

Potential Link between Cu Surface and Selective CO₂ Electroreduction: Perspective on Future Electrocatalyst Designs

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Electrochemical reduction of carbon dioxide (CO₂RR) product distribution has been identified to be dependent on various surface factors, including the Cu facet, morphology, chemical states, doping, etc., which can alter the binding strength of key intermediates such as *CO and *OCCO during reduction. Therefore, in-depth knowledge of the Cu catalyst surface and identification of the active species under reaction conditions aid in designing efficient Cu-based electrocatalysts. This progress report categorizes various Cu-based electrocatalysts into four main groups, namely metallic Cu, Cu alloys, Cu compounds (Cu + non-metal), and supported Cu-based catalysts (Cu supported by carbon, metal oxides, or polymers). The detailed mechanisms for the selective CO₂RR are presented, followed by recent relevant developments on the synthetic procedures for preparing Cu and Cu-based nanoparticles. Herein, the potential link between the Cu surface and CO₂RR performance is highlighted, especially in terms of the chemical states, but other significant factors such as defective sites and roughened morphology of catalysts are equally considered during the discussion of current studies of CO₂RR with Cu-based electrocatalysts to fully understand the origin of the significant enhancement toward C₂ formation. This report concludes by providing suggestions for future designs of highly selective and stable Cu-based electrocatalysts for CO₂RR.

1. Introduction

By the end of this century, the CO₂ concentration in the atmosphere is projected to be three times higher than its record of 270 ppm in the early 1800s, which will be much higher than

the assigned safety limit of 350 ppm.^[1] To help reduce the amount of CO₂ emitted in the atmosphere, extensive research has been carried out on technologies such as carbon capture and sequestration (CCS),^[2] in which CO₂ is stored in cavities under the sea and land, and carbon capture and utilization (CCU),^[3] where CO₂ is used as a valuable carbon source for a variety of chemicals. However, the generation of products from CO₂ as a carbon source is difficult because CO₂ is a thermodynamically stable molecule, which is produced as the result of combustion of various carbon chemicals.^[4] Therefore, the chemical activation or reduction of CO₂ to carbon monoxide or to hydrocarbons requires a large amount of energy input in order to overcome the energy barriers. Electrochemical reduction of CO₂ (CO₂RR) can potentially produce an extensive selection of reduced carbon compounds, containing C–C, C–O, and C–H bonds.^[5] Unfortunately, practical application of CO₂RR has yet to be realized owing to major technological challenges, such as low catalytic activity, poor product selectivity, highly unstable catalyst

structures, and sub-optimal electrode and system designs.^[6] In addition, CO₂RR faces great challenges in both thermodynamic and kinetic terms because the single electron reduction of CO₂ to CO₂^{•−} requires high overpotential, $E = -1.90$ V (vs SHE in water) due to the restructuring of energy between the excessively stable linear molecule and the bent radical anion and also due to the difficulty in assembling the nuclei and forming chemical bonds for the final products.^[7] Furthermore, CO₂RR competes with hydrogen evolution reaction (HER) in an aqueous media, where H₂ formation overpowers CO₂ reduction at low overpotentials.^[8] In order to tackle all these technical problems, it is absolutely necessary to develop electrocatalysts that achieve the maximum CO₂RR activity and selectivity.

Thus far, copper has been the leading metal electrocatalyst toward the electroreduction of CO₂ to highly valued hydrocarbon, fuel, and alcohol products, especially for multi-carbon chemicals.^[9] Various Cu-based electrocatalysts have been developed and can be categorized further as follows: metallic Cu, Cu alloy, Cu compound (Cu + non-metal), and supported Cu-based catalyst (Cu supported by carbon, metal oxides, or polymers).^[10,11] Although there have been momentous

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improvements in the overall performance in CO₂RR, CO₂RR with a Cu-based electrocatalyst is still not a selective process that yields a wide selection of products such as carbon monoxide, formic acid, methane, and ethylene.^[11] Multiple factors such as physicochemical properties (i.e., particle size, morphology, crystal facet, etc.), changes of surface states (Cu⁰, Cu⁺, Cu²⁺), surface defects including phase changes, lattice distortion, grain boundaries, and oxygen or copper vacancies, and even the preparation method used to induce the mentioned factors have been reported to be responsible to modify the catalytic activities of Cu-based electrocatalysts.^[13–17] Furthermore, owing to potential synergistic effects among various structural factors, it is difficult to understand the origin of product selectivity control in CO₂RR on Cu-based electrocatalysts.

A momentous breakthrough in understanding the catalytic activity has been proposed by some theoretical studies of Cu-based electrocatalysts toward CO₂RR. For instance, the structural and oxidation states of the Cu surface could determine the identity of carbon products.^[18–20] Therefore, this progress report intends to provide the potential link between Cu surface and CO₂RR performance. We will investigate the detailed mechanisms for the selective electrochemical reduction of CO₂ on various nanostructured Cu electrodes. Recently developed relevant synthetic procedures for the preparation of Cu and Cu-based NPs will be discussed, and current studies of various Cu-based electrocatalysts in CO₂RR will then be summarized. We believe that highlighting the specific functions of Cu surface during the catalysis reaction will help the future designs of selective and highly stable electrocatalysts toward CO₂RR.

2. Mechanism on CO₂RR on Cu Catalysts

2.1. Brief Introduction of the Overall CO₂RR Mechanism

Understanding the overall CO₂RR mechanism is a challenging topic, owing to the complicated combination of CO₂ and water molecules, which occurs via multiple reaction steps. The selectivity and preferable reaction pathways are reported to be highly dependent on the composition of electrocatalysts and the surrounding conditions, such as pH of the electrolyte and the operating potential. CO₂ can be reduced through two, four, six, eight, or twelve electron pathways, producing chemicals such as formate (HCOO[−]), carbon monoxide (CO), methane (CH₄), ethylene (C₂H₄), methanol (CH₃OH), and ethanol (C₂H₅OH) in meaningful quantities. Despite the variety of the products, CO₂ reduction is commonly initiated by one-electron injection to the CO₂ reactant to form CO₂^{•−}, which typically requires a high overpotential, and its adsorbed species or coordination on the catalyst surface determines the reaction pathways.^[14] Anion radical CO₂^{•−} is very unstable ($E = -1.90$ V vs SHE),^[15] so it is readily protonated or stabilized by adsorption on catalytic active sites for further reduction to products. It can also react with other species, including another CO₂ molecule or surface-adsorbed intermediates. There are three major steps involved for the heterogeneous catalysis process in CO or formate production: 1) chemical adsorption of CO₂ on an electrocatalyst; 2) electron and/or proton transfer, to cleave C–O bonds for



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generating CO or to form C–H for forming formate; and 3) rearrangement of configuration to desorb final products from the electrocatalyst surface and diffuse into the electrolyte.^[16]

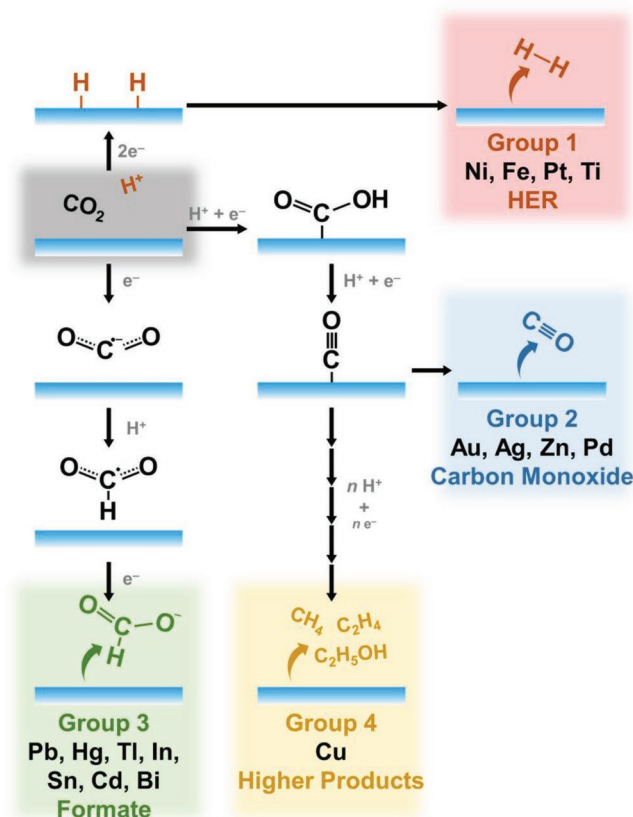


Figure 1. Overall reaction mechanism of electrochemical CO₂ reduction reaction and HER on metal electrodes in aqueous solutions.

However, in the case of hydrocarbon or alcohol production on Cu catalysts, clearly defining each process is a complex task; hence, the mechanisms of C₂ formation will be separately discussed in Section 2.2.

At present, transition-metal elements and their corresponding compounds, such as metal complexes, are being extensively investigated as homogenous electrocatalysts. These metals have available orbitals and active *d* electrons that are assumed to energetically accelerate the formation of the bond between the metal and the intermediates via *C or *O. As shown in Figure 1, these metal elements have been categorized into four main groups depending on their tendency to bind the CO₂⁻ intermediate on their surface, which is either adsorbed as *OCHO or *COOH. While Group 1, which includes Ni, Fe, Pt, and Ti metals, is less active for CO₂ reduction but dominantly favors H₂ formation, the other groups, including Groups 2–4 can generate various products from CO₂ reduction. Group 2, including Au, Ag, Zn, and Pd metals, can reduce the *COOH intermediate to carbon monoxide, but they cannot further reduce the CO intermediate owing to their weak tendency of CO binding to metals surfaces.^[17] Group 3 metals, including Pb, Hg, Tl, In, Sn, Cd, and Bi, can generate formate or formic acid, wherein the CO₂⁻ intermediate is weakly stabilized by *OCHO or *COOH.^[18,19] Because HCOO⁻ formation typically proceeds at −1.5 V or more negative biased potential, free or weakly adsorbed intermediates have been proposed.^[14,20,21] Finally, Group 4, namely,

the prominent Cu metal, can produce CO, formate, various hydrocarbons, and alcohol products through further reduction of the *CO intermediate. The production of C₂⁺ products as building-block chemicals, including ethylene and isopropanol, is challenging but highly desirable owing to the higher energy density and wide applicability.^[22]

2.2. Mechanism of C–C Bond Formation for C₂ Products

The formation of C₂ products such as ethylene and ethanol from the electrochemical reduction of CO₂ with a Cu-based electrocatalyst is a difficult and complicated reaction owing to the competing formation of C–C, C–H, and C–O bonds during CO₂RR. Moreover, the formation of hydrocarbons and alcohols require a greater number of electrons compared to generation of formate, CO, or C₁ products. To design optimal Cu-based electrocatalysts, which will favor the formation of C₂⁺ compounds over C₁ chemicals, understanding the mechanisms of C–C bond formation and modulating the reduction pathway from a key intermediate CO are vital. Here, we focus on the formation pathways to C₂ products of ethylene and ethanol, which are considered to have shared reaction mechanisms.

2.2.1. Ethylene Pathway

Thus far, although C–C coupling has been proposed as the rate-determining step for C₂ products from CO₂RR over Cu catalysts, the representative mechanisms of C–C coupling are still being debated.^[23] While earlier studies proposed that direct coupling of two carbenes (*CH₂) can form C₂H₄,^[24] recent studies attribute the formation of C₂ products more to CO dimerization. Hori et al. also reported the pH independence of C₂H₄ formation,^[25] which differs from the CH₄ formation that depends on the pH value of the electrolyte. This indicates that CH₄ formation and C₂H₄ formation have separate rate-limiting steps and reaction pathways, and thus, the product selectivity between them can be controlled. Proton transfer to *CO is proposed to be involved at the rate-limiting step owing to the pH-dependent activity for CH₄ production, while the pH-independent activity for C₂H₄ indicates that C–C coupling with electron transfer, but decoupled from proton transfer, would determine the activity. Even in the case of the CO dimerization decoupled from proton transfer, there are still debates on whether electron transfer participates in CO coupling or not and on whether the coupling involves two adsorbed *CO species or an adsorbed *CO and a free CO species. Depending on the Cu facets, Koper et al. proposed two different reaction mechanisms for the formation of C₂H₄, based on the experimental works of CO electroreduction.^[26] One pathway has a shared intermediate with the formation of CH₄, which takes place both on Cu (111) and Cu (100) surfaces, while the other pathway involves the formation of a surface-adsorbed CO dimer as the key intermediate to C₂H₄ on the Cu (100) surface, which is the dominant facet for C₂H₄ production. Later, Koper et al. demonstrated that the formation of a negatively charged CO dimer is the most stable on square arrangements

of $*C_2O_2^-$ atoms, showing the observed preferential formation of C_2H_4 on Cu(100) terraces at low potentials, through DFT calculations.^[27]

In addition to experimental studies, other theoretical studies have supported that the CO dimerization pathway is the limiting step for ethylene production.^[28] In CO dimerization, $*CO + *CO$ (or CO_g) (Figure 2a), $*C_2O_2^-$ is generated, which is an intermediate that can exist in either one of two ways: 1) carbon and oxygen atoms from $*C_2O_2^-$ intermediate are bound to the copper surface in a bridging mode (Figure 2b), or 2) the $*C_2O_2^-$ intermediate is bound to the surface by two carbon atoms (Figure 2c). Either way proceeds to further protonation of the $*C_2O_2^-$ intermediate, until the relatively stable intermediates $*CO-COH$ (Figure 2d) or $*COCHO$ are formed.^[29] On the other hand, Goodpaster et al. considered the effect of the applied potential and electrolyte condition, and suggested that C–C bond formation pathways can be different depending on the applied potential.^[30] They proposed that at low overpotential, C–C bond formation occurs via a reaction of two surface-bound $*CO$, while at higher overpotential, the reaction of $*CO$ and $*CHO$ (Figure 2e,f) is preferable because of a large activation barrier to the formation of a CO dimer. Recent studies have presented that further reduction of CO to form $*CHO$ (Figure 2e), followed by the reaction with $*CO$ to form $*COCHO$ (Figure 2g), was more favored over $*CO$ dimerization and subsequent reduction.^[30,31] Although the structures of $*COCO$ H and $*COCHO$ are tautomeric, based on the calculation, the $*COCHO$ structure is preferred more since it does not involve a double bond to the surface or a free radical on the C atom. The $*COCHO$ intermediate is further reduced to $*COCH_2OH$, and then, electron transfer or proton migration can occur to generate the C_2H_4 product.

2.2.2. Ethanol Pathway

Ethanol production is proposed to share the pathways and intermediates with ethylene production; hence, the C–C coupling activity is considered to be important for ethanol production, as well as for other C_{2+} products. However, research is still at too early stages to fully explain the reaction pathways as well as the active descriptors for ethylene and ethanol production. Garaza et al. proposed that $*COCHO$ (Figure 2g) is the key to determining the selectivity on the Cu surface between two major C_2 products, ethylene and ethanol.^[31] The $*COCHO$ intermediate can be reduced to glyoxal ($C_2H_2O_2$) (Figure 2h), and then further reduced to acetaldehyde and ethanol at low and high potentials, respectively. Because most of the glyoxal produced does not leave the surface during the chemical reaction, consumption of glyoxal is thermodynamically favorable. Both oxygen bonds of the *cis*-glyoxal (Figure 2h) form bonds with the surface, leading to stable states, while the carbon atoms in glyoxal form C=C double bonds. The glyoxal is reduced to glycoaldehyde ($C_2H_4O_2$) (Figure 2i), and further to ethylene glycol ($C_2H_6O_2$) or vinyl alcohol (C_2H_4O , which is formed as $CH_2=CHOH$) (Figure 2j) or acetaldehyde (C_2H_4O , which is formed as CH_3COH).^[31,32] However, a related experimental research showed that, while vinyl alcohol and acetaldehyde can be reduced to ethanol on Cu surfaces, ethylene glycol cannot be reduced under the same condition.^[33] Ethylene glycol is not reduced to ethanol because the –OH groups are repelled by the surface, whereas sp^2 hybridized oxygen atoms (=O) exhibit substantial binding with copper. Thus, ethylene glycol is left and not re-adsorbed on the surfaces. Meanwhile, vinyl alcohol is further reduced to ethanol, and acetaldehyde is also considered as a precursor of the ethanol product.

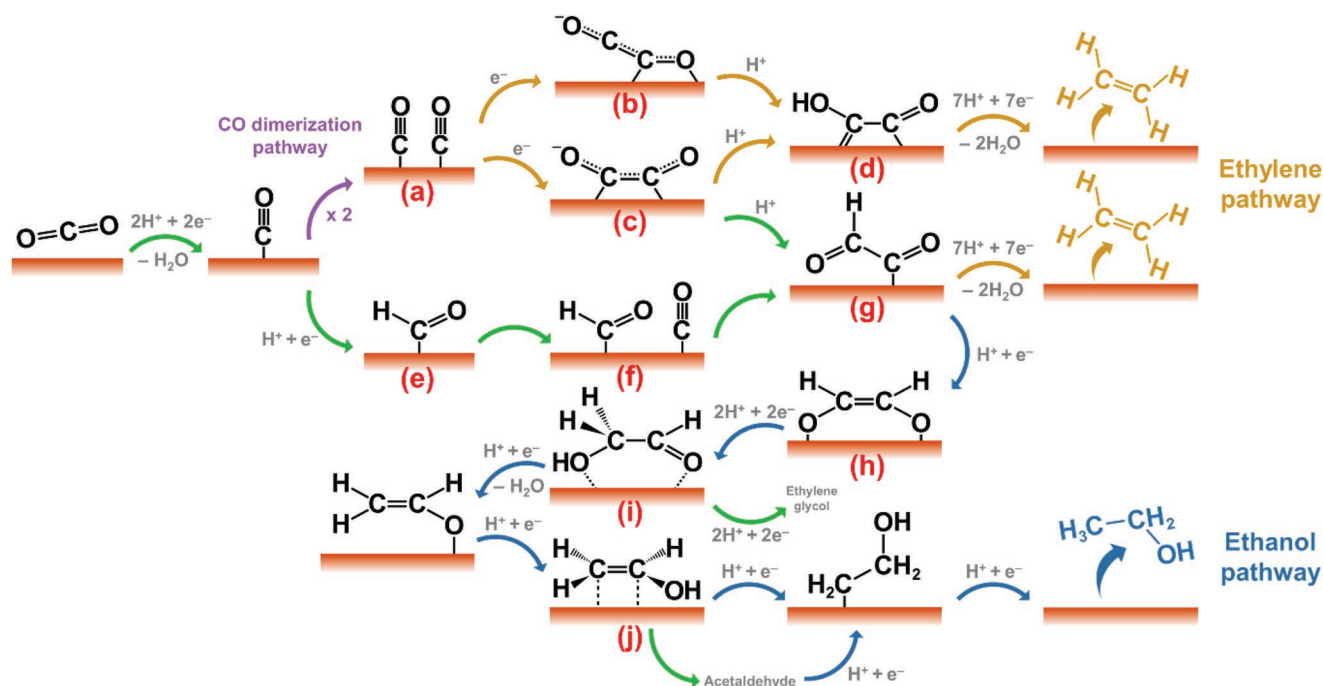


Figure 2. Brief pathways to ethylene and ethanol formation. The brown and blue arrows indicate ethylene pathways^[29] and ethanol pathways,^[31] respectively. The green arrows indicate intermediates of the reaction. Reproduced with permission.^[29,31] Copyright 2019 and 2018, American Chemical Society, respectively.

2.3. Factors Affecting Catalytic Activity/Selectivity of Cu-Based Catalyst

Although some major pathways of CO₂RR to various C₂ products have been deciphered, the overall mechanism is still highly influenced by numerous factors, including the operating conditions (electrolyte pH, cation/anion of electrolyte, and applied overpotential) and properties of the catalyst surface (surface adsorbates, facets, defects, structure, and morphology).^[31] These physical and/or chemical factors significantly affect the thermodynamic adsorption energies of the key intermediates and kinetic barriers of the reactions, leading to alternate reaction pathways. In this section, we will discuss the different factors that influence the mechanism of C₁/C₂ products.

2.3.1. pH Effect

Figure 2 presents the different reaction pathways for the formation of C₂ products, wherein it can be seen that the protonation process involves multiple elemental reduction steps and depends on the products as the numbers of the involved protons vary. Unlike simple H₂O splitting, in which the reduction product is mainly hydrogen, CO₂ reduction, coupled with H₂O, produces various chemicals and involves diverse competitive reaction pathways, as mentioned earlier. Therefore, the proton-transfer ability can affect the relative kinetics of each pathway differently and can affect the product distribution in CO₂RR. Therefore, the effect of the electrolyte conditions, which can change the pH near the catalyst electrode surface, has been methodically investigated in order to control the product distribution, especially toward the suppression of HER and control of the C₁/C₂ product ratio.

In particular, owing to the unbalance between the consumption and supply rate of protons near the electrode surface, the local pH can be different from the bulk pH of the electrolyte. The local pH gradient near the electrode surface can vary in CO₂RR depending on the operation conditions, such as current density, pH of the bulk electrolyte, types of cations or anions, and concentration of the salt in the electrolyte. In addition, the morphology and porosity of the catalyst are also important since the diffusion property is affected by them. For example, under the condition of high current density or porous structure, in which supply of the proton sources can be depleted due to slow mass transfer compared to its fast consumption, the pH gradient can be increased locally near the electrode/electrolyte interface. Understanding the local pH variations in CO₂RR becomes an important factor since it could determine the electrochemical step occurring at the electrode/electrolyte interface and the stability of the reaction intermediates.^[23] Therefore, the use of the suitable electrolytes at the right pH values is critical for determining the operation conditions of effective CO₂RR.

Recently, Wang et al. revealed the role of pH through the comparison of CO₂RR and CO reduction reaction (COR) on planar polycrystalline Cu in an alkaline condition.^[34] They demonstrated that, on the standard hydrogen electrode (SHE) scale, the overpotentials for C₂₊ products in COR are similar to that of CO₂RR, indicating that the rate-determining step

for C₂₊ formation is pH-independent of an absolute potential scale. In contrast, the C₁ product overpotential, which includes CH₄, shows a pH dependence on the SHE scales, leading to a much smaller shift on the RHE scale, compared to C₂₊ products overpotentials. It was concluded that both field stabilization of a rate-limiting chemical reaction (i.e., CO dimerization) or proton–electron transfer from water during the rate-limiting step are plausible explanations for the pH independence of the C₂₊ pathway on the SHE scales.

Furthermore, by considering the kinetic barriers and solvent effects, DFT calculations showed that the C₁ and C₂ pathways on Cu (111) are competitive and the products can be related to the operating pH condition. Xiao et al. presented the atomistic mechanisms underlying CO₂RR on Cu (111): at low local pH, while C₂ (C₃) pathways are kinetically blocked, the C₁ pathway proceeds through *COH intermediate to form CH₄; at neutral pH, the C₁ and C₂ (C₃) pathways share the common intermediate *COH, where the branch to C–C coupling is realized by a CO–COH pathway; and at high pH, early C–C coupling pathways through adsorbed CO dimerization are dominant by kinetically suppressing the C₁ pathways, thereby accelerating selectivity for the C₂₊ products.^[35] Thus, alkaline conditions can be used to increase the energy efficiency of CO and CO₂ reduction to C–C coupled products, when these cathode reactions are coupled to the oxygen evolution reaction at the anode.

2.3.2. Overpotential

In addition to the local pH in electrolytes, the C₁/C₂ pathways can also be affected by the different ranges of the applied overpotentials.^[23,32] DFT calculations show that the preferable pathways to form C–C coupling vary with the applied overpotential.^[36,37] At high overpotentials, the coupling of *CO–COH is dominant, while at low overpotentials, the *CO–CO dimerization pathway is found to be energetically favorable. This can be supported by the experimental observation of the potential dependence of C₂H₄, C₂H₅OH, and CH₄ selectivity on the Cu surfaces. For example, between the potentials of –0.6 and –0.8 V, adsorption of *H and adsorption of *CO compete for surface sites, which decreases the total CO surface coverage and slows down CO dimerization, thus preventing the formation of C₂H₄.^[37] However, when the potential is more positive than –0.6 V, the C–C coupling through *CO–CO, protonation to *CO–COH, and formation of C₂H₄ are favored over CH₄ formation, owing to the lower energy barrier for CO dimerization ($\Delta G^\ddagger = 0.69$ eV). Thus, the C₂H₄ product is generally formed at a higher potential (from –0.9 to 1.35 V).

Moreover, Ren et al. showed the effects of potential on the selectivity of Cu through Cu-based films. At potentials more positive than –0.7 V, CO and HCOO[–] were significantly formed. From –0.8 to –1.1 V, C₂H₄ and C₂H₅OH were produced in great quantities by all the CuO catalysts. As the overpotential was more negative than –1.1 V, CH₄ was selectively produced. The total current density exceeded the limiting current density of –40 mA cm^{–2} after the potential was more negative than –1.1 V, which caused a significant decrease in the CO₂ concentration near the electrode.^[38]

Furthermore, the activity and selectivity of Cu-based catalysts toward the formation of multiple hydrocarbons are also affected by factors like facet dependency, chemical states, and large surface area from defective sites such as the grain boundary and vacancy from low-coordinated sites of catalysts. Based on the studies, mentioned above, on the mechanism of C₂ products, the surface of catalytic sites should be able to pile up large amounts of *CO intermediates to achieve a sufficient surface coverage for further C-C formation or further reduction of CO to *CHO.

2.3.3. Facet Dependency

A number of studies have demonstrated the strong facet-dependent product selectivity of CO₂RR, and the ratio of hydrocarbons (CH₄ or C₂H₄) varies according to the crystal facets of Cu.^[39] It has been confirmed that Cu (100) increases the selectivity for ethylene while Cu (111) favors methane as the main hydrocarbon product, and the activity of C–C coupling on Cu (100) is relatively high compared to Cu (111).^[40] A single crystalline Cu (100) surface showed higher activity for ethylene production, and nanostructured Cu catalysts that have higher exposure of Cu (100) facets showed improved selectivity for C₂ production compared to the bulk polycrystalline Cu surface.^[26,40] Luo et al. conducted density functional theory (DFT) calculations and reported that Cu (111) favors the formation of COH* intermediate, through which methane is produced via a common CH₂ species under high overpotential (<−0.8 V vs RHE).^[36] In addition, under relatively low overpotentials (−0.4 to −0.6 V vs RHE), Cu (100) favors C–C coupling via a series of reduction steps of the C₂ species. Moreover, Kim et al. presented a study via in situ electrochemical scanning tunneling microscopy (EC-STM) wherein they correlated the importance of the crystal facet to the observed structure of the polycrystalline Cu electrode during CO₂RR; polycrystalline Cu experienced stepwise surface reconstruction from Cu(111) to Cu(100).^[41] Meanwhile, Mangione et al. investigated the dual-facet mechanism occurring at the interface between the (100) terraces and (110) edges over Cu nanocubes.^[42] Using DFT calculations and experimental data, they evaluated the selectivity toward C–C dimerization on Cu nanocube electrocatalysts and proposed a synergistic effect between two neighboring facets; the (100)/(110) interface favors the COH-CO coupling. Likewise, the relationship between the CO₂ reduction activity and facet dependency for methanol production was reported by Wu et al.^[43] They observed that the (110) facet of a single Cu₂O electrocatalyst is active for CO₂ reduction to methanol while the (100) facet is inert. The oxidation state of the Cu active sites on the (110) facet changed from Cu⁺ to Cu²⁺ on co-adsorption of CO₂/H₂O and changed from Cu²⁺ to Cu⁺ under 532 nm illumination, which indicates the bond breakage between the CO₂ and Cu (110) active sites.

2.3.4. Defect Sites

Various defect sites from vacancies or grain boundaries (GBs) may lead to the new breakthrough in generating active sites for

ECR catalysts, because those defects can induce a large surface area on the electrocatalysts surface.^[44] Feng et al. showed that CO reduction activity is directly correlated to the density of GBs in Cu nanoparticles.^[45] Increasing the density of GBs could lead to improving CO electroreduction activity because the GBs can alter the surface properties of particles to lower the barrier for CO reduction. Similarly, Li et al. demonstrated that a high density of under-coordinated atoms from Cu catalysts could enhance CO adsorption and stabilize C₂ intermediates, leading to selective n-propanol generation.^[46] On the Cu-based electrocatalysts, the under-coordinated defect sites have been demonstrated to facilitate the C–C bond formation and thus have higher selectivity for C₂₊ production over C₁ or HER, compared to the flat Cu surface.

2.3.5. Chemical States

The oxidation states of copper can easily vary among Cu⁰, Cu⁺, to Cu²⁺, and their oxidation/reduction states reversibly change during electrochemical reaction condition. The catalysts derived from oxidized copper have been observed to improve the activity and selectivity for C₂₊ products, however, the origin of the significant enhancement toward C₂ formation is still debated.^[23] Thus, other factors such as defective sites and roughened morphology of catalysts as well as chemical states should be considered to understand synergy effects to improvement of C₂₊ selectivity.

Via theoretical studies, the presence of metastable states including the residual oxygen, subsurface oxygen, or oxidized copper states have been proposed to be formed under the CO₂ reduction condition: all of which were suggested to stabilize the intermediate species, especially for C–C coupling.^[47,48] The theoretical studies further suggested that the Cu⁺ may interact with Cu to promote CO₂ activation and dimerization of *CO.^[48] During the initial step, CO₂ is favored on top of the Cu⁰ region. Upon the activation of CO₂, the Cu⁺ species existing under the metallic Cu region provides a strong H₂O adsorption site via hydrogen bonds to stabilize the CO₂ molecule. Then, during the CO dimerization step, *CO on Cu⁺ and Cu⁰ can be understood by noting that the C atom of CO on Cu⁺ is positively charged due to back donation (Mulliken charge of +0.11 on Cu⁺ and −0.31 on Cu⁰). Thus, the Cu metal embedded in the oxidized matrix model showed the synergy effect between the surface Cu⁺ and surface Cu⁰, which significantly improved the kinetics and thermodynamics of both CO₂ activation and CO dimerization. In addition, Liu et al. found that oxide-derived copper (OD-Cu) electrocatalysts, possessing subsurface oxygen, increased the maximum adsorption coverage of the important CO intermediate, lowering the activation barrier and the reaction energy due to the reduction of σ -repulsion while the π -attraction is uninfluenced.^[49] Mistry et al. presented a correlation between hydrocarbon selectivity and Cu⁺ on the plasma-activated Cu, wherein Cu⁺ remained on the Cu surface during the reaction, as observed in operando X-ray absorption spectroscopy (XAS).^[50]

Although theoretical studies indicate that Cu⁺ state or subsurface oxygen in OD-Cu induced high selectivity toward C₂ products, experimental studies showed that this high

performance was not directly attributed to the residual Cu⁺ or oxide itself.^[51–53] Using in situ Raman spectroscopy, some experimental studies found that the surface of Cu₂O catalysts reduces to Cu⁰ at negative potentials and are rapidly re-oxidized upon the removal of that condition.^[52,54] The initial oxidation state of the Cu surface maybe then contribute to selective products from CO₂RR, but the method of preservation of the Cu states under the CO₂ reduction condition still needs to be considered. Therefore, the importance of sub-surface oxygen or Cu⁺ sites in influencing the CO₂RR to C₂ products still needs more investigation with careful in situ/operando measurements.

In general, the high C₂ production from CO₂RR was well demonstrated by using the following strategies: inducing high pH near the electrode surface, exposing the (100) facets, utilizing the porous structure, and introducing under-coordinated sites. However, identification of the activation factor of C–C coupling in CO₂RR has been very difficult. In the case of Cu-based catalysts with surface states that can be varied in situ, further in-depth studies have been conducted, wherein in situ/operando measurements have been performed to investigate the catalyst surface.

3. Synthesis of Cu-Based Catalysts

Procedures to synthesize Cu, copper oxide nanocrystals (NCs), OD-Cu, or other Cu-based related catalysts are not very different from those used to prepare other metal NPs. Here, we will focus on the wet-chemical-based copper synthesis method, in which the morphologically and compositionally controlled Cu-based nanoparticles are greatly affected by small changes in the reaction parameters, such as precursors and solvent, and external reagents such as capping agents and reducing agents. The controlled Cu-based catalysts have been used for model catalysts to understand the effects of size, morphology, facets, defects, and composition on the catalytic activity. Typical synthesis evolved around four chemical reaction types, namely: 1) reduction, 2) hydrolysis, 3) condensation, and 4) oxidation, while the techniques applied can vary among the solvothermal method, electrochemical synthesis, photochemical synthesis, and sonochemical method.^[10] **Table 1** provides a summary of recent Cu and Cu-based related catalysts prepared using the various established synthetic procedures, and most of these applied for CO₂RR.

Chemical treatment is the most popular procedure to prepare Cu, copper oxide NCs, and Cu-based related catalysts. It refers to methods in which Cu precursors are treated with external reagents and then subjected to appropriate energy input through calcination, pyrolysis, or microwave-assisted method. For example, highly dense Cu nanowires (NWs) were synthesized by Raciti et al. via a two-step method. Initially, cleaned Cu gauze was placed in oven pre-heated to 600 °C and kept stable for 8 h in air atmosphere.^[55] CuO NWs grown during the oxidation process were further reduced to Cu NWs by either 1) annealing process at 300 °C for 1 h under forming gas (5% H₂/N₂), or 2) electrochemical treatment at –0.4 V in 0.1 M KHCO₃ electrolyte. Different crystalline and surface structures were observed on the final materials, and CuO NWs were reduced by the application of negative potential, showing enhanced CO₂RR

activity toward CO (FE_{CO} = 60% at –0.4 V). To determine the size and shape effect of nanocrystals on CO₂RR, Loidice et al. synthesized Cu nanospheres and nanocubes with varying particle sizes via a colloidal chemistry-based method.^[40] In the typical synthesis procedure, a mixture of CuBr, oleyamine, and trioctylphosphine (TOP) (nanospheres) or trioctylphosphine oxide (TOPO) (nanocubes) in a three-necked flask was submitted to rapid magnetic stirring and refluxed at 260 °C for 3 h. The nanocrystal sizes were varied by adjusting the concentration of the additives. A similar synthesis procedure was adopted by Suen et al. to prepare their Cu nanocrystals with cubic, hexarhombic dodecahedron, and octahedron-like morphologies.^[56] The group modified the standard reflux setup by performing the reaction under N₂ gas at 230 °C (or 270 °C) for 3 h. Excess n-hexane was used to wash the additives. HRTEM images of the above-mentioned Cu nanostructures are shown in **Figure 3a–d**.

Moreover, Sun et al.^[57] demonstrated that in the synthesis of Cu₂O nanoparticles, controlled crystal facets of Cu (100), Cu (111), and Cu (110) can be obtained by treating copper salts with different counter anions, including sulfate (CuSO₄),^[58] nitrate (Cu(NO₃)₂),^[59] chloride (CuCl₂),^[60] and acetate (Cu(CH₃COO)₂)^[61] with different reducing agents or capping agents during the reduction processes under alkaline conditions. Both counter anions from Cu salts and employed reducing/capping agents played major roles in determining the final particle size and shapes. They comprehensively reviewed the various synthetic methods for obtaining polyhedral Cu₂O architectures that are summarized in **Figure 3e**. Likewise, Su et al. showed that controlled morphology and crystal facets of Cu₂O NPs are highly dependent on the ratio of the reducing agent (hydroxylamine hydrochloride) and surfactant (sodium dodecyl sulfate [NH₂OH·HCl: SDS]) with respect to the Cu precursor during hydrothermal treatment.^[62] Initial experiments showed that in the absence of SDS, the morphology of Cu₂O nanocrystals evolved from cubic to 26-facet polyhedron to truncated rhombic dodecahedron with the increasing amount of NH₂OH·HCl, as shown in **Figure 3f**. Upon the addition of SDS, uniform particle size and further evolution of morphology were observed. For instance, with 1:1 ratio of reducing agent and surfactant, the morphology of the Cu₂O nanocrystal changed from truncated rhombic dodecahedron (exposed with 12 (110) facets and 6 (100) facets) to rhombic dodecahedron with only 12 (110) exposed facets. The group suggested that the addition of SDS led to preferential adsorption on different facets, which affected the growth of the nanocrystals. In contrast, Xu et al. synthesized Cu₂O NPs via a surfactant-free room temperature solution-based synthesis.^[63] They found that Cu₂O NPs with cubic, octahedral, spherical, and cuboctahedron shapes can be obtained by facile reduction of Cu(OH)₂ in the presence of reducing agents such as hydrazine hydrate or sodium ascorbate. The reaction atmosphere varied between argon or air conditions. They emphasized the importance of choosing the suitable reducing agent and atmosphere condition to control the morphological structure of NPs. Importantly, this approach did not necessitate the additional structural directing agents.

Electrochemical synthesis of Cu-based NPs involves a constant applied current flowing through an electrolytic cell that contains an aqueous solution of Cu salt. The presence of current in the solution moves electrons from the anode to cathode

Table 1. Summary of Cu and Cu-based related catalysts prepared by using the various established synthetic procedures.

Category	Catalyst	Synthetic method	Precursors	Reaction condition	Structures	Refs.
Metallic Cu	Cu	Thermal treatment, electro-chemical reduction	Cu gauze	600 °C for 8 h, air	Nanowires	[55]
	Cu	Wet-chemical	Cu(NO ₃) ₂ ·xH ₂ O, ethylene glycol, ketjen black, cysteamine	180 °C for 7 h 220 °C for 4 h 200 °C for 1 h	Nanocube Nanosphere	[75]
	Cu ₂ O	Wet-chemical	CuSO ₄ , KOH, ascorbic acid	65 °C for 10 min	50-Facet nanocrystal	[58]
	Cu ₂ O	Wet-chemical, thermal treatment	CuCl ₂ , NaOH, sodium ascorbate, hydrazine hydrate	45 °C for 6 h	Nanocubes, octahedra, cuboctahedra, spheres, facet-etched cubes	[63]
	Cu	Electrodeposition	CuSO ₄ , H ₂ SO ₄ , KBr, carbon paper	90 mA cm ⁻² for 30, 45, and 60 min	Rough particles	[64]
	Cu, Cu ₂ O	Electrodeposition	CuSO ₄ , H ₂ SO ₄ , NaOH, lactic acid	−0.03 V (vs RHE) 0.45 V (vs RHE)	Nanoparticles	[126]
	Cu ₂ O-derived Cu	Hydrothermal treatment	Cu(NO ₃) ₂ ·3H ₂ O, NH ₃ , ethanol, formic acid	145 °C for 90 min	Nanofilm	[59]
	CuO, Cu ₂ O	Microwave assisted	Cu(Ac) ₂ , Cu(acac) ₂ , benzyl alcohol, hydrazine hydrate	700 W for 10 min	Nanosphere, nanocube	[69]
	Cu	Electrochemical reduction	Cu foil, KOH	10 mA cm ⁻² for 60 s	Nanowires	[13]
	Cu	Wet-chemical	CuBr, TOPO, oleylamine	230 °C for 3 h	Nanocubes, hexarhombic dodecahedra, octahedra	[56]
	Cu	Inverse micelle encapsulation	CuCl ₂ , poly(styrene)-block-poly(2-vinylpyridine), PVP, PS	Room T for 48 h	Nanosphere	[12]
	Cu	Electrochemical reduction, plasma treatment	Cu foil, KCl	O ₂ plasma for 20 s, H ₂ /Ar plasma for 4–5 min	Nanocube	[73]
	Cu	Electrodeposition	CuSO ₄ ·5H ₂ O, H ₃ BO ₃ , H ₃ PO ₄ , Cu foils, Janus Green B	−6 mA cm ⁻² for 3 min	Nanoprism	[65]
	Cu	Wet-chemical	CuBr, TOPO, oleylamine	80 °C for 15 min 210 °C for 1 h 260 °C for 3 h	Nanocube, nanosphere	[40]
Cu alloy	Cu/Pt (111), Cu/Pt (211)	Thermal treatment, electrodeposition	Pt(111) and Pt(211) single crystals, CuO, HClO ₄	850 ± 20 in H ₂ + Ar atm for 3 min, 0.32 V (vs RHE) for 2 min	Cu overlayer	[77]
	Cu–Sn	Electrodeposition	Cu sheet, Sn metal sheet, HNO ₃ , HCl, SnCl ₂ ·2H ₂ O, KOH	−0.6 V (vs RHE) for 1 h, −0.8 V (vs RHE) for 1 h under CO ₂	Rough grain-like particles, nanocubes	[89]
	Cu ₂ O-derived Cu/PdCl ₂ dopants	Electrodeposition	Cu discs, H ₃ PO ₄ , CuSO ₄ , NaOH, lactic acid	−0.7 mA for 1200 s, at 60 °C	≈500 nm-sized polyhedrons	[127]
	Au–Cu	Magnetron sputtering co-deposition	Au and Cu	Deposition power and duration were controlled to obtain films with a thickness of 80 nm	Thin films	[128]
	Cu–In	Wet-chemical	InCl ₃ , ethanol, NH ₄ OH, CuCl ₂ trisodium citrate, NaBH ₄	Ice bath for 30 min	Rectangular crystallites	[129]
	AuCu	Wet-chemical	HAuCl ₄ ·3H ₂ O, Cu(acac) ₂ , 1-adamantanecarboxylic acid, 1,2-hexadecanediol, 1-hexadecylamine, diphenyl ether, CTAB	160 °C for 5 h	Nanocubes	[80]
	CuZn	Pulsed laser ablation (PLA) in liquid	Cu, Zn, CuZn, ethanol	1064 nm, 10 Hz, 300 mJ per pulse for 20 min	Nanosphere	[67]
	CuZn@C-N	Wet-chemical, thermal treatment	Cu(NO ₃) ₂ , Zn(NO ₃) ₂ , Na ₂ CO ₃ , 2-methylimidazole	Pre-oxidation: 400 °C for 4 h in N ₂ Hydrothermal: 180 °C for 18 h Carbonization: 500 °C for 1 h	Nanosphere	[70]
	Cu/In	Wet-chemical, thermal treatment	Cu foil, NaOH, (NH ₄) ₂ S ₂ O ₈ , InCl ₃	150 °C for 2 h in air	Nanowires	[90]
	Ag/Cu ₂ O	Wet-chemical, electro-chemical reduction	Cu(Ac) ₂ , AgNO ₃ , hydrazine hydrate	−2.0 V (vs SCE) for 1 h	≈300 nm particles covered by small Ag particles	[83]

Table 1. Continued.

Category	Catalyst	Synthetic method	Precursors	Reaction condition	Structures	Refs.
Cu compound	Ag–Cu	Wet-chemical	Cu(Ac) ₂ ·H ₂ O, CF ₃ COOAg, D-glucose, hexadecylamine, L-ascorbic acid	Oil bath at 150 °C for 20, 12.5, and 8 min	Nanodimers	[84]
	OD-Cu ₂ Zn	Electrodeposition	Cu and Zn film, CuSO ₄ , lactic acid, NaOH, ZnCl ₂	−0.92 mA cm ^{−2} for 600 s	Polyhedral particles	[86]
	Cu/Ni(OH) ₂	Wet-chemical	NiCl ₂ , Cu(acac) ₂ , HCOONa, DMF	160 °C for 30 min	Nanosheets	[79]
	Cu–S	Wet-chemical	Cu(NO ₃) ₂ ·3H ₂ O, urea, thiourea, carbon black	100 °C for 1 h	Nanoparticles	[94]
	Sulfide-derived Cu (SD-Cu)	Electrodeposition	Cu foil, H ₃ PO ₄ , CuS	−0.85 V Ag/AgCl × 10 ms for a total time of 30 min or 2 h	Nanowires	[91]
	Cu ₃ N-derived Cu	Chemical oxidation, electrochemical reduction	Cu foam, ammonium persulfate, KHCO ₃	Oxidation: 300 °C for 1 h, Reduction: −1.2 V	Nanowires	[100]
	S-doped Cu ₂ O-derived Cu	Electrochemical reduction, wet-chemical	Cu discs, ammonium polysulfide solution, KHCO ₃	−0.3 A cm ^{−2} for 50 min	Polyhedral nanoparticles	[93]
	CuS _x	Electrodeposition	Cu discs, CuSO ₄ ·5H ₂ O, thiourea, HCl	−0.54 V (vs RHE) for 10 ms, 0.21 V (vs RHE) for 20 ms	Nanowires, nanoparticles	[95]
	Nitride-derived Cu	Wet-chemical	Cu(NO ₃) ₂ ·3H ₂ O, ethylene glycol, In(OH) ₃ , Cu ₃ N, NH ₄ OH	140 °C for 10 h	Nanoparticles	[130]
	B-doped OD-Cu	Wet-chemical, thermal treatment	Cu foils, NaOH, K ₂ S ₂ O ₈ , B ₂ O ₃	Room T for 4 h, Calcination: 500 °C for 3 h in air	Nanoplate	[105]
Supported Cu	CuS	Wet-chemical	Cu(NO ₃) ₂ ·3H ₂ O, NH ₄ F, urea, Na ₂ S, S, KCl	120 °C for 6 h	Nanosheets	[96]
	Cu ₂ →S	Ligand exchange process	Cu(NO ₃) ₂ ·3H ₂ O, 1-octadecylamine, hexane, NaN ₃ , NMF	150 °C for 10 min, 240 °C for 10 min	Nanosphere	[99]
	Cu/In ₂ O ₃	Wet-chemical	Cu(Ac), tetradecylphosphonic acid, In(acac) ₃ , TOA	130 °C for 30 min, 180 °C for 30 min, 270 °C for 30 min	Core/shell	[131]
	OD-Cu/carbon	Wet-chemical, thermal treatment	Cu(NO ₃) ₂ ·3H ₂ O, benzene-1,3,5-tricarboxylate, ethanol, DMF	Hydrothermal: 100 °C for 24 h, Carbonization: 900, 1000, and 1100 °C for 6 h, respectively, under Ar	Octahedral	[109]
	Carbon-supported Cu	Wet-chemical, electrodeposition	Cu(acac) ₂ , Vulcan carbon, Ketjen black, SWNTs, LiBEt ₃ H, N ₂ H ₄ , NaBH ₄ , oleylamine, oleic acid, hexane	90 °C for 1 h under N ₂ flow, 120 °C for 1 h under N ₂ flow	Nanoparticles	[132]
	Cu/SiO ₂	Precipitation-gel method, thermal treatment	Cu(NO ₃) ₂ , KOH, SiO ₂ , Zn(NO ₃) ₂ , urea	400 °C for 4 h under air, 450 °C for 2 h under air	Nanoparticles	[133]
	Cu NPs on pyridinic-N rich graphene	Wet-chemical, thermal treatment	Melamine, single-layered GO, Cu(Ac), tetradecylphosphonic acid, TOA	180 °C for 30 min, 250 °C for 5 min, Pyrolysis: 900 °C	Nanoparticles	[107]
	Cu NPs in MOF	Wet-chemical	H ₄ TBAP, DMF, benzoic acid, bis(dimethylamino-2-propoxy) copper(II), zirconyl chloride octahydrate	Room temp for 12 h, 80 °C for 2 h, 90 °C for 18 h	Hexagonal microrods	[121]
	Cu/SnO _x -CNT	Wet-chemical	Cu(Ac) ₂ ·2H ₂ O, SnCl ₂ , MWCNT, ethanol, KOH	80 °C for 6 h	Nanoparticles embed on CNT structure	[111]
	CuO _x on CeO ₂ -{111}/{100} and CuO _x on CeO ₂ -{110}/{100}	Wet-chemical thermal treatment	Ce(NO ₃) ₃ ·6H ₂ O, NaOH, glycol, Cu(NO ₃) ₂ ·3H ₂ O, Na ₂ CO ₃	Hydrothermal: 100 °C for 24 h, Calcination: 400 °C for 4 h	Nanosphere, Nanorods	[118]

Table 1. Continued.

Category	Catalyst	Synthetic method	Precursors	Reaction condition	Structures	Refs.
	Cu ₂ O/GO	Wet-chemical, thermal treatment	CuSO ₄ , GO, H ₂ SO ₄ , NaNO ₃ , KMnO ₄ , H ₂ O ₂ , HCl	650 °C for 2 h	Nanosheets with porous structure	[114]
	Cu NPs on pyridoxine-modified GO	Wet-chemical	Cu(NO ₃) ₂ , GO, VB ₆ , DMF, N ₂ H ₄ ·H ₂ O, ethylene glycol	60 °C for 24 h	Cu NPs on nanosheets modified GO	[116]
	Cu ₂ O/polyaniline	Electro-polymerization and pulse deposition	CuSO ₄ , aniline, H ₂ SO ₄ , TBAP, methanol	Electro-polymerization: −0.2 to 0.8 V vs SCE at 50 mV s ^{−1} Electrodeposition: −1.5 mA cm ^{−2} for 100 s	80–100 nm Cu nanoparticles on polyaniline matrix	[134]
	CuO/CeO ₂	Wet-chemical, thermal treatment	Carbon black, Ce(NO ₃) ₃ ·6H ₂ O, Cu(NO ₃) ₂ , Cu(Ac) ₂ ·H ₂ O, NaOH, Na ₂ CO ₃	150 °C for 10 h Calcination: 400 °C in air	Nanocrystal	[119]

and electrochemically reduces the Cu ions to Cu atoms that eventually agglomerate to form Cu NPs.^[64] Jeon et al. utilized one-step electrochemical deposition, which is a synthetic method that produces finer NPs, to obtain prism-shaped Cu NPs that can be used as electrocatalysts for selective CO₂RR toward ethylene.^[65] Initially, two Cu foils were electropolished in 85% phosphoric acid solution for 5 min and then dried with N₂ gas. Two Cu foils were immersed as electrodes in CuSO₄·5H₂O and H₃BO₃ solutions to enable the electrodeposition process with an applied current density of −6 mA cm^{−2} for 3 min. Triangular nanoprisms with different widths and a rough surface were obtained with respect to the concentration of the additive, Janus Green B, which acted as the crystal modifier and induced the preferential deposition of Cu ions. The prism-shaped Cu nanocrystals toward CO₂RR obtained a C₂H₄ FE of 27.8% and remained remarkably stable for over 12 h.

Pulsed laser ablation (PLA) in liquid, a technique that emits photonic energy, has also been adopted by some researchers to prepare NPs with unique morphology and chemical compositions.^[66] In a typical PLA setup, Feng et al. employed a 20-min nanosecond pulsed Nd:YAG laser with 10 Hz and 300 mJ to the metal targets of Cu, Zn, and CuZn alloy with different Cu:Zn ratios.^[67] Homogeneous CuZnO NPs were reduced to the CuZn state via electroreduction and used as the catalyst for selective CO₂RR. The CuZn catalyst showed good selectivity for C₂H₄ products and obtained FE as high as 33.3%. Likewise, microwave (MW) assisted synthesis converts electromagnetic energy into heat, which offers fast reaction rate and narrow particle size distribution during the synthesis of Cu-based NPs.^[68] Nikam et al. reported the controlled synthesis of Cu₂O/CuO nanostructures by using an MW-assisted method, wherein they utilized

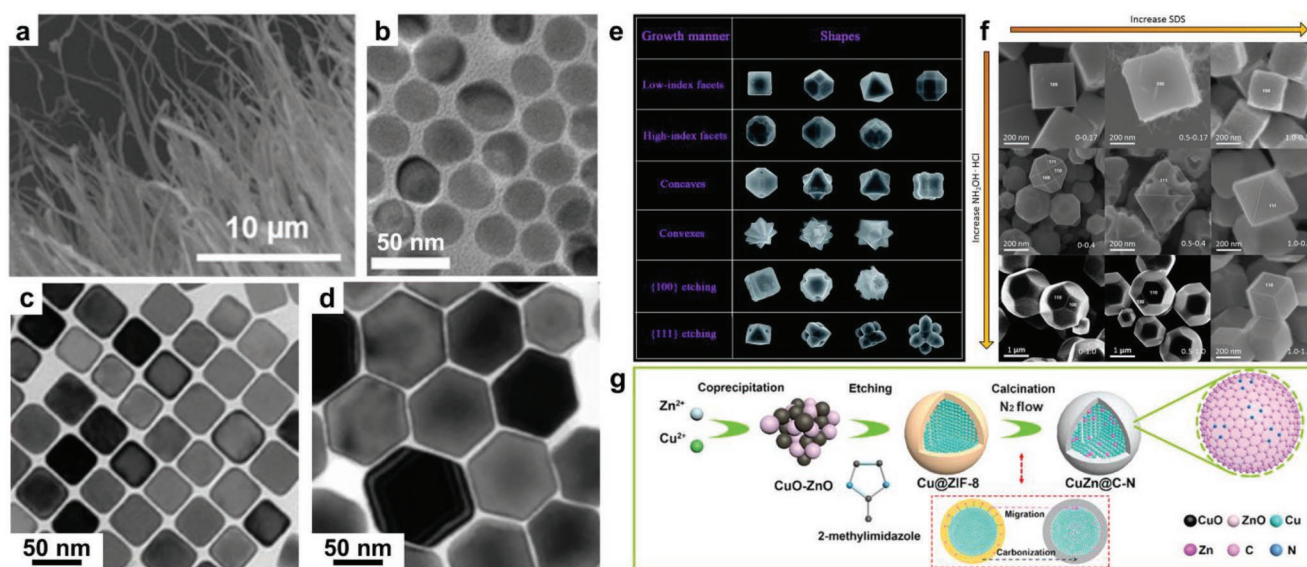


Figure 3. a) CuO-derived Cu nanowires by annealing in the presence of H₂ at 300 °C. Reproduced with permission.^[55] Copyright 2015, American Chemical Society. b) Cu nanospheres with an average diameter of 27 nm. Reproduced with permission.^[40] Copyright 2016, Wiley-VCH. c) Cube-like and d) hexahombic dodecahedron-like Cu nanoscale single crystals. Reproduced with permission.^[56] Copyright 2019, American Chemical Society. e) Various morphologies of Cu₂O crystals. Reproduced with permission.^[57] Copyright 2014, The Royal Society of Chemistry. f) Morphology evolution of Cu₂O nanoparticles under various hydrothermal conditions. Reproduced with permission.^[62] Copyright 2017, American Chemical Society. g) Schematic illustration of the synthetic route for CuZn alloy encapsulated in the N-doped carbon shell layers. Reproduced with permission.^[70] Copyright 2019, American Chemical Society.

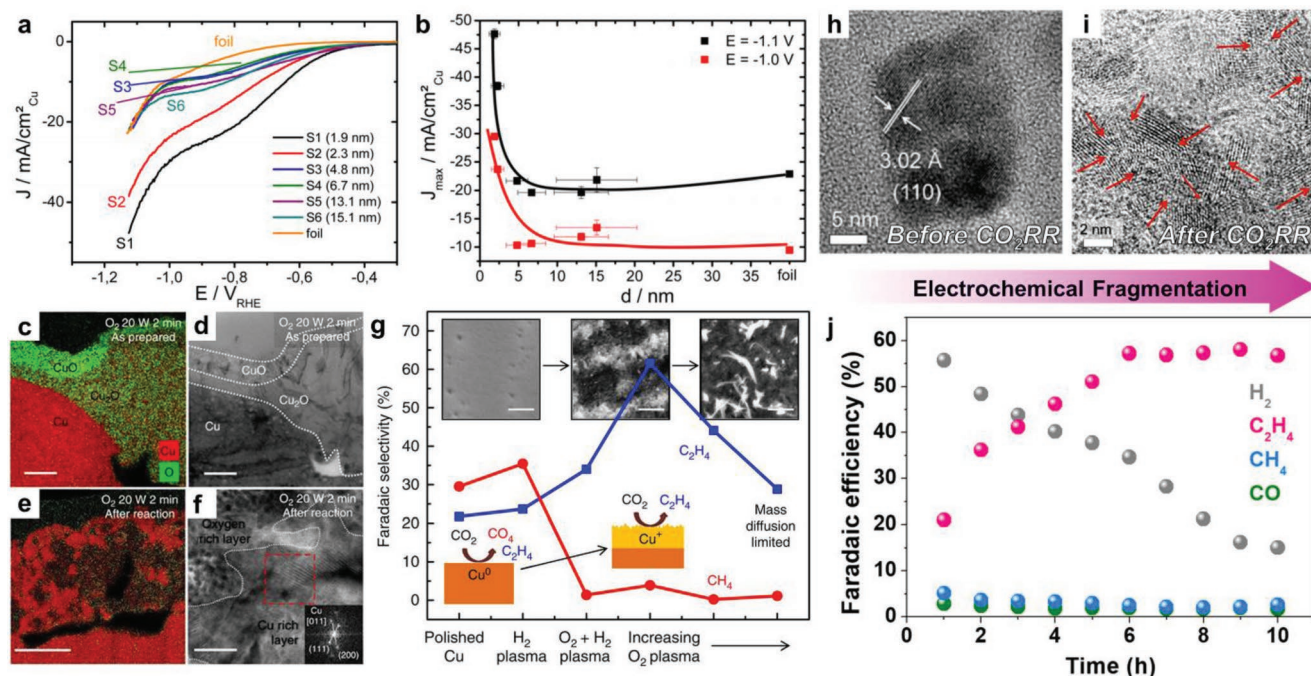


Figure 4. a,b) Size-dependent CO₂RR activities of Cu nanoparticles. a) Linear sweep voltammetry of the CO₂RR on Cu nanoparticle catalysts with different sizes in 0.1 M KHCO₃, room temperature. b) Particle size effect during electrocatalytic CO₂RR. Reproduced with permission.^[12] Copyright 2014, American Chemical Society. c–g) Characterization and CO₂RR activities of plasma-activated Cu foils. c) EDS elemental mapping and d) HRTEM analysis of Cu foils treated with O₂ plasma for 20 W 2 min. e) EDS elemental mapping and f) HRTEM and SAED analysis of plasma-activated Cu foils after CO₂RR for 1 h at -0.91 V versus RHE. The scalebars represent c–e) 300 nm and f) 20 nm, respectively. g) Summary of hydrocarbon selectivity of plasma-treated Cu foils. The scalebar inset represents 500 nm. Reproduced with permission.^[50] Copyright 2016, Nature Publishing Group. h–j) Cu₂O nanoparticles on carbon. HRTEM images of Cu₂O NP/C h) before and i) after CO₂RR for 10 h at -1.1 V versus RHE. j) Faradaic efficiencies of gaseous products for Cu₂O NP/C at -1.1 V versus RHE, depending on reaction time. Reproduced with permission.^[75] Copyright 2019, American Chemical Society.

Cu (II) acetate and Cu (II) acetylacetonate as Cu precursors, and benzyl alcohol as the solvent and reducing agent.^[69] The pH of the solution was varied by introducing small amounts of NaOH, which played an important role in determining the final structure of the products formed. Further, a much more sophisticated technique, that is, encapsulation of CuZn alloy by nitrogen-doped carbon cages, was introduced by Hu et al. to improve the catalytic activity of Cu-based catalyst.^[70] Initially, a solution with equal molar ratio of Cu (II) nitrate and zinc nitrate was added to precipitant Na₂CO₃. The collected precipitate was calcined to form CuZnO_x. Mixed metal oxides (CuO–ZnO) were etched by using 2-methylimidazole to obtain Cu-doped ZIF-8 (Cu@ZIF8) precursor, which was then calcined under N₂ to form CuZn@C–N. Figure 3g shows a schematic illustration of the solvent-free solid-phase synthesis to prepare the CuZn@C–N catalyst. The group suggested that the combined catalytic effects of shell rich with pyridinic N and CuZn alloy core contributed to the significantly enhanced CO₂RR performance, and the core-shell structure protected the metallic alloy core from fast deactivation.

Further detailed discussion of the synthesis of various Cu-based catalysts will be provided in Section 4. In Section 4, we will describe the various kinds of secondary metals and support materials used for the preparation of Cu-based catalysts as well as their roles in improving the catalytic performance of Cu-catalysts for the electroreduction of CO₂.

4. Surface Structure-Dependent Catalytic Activity/Selectivity of Cu-Based Catalysts toward CO₂RR

4.1. Metallic Cu

The earlier works of Hori et al. on Cu single crystals, which showed the significance of crystal facets for a selective electrochemical reduction of CO₂, has been the foundation of numerous studies on Cu-based electrocatalyst over the years.^[71] They found that Cu (111) favors CO protonation, leading to the formation of CH₄, although small amounts of C₂H₄ can also be formed from this pathway. In contrast, Cu (100), with a lower coordination number and higher exergonic adsorption energy than Cu (111), produces C₂H₄ through CO dimerization. Although the facet-dependent product selectivity of CO₂RR has been undeniably proven and the exceptional ability of Cu to reduce CO₂ to multiple valuable products may be due to its negative adsorption energy toward *CO and a positive adsorption energy for *H,^[11,36] other factors described in Section 1, such as physicochemical properties, changes in surface states, surface defects, and preparation methods, should be also considered to understand the product selectivity.

Reske et al. presented the very first study on the catalytic particle size effects in CO₂RR using the Cu NPs with sizes ranging from 2 to 15 nm.^[11] Figure 4a,b shows the linear sweep voltammetry (LSV) and the overall catalytic CO₂RR activity on Cu NPs with decreasing particle size, in comparison to the activity of

a Cu foil electrode as reference. While the decreased particle size could provide high electrochemical active surface area and high catalytic activity, the population of the under-coordinated surface atoms depends on the particle sizes, which could cause significant changes in product selectivity from CO₂RR. As can be seen from the figures, the catalytic activity increased as the size of the Cu NPs decreases, and a drastic increase in Faradaic current density was observed as the particle size decreased from 5 nm to smallest NPs (1.9 nm). In addition, the particle size effect was associated to the product selectivity wherein formation of H₂ and CO products were highly favored as the particle size decreased, but the production of hydrocarbons such as CH₄ and C₂H₄ dropped drastically. The selectivity of hydrocarbons dropped first on the nanoparticles compared to foil and reached a constant plateau. It was suggested that the further hydrogenation was blocked by the reduced mobility of intermediate species on the smaller NPs due to stronger bonding of the under-coordinated atoms, and thus, the H₂ and CO production was preferred. Moreover, Loiudice et al. prepared Cu NCs with spherical and cubic shapes, and varying particle sizes.^[40] Parallel to the earlier discussion, smaller size NCs exhibited higher CO₂RR activity; however, Cu NC with cubic shape showed higher overall activity compared to spherical NC. Among the prepared catalysts, Cu cubes of 44 nm size obtained superior selectivity toward CO₂RR, that is, FE_{CO₂RR} = 80% and FE_{ethylene} = 41%. The group reported that an optimal balance between the edge sites and (100) plane-sites ($N_{\text{edge}}/N_{100} = 0.25$) was observed in the 44-nm Cu cube, which was suggested as a crucial structural parameter to control the product selectivity.

Aside from the structural parameters, such as particle size and shape, changes in the chemical properties (e.g., Cu surface states) were suggested as an important factor to consider for preferential CO₂ reduction. Li et al. prepared a Cu film electrode with μm -thick Cu₂O layer via high temperature annealing.^[51] The presence of Cu⁰ during CO₂ reduction catalysis was highly dependent on the initial properties of the oxide layer. An electrode with a thicker Cu₂O layer not only obtained high FE for CO and HCOOH at low overpotential and produced C₂ hydrocarbons at high overpotential, but also showed great resistance against deactivation for several hours. Such results provided new insights for preparing highly selective CO₂RR electrocatalyst. Following this concept, Mistry et al. synthesized a highly oxidized Cu catalyst through facile and tunable plasma treatments.^[50] O₂ plasma treatment was used to form a nanostructured oxide layer on polycrystalline Cu that possesses highly porous surface with controlled morphology and chemical states. Interestingly, while the surface roughness of the catalyst was suggested to play a minor role in determining the catalytic activity, the presence of Cu⁺ was proposed to decrease the onset potential and contribute to the selective CO₂RR toward ethylene product with FE of 60% at -0.9 V (vs RHE). Based on the EDS elemental mapping and HRTEM analysis of plasma-activated Cu foils before and after the reaction, as shown in Figure 4c–f, Cu oxide species such as Cu₂O (Cu⁺) and CuO (Cu²⁺) were well observed throughout the interlayer and upper layer, respectively. This study proposed that the active Cu surfaces effectively interacted with the negatively charged CO₂ reduction intermediates and played a major role during CO₂RR.^[72] In addition, the surface roughness obtained upon oxidizing the surface with O₂

plasma was partially assigned to a sudden increase in the C₂H₄ formation, as shown in Figure 4g.

To elucidate the effect of different structural (surface) parameters, including crystal facets, surface roughness, and availability of subsurface oxygen, for selective CO₂RR toward hydrocarbons and alcohol products, Gao et al. conducted a well-rounded investigation using plasma-activated Cu nanocubes exposed with a Cu (100) facet.^[73] The group reported that the high influence of surface roughness and specific crystal facet in determining the catalytic activity, and both parameters played a major role during the catalysis reaction. They proposed that oxide-derived natures of copper caused significant lattice strain and affected the binding of *CO intermediate to the catalyst surface, which eventually favored the formation of multiple C₂₊ products.^[74] In related oxidized copper-based catalyst works, Lee et al. investigated the effect of mixed Cu states in an anodized Cu electrocatalyst.^[13] Through facile electrochemical synthesis, they produced an anodized copper (AN-Cu) Cu(OH)₂ catalyst that showed high ethylene FE of 38.1% and outstanding stability even after 40 h of continuous operation. They reported that the highly selective and stable ethylene generation was associated with the initial reduction environment applied to the catalyst, which caused changes in the Cu oxidation states and structure. For instance, Cu(OH)₂ catalyst exposed at low overpotential immediately formed methane products while catalyst exposed at high overpotential was able to extend its durability toward ethylene formation. Cu catalysts were analyzed via ex situ methods, and metastable Cu states were proposed to be related to the stability and selectivity. Later, Jung et al. performed CO₂RR studies with shape-controlled Cu₂O nanoparticles, and monitored the transformation of the catalyst.^[75] HRTEM analyses showed that the Cu₂O NPs with an initial particle size of 20 nm were slowly fragmented into 2–4 nm sized particles after 10 h of continuous CO₂RR, and the CO₂RR activity is highly related with the morphological changes. HRTEM images of catalysts at different elapsed time of CO₂RR show that Cu₂O catalysts collapsed and were fragmented into smaller sizes with compact arrangement and deformed crystal plane, as shown in Figure 4h,i. Electrocatalytic activity for selective C₂H₄ formation was increased and reached FE 57.3%, as shown in Figure 4j. According to in situ/operando X-ray absorption near edge structure (XANES) analysis, the initial oxidation state of Cu⁺ was reduced to form metallic Cu⁰ under the CO₂RR operation condition, indicating that the metallic Cu is the dominant state during CO₂RR even in oxide-derived small-size Cu catalysts. Interestingly, the activated Cu nanoparticles were re-oxidized to Cu⁺ states even without being exposed to air once the initial nanoparticles were transformed into fragmented NPs, while the large nanoparticle remained as Cu⁰ states at the open-circuit voltage condition. These results imply that the fragmented NPs have ready access of oxygen within the fragmented structures although the effects of such structural changes on the catalytic activity have to be investigated further.

4.2. Cu Alloy (Bimetallic Cu-Based Electrocatalyst)

The product selectivity of electrochemical reduction of CO₂ on Cu-based catalysts is highly dependent on the binding energy

of the key intermediates of CO₂RR and competing HER, such as *H, *OCHO (bound to the surface through O), *COOH (bound to the surface through C), *CO, *CHO, or *COH.^[76] Changing the composition of the single Cu crystal catalyst by combining it with a secondary metal might tune the selectivity and activity through optimization of the binding strength of the key intermediates on the catalytic surfaces, and therefore, Cu alloys have attracted considerable attention. The arrangement of the guest metals on the Cu surface can affect the electronic states of the catalyst, geometric distance between the surface atoms, and reaction kinetics between the surface adsorbed intermediates, all of which can modify the binding energies of the intermediates and preferable reaction pathways. Bimetallic Cu-based alloy electrocatalysts depend on the nature of the secondary metal used and are categorized into three main groups, namely 1) Cu + H₂ producing metals (Fe, Ni, Pt, Pd), 2) Cu + CO producing metals (Ag, Au, Zn), and 3) Cu + HCOO⁻ producing metals (In, Sn).^[34]

Cu-based alloy electrocatalysts with Cu and H₂ producing guest metals such as Fe, Ni, Pt, and Pd typically favor HER activity and selectivity because of the excess exposure of these guest metals on the catalyst surface. The earlier work of Varela et al. reported the catalytic activity of CO₂RR on well-defined bimetallic Cu species overlayers on Pt (111) and Pt (211) single crystals.^[77] The main products detected were H₂ and methane on both Cu/Pt (111) and Cu/Pt (211), with very small traces of ethylene products (C₂H₄ FE < 0.6%). The group proposed that during CO₂ reduction, a significant surface restructuring occurred due to the presence of CO intermediates. Although in situ EC-STM analysis revealed that *CO species forced Cu atoms to move closer together, the high binding energy between Pt and CO was anticipated to proceed with the proposed surface restructuring, which exposed more Pt atoms on the catalyst surface.^[78] The final structure of the catalyst was then considered to be the Pt surface partially covered by polycrystalline Cu, and thus, the bimetallic catalyst over exposed with the H₂-producing guest metal strongly favored HER over the production of any hydrocarbon products. This study strongly suggested the importance of choosing the materials with lower affinity toward CO to avoid any surface restructuring and ensure stability under the reduction reaction.

Related to the previous stability challenge on bimetallic Cu-based catalyst with H₂-producing guest metal, Dai et al. demonstrated the enhanced CO₂RR activity with a hybrid of Cu/Ni(OH)₂ nanosheets composed of a Ni(OH)₂-rich core and Cu⁰-rich surface, which were highly stable against air oxidation for several months.^[79] Based on their proposed formation mechanism, a Ni(OH)₂ core was initially formed and then substituted by Cu²⁺ species to form Ni_{1-x}Cu_x(OH)₂ nanosheets. In the presence of sodium formate, which acted as both the reducing agent and protective layer, the Cu²⁺ species were reduced to Cu₂O and then to Cu⁰, ultimately forming ultrathin hybrid Cu/Ni(OH)₂ nanosheets with a thickness less than 3 nm. The formate-protected bimetallic catalyst was reported to have an exceptional ability to maintain Cu⁰ species intact on the surface during the catalysis, which showed remarkable product selectivity to CO at low overpotential (0.39 V) with FE_{CO} of 92% and current density of 4.3 mA cm⁻² was maintained for over 22 h.

Guest metals such as Ag, Au, and Zn are highly capable of producing CO from CO₂RR. By combining these metals with Cu to form alloy or bimetallic structures, the CO₂RR activity was increased. While previous works using these alloyed nanoparticles further improved the selectivity and activity of CO₂RR toward CO at lower overpotential,^[80,128] bimetallic structures have shown promising synergistic effects that lead toward the C–C coupling reaction. Based on a previous report by Kuhl et al. about the electrocatalytic conversion of CO₂ using several transition metal surfaces, including Au, Ag, Zn, Cu, Ni, Pt, and Fe, it was revealed that Cu may not be the only metal that has the ability to catalyze hydrocarbon and alcohol formation. Metals such as Ag, Zn, Ni, and Pt were also capable of producing both methane and methanol.^[81] These findings showed the richer surface chemistry of elemental transition metals and opened new doors for electrocatalyst design.

However, poor multi-carbon product selectivity was continuously observed on Cu alloy based on CO-producing guest metals until the phase-separated structure was applied for catalysis. In other words, even for the same guest metals, the composition ratio of these guest metals to the Cu atom and their mixing structure on the surface sensitively affected whether the CO or hydrocarbon production increased. For instance, in the case of Ag–Cu combination, Clark et al. proposed modification of the surface structure of the catalyst by introducing excess CO-generating metal to Cu, which induced compressive strain in the Cu surface atom.^[82] This compressive strain in Cu shifted the valence band density of states to higher binding energies, such that Cu²⁺/Cu⁺ reduction waves observed during cyclic voltammetry shifted to more anodic potentials over the CuAg bimetallic electrodes. They reported that Ag domains in the bimetallic structure primarily produced CO, and the Cu surface with compressive strain exclusively handled CO reduction and produced carbonyl-containing products.

Recent works on Ag–Cu₂O phase-blended and phase-separated electrodes have shown different CO₂RR activities and CO spillover. Wang et al. analyzed the differences in the structure and electrochemical performance between the Ag/Cu₂O composite and the AgCuO_x alloy electrocatalyst.^[83] Based on SEM, HAADF-STEM, and EDS elemental mappings analysis, as shown in Figure 5a–d, both samples had Ag⁰ and Cu⁺ states, with Ag/Cu composite made up of large Cu particles uniformly covered with tiny Ag particles, while the Ag element in AgCuO_x alloy was evenly embedded in the whole nanoparticle. They revealed that the interface of Ag/Cu composite was necessary to improve selectivity, for ethylene production with FE of 42% and stable operation for over 30 h. Similarly, Huang et al. reported the effect of the interface of Cu metal with Ag NPs in Ag–Cu nanodimers (NDs), which increased the C₂H₄ production up to FE of 40% at –1.1 V.^[84] Using the surface plasmon resonance (SPR) peak obtained in the UV–vis spectra, shown in Figure 5e, they elaborated that the observed blue shift of SPR peak of Ag in the Ag–Cu NDs (with respect to Ag NPs) is correlated to the increased electron density of the Ag domain. The Ag domain in this dimer functioned as electron acceptor for Cu domain, and this phenomenon can only happen if there was a shared interface between Ag and Cu.^[85] The group emphasized that the interface created by Ag–Cu NDs was highly effective in enhancing the intrinsic activity as Ag–Cu NDs exhibited higher

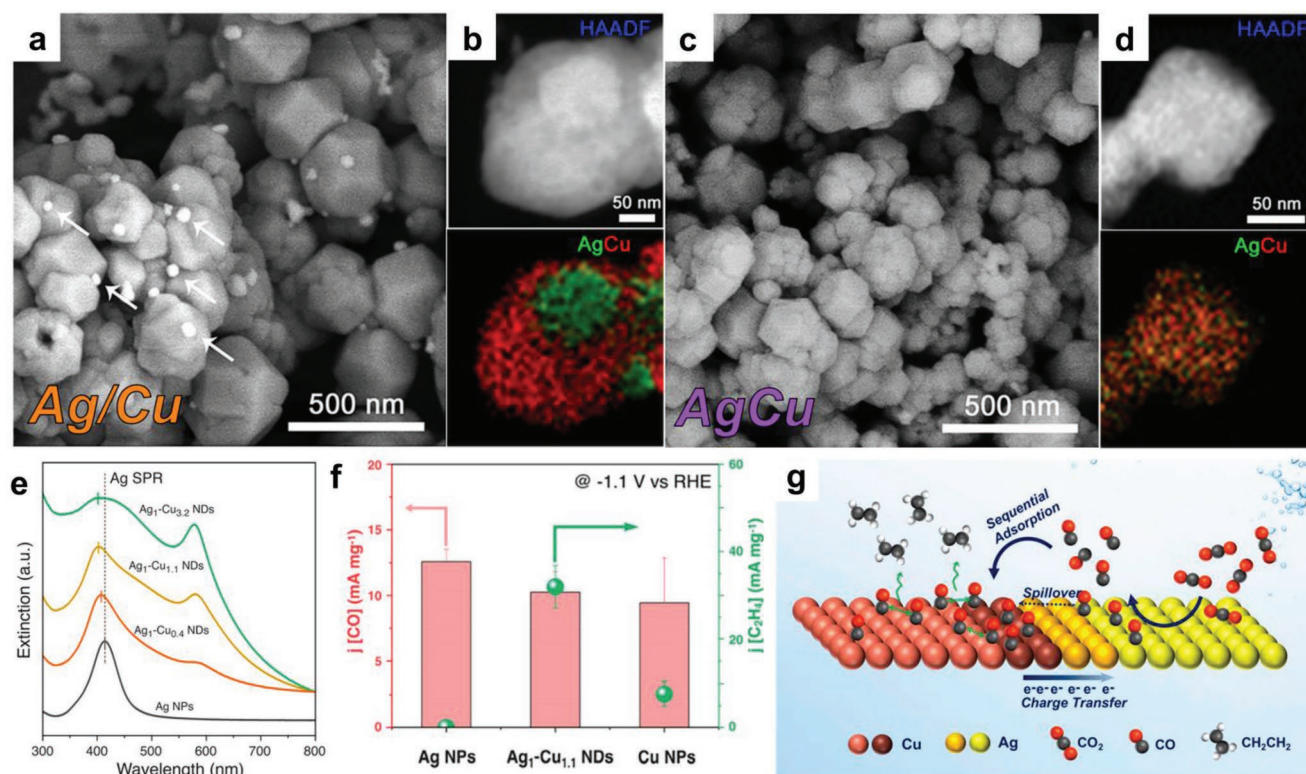


Figure 5. a–d) Ag–Cu bimetallic catalyst with hetero-interfaces. SEM images of a) Ag/Cu₂O and c) AgCuOx pre-catalysts. HAADF-STEM images and corresponding EDS elemental mapping analyses of b) Ag/Cu and d) AgCu catalysts showing elemental distribution of Cu (red) and Ag (green). Reproduced with permission.^[83] Copyright 2019, American Chemical Society. e–g) Ag–Cu nanodimer catalyst. e) UV–vis spectra of the Ag NPs and Ag–Cu NDs. f) CO and C₂H₄ mass activity of Ag NPs, Cu NPs, and Ag–Cu NDs at –1.1 V versus RHE. The mass activity is based on the overall mass of Ag and Cu. g) Schematic representation of the proposed mechanism of ethylene promotion in the Ag–Cu NDs. Reproduced with permission.^[84] Copyright 2019, American Chemical Society.

CO and C₂H₄ mass activity than plain Ag and Cu nanocatalysts, as shown in Figure 5f. CO spillover mechanism was proposed to promote C₂H₄ in the Ag–Cu NDs, as shown in Figure 5g.

Likewise, the phase-segregated oxide-derived Cu with varying amounts of Zn dopants (Cu_xZn) catalyst was prepared by Ren et al., which attained ethanol FE of 29.1% at –1.05 V and remained catalytically stable for at least 5 h.^[86] The presence of distinct Cu⁰ and Zn⁰ demonstrated the phase segregation of Cu and Zn, and that the Cu_xZn did not proceed to the complete formation of alloy structure. Interestingly, Cu and Zn in the Cu_xZn catalyst functioned synergistically, with Zn being solely responsible for promoting the number of free CO molecules at the surface and metallic Cu handled the reduction of CO to ethanol. However, increasing the amount of Zn resulted in a decrease in the Cu surface sites, which leads to an overall lowering of the FE of ethanol.

While homogeneous alloyed structures can tune the delocalized electronic structure via modification of the types of secondary element and its alloyed amounts, these structures have been less effective for increasing the C–C coupling selectivity over H₂ or CO production. Conversely, separated bimetallic phases have demonstrated the feasibility of the CO spillover from the CO-producing guest metal domain to the Cu domain, and indicated that the higher concentration of *CO on the Cu domains contributes to high opportunity for C–C

coupling. Moreover, because the C–C coupling reaction is still expected to occur majorly on the Cu domains, the preferential reaction pathways between ethylene production and ethanol production can then be modified.

Cu metals with HCOO[–]-producing guest metals such as In and Sn are well-known for their combined ability to produce CO, while strongly suppressing HER and C₂₊ products, which are expected due to the decreased binding energies of intermediates.^[87,88] Decreasing the binding energies of *H and *CO would decrease the intrinsic activity for HER and further reduction of *CO to hydrocarbons. Sarfraz et al. aimed to understand the nature of active sites on the Cu–Sn alloy and their role in CO₂RR to CO.^[89] With the optimum Sn loading of ≈3.9 μmol cm^{–2}, the bimetallic catalyst showed CO FE as high as 90% within the potential range –0.4 to –0.8 V (vs RHE), as shown in Figure 6a,b, and remained stable for at least 14 h. The catalytic active sites in the Cu–Sn catalyst can be formed in either of two ways: 1) formation of metallic Sn on top of Cu⁰, or 2) complete formation of Cu–Sn alloy. They demonstrated that only the controlled changes of Sn on the metallic Cu surfaces can lead to efficient and selective CO₂RR. Through DFT calculations, they showed that Sn atom is most active when placed on the surface of the Cu catalyst rather than inside the layers of the catalyst. Similarly, Luo et al. emphasized the advantage of a bimetallic structure with well-deposited secondary metal on the

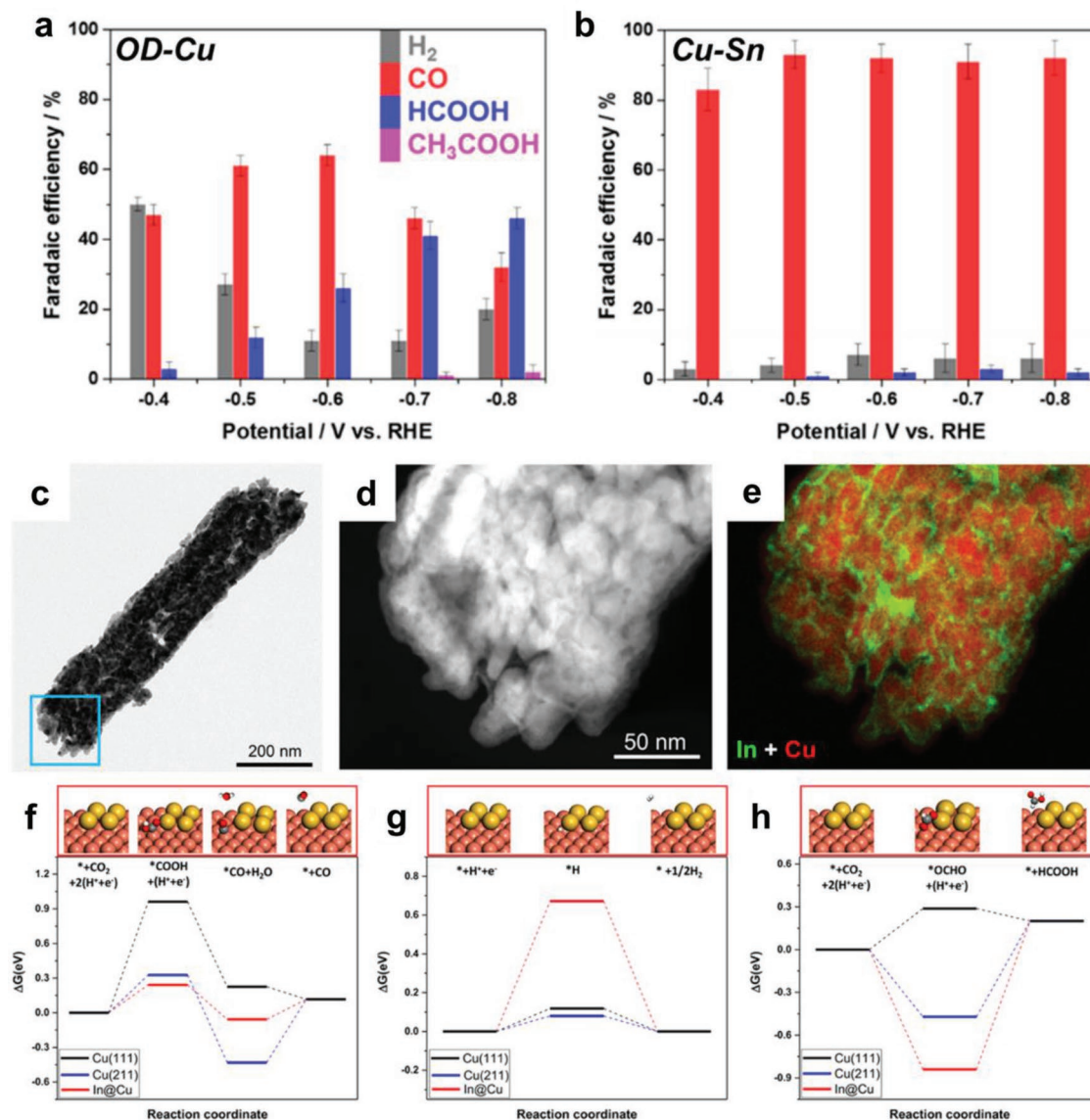


Figure 6. a,b) Cu–Sn catalyst. Faradaic efficiency analysis of a) OD-Cu and b) Cu-Sn catalysts at applied potentials (0.1 M $KHCO_3$, pH 6.8, saturated CO_2). Reproduced with permission.^[89] Copyright 2016, American Chemical Society. c–h) Cu–In catalyst. c) TEM image, d) HAADF-STEM image, and e) corresponding EDS elemental mapping analysis of CuIn20 wire catalyst. Free-energy diagrams for f) CO_2 to CO, g) H_2 evolution, and h) CO_2 to HCOOH on Cu(111), Cu(211), and In@Cu surfaces, at 0 V versus RHE. The upper panels show the DFT-optimized geometries for each reaction step on In@Cu. Cu: reddish-orange, In: yellow, C: dark-gray, O: red, and H: white. Reproduced with permission.^[90] Copyright 2018, American Chemical Society.

surface of the Cu metal.^[90] The group reported a highly stable Cu–In catalyst with a thin layer of In deposited all over the surface of Cu nanowires. Luo et al. performed DFT calculations and several characterization tests to understand the intrinsic property of their synthesized material, wherein they revealed that the catalytic activity of Cu–In catalyst originates from the unique synergy between the two metals. The group demonstrated that the high density of In nanoparticles was evenly adsorbed on the surface of Cu nanowires in the metallic state, instead of forming the Cu–In alloy, as shown in Figure 6c–e. The metallic Cu–In interfaces effectively reduced the free energy barrier for the formation of the $^*COOH$ intermediate during the electroreduction of CO_2 to CO (Figure 6f–h). More

importantly, In nanoparticles protected the metallic Cu from fast deactivation to result in CO FE of $\approx 93\%$ at 0.6 V and a remarkable stability for over 60 h.

4.3. Cu Compound (Cu Metal + Non-Metal)

Other efforts to modify Cu have been made via incorporation of non-metallic elements, such as sulfur, nitrogen, or boron.^[91,130] While the electroreduction of CO_2 on metallic Cu or on OD-Cu catalysts tends to favor the formation of CO, hydrocarbons, and alcohols, the production of formate/formic acid is still limited to lower FE at overpotential around -0.8 V to -1.0 V. Copper

sulfide ($\text{Cu}_2\text{-xS}$) has been considered as highly promising catalyst due to the ability of the S species to stabilize the CO_2^* intermediates and to promote a selective CO_2RR toward formate.^[92] Huang et al. introduced sulfur dopants on the OD-Cu surface and used the as-prepared catalyst toward CO_2RR .^[93] The sulfur-doped Cu_2O -derived catalyst had Cu^+ species in the form of CuS_x and metallic Cu. The S dopants present on the surface of the Cu_2O -derived catalyst remained stable for over 12 h at lower overpotential, in which the HER was synergistically suppressed, the adsorption of carboxyl intermediates was weakened, and the reduction of CO_2 to formate with FE of 75% and current density of -13.9 mA cm^{-2} at -0.9 V was achieved. However, upon the increase in the overpotential, the S dopants started to be removed from the surface of Cu catalyst and were transformed into H_2S or HS^- ions, thus unmasking the catalytic sites of the Cu_2O -derived catalyst and eventually favoring the formation of CO and hydrocarbons. Similarly, Shinagawa et al. prepared sulfur-modified Cu catalyst (Cu-S) via in situ reductive reconstruction of nanosized CuS precursors to further improve the selectivity of formate production from CO_2 .^[94] During the initial electroreduction tests, they observed drastic changes on the particle size wherein the sample material with initial size of $15 \pm 7 \text{ nm}$ was broken down to smaller particles with an average size of 3 nm , while the larger particles ($>20 \text{ nm}$) were retained. This event made the group realize the probable size-activity relationship of Cu-S catalysts during CO_2RR , and therefore, they proceeded to prepare bulk size S-modified Cu catalysts. Auger emission (AE) spectra in the Cu LMM region elucidated the Cu states present on the surface of catalyst, and analyses revealed that Cu^+ and Cu^{2+} species from Cu_2O and CuS, respectively, were present on the surface. The modification of Cu with S affected the energy levels of $^*\text{COOH}$, $^*\text{OCHO}$, or $^*\text{CO}$ intermediates, which inhibited the formation of CO and hydrocarbons,^[72] but activated the pathway toward formate formation with FE as high as 80% at -0.8 V (vs RHE) that remained stable for 12 h. In line with this, Deng et al. reported that the concentration of S dopants on the surface of Cu catalyst is more important than the surface morphology because it can direct the product selectivity.^[95] They conducted DFT calculations to further elaborate the effect of S dopants on the energy levels of $^*\text{COOH}$ and HCOO^* intermediates. Formate formation on Cu (111) and surfaces via HCOO^* intermediates at different potentials revealed that HCOO^* is adsorbed more strongly onto the CuS_1 surface because CuS_1 possesses higher free energy uphill. Likewise, CO formation on bare Cu and sulfur-modified Cu catalysts via $^*\text{COOH}$ intermediates demonstrated that S dopants significantly weaken the adsorption energy of $^*\text{COOH}$.^[18] Overall, at negative potentials, CuS_1 is less favorable toward CO production and more favorable toward formate production. Meanwhile, copper sulfide nanosheet arrays directly grown on the surface of nickel foam substrate (CuS@NF) have shown competitive advantages when used toward electroreduction of CO_2 to CH_4 . Such catalyst design obtained high CH_4 FE of $73 \pm 5\%$, and remained remarkably stable for over 60 h. The high CO_2RR performance was attributed to the obtained nanosheet morphology of CuS and modified intrinsic properties. In particular, the direct growth of CuS nanosheets on the surface of nickel foam substrate eliminated the use of polymer binders and conductive

additives, which provided efficient mass transport over a large electroactive area.^[96] While the nickel from NF substrate might affect the status of copper sulfide and its catalytic activity, the overall mechanism formation of the CO_2RR to CH_4 on the CuS-based electrocatalyst has not been clearly understood. Thus, further investigations to elucidate this new insight about the contribution of copper sulfide to hydrocarbon production via CO_2RR are highly recommended.

Furthermore, Cu_3N is known to be more stable than Cu_2O due to the more covalent nature of nitrides than oxides.^[97] Similarly, the presence of mixed Cu^+ and Cu^0 species on nitride-modified Cu catalysts can possibly promote an efficient selective CO_2RR toward C_{2+} products.^[47] In contrast, a core-shell nanostructure^[98] with a metallic Cu shell protecting the Cu_2O core from further reduction, can modify the electronic structure of the surface catalyst and eventually influence the chemisorption of the intermediates in the electrocatalytic reaction. Related to these possibilities, Liang et al. designed a novel catalyst composed of Cu deposited on Cu_3N .^[99] Figure 7a shows a schematic diagram of the Cu-on- Cu_3N catalyst preparation. Initially, the long-chain octadecylamine ligands on the surface of the Cu_3N nanocrystals were replaced with short-chain azide (N^{3-}) while being exposed to ambient air so that an outer oxide layer could be simultaneously formed. Then, the modified Cu_3N crystals went through facile electroreduction process to produce the active Cu-on- Cu_3N catalyst. After the initial reduction process, XPS spectra of Cu 2p showed the existence of both Cu^+ and Cu^0 while HRTEM with electron energy loss spectroscopy showed that the Cu atoms were well-distributed all over the nanoparticle and N atoms were concentrated in the core. Compared to Cu on Cu_2O , Cu on Cu_3N led to 6.3 times enhancement in the ratio of C_{2+} to CH_4 products, and this result was suggested to be related to the stabilized Cu^+ from Cu_3N support and the suppressed reduction of Cu_3N support (Figure 7b). DFT calculations revealed that Cu^+ on Cu_3N achieved the highest energy barrier for the C_1 pathway and the lowest CO dimerization energy barrier because of its modulated partial oxidation state (Figure 7c). Both factors led to high selectivity of CO_2 to C_{2+} products with FE of $64 \pm 2\%$ at -0.95 V and outstanding stability for over 30 h. Correspondingly, Mi et al. synthesized Cu_3N -derived Cu nanowires (NW) via electrochemical reduction of Cu_3N NWs.^[100] They discussed that the existence of abundant grain boundaries was mainly attributed to the fast release of N^{3-} during the reduction of Cu^+ species to metallic Cu, which started the surface reconstruction upon the introduction of a large negative voltage. The resultant grain boundaries increased the electrochemically active surface area (ECSA) by introducing additional catalytic sites. With a high density of electrocatalytic active sites, the affinity to $^*\text{CO}$ and $^*\text{COH}$ intermediates became stronger, which then facilitated the formation of C_{2+} products.^[101] The modified catalyst exhibited selective electroreduction of CO_2 to ethylene with FE of 66% at -1.0 V (vs RHE) and remarkable stability even after 28 h.

Although the presence of oxidized $\text{Cu}^{\delta+}$ species in the Cu-based catalyst has been theoretically proposed to possibly increase the production of C_{2+} products during CO_2RR , such species are not stable enough to survive at high negative potentials, which made it challenging to provide a straightforward link between the Cu surface states and CO_2RR performance.^[51,73]

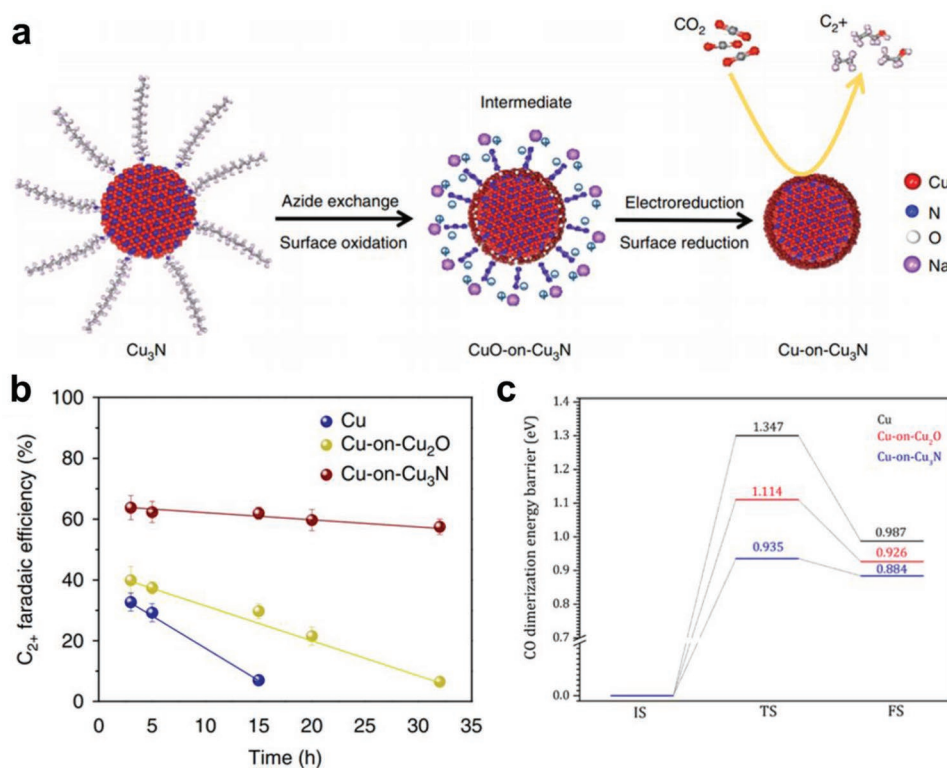


Figure 7. Cu-on-Cu₃N catalyst. a) Schematic diagram of preparing Cu-on-Cu₃N catalyst. b) Stability test of C₂⁺ selectivity on the Cu, Cu-on-Cu₂O, and Cu-on-Cu₃N catalysts at −0.95 V versus RHE. c) Activation energy barrier for CO dimerization demonstrated for Cu (100), Cu-on-Cu₂O, and Cu-on-Cu₃N. IS stands for initial state of two adsorbed CO, TS stands for the transition state, and FS stands for final state of OCCO intermediate. Reproduced with permission.^[99] Copyright 2018, Nature Publishing Group.

To overcome this and stabilize the oxidized Cu^{δ+} species for a longer time, incorporation of modifier elements such as boron (B) atoms into Cu-based catalyst was proposed.^[102] This proposal was based on the recent studies on B-doped Pd catalyst and B-doped nanodiamond electrodes, which successfully increased formate and formaldehyde production within a wide potential window, respectively.^[103,104] Chen et al. postulated that incorporating B atoms into the surface of OD-Cu will affect the electronic configuration of the surrounding atoms.^[105] In a typical synthesis, Cu foils were immersed into a chemical bath for 4 h to form the initial Cu(OH)₂ film, and then, B₂O₃ solution was poured onto the surface of the films. The as-prepared films were calcined at 500 °C under air, and then electrochemically reduced to obtain the final B-doped OD-Cu (B-OD-Cu) catalyst. While XPS analysis of B-OD-Cu revealed that B species available on the surface of catalyst existed between B⁰ and B³⁺, which suggests that B atoms are sub-oxidized and can promote effective electron transfer from Cu to B. Auger Cu LMM line analysis confirmed that Cu⁺ was the main species in the catalyst with a very small amount of Cu⁰, which may indicate the ability of B atoms to stabilize the Cu⁺ species. The presence of B atoms in OD-Cu decreased the applied potential and promoted selective CO₂RR with FE of 27.1% for C₂ products even at low applied potential of −0.7 V (vs RHE). According to Bader charge analysis by Zhou et al., B-doping can effectively tune the structure of Cu-based catalyst since B atoms show a good adsorption behavior on the Cu (111) surface. Cu atoms near the B atoms

are more positively charged, and the binding energy of CO over the B-doped Cu surface is stronger as compared to pristine Cu. More importantly, the presence of B atoms can increase the reaction energy required for the CO* + H* → CHO step (CO₂ to C₁ pathway) but decrease the reaction energy required for the CO* + CO* → OCCO* step to enhance CO₂ to C₂ selectivity.^[102]

4.4. Supported Cu-Based Catalyst

For the use of electrocatalysts, catalysts can be loaded on the support materials, which can be categorized into three different materials, namely 1) carbon-supported Cu-based NPs, 2) metal-oxide-supported Cu NPs, and 3) polymer-supported Cu NPs.^[10] The interactions between Cu and supporting materials have varying degrees of effects on the final physicochemical properties of the Cu-based catalyst.

Carbon materials are the most popular supporting materials. Activated carbon, carbon nanotubes (CNTs), graphene, graphite, and N-doped graphene have distinct properties such as high conductivity, high surface area, and low background activity that make them a valuable choice as supporting materials.^[106] Some of the above-mentioned Cu-based electrocatalysts were loaded onto a carbon support for CO₂RR testing, similar to those prepared electrodes for other applications such as fuel cells or water electrolysis. The carbon support can be effective to increase and utilize the surface of the Cu-based

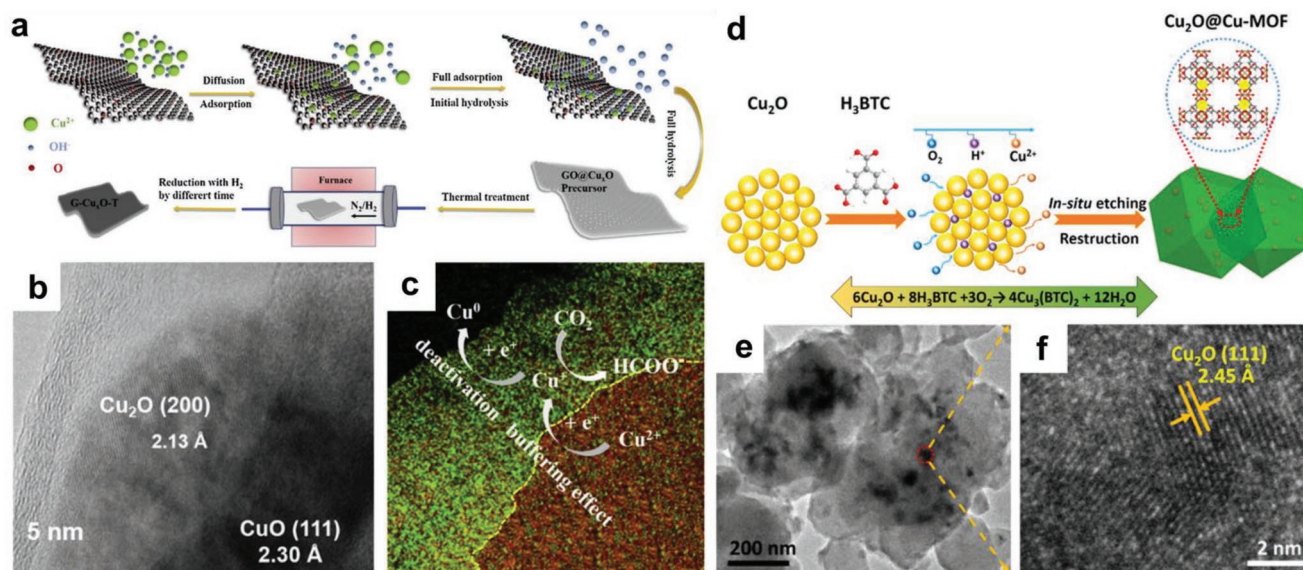


Figure 8. a–c) Cu₂O decorated graphene oxide catalysts (G-CuxO-T). a) Schematic illustration for synthesis of G-CuxO-T catalysts. b) HRTEM image of G-CuxO-2 h catalyst. c) A proposed "buffering effect" illustrating the origin of durability of G-CuxO-T catalysts. Reproduced with permission.^[114] Copyright 2019, Elsevier. d–f) Cu₂O@Cu-MOF catalyst. d) Schematic illustration of the process to synthesize Cu₂O@Cu-MOF catalyst. e) TEM and f) HRTEM images of Cu₂O@Cu-MOF catalysts. Reproduced with permission.^[122] Copyright 2019, American Chemical Society.

particle catalysts, and its chemical and morphological properties can be easily modified by varying the local pH near electrocatalyst/electrolyte interfaces, electronic states, and morphology transformation of Cu-based catalysts.^[107] Notably, recent studies have shown that as-received carbon supports, specifically graphene oxide, can contain trace metal impurities such as Cu which dramatically alter CO₂RR catalytic activity and induce CH₄ formation. Therefore, special cares have to be paid not to mislead the origin of CO₂RR activity when carbon-based materials are employed as support materials of electrocatalysts. Pre-washing them in ultrapure nitric acid before employing as the support material is highly recommended to decrease effects by metallic impurities.^[108] Furthermore, direct deposition or tailoring of Cu-based nanoparticles to the structure of cleaned carbon supports to form Cu/C-based electrocatalyst could be beneficial toward the improvement of the CO₂RR performance. Recently, Zhao et al. reported on an OD-Cu/carbon catalyst, which showed significant improvement in the activity and selectivity toward alcohol generation.^[109] The synergistic effect between the Cu particle size, high Cu₂O content, and highly porous carbon matrix were suggested to be responsible for electroreduction of CO₂ to alcohol with a total FE of 45.2–71.2% at –0.1 to –0.7 V (vs RHE). In this study, the carbon support was derived through the facile carbonization of Cu-based metal organic framework precursor (MOF, HKUST-1), and the induced porous structure reduced the diffusion resistance for overall mass transfer which resulted in a faster movement of CO₂ and alcohol species. In addition, the presence of Cu⁺ species was suggested to allow the valence band electrons to contribute to the CO₂ or CO adsorption, which caused strong adsorption of atomic O onto the Cu⁺ surface, and this initiated the alcohol formation at low overpotential.^[110] Similarly, Huo et al. designed a catalytic system of Cu/SnO_x NPs tailored on the surface of CNTs, in which the CNTs not only functioned

as a support to attach the oxide nanoparticles but also provided an efficient electron conductive pathway during the reduction reaction.^[111] They observed that product selectivity changed from hydrocarbons to CO to formic acid by only adjusting the Cu/SnO_x ratio in the material structure. Cu NPs with optimum concentration of SnO_x and tailored to CNTs electrochemically reduced CO₂ to formic acid with FE as high as 77% and partial current density of 4.0 mA cm⁻² at potential –0.99 V (vs RHE). Well-deposited Cu/SnO_x NPs on the surface of CNTs provided favorable electronic interactions and geometric synergistic effects, which possibly enhanced the catalytic selectivity.

Moreover, graphene-based materials have extremely high surface area of ≈2600 m² g⁻¹, ultrathin layers, high thermal/electrical conductivity, remarkable stability, and low background activity: all of which are suitable characteristics of carbon material to support Cu-based electrocatalyst.^[112] Cao et al. utilized the reduced graphene oxide (rGO) decorated with Cu NPs as electrocatalysts toward CO₂RR.^[113] They secured the strong adsorption of Cu²⁺ cations on the surface of GO by initially modifying its surface with chitosan, and then, Cu²⁺ cations on GO were reduced via microwave treatment to form the Cu NPs/rGO nanohybrid. The presence of oxidized metallic Cu NPs on the ultrathin structure of rGO, and the increased grain boundaries on the surface of the catalyst were suggested to be responsible for the overall performance of CO₂RR. However, the group failed to electrochemically reduce the CO₂ to any C₂₊ products, and only detected H₂, CO, and HCOOH products. In a related work on GO materials, Ni et al. presented an interesting insight on the role of multivalent Cu in the selectivity and durability toward CO₂RR.^[114] They utilized Cu_xO NPs decorated on the surface of GO and named it G-CuxO-T for easy tagging, where T corresponds to the reduction time of catalyst in hydrogen. Figure 8a shows a schematic illustration for the synthesis of G-CuxO-T catalysts. They reported that by adjusting

the reduction time, ratios of multivalent Cu ions in the catalyst can be easily controlled, and with 2 h reduction time, they obtained the highest selectivity toward formic acid with FE of 81% and current density of 19.3 mA cm^{-2} at -0.8 V (vs RHE). The material exhibited an impressive stability of 87.2% retention even after 9 h of continuous operation. Figure 8b,c shows a TEM image of the catalyst and the proposed “buffering effect”, illustrating the origin of durability of the catalysts. The constant concentration of Cu^+ species at the surface effectively sustained the overall activity and stability of the electrocatalyst during the electrochemical reduction reaction. In addition, the deactivation of the material started the formation of the Cu^0 species.

In contrast, Cu supported on the modified carbon support by nitrogen doping can induce the synergic effect for enhanced CO_2 reduction activity.^[115] Incorporating N-atoms into the graphene lattice to develop N-doped graphene materials has led to impressive catalytic properties for CO_2 RR. Yuan et al. designed a hybrid nanocatalyst consisting of Cu NPs uniformly dispersed on the surface of sheet-like-pyridoxine (VB_6)-modified GO, GO- VB_6 -Cu; pyridoxine was used as the nitrogen rich precursor to the N-functionalized graphene sheet.^[116] The resultant catalyst showed outstanding catalytic activity toward the electrochemical reduction of CO_2 to ethanol with FE of 56.3% at low overpotential of -0.250 V (vs RHE). The remarkable catalytic performance of GO- VB_6 -Cu electrocatalyst was attributed to the presence of pyridinic N species, increased electrochemical active surface area (ECSA), and the presence of metallic Cu during the final reductive activation step. The metallic Cu uniformly embedded on the graphene surface was suggested to stimulate the C–C coupling reactions, which is the most vital step for CO_2 reduction to ethanol.^[117]

Meanwhile, the interaction of metal oxide support with Cu may help to stabilize the NPs size and morphology, O_2 spillover during catalysis reaction, or even the electronic interaction.^[6] In particular, CeO_2 NPs supported on the Cu surface have received widespread attention due to the capability of Ce^{3+} species to supply sufficient O_2 molecules to neighboring Cu.^[118] In addition, metal-oxide interfaces such as Au- CeO_x and Ag- CeO_x were proposed to utilize CO_2 adsorption and the activation ability of CeO_x and were successfully demonstrated to have improved CO partial current density as well as CO Faradaic efficiency.

Lee et al. presented a related work on CeO_2/Cu interfaces for selective electrochemical C–C coupling reactions.^[119] Through the addition of Cu precursors into the hydrothermally prepared Ce/C solution and followed by calcination under air atmosphere, they were able to obtain high density and nanoscale interfaces of Cu/Ce catalyst with a Cu surface rich with Cu^{2+} species while Ce with mixed metal valences of Ce^{3+} and Ce^{4+} . The Cu/Ce catalyst increased the FE of ethanol from 38.8% to 64.7%, with respect to performance of pure Cu catalyst. Based on DFT calculations, Ce NPs interacted with hydrogen bonding while the Cu surface stabilized the $^*\text{OCCO}$ intermediate at Cu/Ce interface, providing an ideal atomic environment. The synergistic effects on the Cu/Ce catalyst were proposed to be responsible for the improvement of selectivity toward C_2 products.^[120] In addition, when the Cu amounts were not sufficient to form the Cu–Cu structure with Cu-doped CeO_2 , the relative activity for CH_4 production over C_2H_4 was increased. The atomic distribution and domain formation of Cu can then be

influenced by the surrounding CeO_2 support, which affects the C–C coupling activity.

Furthermore, metal–organic frameworks (MOFs), which are porous crystalline materials with a 3D framework of metal ions or clusters connected by stiff bi- or multipodal organic linkers, are also recognized as important supporting materials.^[121] Tan et al. reported a $\text{Cu}_2\text{O}@\text{Cu-MOF}$ restructured catalyst with a unique CO_2 -adsorption ability and demonstrated outstanding performance with a total FE of 79.4% toward hydrocarbon products.^[122] Figure 8d shows a schematic illustration of the process of $\text{Cu}_2\text{O}@\text{Cu-MOF}$ catalyst synthesis. Based on the TEM and HRTEM images of the catalyst, shown in Figure 8e,f, the residual oxidized Cu derived from the Cu^+ species on the surface of initially formed Cu_2O nanospheres that fully coated the Cu-MOF, wherein trimesic acid (H_3BTC) functioned as both an etching agent and an organic ligand for the formation of the Cu-MOF hybrid.

However, the development of Cu-based catalyst is still hindered because of the fast deactivation through oxidation, corrosion from the heavy metal contaminants, and the general electrode poisoning from reaction products such as carbon.^[123] Thus, designing a catalyst that has protection against these mentioned deactivation factors is highly necessary. Ponnurangam et al. revealed that protecting Cu-based electrode with a layer of μm -thick film of poly(4-vinyl pyridine) (P4VP) can effectively slow down the corrosion process of the Cu electrode due to the presence of free pyridyl groups that firmly bind to the heavy metal contaminants such as lead.^[124] The addition of the protective polymer layer to the surface of Cu-based electrode enhanced the selectivity toward formic acid and exhibited an outstanding stability even after 30 h of continuous operation. More importantly, Cu^0 - and Cu^+ -P4VP complex has a higher electronegativity and a stronger affinity to interact with $\text{CO}_2/\text{HCO}_3^-$ intermediates compared to pure metallic Cu.^[125] Such properties of Cu-P4VP catalyst lead to lower overpotential and suppression of HER during the electrochemical reduction of CO_2 to formic acid.

5. Summary and Outlook

As described in this progress report, Cu has the unique ability to electrochemically reduce CO_2 to different highly valued products, including CO, HCOO^- , C_2H_4 , $\text{C}_2\text{H}_5\text{OH}$, and CH_4 . Figure 9a,b presents the summarized performance of CO_2 RR on various Cu-based catalysts, all measured in an H-cell type with CO_2 gas bubbling through a liquid electrolyte for comparison. We plotted the maximum FE against 1) its corresponding overpotential and 2) the total current density, in order to provide a visual illustration of the latest trend of product generations via CO_2 RR with respect to the category of Cu (metallic Cu, Cu alloy, Cu compounds, and supported Cu). To interpret the provided graphs, we will first discuss the present conditions of each generated primary carbon product in terms of the relationship of FE, overpotential, and total current density, and then suggest ways to further improve the selective CO_2 RR performance. Production of CO and HCOO^- products has been reported with stable and high FE at considerably lower overpotentials, but with limited current density; this phenomenon is understood

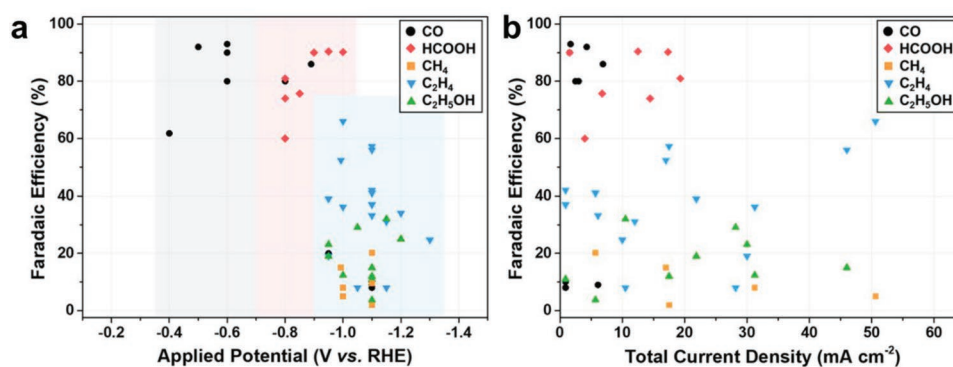


Figure 9. Summary of recent CO₂RR performance on various Cu-based catalysts a) maximum FE versus overpotential and b) maximum FE versus total current density.

because current density is dependent on the applied potential, and further reduction of *CO to hydrocarbon requires a higher overpotential. One of the major challenges in CO₂RR to CO or HCOO⁻ is to overcome the competing H₂ generation, because a further decrease in the overpotential induces a relative increase in the HER selectivity. To improve the CO₂RR performance for these products, finding the optimum overpotential and current density with respect to FE is very important, especially in the case of HCOO⁻ formation, because it still occurs at relatively higher overpotentials compared with CO formation.

In contrast, for the generation of C₁ and C₂ products such as CH₄, C₂H₄, and C₂H₅OH, it is still difficult to achieve high FE at low overpotential. These products are generally produced at higher potentials (around -1.1 V vs RHE), since it is required to overcome the kinetic barriers of related CO₂ intermediates to proceed to the C₁ or C₂ pathway. To obtain high selectivity for CH₄ production, an even higher applied potential is needed. Because the applied potential range is wider, the current density during the generation of these products is relatively higher compared to those of CO or HCOO⁻ products. However, only two electrons are involved for the production of the one molecule of CO or HCOO⁻, whereas 8e⁻ and 12e⁻ are involved for the production of CH₄ or C₂H₄, and hence, the production rates of product moles are of similar level if the involved electron numbers are being considered. Obvious challenges for C₂ chemical generation are finding ways to increase the maximum FE and promote the intrinsic activity for C–C bond formation.

Based on the understanding of fundamental mechanisms, the catalytic activity and selectivity of CO₂RR on Cu catalysts are highly dependent on the composition of electrocatalysts and surrounding conditions, such as pH of the electrolyte and the operating potential. Although there are multiple factors reported to be responsible for the modification of the catalytic activities of Cu-based electrocatalysts, the potential synergistic effects among various structural factors make it more complex to identify the catalytic center that drives the CO₂RR performance. While the sufficient and stable supply of Cu⁰ and oxidized Cu (Cu⁺ or Cu²⁺) during catalysis reaction has been proposed to determine the identity of carbon products, other significant factors such as particle size, surface area, facet, defect, and morphological effects are associated to the excellent CO₂RR performances of the Cu-based electrocatalysts. Therefore, understanding the link between the Cu surface and

CO₂RR activity is important for the future design of CO₂RR electrocatalyst.

The particle size and shape of single Cu nanocrystals are highly crucial to control the product selectivity of CO₂RR, since facile alteration of these structural parameters could lead to different reaction pathways. Smaller nanocrystals could exhibit higher overall CO₂RR activity, given that they provide higher electrochemical active surface area; however, non-faceted spherical Cu nanocrystals could hinder the formation of hydrocarbon products owing to the stronger bonding of the increased under-coordinated atoms, which blocks the subsequent hydrogenation of CO. Furthermore, drastic changes in the particle size during catalysis reaction, wherein the initial Cu bulk particle was broken down to smaller particle sizes, were observed to create additional active sites and access of metastable oxidized states in the defective structures, which was beneficial for improving the selectivity and stability of CO₂RR. Likewise, availability of oxygen in the subsurface level was also proposed to induce significant changes on the Cu surface for selective CO₂RR toward hydrocarbons and alcohol products.

Altering the composition of the single Cu crystal catalyst by combining it with secondary metals such as Pt, Pd, Ag, Au, Zn, In, or Sn, or with elements such as sulfur, nitrogen, or boron, seemed to be an effective approach because CO₂RR on Cu alloy and Cu compound (Cu + non-metal) have shown remarkable selectivity and stability toward CO, HCOO⁻, C₁, and C₂ products. While the roles of secondary metal and non-metal elements on the modified catalysts were dependent on their nature, the arrangement of these guest metals on the Cu surface can affect the electronic states of the catalyst, the geometric distance between the surface atoms, and the reaction kinetics between the surface adsorbed intermediates, all of which can alter the binding energies of the intermediates and preferable reaction pathways. For instance, the created interfaces by metallic Cu with secondary metals such as Au, Ag, and Zn can promote their intrinsic activity by modifying the electronic structure or provide tandem catalytic reaction pathways across each domain. In particular, separated bimetallic phases could promote CO spillover from CO producing guest metal domain to Cu domain, and the higher concentration of *CO on the Cu domains could contribute to a high opportunity for C–C coupling. Owing to the more covalent characteristics of nitrides compared to oxides, Cu⁺ species from Cu₃N showed more

stability than those from Cu₂O. Similarly, the modification of Cu with sulfur was considered promising due to the ability of S species to affect the energy levels of CO₂* intermediates and activate the pathway toward formate formation. B-doping was proposed to be an effective approach to promote CO₂ to C₂ selectivity since boron atoms show good adsorption behavior on the Cu surface. Meanwhile, the interactions between Cu and supporting materials such as carbon nanotubes, N-doped graphene, metal oxides, and polymers, have different degrees of effects on the final physicochemical properties of the Cu-based catalyst. For instance, carbon materials could not only function as the substrate and electron conductive pathway during the reduction reaction, but also increase the active surface and modify the electronic states of the Cu-based particle catalysts. The synergistic interaction of metal oxide support with Cu may help stabilize the NP size and morphology, O₂ spillover during catalysis reaction, or even the electronic interaction.

The production of CO from CO₂ reduction has increased considerably with FE as high as unity at low overpotentials. Meanwhile, the formation of formate/formic acid is still limited at overpotential around −0.8 V to −1.0 V, and the performance of CO₂RR toward C₂₊ products including ethylene and isopropanol is still very limited due to poor product selectivity and highly unstable electrocatalyst. Modification of the structural properties of Cu-based catalyst by methods that involve pursuing controlled morphology and particle size with larger efficient active sites, or promoting surface defects, is the most sought research direction since these methods have shown significant improvement in the CO₂RR performance. For instance, engineering the defects or oxygen/metal vacancies on the surface of Cu catalyst could promote additional efficient active sites, and possibly provide continuous supply and adequate amount of Cu⁰ and Cu⁺ species. However, identification of these active species via careful in situ analysis techniques is highly needed in order to elucidate the effect of Cu surface states to CO₂RR performance. Furthermore, protecting these active sites and species from fast structural deterioration is as important as inducing one. The core-shell nanostructure of Cu-based electrocatalysts with nitrogen-doped carbon cages or a pyridyl-rich polymer shell protecting the metallic Cu or oxide-derive Cu core, could protect the catalyst from fast deactivation or corrosion due to the ability of shell compounds to bind with heavy metal contaminants. In addition, tailoring the Cu-based electrocatalyst to support materials such as carbon or transition metal oxides could preserve the catalyst structure and provide beneficial synergistic effects for improving the catalytic activity. Finally, employing nanostructural engineering to form a Cu alloy catalyst with precise hollow nanostructure, in the form of nanocages or nanoframes, and with a controlled order of alloy composition, could be a promising research direction. While hollow nanostructure provides extreme high surface area and multiple active sites, they are susceptible to structural deterioration due to the harsh conditions during the catalysis reaction. Thus, investigating the effects of de-alloying process or phase segregation after the collapse of the hollow nanostructure during CO₂RR is highly relevant to understand its benefits (or disadvantages) to the catalytic activity. Finally, we hope that this progress report stimulates new ideas for the future designs of Cu-based electrocatalysts in order to improve the performance of CO₂RR toward C₂₊ products.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

catalyst surfaces, CO₂ electroreduction, copper, oxidation states, selectivity

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