



Size, alloy and interface effects on Cu-based catalysts for enhancing electrochemical reduction of CO₂

Fei Guo, Guanjie He^{*}

Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK

ABSTRACT

The electrochemical reduction of CO₂ (CO₂RR) is a significant pathway for converting CO₂ into valuable fuels and promoting the sustainability of energy and environment. In recent years, there has been a growing interest in copper-based CO₂ conversion electrocatalysts due to their high activity and selectivity to generate various products from CO₂ reduction. This review paper focuses on the systematic design of Cu-based CO₂RR electrocatalysts, with a specific emphasis on size regulation, alloying strategies, and interface engineering. Furthermore, the stability, activity, catalytic performance, and underlying mechanisms of these Cu-based electrocatalysts are extensively discussed. Finally, the potential applications and existing challenges associated with copper-based electrocatalysts are summarized, aiming to guide the design of high-performance CO₂RR electrocatalysts.

1. Introduction

In recent decades, the world's primary source of energy has been predominantly dependent on fossil fuels [1–3], which contribute significantly to the emission of substantial amounts of greenhouse gases [4,5]. Among these gases, carbon dioxide (CO₂) is widely recognized as one of the most detrimental greenhouse gases [6], responsible for disrupting the natural carbon cycle [7], causing acidification of seawater, and contributing to climate change [8]. According to the Intergovernmental Panel on Climate Change (IPCC) [9–11], the challenge of global warming is becoming increasingly complex and difficult to manage. Up to this year, 2023, the global average atmospheric concentration of CO₂ has reached a historically elevated level of 423.45 parts per million (ppm), representing a notable increase of 2.82 ppm compared to the corresponding period in the previous year. Consequently, it is imperative to reduce the CO₂ concentration in the atmosphere, with a targeted goal of achieving net-zero CO₂ emissions by 2050. However, as the global economy continues to expand, accompanied by a corresponding rise in energy demand from industrial processes that emit CO₂, effectively mitigating the atmospheric CO₂ content has become a critical and pressing area of research. To address this issue, researchers have proposed various potential solutions, including physical capture [12,13], chemical conversion [14,15], and enhancing the efficiency of internal combustion engine [16]. However, among these approaches, electrochemical CO₂ reduction reaction (CO₂RR) emerges as a promising and viable method for reducing CO₂ emissions and efficiently converting them into alternative sustainable energy sources [17,18]. Furthermore,

the CO₂RR facilitates the recycling of carbon, effecting a transformation of a greenhouse gas into a repertoire of valuable chemical compounds and fuels. This overarching paradigm seamlessly aligns with the foundational tenets of the circular economy and sustainability, as it affords us the opportunity to harness CO₂ as a substantive resource rather than a noxious pollutant. Notably, CO₂RR exhibits synergy with renewable energy sources, such as solar and wind power. This synergistic coupling permits the efficient storage of surplus renewable energy, converting it into chemical energy embedded within the products of CO₂RR. In essence, this process not only offers a means to store intermittent renewable energy efficiently but also provides a pathway toward mitigating the pressing global imperatives of climate change, sustainable energy production, and responsible environmental stewardship. In doing so, it heralds a pivotal trajectory toward the reduction of CO₂ emissions, the cyclical utilization of carbon, and the overarching transition toward a sustainable, low-carbon future.

Furthermore, this methodology facilitates the conversion of carbon dioxide into other valuable chemicals, such as formic acid, acetic acid, ethanol, and more, through a facile electrochemical process [19]. In recent years, CO₂RR has garnered significant research attention due to its straightforward catalytic system and potential for large-scale implementation. For instance, the combination of a gas diffusion electrode (GDE) [20] and an electrolyte fluid system enables stable CO₂RR operation at high current densities [21]. Nonetheless, the overall energy efficiency of the reaction and the selectivity [22,23] towards desired products remain inadequate, primarily due to the absence of efficient and stable catalysts. Additionally, it is imperative to effectively mitigate

^{*} Corresponding author.

E-mail address: g.he@ucl.ac.uk (G. He).

the occurrence of the hydrogen evolution reaction at the reduction potential during the electrochemical process [24–26]. Furthermore, the substantial energy barrier associated with CO₂ activation and the involvement of multi-electron transfer pathways contribute to sluggish reaction kinetics, significant overpotentials, and low selectivity in CO₂RR [27]. Therefore, the key to CO₂RR critically hinges upon the utilization of suitable catalysts that can minimize overpotentials, accelerate reaction kinetics, and enhance the selectivity of desired target products [28].

Currently, extensive research in the literature has focused on investigating various CO₂RR electrocatalysts, including metals, metal oxides, metal alloys, metal chalcogenides, and metal-free carbon-based materials. Among these materials, the incorporation of suitable metal [29,30] or semiconductor nanoparticles [31,32] enables the conversion of CO₂ into valuable fuels and feedstock chemicals [33]. However, it is important to note that different metals exhibit distinct selectivity in the electrochemical CO₂ reduction reaction (CO₂RR). Noble metals such as gold (Au) [34,35], palladium (Pd) [36,37], platinum (Pt) [38,39] and silver (Ag) [40,41] exhibit high selectivity towards CO formation, while certain transition metals like iron (Fe) [42,43] and cobalt (Co) [44,45] selectively convert CO₂ to CO as well. On the other hand, metals like tin (Sn) [46,47], indium (In) [48,49], and lead (Pb) [50,51] demonstrate a high selectivity for the formation of formate ions (HCOO⁻). Notably, recent studies have revealed that copper (Cu) [52–55] is a unique heterogeneous metal catalyst capable of facilitating the production of various oxygenate and hydrocarbon fuels [56], including ethylene (C₂H₄) [57–59], ethanol (C₂H₅OH) [60–62], and propanol (C₃H₇OH) [63,64], through catalytic CO₂ reduction.

In the catalytic conversion of CO₂, both divalent copper (Cu(II)) and monovalent copper (Cu(I)) play significant roles, both of which exhibit distinct catalytic mechanisms and effects [65]. Monovalent copper is commonly employed as a catalyst precursor due to its ability to be reduced to active intermediates, namely copper ions and copper clusters [66]. These intermediates effectively react with CO₂ and catalyze the reduction of carbon dioxide. The monovalent copper typically demonstrates high catalytic activity but limited selectivity. In contrast, divalent copper exhibits superior selectivity and can selectively reduce CO₂ to specific chemicals [67]. In catalytic reactions, divalent copper predominantly operates through a redox cycle, involving the alternating conversion between divalent copper ions (Cu(II)) and monovalent copper ions (Cu(I)) [68–70]. This catalytic mechanism is commonly referred to as the "redox mechanism." Divalent copper can also form a surface reducing agent by combining with a reductant, thereby enhancing the efficiency and selectivity of the catalytic reaction. Consequently, although both monovalent copper and divalent copper can catalyze the CO₂ reduction reaction, their catalytic mechanisms and effects differ significantly, necessitating the selection of an appropriate catalyst based on specific application requirements. Given this distinct property, Cu-based nanoparticles have garnered significant attention in the field of CO₂ emission reduction [71–73].

In this review, we will commence by providing a concise overview of the fundamental principles underlying the CO₂RR and subsequently outline the recent advancements made in the realm of Cu-based catalysts with diverse structures for facilitating CO₂ conversion. Subsequently, we will introduce several noteworthy Cu-based nanomaterials, shedding light on the pivotal role played by size and structure in enhancing the kinetics of CO₂RR and optimizing selectivity towards desired target products. In conclusion, this paper will comprehensively review the current research progress pertaining to Cu-based nanomaterials in CO₂RR, critically assess existing challenges, and propose viable directions for future advancements in the development of highly active and selective CO₂RR catalysts.

2. Mechanism of CO₂RR

Ordinarily, the dissociation of a carbon dioxide molecule necessitates

substantial amount of energy, as the C=O bond possesses a formidable bond energy of approximately 750 kJ mol⁻¹. The electrochemical reduction of CO₂ in the electrolyte involves the transfer of multiple electrons (2, 4, 6, 8, and 12 electrons), enabling the conversion of gaseous CO₂ into various chemical species [74,75] (as illustrated in Fig. 1). In Table 1, the electrochemical reactions of the principal C₁ and C₂ products achievable through CO₂RR in aqueous solutions are summarized, along with their corresponding equilibrium potentials referenced against the standard hydrogen electrode [76].

Electrocatalysts have undergone extensive investigation for the conversion of CO₂ into hydrocarbons in solution, encompassing different pH conditions [77–79]. This electrochemical process is fundamentally centered on the conversion of CO₂ into high-value chemical compounds, predominantly facilitated by the judicious application of electrical energy and a catalyst. A comprehensive comprehension of the intricate CO₂RR mechanism, encompassing the elucidation of key intermediates and discernment of influential factors governing the reaction pathway, stands as a paramount imperative. This profound understanding serves as the cornerstone for the refinement and optimization of the CO₂RR process, fostering its applicability across a diverse spectrum of domains, including carbon capture and utilization, sustainable energy storage, and the synthesis of invaluable chemical commodities. During the CO₂RR process, CO₂ molecules would be adsorbed onto the catalyst surface. The interaction between CO₂ and the Cu surface plays a crucial role in initiating the reaction. Adsorbed CO₂ can undergo dissociation to form adsorbed CO₂ species. Protons (H⁺) from the surrounding electrolyte adsorb onto the Cu surface or interact with the CO₂* species to form bicarbonate (HCO₃⁻) or carbonic acid (H₂CO₃). Electrons are supplied from an external source, such as an electrode, to reduce the adsorbed CO₂* species. This results in the formation of carbonaceous intermediates. One common intermediate in the CO₂RR on Cu-based catalysts is CO. This intermediate can be further reduced to other products or evolve into gaseous CO. Under certain conditions, CO can undergo additional reduction steps to form hydrocarbons such as CH₄, C₂H₄, and so on. In some cases, HCOO⁻ can be an intermediate or a product in the CO₂RR on Cu catalysts. Depending on the reaction conditions and electrode potential, the hydrogen evolution reaction (HER) may also compete with the CO₂RR.

Nevertheless, the CO₂RR remains subject to a myriad of influencing factors. The applied voltage or electrode potential plays a pivotal role in governing the thermodynamic aspects of this reaction, and the deliberate modulation of electrode potential can exert discernible influence over the selectivity of CO₂RR products. Furthermore, the expedient transport of CO₂, protons, and intermediary species to and from the electrode surface stands as a critical imperative. This necessitates meticulous consideration of electrode design and the implementation of well-designed flow systems to augment mass transport and, consequently, reaction rates. Equally vital is the accessibility of CO₂ at the electrode surface, a determinant that assumes profound significance. Optimization of gas diffusion rates emerges as an efficacious strategy to ameliorate overall reaction efficiency. Compounding these challenges are the advent of side reactions, such as the Hydrogen Evolution Reaction (HER), which may act in competition with CO₂RR, thereby exerting notable impacts on the selectivity of ensuing products. Therefore, in order to optimize the efficiency of CO₂RR, a comprehensive understanding of their catalytic activity and selectivity towards different target products is imperative. As Cu-based catalysts in distinct chemical states exhibit notable selectivity towards specific products [80–82], researchers have commenced their investigations by focusing on the reactive sites, enabling precise control over the size, composition, and structure of Cu-based nanomaterials [83–85]. This meticulous control has led to the development of highly active and selective CO₂RR electrocatalysts. This paper provides an overview of recent research endeavors pertaining to the size regulation, alloying, and interface engineering strategies employed in Cu-based catalysts. Additionally, it presents a comprehensive summary of the prevailing challenges,

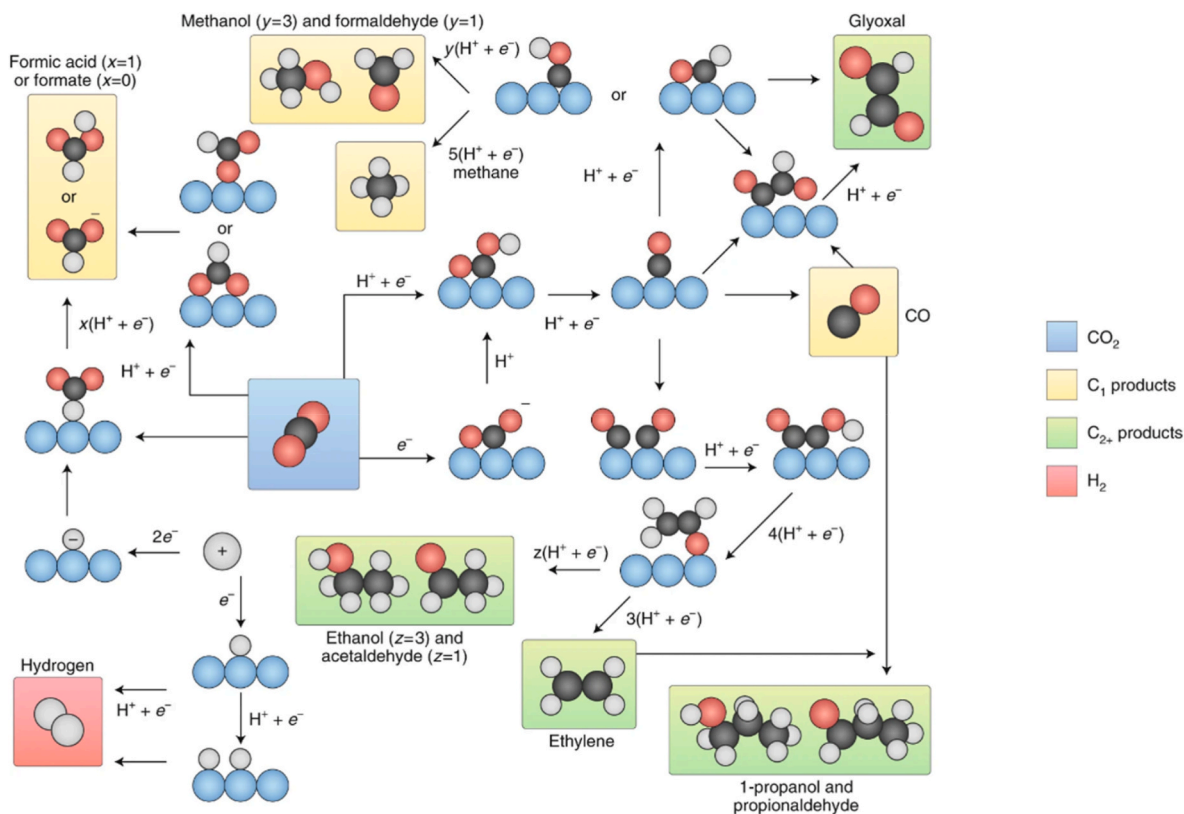


Fig. 1. The reaction pathways for the conversion of CO₂ to different C₁/C₂ products through CO₂RR [74]. Reproduced with permission. Copyright 2019, Springer Nature.

Table 1

The reactions, corresponding overpotentials and number of transferred electrons at 1.0 atm and 25 °C [76]. Reproduced with permission. Copyright 2014, the Royal Society of Chemistry.

Electrons	Reaction	Overpotential (V vs. SHE)
2	$\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{HCOOH}(\text{l})$	-0.250
2	$\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- = \text{HCOO}^-(\text{aq}) + \text{OH}^-$	-1.078
2	$\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$	-0.106
2	$\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- = \text{CO}(\text{g}) + 2\text{OH}^-$	-0.934
2	$2\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{C}_2\text{O}_4(\text{aq})$	-0.500
2	$2\text{CO}_2(\text{g}) + 2\text{e}^- = \text{C}_2\text{O}_4^{2-}(\text{aq})$	-0.590
4	$\text{CO}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- = \text{C}(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	0.210
4	$\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- = \text{C}(\text{s}) + 4\text{OH}^-$	-0.627
4	$\text{CO}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- = \text{CH}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{l})$	-0.070
4	$\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) + 4\text{e}^- = \text{CH}_2\text{O}(\text{l}) + 4\text{OH}^-$	-0.898
6	$\text{CO}_2(\text{g}) + 6\text{H}^+ + 6\text{e}^- = \text{CH}_3\text{OH}(\text{l}) + \text{H}_2\text{O}(\text{l})$	0.016
6	$\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l}) + 6\text{e}^- = \text{CH}_3\text{OH}(\text{l}) + 6\text{OH}^-$	-0.812
8	$\text{CO}_2(\text{g}) + 8\text{H}^+ + 8\text{e}^- = \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	0.169
8	$\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) + 8\text{e}^- = \text{CH}_4(\text{g}) + 8\text{OH}^-$	-0.659
12	$2\text{CO}_2(\text{g}) + 12\text{H}^+ + 12\text{e}^- = \text{CH}_2\text{CH}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$	0.064
12	$2\text{CO}_2(\text{g}) + 8\text{H}_2\text{O}(\text{l}) + 12\text{e}^- = \text{CH}_2\text{CH}_2(\text{g}) + 12\text{OH}^-$	-0.764
12	$2\text{CO}_2(\text{g}) + 12\text{H}^+ + 12\text{e}^- = \text{CH}_3\text{CH}_2\text{OH}(\text{l}) + 3\text{H}_2\text{O}(\text{l})$	0.084
12	$2\text{CO}_2(\text{g}) + 9\text{H}_2\text{O}(\text{l}) + 12\text{e}^- = \text{CH}_3\text{CH}_2\text{OH}(\text{l}) + 12\text{OH}^-$	-0.744

reaction mechanisms, and design considerations relevant to Cu-based catalysts in the context of the CO₂RR.

3. Size effect on Cu-based catalysts

The size effect of Cu-based electrocatalysts in the CO₂RR has garnered extensive research attention due to its significant impact on catalytic activity and selectivity [86–89]. The size of Cu nanoparticles (NPs) has emerged as a crucial parameter governing the efficiency of CO₂ conversion, necessitating a comprehensive understanding of this relationship. As the size of Cu NPs decreases, the surface-to-volume ratio increases, resulting in a higher density of active sites available for catalysis. This enlarged surface area facilitates the adsorption of reactant molecules, particularly CO₂, enhancing their interaction with the catalytic surface. Furthermore, the electronic properties of Cu nanoparticles play a pivotal role in their catalytic behavior. Quantum confinement effects at the nanoscale alter the electronic structure of Cu, leading to changes in energy levels and electronic states [90]. These modifications influence the adsorption energy of reaction intermediates, thereby regulating reaction kinetics and determining the selectivity of C₁ and C₂ products [91–93]. Notably, smaller Cu NPs may possess a higher abundance of low-coordination sites, which promote the formation of specific intermediates and impact product selectivity [94,95]. Additionally, the size-dependent morphology of Cu NPs profoundly affects their catalytic performance. The anisotropic shape of Cu electrocatalysts also influences the diffusion and transport of reactants and intermediates, thereby modulating reaction kinetics and product selectivity.

As shown in Fig. 2 [94], Strasser et al. investigated the influence of particle size on the catalytic performance of Cu NPs in the CO₂RR. Cu NPs catalysts with precisely controlled sizes ranging from 2 to 15 nm were synthesized, and their catalytic activity and selectivity in the CO₂RR process were systematically analyzed and compared with bulk

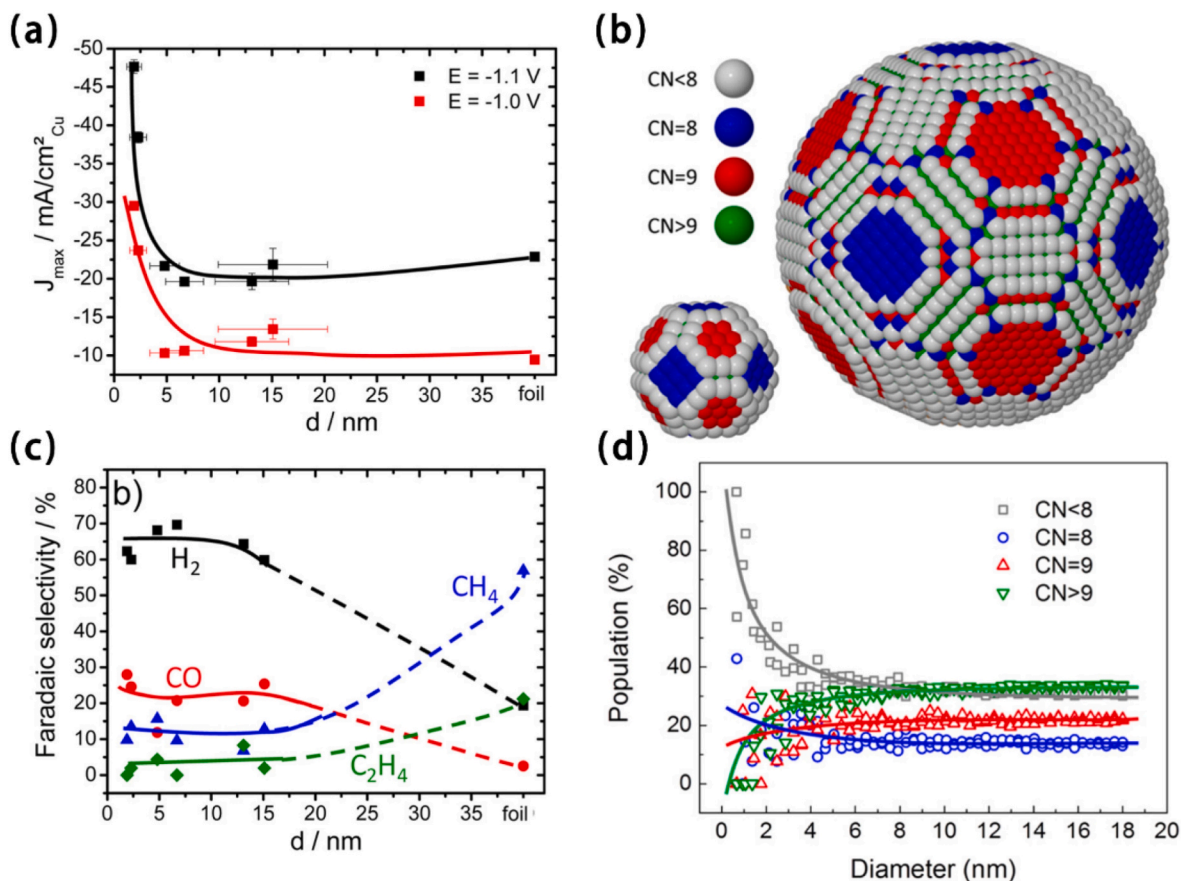


Fig. 2. (a) CO₂RR Faradaic current density at -1.1 and -1.0 V vs. RHE as a function of the particle size of Cu NPs in 0.1 M KHCO₃ (pH 6.8) at 25 °C. (b) Ball models of spherical Cu NPs with 2.2 and 6.9 nm diameters. Surface atoms are color-coded according to their first neighbor coordination number (CN), CN < 8 (gray), CN = 8 (blue), CN = 9 (red), CN > 9 (green). (c) Faradaic selectivity of H₂, CO, CH₄, and C₂H₄ during the CO₂RR on Cu NPs. (d) Population (relative ratio) of surface atoms with a specific CN as a function of particle diameter [94]. Reproduced with permission. Copyright 2014, American Chemical Society. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Cu electrodes. In Fig. 2a, the Faradaic current density of Cu NPs is normalized to the surface area of Cu NPs and plotted against the diameter of the nanoparticles. It is observed that the current density exhibits an increasing trend as the size of the copper nanoparticles decreases, with a more pronounced effect when the nanoparticles are smaller than 5 nm. The surface atomic coordination of spherical Cu NPs is depicted in Fig. 2b, as revealed by the DFT model. The Faradaic selectivity of H₂, CO, CH₄, and C₂H₄ is presented in Fig. 2c. It is noteworthy that larger-sized Cu foils preferably produce CH₄ and C₂H₄. However, as the size of Cu NPs decreases to approximately 15 nm or smaller, H₂ and CO become the dominant products. This finding suggests that the CO₂RR performance of Cu NPs is contingent upon the presence of low-coordination Cu sites, which exhibit high selectivity towards H₂ and CO (Fig. 2d). The particle size effect has been systematically investigated in the context of the catalytic electroreduction of CO₂ on Cu NPs within the size range of 2 – 15 nm, with comparisons made to bulk Cu. Further, researchers thus concluded that the catalytic performance of Cu NPs in CO₂RR is strongly influenced by the size-dependent distribution of low-coordination Cu sites, which play a pivotal role in dictating the selectivity towards H₂ and CO. As the Cu particle size decreases, the catalytic activity and selectivity toward H₂ and CO increase significantly, especially for NPs smaller than 5 nm. Nanoscale Cu surfaces are increasingly less selective for hydrocarbons. The results indicate that nanometer-sized Cu NPs exhibit a remarkable augmentation in overall catalytic activity, as evidenced by the increase in faradaic current. Subsequent selectivity analysis elucidates that this heightened catalytic activity primarily stems from an enhanced

production of CO and H₂ on the Cu NPs. The selectivity towards hydrocarbons, initially responsive to particle size, ultimately stabilizes at a reduced constant plateau, and eventually diminishes to negligible levels for NP sizes at or below 2 nm.

One drawback of reducing the size of Cu NPs in CO₂RR is the potential decrease in stability and durability. One of the principal structural transformations discerned within Cu-based catalysts during the course of the CO₂RR is surface reconstruction. This intricate process involves the reconfiguration of surface atomic arrangements, giving rise to novel facets or phases in response to the electrochemical milieu. Notably, this reconstruction is instigated by the adsorption of CO₂ molecules and reaction intermediates onto the Cu surface, which engenders mechanical strain and prompts the reorganization of the surface morphology. Concurrently, the advent of CO₂ and reaction intermediates has the propensity to yield catalytically active sites on the Cu surface. These sites assume critical importance in expediting the reduction reactions. For instance, the adsorption of CO₂ may incite dissociation, culminating in the formation of adsorbed carbon species (C*) on the Cu surface. These C* species subsequently participate in successive reaction steps, signifying their pivotal role in the CO₂RR mechanism. Furthermore, the realm of Cu-based catalysts in CO₂RR is punctuated by instances of oxidative transformation. Under specific conditions, the development of a thin layer of copper oxide, such as Cu₂O or CuO, on the catalyst's surface ensues. This oxide overlayer exerts a discernible influence over the kinetics of the reaction and the selectivity of product formation, as it functions as an active site for distinct CO₂RR pathways. Extended exposure to the CO₂RR milieu can

further precipitate the aggregation of Cu nanoparticles or give rise to alterations in the catalyst's morphology. These morphological transitions have the potential to exert profound ramifications on the catalyst's activity and stability, thus underscoring the imperative need to unravel and comprehend the intricacies of structural dynamics in Cu-based catalysts deployed for CO₂RR applications. For instance, smaller nanoparticles generally possess a larger fraction of surface atoms, which are more susceptible to oxidation and degradation under the harsh reaction conditions. This can lead to a loss of catalytic activity over time and limit the practical application of Cu NPs in CO₂RR. To overcome this, Duan's team [90] used the alkyne bond induction-site trapping method to synthesize Cu catalysts supported on graphdiyne (GDY) with three different sizes: 1–1.5 nm nanoclusters (NCs, Cu_{45.2}/GDY), 0.5–1 nm sub-nanoclusters (SCs, Cu_{6.0}/GDY), and single-atom catalysts (SAs, Cu_{1.5}/GDY). As the size of the Cu species decreased, the atomic surface energy increased. Conventional synthesis methods often struggle to precisely control the agglomeration of metal atoms, resulting in the formation of metal particles. However, with the acetylenic bond induction-site trapping method, they achieved synchronous growth of

metal atoms with the substrate, enabling better control over the cluster growth rate and size. Fig. 3b illustrates the electrochemical reduction performance of CO using these catalysts. Their findings revealed that Cu SAs predominantly produced C₁ (CH₄) and only a small amount of C₂ products during CO reduction, with no C₃ product observed. As the cluster size increased, the yield of C₂₊ products gradually increased. Notably, at –1.0 V, the C₂₊/C₁ ratio in the product obtained by the Cu NCs catalyst reached 398.5, indicating nearly complete elimination of the C₁ component. In a 1.0 M KOH electrolyte, the current density of C₂₊ reached 312 mA cm⁻², with a Faradaic efficiency of 91.2 %. Remarkably, Cu NCs exhibited exceptional stability at high current densities of 150–200 mA cm⁻². Duan's results highlight the importance of size control in designing efficient catalysts for CO₂ reduction. The adeptness to meticulously control the dimensions of copper species through the alkyne bond induction-site trapping technique has resulted in heightened selectivity towards targeted products and increased stability under elevated current densities. This investigation offers significant insights into the systematic formulation of nanocluster catalysts for the electrochemical reduction of CO, thereby unlocking novel avenues for the

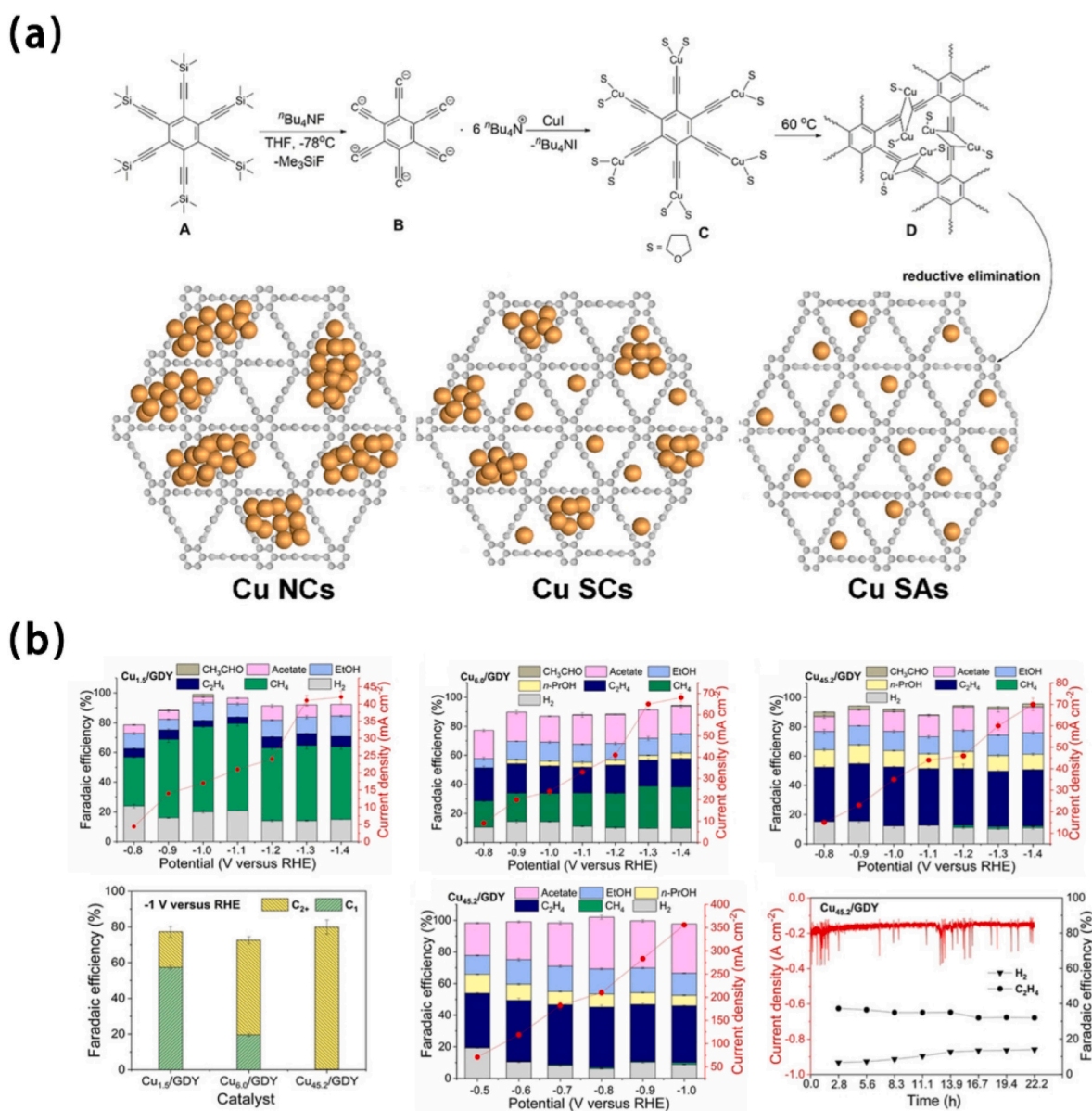


Fig. 3. (a) Schematic illustration for the synthesis of Cu/GDY. (b) CO electrochemical reduction performance of Cu/GDY [90]. Reproduced with permission. Copyright 2020, Wiley-VCH.

advancement of exceptionally efficient and enduring electrocatalytic systems.

However, another challenge related to the size effect is the difficulty in achieving precise control over the particle size distribution. The synthesis of uniform copper nanoparticles with well-defined sizes can be

challenging and may require sophisticated fabrication techniques. Variations in particle size and size distribution can significantly influence the catalytic performance and selectivity, making it essential to achieve reproducible and controlled synthesis methods. Furthermore, the size-dependent catalytic behavior of Cu NPs in CO₂RR is not a linear

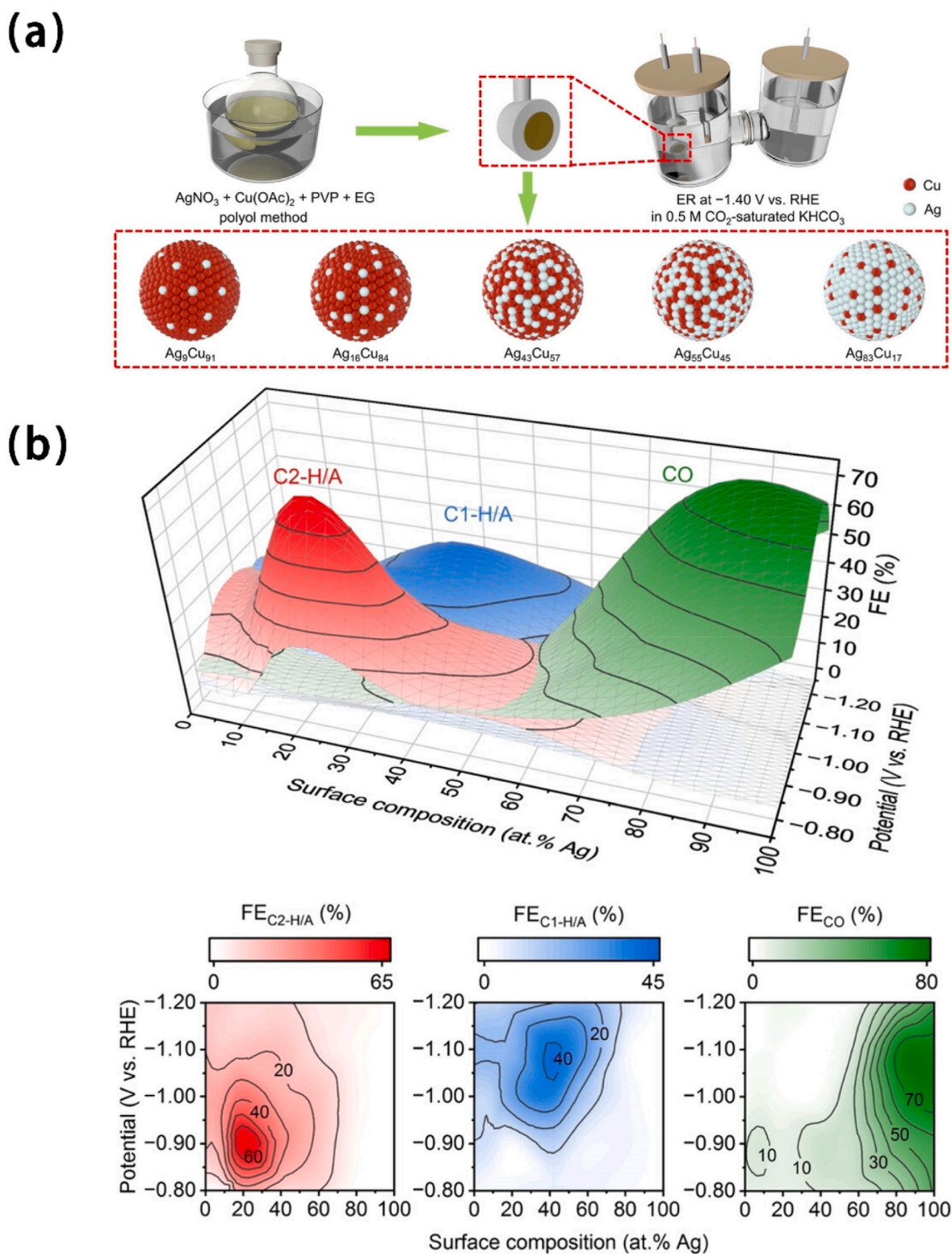


Fig. 4. (a) Schematic of the synthetic process of Ag–Cu surface alloys. PVP: polyvinyl pyrrolidone. EG: ethylene glycol. (b) 3D colormap surface plot and corresponding colortour maps for FE towards different products (i.e., C₂-H/A, C₁-H/A and CO) versus surface compositions and applied cathodic potentials [102]. Reproduced with permission. Copyright 2023, Wiley-VCH.

relationship. While smaller nanoparticles generally exhibit higher activity, there is an optimum size range for achieving the highest catalytic performance. Beyond this range, further reduction in size may not lead to significant improvements or can even result in reduced activity and selectivity. Understanding the optimal size range for Cu NPs in CO₂RR and its underlying mechanisms is crucial for effective catalyst design and development. In summary, the size-dependent selectivity findings presented herein contribute significantly to a more comprehensive mechanistic comprehension of the electroreduction of CO₂. The catalyst materials, their structural configurations, and the prevailing reaction conditions readily lend themselves to validation through Density Functional Theory (DFT) simulations, thereby enabling a refined mechanistic elucidation. Delving into the behavior of particles measuring below 2 nm, a computational domain now accessible to theoreticians employing ab initio computational methods. This, in turn, extends the prospects for further comprehensive DFT investigations within the context of the current electroreduction system. It is evident that when the production of hydrocarbons holds paramount significance, the utilization of very small (<3 nm) nanoscale copper catalysts should be avoided. Given the growing recognition of this reaction as a pivotal process for the chemical storage of electricity, it becomes imperative to comprehensively understand the reactivity and selectivity of this process on the nanoscale catalysts.

4. Alloy effect on Cu-based catalysts

Cu-based alloy electrocatalysts have garnered significant attention for their potential in CO₂RR. The incorporation of different metals into the copper lattice can modify its catalytic properties, enabling enhanced activity, selectivity, and stability in CO₂RR. This section explores the advancements in Cu-based alloy electrocatalysts for CO₂RR and their potential applications in sustainable energy conversion.

One prominent example of Cu-based alloy electrocatalysts is the incorporation of noble metals such as Au, Ag, or Pd etc. into the structure of Cu. These bimetallic catalysts have shown improved selectivity towards desired CO₂RR products. For instance, Au–Cu alloys have exhibited enhanced activity and selectivity for the production of C₂H₄ and C₂H₅OH [96]. Ag–Cu alloys have demonstrated high selectivity towards the formation of CO and H₂ [97]. Pd–Cu alloys have displayed an excellent catalytic performance in reducing CO₂ to CH₄ [98]. The alloying of Cu with noble metals not only alters the electronic structure of the catalyst but also facilitates the optimization of reaction intermediates and surface adsorption, leading to enhanced CO₂RR performance. Additionally, Cu-based alloys with transition metals have been explored for CO₂RR. These alloys exhibit unique catalytic properties and selectivity towards specific CO₂RR products. Fe–Cu alloys have shown selectivity towards CO production [99], while Co–Cu alloys have demonstrated enhanced activity for C₂H₄ production [100]. Furthermore, Ni–Cu alloys have exhibited improved selectivity towards CH₄ formation [101]. The incorporation of transition metals into the copper lattice not only influences the electronic structure but also enhances the adsorption and activation of CO₂ molecules, facilitating efficient CO₂RR.

As depicted in Fig. 4a [102], Shen's research group introduced Ag, a metal known for its weak *CO binding strength, into the Cu-based catalyst to form an Ag–Cu bimetallic surface alloy (Ag_xCu_{100-x}) with precisely tailored surface compositions, ranging from Cu-rich to Ag-rich variants. Through the adjustment of the surface alloy composition and applied voltage, they successfully achieved controllable selective production of C₂ hydrocarbon/alcohol products (such as C₂H₄ and C₂H₅OH), C₁ hydrocarbon/alcohol products (such as CH₄ and CH₃OH), and CO in the CO₂RR. Fig. 4b illustrates that the surface rich in Cu of the Ag_xCu_{100-x} catalyst (with 14 < x < 34) exhibits favorable characteristics for the reduction of CO₂ to C₂ hydrocarbon/alcohol products with high selectivity in the voltage range of –0.85 to –1.00 V vs. RHE. On the other hand, the Ag-rich surface of the Ag_xCu_{100-x} catalyst (with 27 < x <

55) promotes the selective production of C₁ hydrocarbon/alcohol products in the voltage range of –1.00 to –1.10 V vs. RHE. Moreover, Ag_xCu_{100-x} catalysts with higher Ag content (x > 74) tend to facilitate the reduction of CO₂ to CO with high selectivity in the voltage range of –0.90 to –1.15 V vs. RHE in this work. These materials were engineered to showcase remarkable performances in the CO₂RR while enabling the controllable selection of various value-added products, including C₂-hydrocarbons/alcohols, C₁-hydrocarbons/alcohols, and carbon monoxide (CO), according to specific preferences. Shen's comprehensive investigation, which incorporated in situ spectral examinations and theoretical calculations, unveiled that modifying the surface composition of Ag_xCu_{100-x} surface alloys from Cu-rich to Ag-rich results in a deliberate adjustment of the d-band center, thereby modulating the binding strength of *CO intermediates from strong to weak. This strategic manipulation effectively governs subsequent *CO reaction pathways, consequently influencing product selectivity. Further customization of the applied cathodic potentials permits the fine-tuning of the energy levels of electrons engaged in *CO reactions, facilitating the realization of tunable CO₂RR selectivity toward desired products. Moreover, they have introduced a prominent region map and proposed the indicator P_p as a means to evaluate the thermodynamic predominance of the *CO-to-ρ conversion in the competition among three plausible reactions involving *CO intermediates. This theoretical framework serves as a predictive tool for achieving controlled CO₂RR product selectivity.

Lee et al. [103] successfully synthesized CuNi bimetallic nanosheets using a ligand π-π stacking self-assembly method. The nanochips exhibit a thin regular hexagonal morphology with a thickness of tens of atomic layers, a uniform size distribution, and a stable crystal structure resulting from the bimetallic fusion (as depicted in Fig. 5a). Among the synthesized nanosheets (Fig. 5b), CuNi demonstrated remarkable catalytic activity and Faradaic efficiency. This enhanced performance can be attributed to several factors, including its optimized d-orbital structure, efficient adsorption of reaction intermediates, rapid desorption of product species, efficient electron transfer processes, abundant active sites, and excellent surface area and conductivity. The optimized d-orbital structure of CuNi contributes to the favorable interaction between the catalyst and reactant molecules, facilitating the adsorption of carbon dioxide and reaction intermediates. The fast electron transfer processes enable efficient charge transfer during the electrocatalytic reaction, enhancing the catalytic activity. The presence of a profusion of active sites on the nanochips serves to promote the exposure of catalytically active moieties, thereby augmenting the reservoir of available active sites conducive to CO₂ reduction. Furthermore, the expansive surface area offered by the nanosheets facilitates heightened mass transport and accelerates reaction kinetics. The heightened conductivity inherent to CuNi further expedites the electron transfer process, thus ensuring the proficient conversion of CO₂. In its entirety, the exceptional catalytic efficacy exhibited by CuNi nanosheets in the electrocatalytic reduction of CO₂ can be ascribed to their meticulously engineered structural attributes, the expeditiousness of charge transfer processes, and the abundance of active sites. These discerned outcomes contribute significantly to the advancement of bimetallic catalysts tailored for CO₂ conversion, holding promise for the progression of efficient and sustainable energy conversion technologies.

However, Cu-based alloy catalysts for CO₂RR are still limited by their stability and durability under harsh reaction conditions. The CO₂RR involves complex reaction pathways and generates various reaction intermediates, which can cause surface reconstruction, particle agglomeration, and catalyst deactivation over time. Cu-based alloys, especially those with high surface area and active sites, are prone to surface oxidation, dissolution, and structural changes, leading to reduced catalytic activity and selectivity. Moreover, the optimization of selectivity towards specific CO₂RR products. While Cu-based alloys can exhibit improved selectivity compared to pure Cu catalysts, achieving high selectivity for desired products remains a significant challenge. The

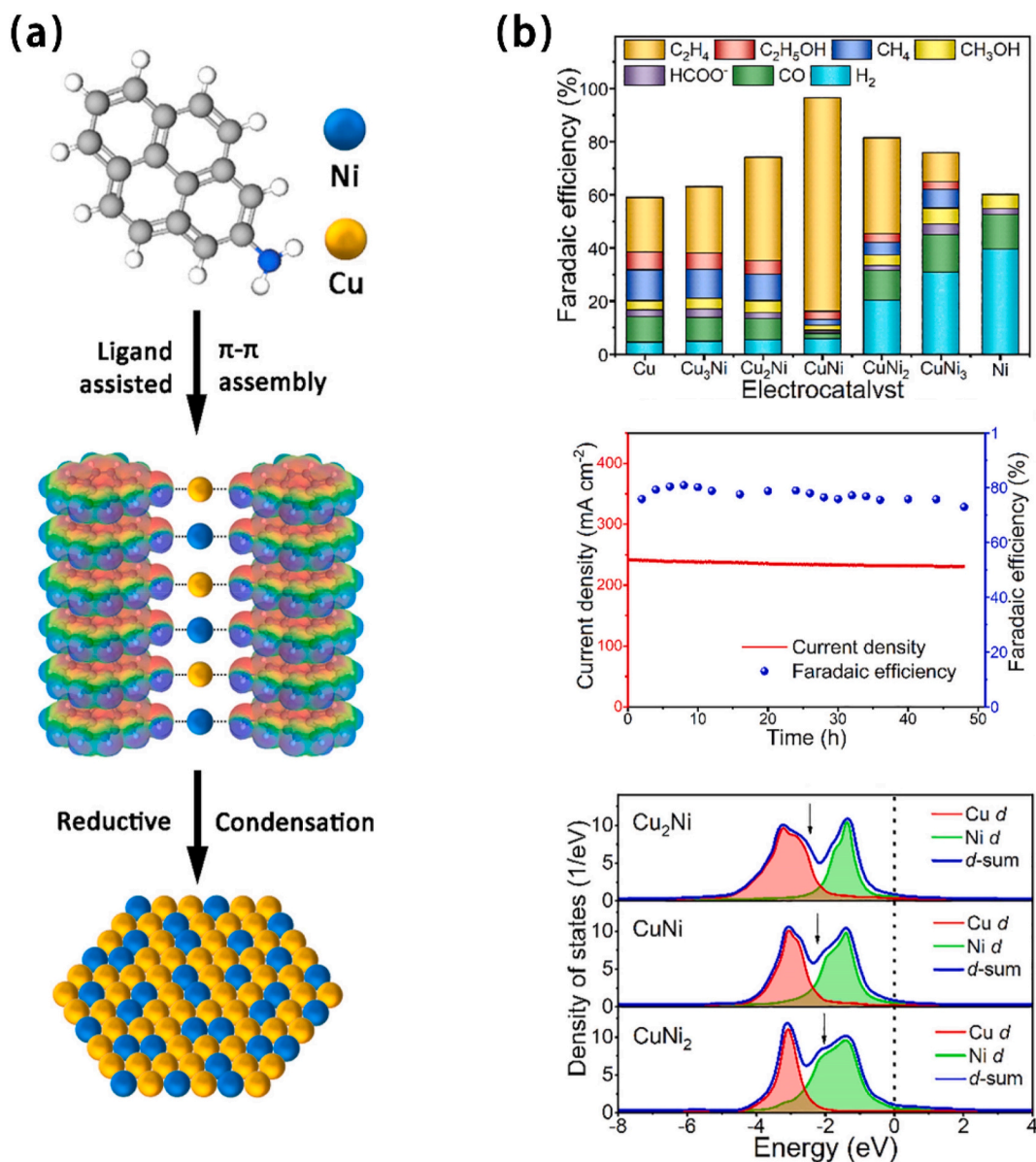


Fig. 5. (a) Scheme for the generation mechanism of the CuNi nanosheets. (b) Faradaic efficiency of each product using various electrocatalysts at -1.5 V vs RHE, Faradaic efficiency for C_2H_4 (blue) and current density (red) using the CuNi catalyst for over 48h electrolysis. (f) Density of states for the Cu_2Ni , $CuNi$, $CuNi_2$ d-bands [103]. Reproduced with permission. Copyright 2021, American Chemical Society. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

control of reaction pathways and intermediate species is intricate, and the presence of different metal components in the alloy can influence the adsorption and activation of reaction intermediates, leading to varied product distributions. Achieving precise control over selectivity for specific target products, such as C_2 hydrocarbon/alcohol or C_1 hydrocarbon/alcohol, still requires further understanding and design strategies. Furthermore, the scalability and cost-effectiveness of Cu-based alloy catalysts need to be addressed. Many Cu-based alloys contain noble metals or transition metals, which can be expensive and limited in availability. Developing cost-effective and scalable synthesis methods for Cu-based alloys with desirable properties is crucial for their practical implementation in large-scale CO_2RR applications. Additionally, the mechanistic understanding of the CO_2RR process on Cu-based alloy catalysts is still evolving. Despite significant progress in characterizing the catalytic behavior and reaction pathways, there are still gaps in the understanding of the active sites, surface reactions, and structure-activity relationships of Cu-based alloys during CO_2RR . Further

research efforts, including advanced characterization techniques and theoretical modeling, are needed to elucidate the mechanistic aspects and guide the rational design of Cu-based alloy catalysts. Addressing these limitations and challenges will pave the way for the development of more efficient, selective, and stable Cu-based alloy catalysts for CO_2RR , enabling their widespread application in sustainable energy conversion and carbon utilization. Thus, designing high-efficiency Cu-based alloy catalysts for the CO_2RR is a multifaceted process that demands a judicious selection of materials and meticulous optimization of catalyst properties. Cu has been a common choice for CO_2RR catalysts because it can catalyze the reduction of CO_2 to various C_1 , C_2 and C_2+ products. Start with pure copper and then consider alloying it with other metals to enhance its catalytic properties. Identify alloying elements that can improve the catalytic activity, selectivity, and stability of copper. Common alloying elements include Ag, Au, and transition metals like Ni or Co. The choice of alloying elements should be based on their known catalytic properties and their compatibility with Cu. Determine the

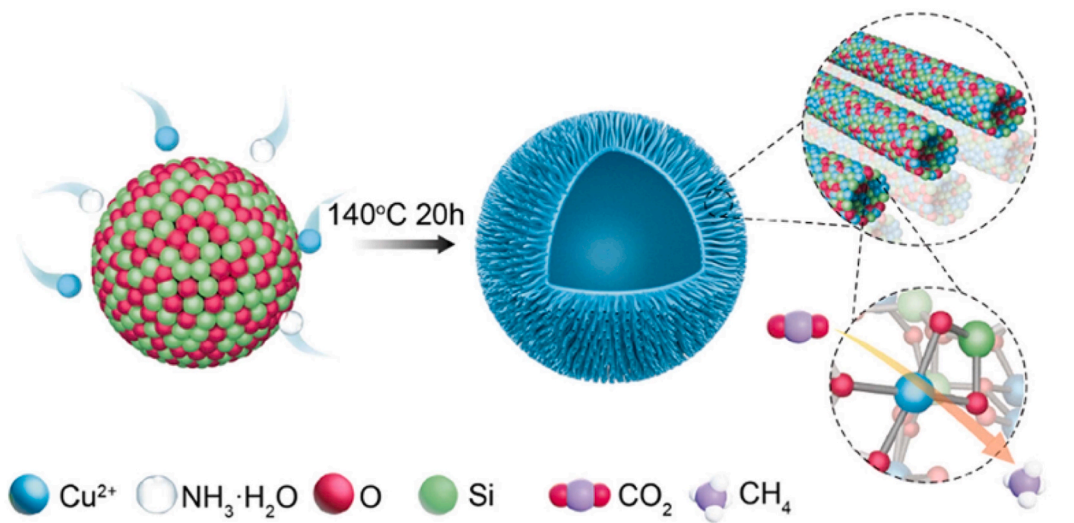
optimal composition of the Cu-based alloy. This can involve varying the ratio of copper to alloying elements to achieve the desired catalytic performance, which could be predicted by DFT simulation.

5. Interface effect on Cu-based catalysts

The interface effect on Cu-based catalysts for CO₂RR has been a

subject of significant research interest. The interface effect between different components of Cu-based catalysts plays a crucial role in the process of CO₂RR, which is a promising strategy for converting CO₂ into value-added chemicals and fuels using renewable energy sources. In CO₂RR, the goal is to utilize an electrochemical reaction to convert CO₂ into useful products such as CO, CH₄, C₂H₄, and more, thereby contributing to both CO₂ mitigation and fuel production. Therefore, Cu-

(a)



(b)

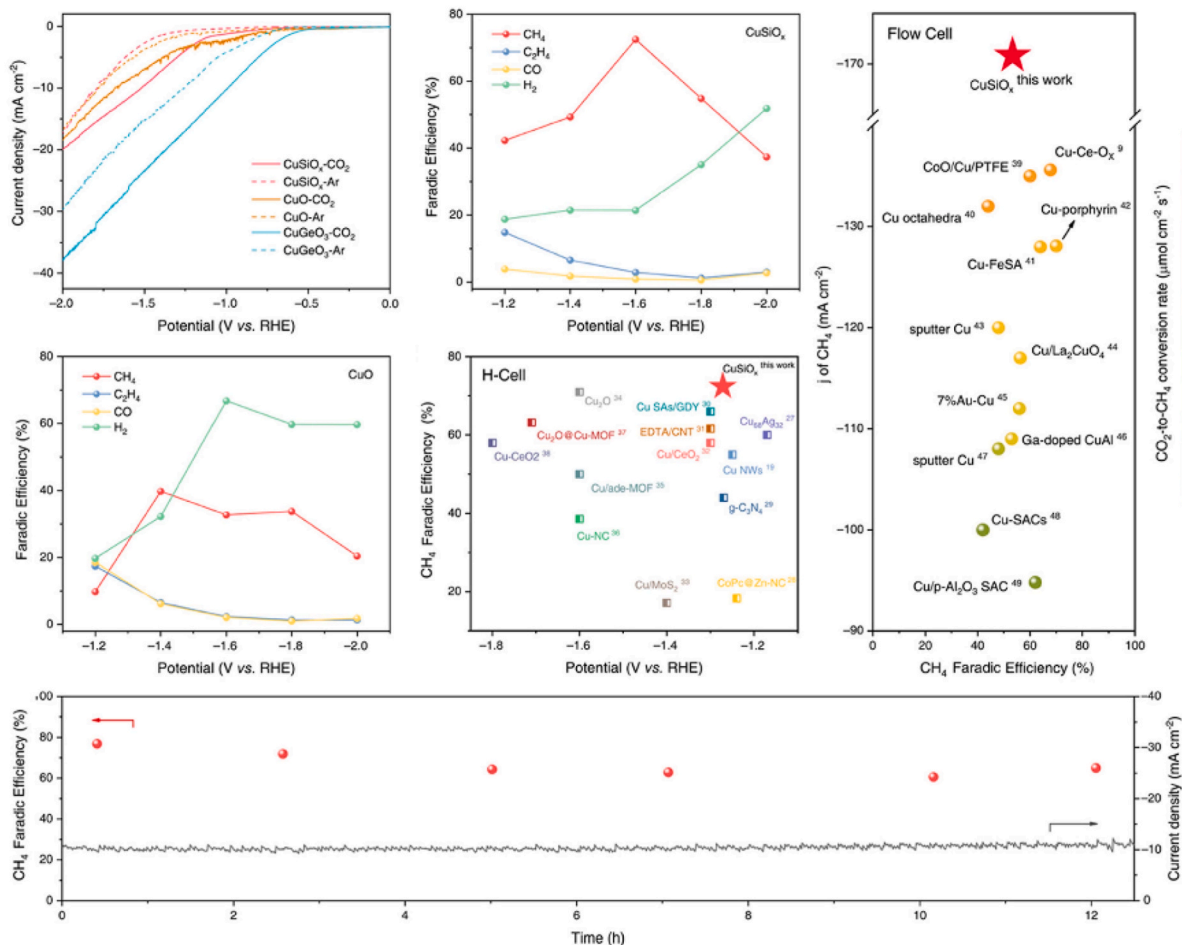


Fig. 6. (a) Schematic illustration of the CuSiO_x synthetic process. (b) Electrochemical CO₂RR performance [104]. Reproduced with permission. Copyright 2023, American Chemical Society.

based catalysts are widely studied for CO₂RR due to their ability to selectively produce specific target products. However, the catalyst's performance is significantly influenced by the interfaces between Cu-based materials with various components [104–107]. At the interface, several factors come into play. One key factor is the adsorption of reactant molecules on the catalyst surface. The interface influences the strength and orientation of adsorption, which in turn affects the reaction kinetics and selectivity [108,109]. Cu-based catalysts with tailored interfaces can promote the adsorption of CO₂ and reaction intermediates, leading to enhanced CO₂RR activity and selectivity towards desired products [110,111]. The interfacial interaction between Cu-based catalysts and support materials is a pivotal determinant in enhancing the efficiency of the electrochemical process of CO₂RR [112]. Support materials serve as platforms for optimizing the dispersion, stability, and catalytic activity of Cu-based catalysts, thereby playing a crucial role in augmenting CO₂RR performance. Support materials confer an elevated surface area and specialized structural characteristics that facilitate the even distribution of Cu nanoparticles [113]. This uniform dispersion of Cu catalysts on the support surface substantially enhances the density of active sites available for CO₂RR, which in turn leads to an amplification of the overall catalytic activity. Further, the interface established between Cu and the support materials effectively mitigates the aggregation and coarsening of Cu nanoparticles during the course of electrochemical reactions. This stabilization mechanism prolongs the catalytic lifespan by impeding the diminishment of performance attributes over time. Moreover, the interfacial region between Cu and the supporting substrate expedites the transfer of electrons between the catalyst and the electrode surface. This expeditious electron transfer kinetics are indispensable for sustaining optimal reaction rates throughout CO₂RR. The interplay between Cu and the support modulates the electronic and geometric characteristics of the catalytic active sites. This tailored modification of active sites influences the adsorption energies of intermediate reaction species, thereby enabling fine-tuning of the selectivity

of CO₂RR toward desired products. Also, interfaces provide an avenue for the deliberate generation of defects, steps, and specialized crystallographic facets on the Cu surface. These structural attributes serve as unique active sites for CO₂RR, conferring the capability to modulate product distribution and overall catalytic performance.

Chen et al. [104] successfully synthesized an amorphous CuSiO_x catalyst, where Cu species were uniformly dispersed within the silica matrix, accompanied by abundant atomic Cu–O–Si interface sites (Fig. 6a). The presence of these unique atomic interface sites confers high selectivity (72.5 %) and stability (FE_{CH₄} remains above 60 % after 12 h of testing) to the CuSiO_x catalyst in the CO₂ to CH₄ conversion (Fig. 6b). The interface between Cu and silica enhances the Cu–O bond strength, thereby improving the resistance to Cu species reconstitution. In terms of reaction thermodynamics, the Cu–O–Si interfacial sites favor the protonation of *CO to *COH, leading to methane formation instead of hydrogen evolution or C–C coupling. In summary, Chen's team have proposed an effective strategy for enhancing the stability of Cu-based electrocatalysts for CO₂RR by introducing Cu–O–Si interfaces. They successfully synthesized a novel amorphous CuSiO_x catalyst possessing a profusion of atomic-level Cu–O–Si interfacial sites. Their comprehensive electrochemical assessments unveiled that these Cu–O–Si interfacial sites exhibit exceptional electrochemical robustness and deliver outstanding electrocatalytic performance for CO₂RR, particularly in the context of methanation. Theoretical calculations have substantiated the presence of a robust interfacial interaction between copper and silica, leading to an enhancement in the strength of Cu–O bonds and an augmentation in the reconstruction resistance of Cu–O–Si interface sites. This discovery represents a highly effective approach to mitigate the stability challenges encountered by Cu-based CO₂RR electrocatalysts, while concurrently offering insights into the design of novel catalytically active sites.

Chen's research team [110] achieved efficient conversion of CO₂ into C₂₊ products by manipulating the surface interface structure of the Cu

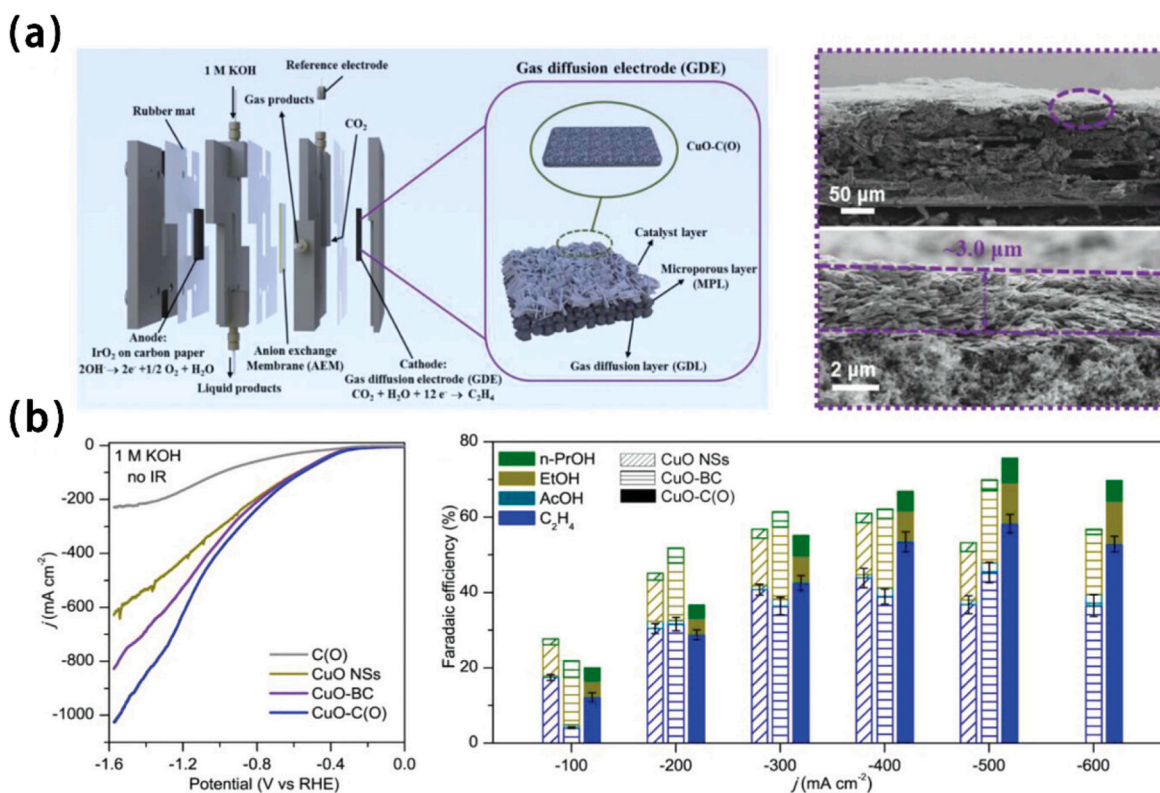


Fig. 7. (a) Schematic diagram of the flow cell used for CO₂RR studies, and cross-sectional SEM image of CuO–C(O) electrode. (b) LSV curves for different catalysts in a flow cell with a 1 m KOH electrolyte and flowing CO₂ and FEs to C₂₊ products [110]. Reproduced with permission. Copyright 2023, Wiley-VCH.

catalyst and the solid-gas-liquid interface on the gas diffusion electrode (GDE) within the CO₂ reduction flow electrolysis cell (Fig. 7a). They successfully prepared CuO–C(O) catalysts with abundant Cu–O–C interfaces through in situ electrochemical reduction of CuO nanosheets/graphene oxide dots (CuO–C(O)). As illustrated in Fig. 7b, the CuO–C(O) catalyst exhibits a remarkable Faradaic efficiency of 77.4 % towards C₂₊ products (with FE-C₂H₄ approximately 60 %) during CO₂RR at a current density of 500 mA cm⁻². The surface of the CuO–C(O) catalyst is rich in Cu⁺ species and Cu⁰/Cu⁺ interfaces, which enhance the adsorption and surface coverage on the Cu catalyst during the electrocatalytic reduction process, thereby facilitating the C–C coupling reaction. In this study, Chen's team present a noteworthy Cu–O–C interfacial phenomenon that significantly enhances the electrocatalytic conversion of CO₂RR into C₂₊ products. The Cu–O–C interfaces were meticulously engineered through a sequence of steps, beginning with the electrostatic deposition of graphene oxide dots onto the surface of CuO nanosheets (NSs), followed by the electroreduction of the resulting CuO–C(O) hybrid material. These Cu–O–C interfaces played a pivotal role in inducing topological transformations in the CuO nanosheets, and Cu⁺/Cu⁰ interfaces during the electroreduction process. The resultant catalyst exhibited remarkable electrocatalytic performance, with a high Faradaic efficiency of 60 % for C₂H₄ production achieved at a potential of –0.82 V, and an impressive maximum ethylene partial current density of 316.8 mA cm⁻² observed at –0.93 V. Furthermore, the hydrophobic nature and stability of the Gas Diffusion Electrode (GDE) were substantially improved through the incorporation of hydrophobic Cu–C(O) interfaces. The substantial presence of Cu⁰/Cu⁺ interfaces within the catalyst led to enhanced adsorption and surface coverage of carbon monoxide (CO), consequently promoting the dimerization reaction of two adsorbed *CO molecules. This mechanistic feature facilitated the selective production of ethylene with high yield.

The interface plays a crucial role in the performance of Cu-based catalysts for CO₂RR, but it also presents some limitations. One of the main challenges is achieving and maintaining a stable and active interface. Over time, the interface can undergo structural changes, leading to reduced catalytic activity and selectivity. Moreover, the interface may be prone to degradation or poisoning by reaction intermediates or side products, which can further hinder the efficiency of CO₂RR. Another limitation is the difficulty in precisely controlling and optimizing the interface structure. Designing Cu-based catalysts with well-defined interfaces requires sophisticated synthesis techniques and precise control over the composition, morphology, and spatial arrangement of the interface. Achieving such control can be challenging, and variations in the interface structure can significantly affect the catalytic performance, leading to inconsistent results.

6. Summary and perspective

In summary, Cu-based catalysts have shown great potential for CO₂RR, offering opportunities to convert CO₂ into valuable chemicals and fuels. They exhibit favorable catalytic activity and selectivity, making them a promising candidate for sustainable energy conversion. One of the key advantages of Cu-based catalysts is their tunability through alloying or interface engineering, enabling enhanced performance and selectivity. Bimetallic Cu alloys, such as Cu–Au, Cu–Ag, and Cu–Pd, have demonstrated improved selectivity towards specific CO₂RR products. The incorporation of transition metals into the Cu lattice has also shown promising results. Furthermore, interfaces, such as Cu–O–Si and Cu–O–C, have been explored to enhance catalytic activity and stability.

However, there are still several challenges and limitations to address in Cu-based catalysts for CO₂RR. Stability and durability remain critical factors, as catalyst degradation and fouling can significantly impact their performance over time. Precise control over catalyst morphology, composition, and interface structure is necessary to optimize catalytic activity and selectivity. Further research is needed to deepen our

understanding of the fundamental mechanisms underlying Cu-based catalysts' performance in CO₂RR. This includes elucidating the reaction pathways, identifying active sites, and uncovering the role of intermediates and surface species. Computational modeling and in-depth experimental investigations will be crucial in advancing our knowledge in this field.

Currently, most Cu-based catalysts show enhanced C₂₊ product formation under alkaline conditions, which may limit their practicality and efficiency for certain applications. The significance of developing catalysts for the electrochemical reduction of carbon dioxide (CO₂RR) that can produce C₂₊ (C₂ and higher) products in a neutral medium, rather than just an alkaline medium, is a critical aspect in advancing the commercial application of CO₂RR technology. The importance of developing neutral medium-compatible catalysts could be essential for the following reasons: Firstly, neutral pH conditions are prevalent in a variety of industrial processes and applications. Catalysts that can operate in a neutral medium would find broader use across different industries and electrochemical setups, making CO₂RR technology more adaptable and versatile. Secondly, alkaline conditions often require additional energy inputs for pH adjustment and maintenance. Catalysts that function effectively in neutral conditions can reduce the energy requirements for pH control, contributing to overall process efficiency. Thirdly, neutral pH is more environmentally benign compared to alkaline conditions, which may involve the use of caustic substances. Catalysts that operate in a neutral medium align better with sustainability goals and minimize potential environmental impacts. Also, catalysts compatible with neutral media could more easily integrate with existing chemical processes, allowing for seamless integration into industrial operations without the need for major modifications. Further, some C₂₊ products, like ethylene and ethanol, are valuable chemicals with diverse industrial applications. Developing catalysts that can selectively generate C₂₊ products under neutral conditions enhances the potential for cost-effective production of these high-value chemicals from CO₂. Moreover, the electrolyzers designed for neutral pH conditions might have different engineering requirements than those optimized for alkaline conditions. Catalysts tailored for neutral pH can enable the design of more efficient and durable electrolyzer systems. Furthermore, operating in neutral conditions could potentially reduce unwanted side reactions that might occur under alkaline conditions. This can lead to higher selectivity towards desired C₂₊ products and better overall catalytic performance. Finally, compliance with regulations and safety standards might be easier to achieve when working with neutral pH conditions, simplifying the approval process for CO₂RR technologies.

In summary, emphasizing the importance of developing catalysts capable of producing C₂₊ products in a neutral medium is crucial for advancing the commercial viability of CO₂RR technology. Such catalysts have the potential to enhance applicability, energy efficiency, environmental compatibility, and product selectivity, ultimately accelerating the integration of CO₂ conversion processes into industrial settings and contributing to a more sustainable future.

In terms of practical applications, scale-up and cost-effectiveness are essential considerations for Cu-based catalysts. Developing scalable synthesis methods and exploring cost-efficient catalyst designs are necessary for their successful implementation in industrial settings. There are several limitations and challenges that need to be addressed:

Efficiency: The efficiency of CO₂RR devices, particularly in terms of conversion efficiency and energy efficiency, needs improvement. Enhancing the overall efficiency of the process is crucial for the practical implementation of CO₂RR technologies. **Durability and Longevity:** The long-term durability and stability of CO₂RR devices are critical for their practical application. Catalyst degradation, fouling, and electrode passivation can hinder the device's performance and lifespan. Finding strategies to improve the durability and longevity of CO₂RR devices is essential. **Scalability and Cost-effectiveness:** The scalability and cost-effectiveness of CO₂RR devices are important considerations for large-scale implementation. Developing manufacturing processes that are

scalable, cost-efficient, and utilize abundant and inexpensive materials is crucial to make CO₂RR technologies economically viable. Reaction Kinetics and Mass Transport: Understanding the reaction kinetics and mass transport phenomena in CO₂RR devices is crucial for optimizing their performance. Improving the reaction kinetics and mass transfer efficiency can enhance the overall performance and productivity of CO₂RR devices. Integration with Renewable Energy Sources: Integrating CO₂RR devices with renewable energy sources, such as solar or wind power, can enhance their sustainability and reduce their carbon footprint. Developing efficient and effective coupling strategies between CO₂RR devices and renewable energy systems is an important area of research. Addressing these limitations and challenges requires multidisciplinary efforts, including advances in catalyst design, materials engineering, electrochemical techniques, system optimization, and collaboration between academia, industry, and policymakers. Overcoming these hurdles will pave the way for the practical implementation of CO₂RR devices and contribute to the mitigation of carbon dioxide emissions.

In conclusion, Cu-based catalysts hold significant promise for CO₂RR, but further research is required to address challenges related to stability, precise control, and fundamental understanding. With continued efforts in these areas, Cu-based catalysts have the potential to contribute to the development of sustainable energy conversion technologies and the mitigation of carbon dioxide emissions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgement

The authors would like to acknowledge Engineering and Physical Sciences Research Council (EPSRC) (EP/V027433/3) and UK Research and Innovation (UKRI) under the UK government's Horizon Europe funding guarantee (101077226; EP/Y008707/1), and the Royal Society (IES/R2/212115; IEC/NSFC/211019; RGS/R1/211080) for funding support.

References

- [1] J. Zhu, L. Xia, R. Yu, R. Lu, J. Li, R. He, Y. Wu, W. Zhang, X. Hong, W. Chen, Y. Zhao, L. Zhou, L. Mai, Z. Wang, *J. Am. Chem. Soc.* 144 (2022), 15529.
- [2] F. Guo, T.J. Macdonald, A.J. Sobrido, L. Liu, J. Feng, G. He, *Adv. Sci.* (2023), e2301098, <https://doi.org/10.1002/advs.202301098>.
- [3] L. Lv, R. Lu, J. Zhu, R. Yu, W. Zhang, E. Cui, X. Chen, Y. Dai, L. Cui, J. Li, L. Zhou, W. Chen, Z. Wang, L. Mai, *Angew. Chem., Int. Ed. Engl.* 62 (2023), e202303117.
- [4] D.H. Nam, P. De Luna, A. Rosas-Hernandez, A. Thevenon, F. Li, T. Agapie, J. C. Peters, O. Shekhan, M. Eddaoudi, E.H. Sargent, *Nat. Mater.* 19 (2020) 266.
- [5] F. Guo, Z. Zou, Z. Zhang, T. Zeng, Y. Tan, R. Chen, W. Wu, N. Cheng, X. Sun, *J. Mater. Chem. A* 9 (2021) 5468.
- [6] J. Zhu, S. Mu, *Adv. Funct. Mater.* 30 (2020), 2001097.
- [7] A. Tripathi, R. Thapa, *Carbon* 208 (2023) 330.
- [8] K. He, Z. Mi, J. Zhang, J. Li, D. Coffman, *Environ. Sci. Technol.* 57 (2023) 4406.
- [9] M. Honegger, *Nat. Commun.* 14 (2023) 534.
- [10] A.L. Fanning, J. Hickel, *Nat. Sustain.* (2023), <https://doi.org/10.1038/s41893-023-01130-8>.
- [11] R.E. Kopp, M. Oppenheimer, J.L. O'Reilly, S.S. Drijfhout, T.L. Edwards, B. Fox-Kemper, G.G. Garner, N.R. Golleger, T.H.J. Hermans, H.T. Hewitt, B.P. Horton, G. Krinner, D. Notz, S. Nowicki, M.D. Palmer, A.B.A. Slangen, C. Xiao, *Nat. Clim. Change* (2023), <https://doi.org/10.1038/s41558-023-01691-8>.
- [12] C. Quan, Y. Zhou, J. Wang, C. Wu, N. Gao, *J. CO₂ Util.* 68 (2023), 102373.
- [13] X. He, H. He, F. Barzagli, M.W. Amer, C.e. Li, R. Zhang, *Energy* 270 (2023), 126903.
- [14] S. Ren, E.W. Lees, C. Hunt, A. Jewlall, Y. Kim, Z. Zhang, B.A.W. Mowbray, A. G. Fink, L. Melo, E.R. Grant, C.P. Berlinguette, *J. Am. Chem. Soc.* 145 (2023) 4414.

- [15] S. Cao, H. Chen, Y. Hu, J. Li, C. Yang, Z. Chen, S. Wei, S. Liu, Z. Wang, D. Sun, X. Lu, *Chem. Eng. J.* 461 (2023), 141936.
- [16] H. Chehrmonavari, A. Kakaee, S.E. Hosseini, U. Desideri, G. Tsatsaronis, G. Floerchinger, R. Braun, A. Paykani, *Renewable Sustainable Energy Rev.* 171 (2023), 112982.
- [17] M. Sun, H.H. Wong, T. Wu, Q. Lu, L. Lu, C.H. Chan, B. Chen, A.W. Dougherty, B. Huang, *Adv. Energy Mater.* 13 (2022), 2203858.
- [18] S. Cao, S. Zhou, H. Chen, S. Wei, S. Liu, X. Lin, X. Chen, Z. Wang, W. Guo, X. Lu, *Energy Environ. Mater.* 6 (2022), e12287.
- [19] Q. Zhang, P.A. Hu, Z.Y. Xu, B.B. Tang, H.R. Zhang, Y.H. Xiao, Y.C. Wu, *Nanoscale* 15 (2023) 4991.
- [20] Z. Zhang, X. Huang, Z. Chen, J. Zhu, B. Endrodi, C. Janaky, D. Deng, *Angew. Chem., Int. Ed. Engl.* (2023), e202302789, <https://doi.org/10.1002/ange.202302789>.
- [21] Q. Wan, G. Zhu, T. Li, Y. Liu, D. Ye, A. Wang, J. Hou, Y. Peng, C. Deng, X. Zhuang, J. Zhang, C. Ke, *J. Power Sources* 572 (2023), 233106.
- [22] X. Zhang, Z. Wu, X. Zhang, L. Li, Y. Li, H. Xu, X. Li, X. Yu, Z. Zhang, Y. Liang, H. Wang, *Nat. Commun.* 8 (2017), 14675.
- [23] T. Zheng, K. Jiang, N. Ta, Y. Hu, J. Zeng, J. Liu, H. Wang, *Joule* 3 (2019) 265.
- [24] A. Goyal, G. Marcandalli, V.A. Mints, M.T.M. Koper, *J. Am. Chem. Soc.* 142 (2020) 4154.
- [25] F. Guo, Z. Zhang, R. Chen, Y. Tan, W. Wu, Z. Wang, T. Zeng, W. Zhu, C. Lin, N. Cheng, *Mater. Horiz.* (2023), <https://doi.org/10.1039/D3MH00416C>.
- [26] T. Wang, L. Zhou, S. Xia, L. Yu, *J. Phys. Chem. C* 127 (2023) 2963.
- [27] X. Han, T. Zhang, M. Biset-Peiro, X. Zhang, F. Li, W. Tang, P. Tang, J.R. Morante, J. Arbiol, *ACS Appl. Mater. Interfaces* 14 (2022), 32157.
- [28] M. Ferri, L. Delafontaine, S. Guo, T. Asset, P. Cristiani, S. Campisi, A. Gervasini, P. Atanassov, *ACS Energy Lett.* 7 (2022) 2304.
- [29] L. Zhang, F. Mao, L.R. Zheng, H.F. Wang, X.H. Yang, H.G. Yang, *ACS Catal.* 8 (2018), 11035.
- [30] T. Wu, M. Sun, B. Huang, *Angew. Chem., Int. Ed. Engl.* 60 (2021), 22996.
- [31] T.S. Bui, E.C. Lovell, R. Daiyan, R. Amal, *Adv. Mater.* (2023), e2205814.
- [32] Z. Zhuang, Y. Zhang, L. Hu, H. Ying, W. Han, *Chem. Asian J.* 15 (2020) 2153.
- [33] S. Nellaippan, N.K. Katiyar, R. Kumar, A. Parui, K.D. Malviya, K.G. Pradeep, A. K. Singh, S. Sharma, C.S. Tiwary, K. Biswas, *ACS Catal.* 10 (2020) 3658.
- [34] R. Shi, J. Guo, X. Zhang, G.I.N. Waterhouse, Z. Han, Y. Zhao, L. Shang, C. Zhou, L. Jiang, T. Zhang, *Nat. Commun.* 11 (2020) 3028.
- [35] J. Fu, W. Zhu, Y. Chen, Z. Yin, Y. Li, J. Liu, H. Zhang, J.J. Zhu, S. Sun, *Angew. Chem., Int. Ed. Engl.* 58 (2019), 14100.
- [36] D. Gao, H. Zhou, F. Cai, J. Wang, G. Wang, X. Bao, *ACS Catal.* 8 (2018) 1510.
- [37] J. Wang, S. Kattel, C.J. Hawxhurst, J.H. Lee, B.M. Tackett, K. Chang, N. Rui, C. J. Liu, J.G. Chen, *Angew. Chem., Int. Ed. Engl.* 58 (2019) 6271.
- [38] Z. Jia, M. Peng, X. Cai, Y. Chen, X. Chen, F. Huang, L. Zhao, J. Diao, N. Wang, D. Xiao, X. Wen, Z. Jiang, H. Liu, D. Ma, *ACS Catal.* 12 (2022) 9602.
- [39] M. Dunwell, Y. Yan, B. Xu, *ACS Catal.* 7 (2017) 5410.
- [40] L. Xiong, X. Zhang, L. Chen, Z. Deng, S. Han, Y. Chen, J. Zhong, H. Sun, Y. Lian, B. Yang, X. Yuan, H. Yu, Y. Liu, X. Yang, J. Guo, M.H. Rummeli, Y. Jiao, Y. Peng, *Adv. Mater.* 33 (2021), e2101741.
- [41] W. Deng, L. Zhang, H. Dong, X. Chang, T. Wang, J. Gong, *Chem. Sci.* 9 (2018) 6599.
- [42] W. Ni, Z. Liu, Y. Zhang, C. Ma, H. Deng, S. Zhang, S. Wang, *Adv. Mater.* 33 (2021), e2003238.
- [43] W. Ren, X. Tan, W. Yang, C. Jia, S. Xu, K. Wang, S.C. Smith, C. Zhao, *Angew. Chem., Int. Ed. Engl.* 58 (2019) 6972.
- [44] C. He, Y. Zhang, Y. Zhang, L. Zhao, L.P. Yuan, J. Zhang, J. Ma, J.S. Hu, *Angew. Chem., Int. Ed. Engl.* 59 (2020) 4914.
- [45] F. Pan, H. Zhang, K. Liu, D. Cullen, K. More, M. Wang, Z. Feng, G. Wang, G. Wu, Y. Li, *ACS Catal.* 8 (2018) 3116.
- [46] T. Tsujiguchi, Y. Kawabe, S. Jeong, T. Ohto, S. Kukunuri, H. Kuramochi, Y. Takahashi, T. Nishiuchi, H. Masuda, M. Wakisaka, K. Hu, G. Elumalai, J.-i. Fujita, Y. Ito, *ACS Catal.* 11 (2021) 3310.
- [47] J. Jiang, B. Huang, R. Daiyan, B. Subhash, C. Tsounis, Z. Ma, C. Han, Y. Zhao, L. H. Effendi, L.C. Gallington, J.N. Hart, J.A. Scott, N.M. Bedford, *Nano Energy* 101 (2022), 107593.
- [48] L. Ma, N. Liu, B. Mei, K. Yang, B. Liu, K. Deng, Y. Zhang, H. Feng, D. Liu, J. Duan, Z. Jiang, H. Yang, Q. Li, *ACS Catal.* 12 (2022) 8601.
- [49] W. Ma, S. Xie, X.G. Zhang, F. Sun, J. Kang, Z. Jiang, Q. Zhang, D.Y. Wu, Y. Wang, *Nat. Commun.* 10 (2019) 892.
- [50] C. Kim, F. Dionigi, V. Beermann, X. Wang, T. Moller, P. Strasser, *Adv. Mater.* 31 (2019), e1805617.
- [51] W. Yu, L. Wen, J. Gao, S. Chen, Z. He, D. Wang, Y. Shen, S. Song, *Chem. Commun.* 57 (2021) 7418.
- [52] Y. Yang, S. Louisia, S. Yu, J. Jin, I. Roh, C. Chen, M.V. Fonseca Guzman, J. Feijoo, P.C. Chen, H. Wang, C.J. Pollock, X. Huang, Y.T. Shao, C. Wang, D.A. Muller, H. D. Abruna, P. Yang, *Nature* 614 (2023) 262.
- [53] W. Ma, X. He, W. Wang, S. Xie, Q. Zhang, Y. Wang, *Chem. Soc. Rev.* 50 (2021), 12897.
- [54] J. Hao, Z. Zhuang, J. Hao, C. Wang, S. Lu, F. Duan, F. Xu, M. Du, H. Zhu, *Adv. Energy Mater.* 12 (2022), 2200579.
- [55] F. Zhang, P. Wang, R. Zhao, Y. Wang, J. Wang, B. Han, Z. Liu, *ChemSusChem* 15 (2022), e202201267.
- [56] Y.N. Xu, W. Li, H.Q. Fu, X.Y. Zhang, J.Y. Zhao, X. Wu, H.Y. Yuan, M. Zhu, S. Dai, P.F. Liu, H.G. Yang, *Angew. Chem., Int. Ed. Engl.* 62 (2023), e202217296.
- [57] T. Yan, P. Wang, W.Y. Sun, *Small* 19 (2023), e2206070.

- [58] L.L. Zhuo, P. Chen, K. Zheng, X.W. Zhang, J.X. Wu, D.Y. Lin, S.Y. Liu, Z.S. Wang, J.Y. Liu, D.D. Zhou, J.P. Zhang, *Angew. Chem., Int. Ed. Engl.* 61 (2022), e202204967.
- [59] D.H. Nam, O. Shekhah, A. Ozden, C. McCallum, F. Li, X. Wang, Y. Lum, T. Lee, J. Li, J. Wicks, A. Johnston, D. Sinton, M. Eddaoudi, E.H. Sargent, *Adv. Mater.* 34 (2022), e2207088.
- [60] M. Li, N. Song, W. Luo, J. Chen, W. Jiang, J. Yang, *Adv. Sci.* 10 (2023), e2204579.
- [61] C. Liu, M. Zhang, J. Li, W. Xue, T. Zheng, C. Xia, J. Zeng, *Angew. Chem., Int. Ed. Engl.* 61 (2022), e202113498.
- [62] T. Tang, Z. Wang, J. Guan, *Adv. Funct. Mater.* 32 (2022), 2111504.
- [63] P. Prabhu, J.-M. Lee, *Chem Catal.* (2023) 3.
- [64] R. Sun, C. Wei, Z. Huang, S. Niu, X. Han, C. Chen, H. Wang, J. Song, J.-D. Yi, G. Wu, D. Rao, X. Zheng, Y. Wu, G. Wang, X. Hong, *Nano Res.* 16 (2022) 4698.
- [65] X. Ma, Y. Zhang, T. Fan, D. Wei, Z. Huang, Z. Zhang, Z. Zhang, Y. Dong, Q. Hong, Z. Chen, X. Yi, *Adv. Funct. Mater.* 33 (2023), 2213145.
- [66] Q. Wu, R. Du, P. Wang, G.I.N. Waterhouse, J. Li, Y. Qiu, K. Yan, Y. Zhao, W.-W. Zhao, H.-J. Tsai, M.-C. Chen, S.-F. Hung, X. Wang, G. Chen, *ACS Nano* (2023), <https://doi.org/10.1021/acsnano.3c04951>.
- [67] Z. Wei, J. Ding, X. Duan, G.-L. Chen, F.-Y. Wu, L. Zhang, X. Yang, Q. Zhang, Q. He, Z. Chen, J. Huang, S.-F. Hung, X. Yang, Y. Zhai, *ACS Catal.* 13 (2023) 4711.
- [68] J. Li, K. Xu, F. Liu, Y. Li, Y. Hu, X. Chen, H. Wang, W. Xu, Y. Ni, G. Ding, T. Zhao, M. Yu, W. Xie, F. Cheng, *Adv. Mater.* (2023), e2301127, <https://doi.org/10.1002/adma.202301127>.
- [69] T. Zhao, J. Li, J. Liu, F. Liu, K. Xu, M. Yu, W. Xu, F. Cheng, *ACS Catal.* 13 (2023) 4444.
- [70] J. Wang, H.Y. Tan, Y. Zhu, H. Chu, H.M. Chen, *Angew. Chem., Int. Ed. Engl.* 60 (2021), 17254.
- [71] L. Li, S. Wang, C. Wan, C. Xu, M. Zuo, Y. Sun, Y. Xie, *Energy* 1 (2023), 100027.
- [72] H. Li, S. Cao, H. Sun, Y. Lu, Y. Zhang, X. Lu, J. Zeng, Z. Yan, *Appl. Catal., B* 320 (2023), 121948.
- [73] H. Xiong, J. Li, D. Wu, B. Xu, Q. Lu, *Chem. Commun.* 59 (2023) 5615.
- [74] Y.Y. Birdja, E. Pérez-Gallent, M.C. Figueiredo, A.J. Göttle, F. Calle-Vallejo, M.T. M. Koper, *Nat. Energy* 4 (2019) 732.
- [75] M. Jun, D. Kim, M. Kim, M. Kim, T. Kwon, K. Lee, *ACS Omega* 7 (2022), 42655.
- [76] J. Qiao, Y. Liu, F. Hong, J. Zhang, *Chem. Soc. Rev.* 43 (2014) 631.
- [77] Z. Zhang, L. Melo, R.P. Jansonius, F. Habibzadeh, E.R. Grant, C.P. Berlinguette, *ACS Energy Lett.* 5 (2020) 3101.
- [78] F. Zhang, A.C. Co, *Angew. Chem., Int. Ed. Engl.* 59 (2020) 1674.
- [79] T.K. Todorova, M.W. Schreiber, M. Fontecave, *ACS Catal.* 10 (2019) 1754.
- [80] D. Ren, J. Fong, B.S. Yeo, *Nat. Commun.* 9 (2018) 925.
- [81] Q. Lei, L. Huang, J. Yin, B. Davaasuren, Y. Yuan, X. Dong, Z.P. Wu, X. Wang, K. X. Yao, X. Lu, Y. Han, *Nat. Commun.* 13 (2022) 4857.
- [82] T. Zheng, C. Liu, C. Guo, M. Zhang, X. Li, Q. Jiang, W. Xue, H. Li, A. Li, C.W. Pao, J. Xiao, C. Xia, J. Zeng, *Nat. Nanotechnol.* 16 (2021) 1386.
- [83] S. Mu, H. Lu, Q. Wu, L. Li, R. Zhao, C. Long, C. Cui, *Nat. Commun.* 13 (2022) 3694.
- [84] X. Wang, Q. Hu, G. Li, H. Yang, C. He, *Electrochem. Energy Rev.* 5 (2022), <https://doi.org/10.1007/s41918>.
- [85] H. Sun, L. Chen, L. Xiong, K. Feng, Y. Chen, X. Zhang, X. Yuan, B. Yang, Z. Deng, Y. Liu, M.H. Rummeli, J. Zhong, Y. Jiao, Y. Peng, *Nat. Commun.* 12 (2021) 6823.
- [86] P. Grosse, D. Gao, F. Scholten, I. Sinev, H. Mistry, B. Roldan Cuenya, *Angew. Chem., Int. Ed. Engl.* 57 (2018) 6192.
- [87] H. Xie, T. Wang, J. Liang, Q. Li, S. Sun, *Nano Today* 21 (2018) 41.
- [88] G.M. Tomboc, S. Choi, T. Kwon, Y.J. Hwang, K. Lee, *Adv. Mater.* 32 (2020), e1908398.
- [89] S. Li, A.V. Nagarajan, X. Du, Y. Li, Z. Liu, D.R. Kauffman, G. Mpourmpakis, R. Jin, *Angew. Chem., Int. Ed. Engl.* 61 (2022), e202211771.
- [90] W. Rong, H. Zou, W. Zang, S. Xi, S. Wei, B. Long, J. Hu, Y. Ji, L. Duan, *Angew. Chem., Int. Ed. Engl.* 60 (2021) 466.
- [91] T. Wu, M.Y. Han, Z.J. Xu, *ACS Nano* 16 (2022) 8531.
- [92] V. Indira, K. Abhitha, *Results Eng* 17 (2023), 100886.
- [93] C. Xiao, J. Zhang, *ACS Nano* 15 (2021) 7975.
- [94] R. Reske, H. Mistry, F. Behafarid, B. Roldan Cuenya, P. Strasser, *J. Am. Chem. Soc.* 136 (2014) 6978.
- [95] F. Calle-Vallejo, M.T. Koper, *Angew. Chem., Int. Ed. Engl.* 52 (2013) 7423.
- [96] S. Kuang, M. Li, X. Chen, H. Chi, J. Lin, Z. Hu, S. Hu, S. Zhang, X. Ma, *Chin. Chem. Lett.* 34 (2023), 108013.
- [97] P. Iyengar, M.J. Kolb, J.R. Pankhurst, F. Calle-Vallejo, R. Buonsanti, *ACS Catal.* 11 (2021) 4456.
- [98] N. Zhang, X. Zhang, Y. Kang, C. Ye, R. Jin, H. Yan, R. Lin, J. Yang, Q. Xu, Y. Wang, Q. Zhang, L. Gu, L. Liu, W. Song, J. Liu, D. Wang, Y. Li, *Angew. Chem., Int. Ed. Engl.* 60 (2021), 13388.
- [99] F. Wang, H. Xie, T. Liu, Y. Wu, B. Chen, *Appl. Energy* 269 (2020), 115029.
- [100] Y. Yan, Z. Zhao, J. Zhao, W. Tang, W. Huang, J.-M. Lee, *J. Mater. Chem. A* 9 (2021) 7496.
- [101] J. Zhu, M. Xiao, D. Ren, R. Gao, X. Liu, Z. Zhang, D. Luo, W. Xing, D. Su, A. Yu, Z. Chen, *J. Am. Chem. Soc.* 144 (2022) 9661.
- [102] D. Wei, Y. Wang, C.L. Dong, Z. Zhang, X. Wang, Y.C. Huang, Y. Shi, X. Zhao, J. Wang, R. Long, Y. Xiong, F. Dong, M. Li, S. Shen, *Angew. Chem., Int. Ed. Engl.* 62 (2023), e202217369.
- [103] Y. Yan, Z. Zhao, J. Zhao, Y. Xu, Y. Xu, Y. Zhao, W. Tang, J.-M. Lee, *ACS Mater. Lett.* 3 (2021) 1143.
- [104] X. Tan, K. Sun, Z. Zhuang, B. Hu, Y. Zhang, Q. Liu, C. He, Z. Xu, C. Chen, H. Xiao, C. Chen, *J. Am. Chem. Soc.* 145 (2023) 8656.
- [105] C. Choi, J. Cai, C. Lee, H.M. Lee, M. Xu, Y. Huang, *Nano Res.* 14 (2021) 3497.
- [106] X.-Q. Li, G.-Y. Duan, J.-W. Chen, L.-J. Han, S.-J. Zhang, B.-H. Xu, *Appl. Catal., B* (2021) 297.
- [107] S. Banerjee, C.S. Gerke, V.S. Thoi, *Acc. Chem. Res.* 55 (2022) 504.
- [108] J.X. Wu, S.Z. Hou, X.D. Zhang, M. Xu, H.F. Yang, P.S. Cao, Z.Y. Gu, *Chem. Sci.* 10 (2019) 2199.
- [109] A.R. Woldu, Z. Huang, P. Zhao, L. Hu, D. Astruc, *Coord. Chem. Rev.* 454 (2022), 214340.
- [110] R. Du, Q. Wu, S. Zhang, P. Wang, Z. Li, Y. Qiu, K. Yan, G.I.N. Waterhouse, P. Wang, J. Li, Y. Zhao, W.W. Zhao, X. Wang, G. Chen, *Small* (2023), e2301289, <https://doi.org/10.1002/smll.202301289>.
- [111] Y. Xia, Q. Zhang, F. Guo, J. Wang, W. Li, J. Xu, *Vacuum* 196 (2022), 110767.
- [112] D. Zang, Q. Li, G. Dai, M. Zeng, Y. Huang, Y. Wei, *Appl. Catal., B* 281 (2021), 119426.
- [113] X. Wei, Z. Yin, K. Lyu, Z. Li, J. Gong, G. Wang, L. Xiao, J. Lu, L. Zhuang, *ACS Catal.* 10 (2020) 4103.