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# Engineering Strategies in Rational Design of Cu-Based Catalysts for Electrochemical CO<sub>2</sub> Reduction: From Doping of Elements to Defects creation

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## Abstract

Copper (Cu)-based catalyst design for electrochemical CO<sub>2</sub> reduction (e-CO<sub>2</sub>R) has attracted much interest. This is because it could help climate change by converting CO<sub>2</sub> into useful chemical products. This study considers a range of techniques used to optimize Cu-based catalysts, from element doping to defect engineering. Each technique has its advantages as well as its own unique problems. Doping Cu with noble metals such as silver (Ag) can give very

high catalytic activity and selectivity, but it also has disadvantages in terms of cost and long-term stability. In contrast, defect engineering which uses Cu as a material is both economically viable and sustainable. Maintaining stability and reliability are demanding tasks that require precise control. In addition, the single-atom approach has been a breakthrough method. It can efficiently and cheaply accommodate multiple carbon materials from CO<sub>2</sub>, and other than this it's quite stable and steady. It is possible for us to gain control over the active sites on an atomic level, even if we have inefficiency and selectivity problems that remain to be resolved. Due to this method, the chemical toolbox for Cu-based catalyst design has been expanded with many other tricks in addition. As they are flexible and can be tailored to specific applications or requirements, new types of Cu-based catalysts will be able to help in e-CO<sub>2</sub>R. When technologies mature, their sustainable deployment and global impact will depend on rigorous environmental impact assessments. It is important to emphasize the importance of Cu-based catalysts in the fight against climate change. In this crucial undertake--the paper also highlights the need for further research, innovations, and collaboration between nations.

## 1. Introduction

As global carbon dioxide (CO<sub>2</sub>) levels rise and climate change becomes more entrenched the world faces an ongoing dilemma of how to cope with environmental problems. Very recently, there has been considerable consultation into sustainable technologies [1]. These copper-containing catalysts are totally unique as they convert CO<sub>2</sub> into feedstocks for chemical production. Here's a new way of thinking: Where CO<sub>2</sub> is concerned as a resource, not a pollutant. This novel approach to carbon economy has the potential of being both sustainable and circular [2]. This review focuses on Cu-containing catalysts and how much they have ventured into e-CO<sub>2</sub>R. It delves into the skills of engineering designed for affecting these catalysts intentionally. Engineering strategies include techniques such as selectively adding elements through doping, inducing defects within crystal lattices and using the single-atom approach to control overactive sites for innovation in precision. Conversion of CO<sub>2</sub> to beneficial compounds through reactions is the focus of e-CO<sub>2</sub>R. This entire area of research has the urgency to find some solution as the emissions are becoming an issue for global warming today. This is done through capturing CO<sub>2</sub> from sources such as power plants, industrial processes and the atmosphere. These captures CO<sub>2</sub> are converted into products that have various uses. Different methods could be used to collect CO<sub>2</sub> which are post-combustion capture, pre-combustion capture, and direct air capture [3].

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Capturing and storage of carbon is an essential step in limiting CO<sub>2</sub> emissions. CO<sub>2</sub> can be employed in the production of goods in transformation processes. The output depends on which products they want to create as well as what resources are available. Common types of CO<sub>2</sub> conversion include electrochemical, photocatalyst and biological reduction, using different reaction agents, such as metal coatings in the nanoscale [4]. Catalysts such as copper and silver metal catalysts for electrochemical reduction are very important [5, 6]. And semiconductor materials are important in these strategies. It is essential to supply energy to drive these conversion reactions, which can be sourced from diverse renewable sources like geothermal, wind, or residual energy from industrial processes. Energy sources that prioritize both efficiency and sustainability not only promote CO<sub>2</sub> emissions reduction but also contribute to lowering the overall carbon footprint.

Carbon dioxide reduction can produce various valuable products such as fuels, chemicals, and materials. Typical outputs comprise of methane, methanol, formic acid, carbon monoxide, and diverse hydrocarbons. Product selection is influenced by market demand, feasibility of application, and environmental factors. It has the potential to mitigate climate change by reducing greenhouse gas emissions [7]. The environmental impact of CO<sub>2</sub> conversion processes must be assessed, taking into account resource availability, energy efficiency, and waste management. This review centers on the investigation of engineering approaches in the logical design of Cu-based catalysts for e-CO<sub>2</sub>R. This review seeks to clarify the complex world of catalyst optimization with a wide range of techniques covered, from element doping to defect engineering. By exploring the underlying theories and mechanisms of e-CO<sub>2</sub>R, it establishes the foundation for a sophisticated comprehension of the various approaches used in catalyst design. The aim of this endeavor is to create a comprehensive resource for researchers, engineers, and policymakers to guide future advancements in the field by consolidating and synthesizing the wealth of knowledge accumulated across various research domains.

## 2. Fundamentals and mechanisms involved in electrochemical CO<sub>2</sub> Reduction

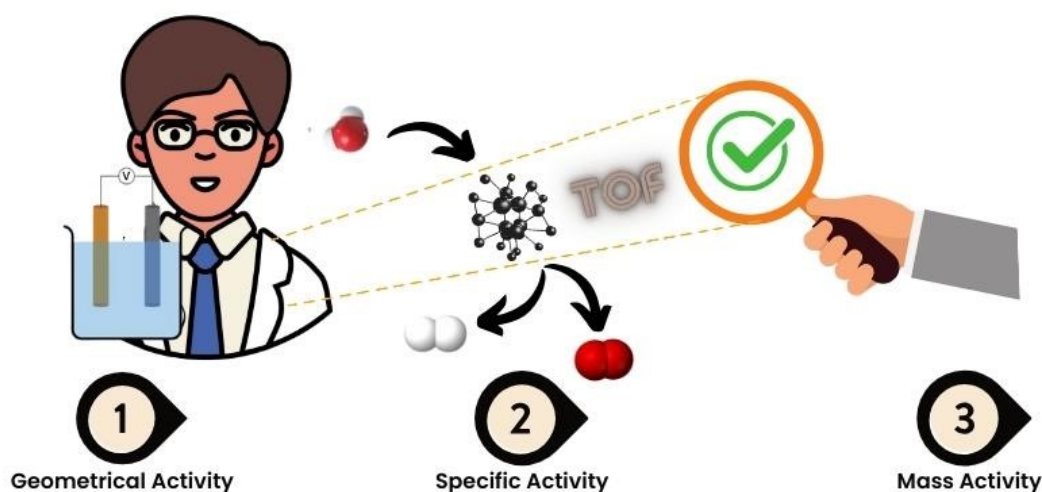
To assess the performance of a system and to determine the effectiveness of an electrocatalyst, several fundamental parameters could be considered for evaluation of e-CO<sub>2</sub>R process. Their assessments are done using some common key parameters employed in evaluating reaction. Faradaic efficiency gives the ratio of electrons employed in generating desired CO<sub>2</sub>R products with respect to the total number electrons that flow through the system and therefore can be used as an indication of selectivity for specific products [8]. The rate at which electrons are

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transferred by electron transfer processes occurring inside a particular unit surface area was reported as a current density and given in  $\text{mAcm}^{-2}$ . Higher current densities would indicate faster kinetics for  $\text{CO}_2\text{R}$  and higher catalytic activity [9, 10].

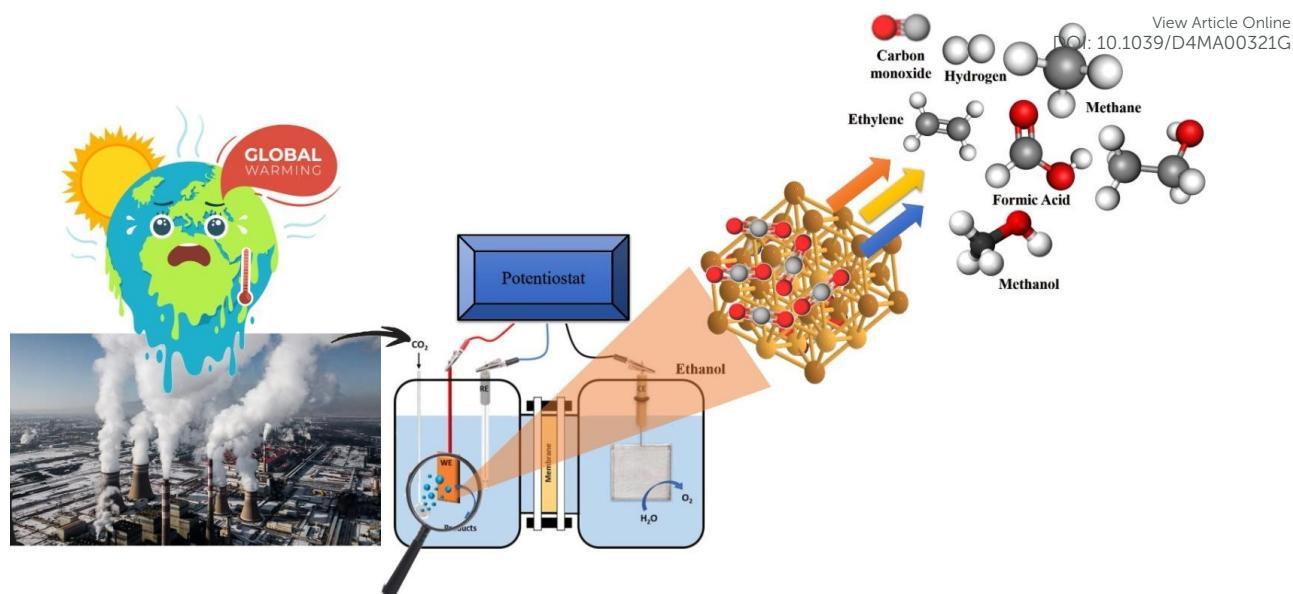
Further, the energy efficiency assesses the energy consumption of the electrochemical  $\text{CO}_2$  reduction process. It quantifies the amount of electrical energy required to produce a certain amount of desired products. Higher energy efficiency indicates a more sustainable and economically viable process [11, 12]. The TOF represents the number of  $\text{CO}_2$  molecules converted into the desired product per active site on the catalyst per unit time [13]. It provides information about the intrinsic catalytic activity of the electrocatalyst, independent of the electrode size or current density [14]. Further, its dependence over geometrical activity, specific activity and mass activity is schematically shown in Figure 1.



**Figure 1:** Dependence of TOF in terms of geometrical activity, specific activity and mass activity.

Product selectivity refers to the distribution of different carbonaceous products obtained during  $\text{CO}_2$  reduction. It evaluates the electrocatalyst's ability to favor specific target products over others. Selectivity can be determined through product analysis using techniques such as gas chromatography, mass spectrometry, or NMR spectroscopy. Figure 2 shows the schematic representation of production of various organic products during electrocatalysis based experiment [15, 16].





**Figure 2:** Schematic illustration of production of different gaseous and liquid products over the surface of electrocatalyst's active sites.

The electrocatalyst's stability and durability are important for long-term operation. Evaluating the catalyst's performance over time and different operating conditions helps determine its durability and potential for practical use [17]. The catalyst loading is the amount of material used on an electrode. Electrolysing the catalyst loading improves the electrode's efficiency and the usage of the catalyst. Learning about the kinetics of CO<sub>2</sub>R can tell us important information about the mechanisms and rate-limiting steps [18]. We can use cyclic voltammetry and electrochemical impedance spectroscopy to analyse reaction kinetics. A comparative study can help to give an idea of how well an electrocatalyst is performing according to different catalyst materials and electrode configurations as well as working modes. Because evaluation procedures vary according to study objectives and desired CO<sub>2</sub>R products. But it's also because the choice of evaluation parameters should suit the study objectives and the products of CO<sub>2</sub>R that are wanted. The performance, selectivity and potential of e-CO<sub>2</sub>R technology can be evaluated by analysing these parameters.

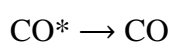
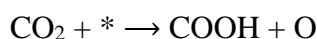
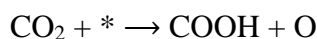
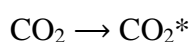
A multitude of intermediate products and steps lies in the reduction of CO<sub>2</sub> on the electrocatalyst's surface. Catalyst material and experimental conditions affect the catalysis mechanism. Generally, certain key steps are taken to be necessary. First, CO<sub>2</sub> molecules come to rest on the electrocatalyst's surface. Adsorption happens due to weak interactions, such as forces of van der Waals, or chemisorption, in which CO<sub>2</sub> forms chemical bonds on the surface of the catalyst. The adsorbed carbon dioxide is activated by breaking its C=O bond, allowing subsequent reduction. To carry out this process energy must be provided, and both the potential applied and the electronic properties of the catalyst can affect it [19].



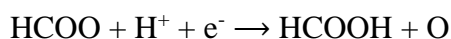
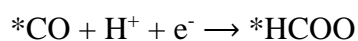
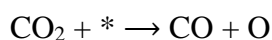
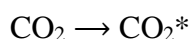


Activated CO<sub>2</sub> can undergo intermediate formation steps, resulting in the production of various reaction intermediates. Frequently encountered intermediates comprise, carbon monoxide (\*CO), formate (\*HCOO) [20], formyl (\*CHO) [21], and carboxyl (\*COOH) species [5]. Electrons from the cathode electrode are transferred to the adsorbed reaction intermediates. The electron transfer is facilitated by the potential difference applied to the electrochemical cell. Protons from aqueous electrolytes can participate in the reactions. Protons react with adsorbed intermediates to produce reduced carbon compounds. The electrochemical reduction of CO<sub>2</sub> generates reduced carbon compounds that subsequently desorb from the catalyst surface. This step facilitates the collection of products for subsequent utilization or analysis. Electrochemical CO<sub>2</sub> conversion involves a range of mechanistic pathways leading to the formation of various products. Here are different mechanisms for the electrochemical CO<sub>2</sub> conversion to different products. CO<sub>2</sub> reduction to CO typically involves a 2-electron transfer process. Mechanistically, CO<sub>2</sub> is first adsorbed onto the catalyst surface, followed by the electrochemical reduction of CO<sub>2</sub> to carboxyl intermediate. The carboxyl intermediate further undergoes protonation and electron transfer steps to form CO and water.

This mechanism is preferred at low overpotentials and in the absence of other competing reduction pathways. It occurs most often on Cu-based catalysts.



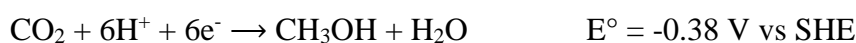
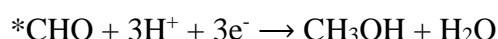
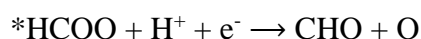
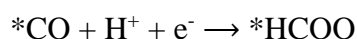
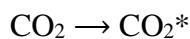
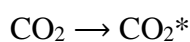
The conversion of CO<sub>2</sub> to formic acid (HCOOH) via reduction usually involves a process of 4 electron transfer. First, CO<sub>2</sub> is reduced to CO, which then undergoes further reduction, being protonated and losing an electron to produce CHO. The formyl intermediate is then further protonated and accepts an electron, forming acid and water. More overpotentials and under acidic environment favors the formation of formic acid. At the same time, some catalysts such as Ag, Au, or Pd exhibit a higher selectivity for formic acid.



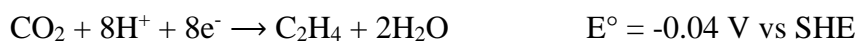
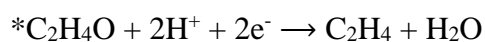
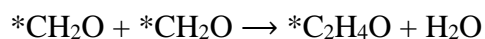
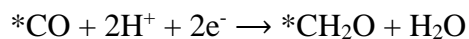
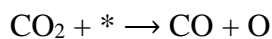
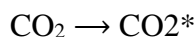


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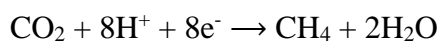
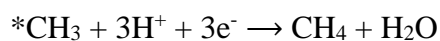
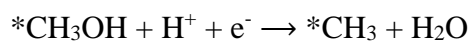
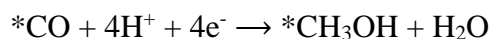
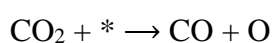
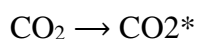
Usually, there is a complex process of creating methanol ( $\text{CH}_3\text{OH}$ ) from  $\text{CO}_2$ . The typical course of conversion of  $\text{CO}_2$  is this: first, it is reduced to  $\text{CO}$  in a two-step reaction sequence, and then goes into the formation of  $\text{HCOO}$ . The  $\text{HCOO}$  intermediate then takes on additional reductions with protonation and electron transfer, leading to formaldehyde. Formaldehyde, in turn, has a series of hydrogenation reactions which consist of multiple protonation and electron transfer steps, and ends in methanol production. In the generation of methanol, the overpotentials that are higher and the more reducing environment the more likely. Quite a number of Cu-based catalysts have shown high methanol selectivity, especially those with alloying elements.



Turning  $\text{CO}_2$  into hydrocarbons such as ethylene ( $\text{C}_2\text{H}_4$ ) through electrochemical reduction typically involves multiple steps.  $\text{CO}_2$  is first reduced to  $\text{CO}$ , and this species can then undergo hydrogenation as well as C-C coupling reactions.  $\text{CO}$  can transform by a series of protonation, electron transfer, and bond formation steps to  $*\text{C}_2\text{H}_x$  (ethylene precursor). Further hydrogenation reactions produce ethylene. At high cathodic potentials in general alkaline conditions favor of the formation of ethylene. Transition metals like Cu assist in C-C coupling and catalyze  $\text{CO}_2$  activation; these enhance ethylene production.

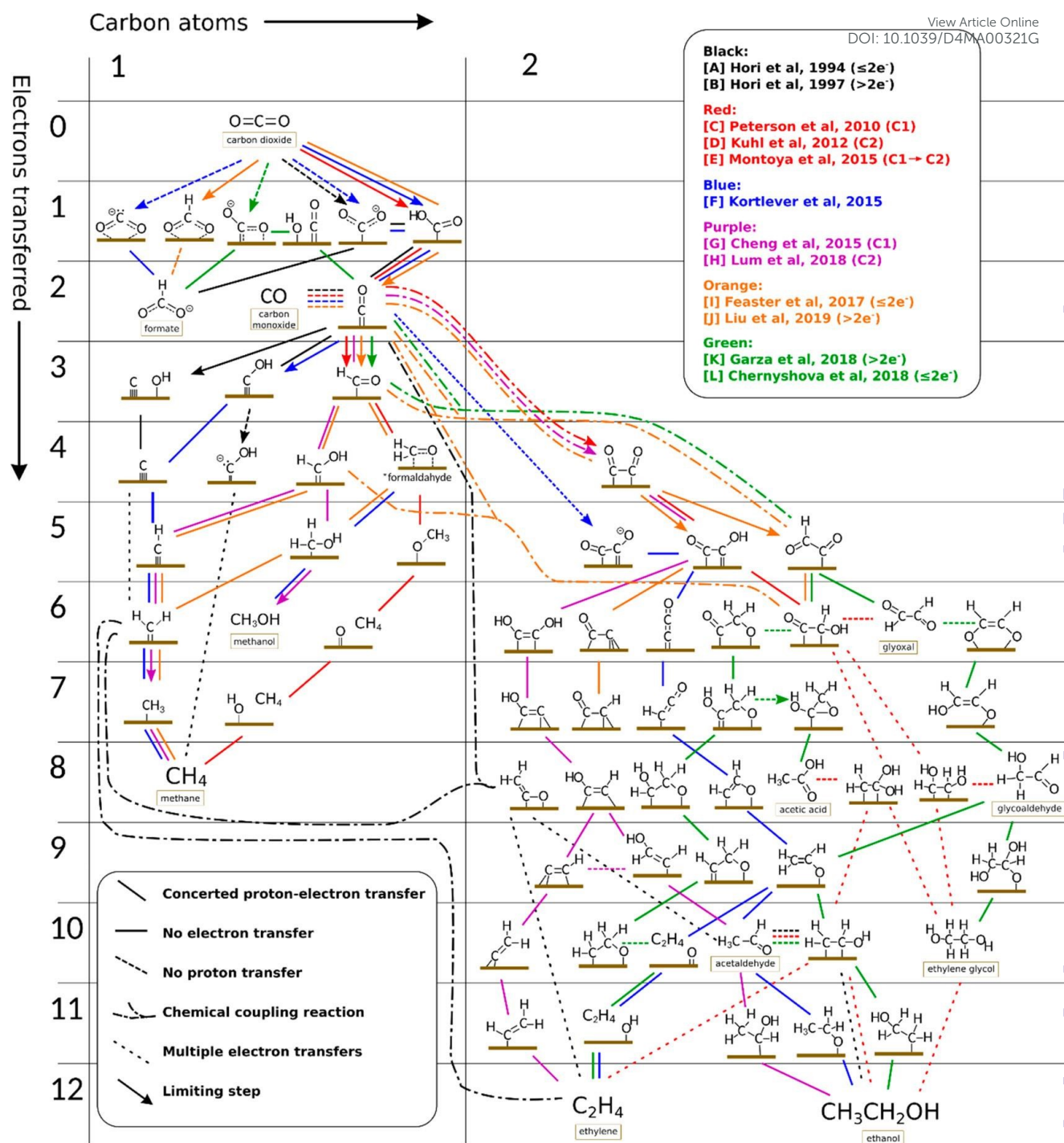


The formation of methane (CH<sub>4</sub>) by the reduction of CO<sub>2</sub> is typically accomplished through a complex series of reactions. In the beginning, CO<sub>2</sub> is turned into CO, which is then hydrogenated to produce CHO (formyl intermediate). The \*CHO intermediate can be further reduced to \*CH<sub>3</sub> (methyl intermediate) through protonation and electron transfer steps. Subsequent hydrogenation reactions lead to the formation of methane. Methane formation is favored at high cathodic potentials and under reducing conditions. Catalysts like Ni, Cu, or bimetallic systems often exhibit higher methane selectivity. All mechanisms for e-CO<sub>2</sub>R to C<sub>1</sub> and C<sub>2</sub> products are schematically shown in Figure 3.



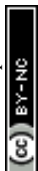
$$E^\circ = -0.24 \text{ V vs SHE}$$





**Figure 3:** Possible different routes for the production of C<sub>1</sub> and C<sub>2</sub> products over the surface of polycrystalline copper upon e-CO<sub>2</sub>R. Reproduced with permission from Ref. [11] Copyright 2023, American Chemical Society.

The electrocatalyst selectivity and activity have a significant impact on the reaction pathway and the resulting product distribution. The catalyst's material, composition, and surface structure significantly impact the CO<sub>2</sub> reduction's efficiency and selectivity. The reaction



mechanism can be complex, with multiple competing pathways occurring simultaneously. The catalyst's surface morphology and defects, as well as reaction conditions such as temperature, pressure, and pH, can affect the reaction mechanism and product distribution [22].

Modern electrocatalysis research aims to enhance comprehension of these mechanisms and create efficient catalysts that can boost CO<sub>2</sub> reduction selectivity and activity. This will facilitate the development of sustainable and economically possible carbon capture and utilization technologies.

### 3. Importance of Cu-based catalysts in e-CO<sub>2</sub>R

Cu-based catalysts have gained significant importance in electrochemical CO<sub>2</sub> reduction for several reasons like. Their high Selectivity for C-C Bond Formation. Copper-based electrocatalysts show a great deal of selectivity in the formation of C-C bonds during the reduction of CO<sub>2</sub> [23]. By this means it is possible to synthesize valuable hydrocarbon compounds such as ethylene (C<sub>2</sub>H<sub>4</sub>) and methane (CH<sub>4</sub>), highly varied in industrial applications as fuels or for use with chemical feedstocks. Natural limit defects of these Cu nanosheets (2-14 nm) were designed to produce ethylene with a high ethylene Faradaic efficiency or 83.2% from carbon dioxide. These defects enhance the formation of ethylene by promoting C-C coupling through reaction intermediates and hydroxyl ions [24]. In the same way, CuO nanoparticles were made and deposited on conductive carbon materials, resulting in a higher Faradaic efficiency (FE) of over 70% for ethylene but only 30% for hydrogen.

The catalyst exhibited durability and selectivity for ethylene production, due to its active domains and high local pH [25]. The Cu-polyamine hybrid catalyst significantly improves ethylene production selectivity by 87% at -0.47V. Additionally, the full-cell energetic efficiency reaches 50%. Raman measurements indicate that incorporating polyamine on a Cu electrode enhances surface pH, CO content, and intermediate stabilization. This demonstrates the positive effect of polymer incorporation on product selectivity [26]. The tw-Cu foil electrocatalyst has dense twin boundaries and shows a Faradaic efficiency of  $86.1 \pm 5.3\%$  for CH<sub>4</sub>. It also reduces the barrier for reduction and has high selectivity for CH<sub>4</sub> [27]. Moreover, copper-based catalysts have shown favorable kinetics for CO<sub>2</sub> reduction reactions [28]. Lower overpotentials are possessed by them, resulting in a reduced energy requirement for driving the desired electrochemical reactions. This characteristic is responsible for increment in process's energy efficiency.

Copper-based catalysts can have different oxidation states and undergo structural changes during electrochemical processes [29, 30]. The versatility of Cu catalysts makes them able to form and react with a greater variety of intermediates, leading different products from the same source. Copper, widely available and plentiful, is an inexpensive choice for massive carbon dioxide reduction.



Copper catalysts have low cost and can be used widely. Cu-based electrocatalysts are preferred for the ability to have adjustable catalytic properties. It is possible to change the catalytic properties of Cu-based catalysts by controlling particle size, morphology, and surface composition. Researchers can optimize catalyst performance and customize selectivity for specific CO<sub>2</sub> reduction products. Copper catalysts are stable and durable for electrochemical CO<sub>2</sub> reduction. They resist deactivation and degradation, allowing them to operate efficiently for a long time. Cu-based catalysts are important in electrochemical CO<sub>2</sub> reduction because they can efficiently produce valuable carbon-based compounds with high selectivity. Their abundance, cost-effectiveness, tunable properties, and stability make them ideal for scaling up CO<sub>2</sub> reduction technologies and using carbon dioxide sustainably in various industrial processes [31, 32].

While Cu-based electrocatalysts show promise for CO<sub>2</sub> conversion, there are still some challenges and current issues that need to be addressed. The key issues associated with Cu-based electrocatalysts for CO<sub>2</sub> conversion include their low faradaic efficiency. Cu catalysts often exhibit low faradaic efficiency for specific CO<sub>2</sub> reduction products like C<sub>2</sub> products [33-35]. Undesired side reactions, such as hydrogen evolution and competitive reduction pathways, can limit the selectivity towards desired products like ethylene or methane [36]. Enhancing the faradaic efficiency and selectivity for these materials remain a major challenge. Cu based electrocatalysts can suffer from stability issues during prolonged CO<sub>2</sub> conversion reactions [37, 38]. A hydrophobic coating of long-chain alkanethiols on Cu dendrite enhances CO<sub>2</sub> reduction selectivity by creating a plastron effect. This creates a gas layer on the electrode, which increases the concentration of CO<sub>2</sub> in that area. The current electrode has drawbacks. Future work should focus on promoting stable hydrophobicity on high-surface-area microporous electrodes. This supports the idea that gas diffusion electrodes can produce stable C<sub>2</sub> products, which may explain the low long-term stability of electrocatalytic surfaces [39]. Surface restructuring, agglomeration, or dissolution of Cu nanoparticles may occur, leading to decreased catalytic activity and selectivity over time [40]. Improving the stability of Cu-based catalysts under harsh reaction conditions is critical for their practical applications. Additionally, the reduction of CO<sub>2</sub> on Cu surfaces often requires high overpotentials, meaning a higher energy input is needed to drive the electrochemical reactions efficiently. Reducing the overpotentials would enhance the energy efficiency of the process and make it more economically viable [41]. Diffusion of CO<sub>2</sub> to the catalyst surface can be a limiting factor, especially in dense electrode structures or with thick catalyst layers. Insufficient CO<sub>2</sub> transport to the catalyst surface can lower reaction rate and efficiency. Efficient CO<sub>2</sub> mass transport is important for catalyst designs and electrode architectures [42].



Cu-based electrocatalysts are susceptible to poisoning or deactivation by adsorbed species or impurities in the reaction environment [43, 44]. Oxygen or sulfur-containing species that are adsorbed can block active sites or alter the electronic properties of the catalyst, leading to reduced activity and selectivity [45]. Mitigating catalyst poisoning effects is crucial for ensuring long-term performance. Despite the abundance and cost-effectiveness of copper (Cu), scaling up copper-based catalysts for large-scale CO<sub>2</sub> conversion processes is still challenging. Innovative synthesis approaches are important for addressing challenges in CO<sub>2</sub> conversion with Cu-based electrocatalysts. Various synthesis techniques can precisely control catalyst composition, morphology, and structure. These approaches improve the selectivity and activity of Cu-based catalysts by giving them specific properties. Metals can be added through alloying or surface modification. Bimetallic or composite catalysts can improve catalytic performance and selectivity by leveraging the synergistic effects between Cu and other metals. Bottom-up assembly methods can be used to develop nanostructured Cu catalysts, providing control over particle size, shape, and surface properties. This leads to improvements, in both the efficiency and stability of reactions. Researchers have the opportunity to employ synthesis techniques in order to design electrocatalysts based on copper that exhibit performance, selectivity, stability and scalability for efficient conversion of CO<sub>2</sub>.

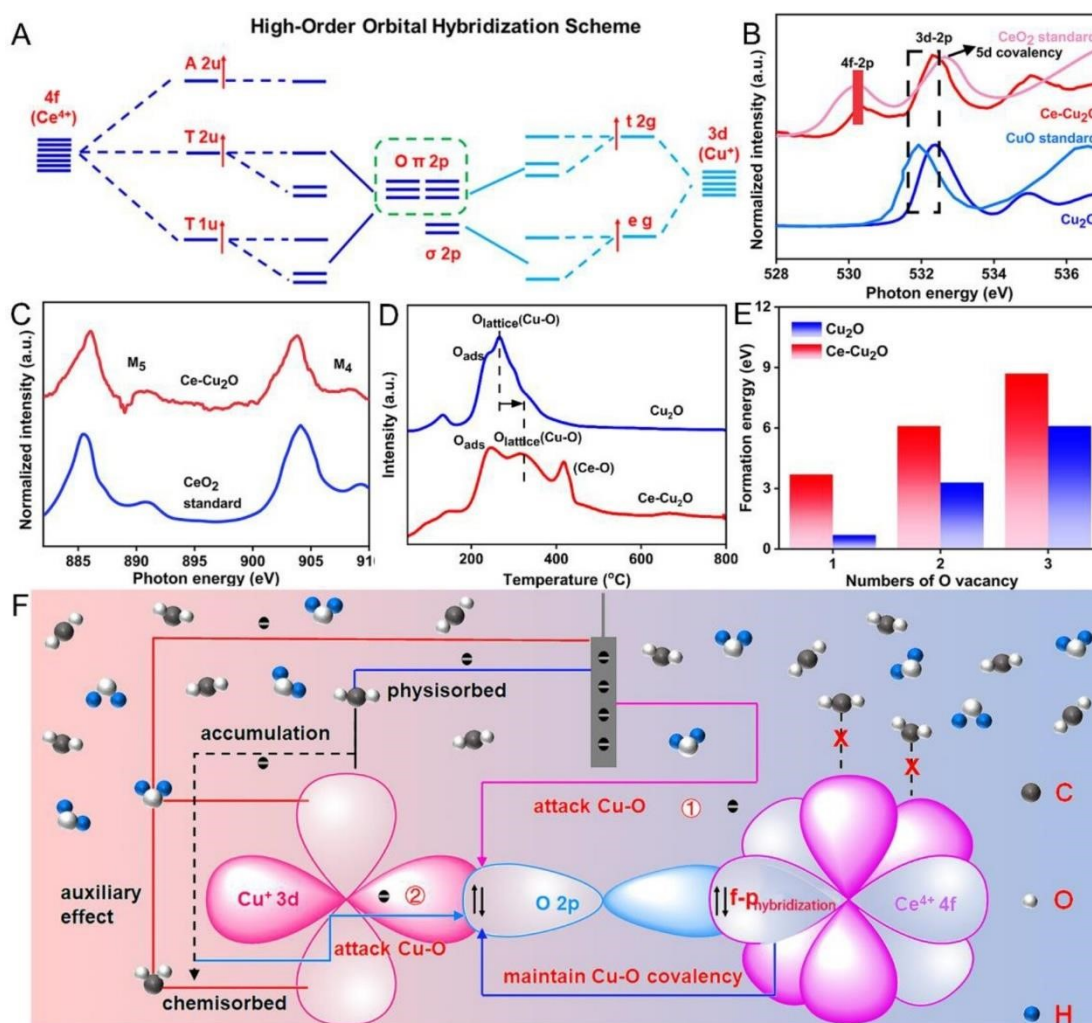
#### 4. Mechanistic Insights from Spectroscopic Techniques

Recent discoveries and developments from spectroscopic techniques such as XAS, Raman and IR spectroscopy have provided mechanistic knowledge of CO<sub>2</sub> reduction on Cu-based electrode catalysts. XAS, especially the XANES and EXAFS, demonstrates the change of the Cu oxidation state and the ability of local geometry around Cu, which represents the transition from Cu(II), Cu(I) to active Cu(0) during the catalytic process. The Raman spectroscopy identifies surface species such as CO and CHO which play important roles in the reaction route map while the IR spectroscopy is useful in gaining information on the adsorbed species and reaction intermediates. Each of these spectroscopic strategies combined provides a detailed description of the dynamic processes occurring at the catalyst surface and with CO<sub>2</sub>, which is profitable for the development of enhanced and selective electrocatalysts. EC-RSoXS was employed to study the real-time and real-space particle interactions as well as the chemical surroundings of Cu nanocatalysts in e-CO<sub>2</sub>R. The changes of Cu nanoparticle properties depending on the particles size and interaction with soft X-ray beams were analyzed. The 7-nanometer nanoparticles were primarily oxidized to CuO, whereas the larger 18-nanometer particles showed more resistance to damage. EC-RSoXS combines soft XAS (X-ray

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Absorption Spectroscopy) and SAXS (Small-Angle X-ray Scattering) methods to give a complete picture of how chemical and physical states affect the interparticle dynamics of nanocatalysts [46]. Furthermore, another research has showcased that the utilization of Ce-Cu<sub>2</sub>O, a catalyst characterized by a unique orbital coupling between high-order Ce<sup>4+</sup> 4f and O 2p, brings about significant improvements in e-CO<sub>2</sub>RR (Figure 4). Throughout a 7-hour operational run, the as-synthesized CeCu<sub>2</sub>O sample consistently generated C<sub>2</sub>H<sub>4</sub> and demonstrated a C<sub>2</sub>H<sub>4</sub>/CO ratio 1.69 times higher than that of the Cu<sub>2</sub>O catalyst. The Ce-Cu<sub>2</sub>O catalyst maintained stable Cu<sup>+</sup> species during the entire CO<sub>2</sub>RR process [47].



**Figure 4:** Molecular orbital representation of Ce<sup>4+</sup> 4fO 2pCu<sup>+</sup> 3d coupling (A). Ex situ sXAS measurements of the O-K edge in CeCu<sub>2</sub>O and Cu<sub>2</sub>O catalysts (B). Ex situ sXAS at the Ce-M<sub>4,5</sub> edge in Ce-Cu<sub>2</sub>O (C). Ce-Cu<sub>2</sub>O and Cu<sub>2</sub>O O<sub>2</sub>-TPD spectra (D). Energy dissipated in the production of OV<sub>s</sub> in Ce-Cu<sub>2</sub>O and Cu<sub>2</sub>O, as calculated by E. F) A schematic showing how the connection between the high-order orbitals 4f and 2p in Ce-Cu<sub>2</sub>O prevents CuO deactivation





*and shields the Cu<sup>+</sup> site from electron attack during the CO<sub>2</sub>RR. Reproduced with permission from Ref. [47] Copyright 2023, American Chemical Society.*

In another facet of this research, pure Cu, a metal known for catalyzing the conversion of CO<sub>2</sub> to hydrocarbons with high FE, was utilized for e-CO<sub>2</sub>RR. Researchers closely monitored the structural dynamics of Cu during the electrochemical process using techniques such as electrochemical scanning tunneling microscopy and Raman spectroscopy. Through control of polarization potential and in situ synthesis time, it was discovered that polycrystalline Cu surfaces could give rise to Cu nano-cuboids. Additionally, a graphene monolayer was grown on the Cu surface to create smaller features with enhanced catalytic activity [48].

Furthermore, the study employed in situ HERFD XAS to investigate the potential dependency of a single Cu layer, revealing significant differences compared to bulk Cu electrodes. Unlike thick Cu electrodes, which exhibit two redox transitions, only one redox transition was observed for 1 ML Cu/Au(111) and 1 ML Cu/Pt. This single Cu layer exhibited an anodic shift in the onset of Cu oxidation. The considerable tensile strain experienced by a single Cu monolayer when deposited on Au, Pt, and platinum-group metals was found to influence the redox behavior and interaction with e-CO<sub>2</sub>R intermediates. This tensile strain allowed for tunability in the ratio of methane to ethylene formed [49]. Moreover, the research demonstrated that the incorporation of s-ZnO into s-CuO during the fabrication of a series of sputtering electrocatalysts significantly altered the product profile of the CO<sub>2</sub>RR reaction. Specifically, the efficiency of CH<sub>4</sub> generation increased, while the production of C<sub>2+</sub> products decreased under ideal conditions. In situ XAS analysis revealed that the coordination number of Cu sites played a crucial role in CH<sub>4</sub> formation, which was influenced by the presence of Zn sites and led to a reversal of Ostwald ripening during the CO<sub>2</sub>RR [50].

Furthermore, another research confines a copper-complex catalyst in a membrane electrode assembly, scientists employed a carbon nanoparticle moderator method. Real-time XAS experiments demonstrated that increased carbon nanoparticle loadings reduced the coordination number of metallic copper. The system operated continuously for over 110 hours, achieving a CO<sub>2</sub>-to-methane selectivity of 62%, a methane partial current density of 136 mA cm<sup>-2</sup>, and a copper coordination number of 4.2 [51]. Lei et al. have designed nanocrystals of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>, Cu(OH)<sub>2</sub>, and CuO for e-CO<sub>2</sub>R. In-situ XRD and Raman spectroscopy confirmed the complete reduction of precursors to Cu(0), and Cu(0) was identified as the active species responsible for the improved selectivity. Initially, the strong C<sub>2+</sub> selectivity was



attributed to the small grain size of the resulting Cu. Interestingly, Cu nanocrystals synthesized from Cu(OH)<sub>2</sub> and Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> were found to possess substantial tensile stresses, as indicated by in-situ XRD. These stresses play a crucial role in promoting hydrogenation of \*CO and C-C coupling, ultimately enhancing the overall e-CO<sub>2</sub>RR selectivity while reducing HER rates [52].

## 5. Theoretical Calculations and Computational Studies

Theoretical calculations and computational studies, particularly those involving density functional theory (DFT), play a crucial role in the design and optimization of catalysts for CO<sub>2</sub> reduction. These approaches allow researchers to model and predict the electronic structure, potential energy surfaces, and reaction pathways of catalyst materials at an atomic level. A DFT study found that Cu-M bimetal catalysts have notable effects on the reaction barrier and catalytic activity of CO<sub>2</sub>RR and HER. The Cu-Pd catalyst is better for CO<sub>2</sub>RR than HER. This information can help in designing effective electrocatalysts and syngas production applications [53]. By simulating interactions between CO<sub>2</sub> and catalyst surfaces, computational studies can identify active sites, determine the most favorable reaction intermediates, and predict product selectivity. This theoretical insight complements experimental findings, guiding the rational design of catalysts with enhanced activity and selectivity. For instance, DFT calculations have helped in optimizing the composition and structure of Cu-based catalysts to improve their performance, ensuring a more efficient conversion of CO<sub>2</sub> to valuable chemicals.

The self-supporting and through-hole structure of CuSAs/TCNFs facilitated an increase in the number of useful Cu atoms while simultaneously reducing the number of incorporated metal atoms in the material. These individual Cu atoms played a pivotal role in the e-CO<sub>2</sub>RR reaction. Notably, the process yielded stable C<sub>1</sub> products with a current density of -93 mA cm<sup>-2</sup>, maintaining stability in water for over 50 hours. DFT simulations suggested relatively high binding energy for the \*CO intermediate in isolated Cu atoms. These findings suggest the potential for CO conversion into other valuable products, such as methanol, contributing to the reduction of CO levels [54]. Besides, ethanol synthesis emerged as one focal point: copper nitrogen-doped carbon materials with porphyrin-like Cu graphene structures played a critical role. The reversible transformation of porphyrin-like Cu sites to metallic copper nanoclusters complicates understanding their specific activities. A computational method was used to model the structure of the Cu-N-C material. Employing DFT calculations, the main focus of the work was on e-CO<sub>2</sub>R for ethanol and ethylene production. In both CO reduction and ethanol production, Cu nanoclusters are significantly better than single sites. This all-encompassing



piece of research helps to further our knowledge of Cu-based catalysts for many different CO<sub>2</sub> conversion processes [55].

Further expanding the investigation, the research delved into the CO<sub>2</sub>RR process catalyzed by a material housing a single Cu site within an N-doped carbon surface. Utilizing periodic DFT computations, distinct surface models were developed for the first CuN<sub>4</sub> site and a secondary Cu cluster at negative potentials. While the feasibility of the single-site surface was found to be thermodynamically challenging, the mechanistic study highlighted the significant activity of the Cu<sub>13</sub>N<sub>4</sub> nanocluster surface in driving CO<sub>2</sub>R. Notably, the catalytic activity of the Cu, N-doped carbon with a single site heavily depended on the presence of Cu<sub>13</sub>N<sub>4</sub> nanoclusters on its surface, owing to their unique capability to facilitate the crucial C-C coupling reactions required for C<sub>2</sub> product formation [55].

DFT simulations were also employed to investigate the binding energies of CO<sub>2</sub>R intermediates. Surface slab models for Cu(111), Sn(200), and Cu<sub>3</sub>Sn(002) were constructed based on XRD data. The binding energy of H\* on Cu<sub>3</sub>Sn(002) was similar to that on Cu(111), while CO\* binding energy on Cu<sub>3</sub>Sn(002) was lower. This difference, along with the energetically preferable CO desorption process over CO\* reduction, contributed to improved CO selectivity compared to Cu(111). The presence of surface Sn dramatically impacted HCOOH formation selectivity, allowing for control over two-electron reduction product selectivity through Cu-Sn alloying [56]. In this same study, DFT calculations were employed to examine the adsorption properties of CO<sub>2</sub> on clusters of Cu<sub>55</sub>, Cu<sub>54</sub>Ni<sub>1</sub>, and Cu<sub>42</sub>Ni<sub>13</sub>, featuring highly symmetric cub-octahedral, decahedral, and icosahedral structures. The composition of these clusters was found to influence the energy required for CO<sub>2</sub> adsorption, with the icosahedral Cu<sub>42</sub>Ni<sub>13</sub> cluster demonstrating the highest CO<sub>2</sub> adsorption capacity [57].

Further, using DFT calculations, the the impact of Zr doping on CO<sub>2</sub> hydrogenation to CHO in icosahedral Cu NPs was investigated. The findings indicated that Zr doping of Cu NPs improved CO<sub>2</sub> adsorption and hydrogen dissociation. Zr atoms played a crucial role in stabilizing chemical intermediates by lowering energy barriers [58]. Additionally, the B-doped copper surface (B@Cu(111)) catalyst's structure, activity, and selectivity were probed with DFT simulations. It was revealed that CO adsorption and activation occurred at the B site, with CO favoring coupling to \*C<sub>2</sub>O<sub>2</sub>. B played a crucial role in the conversion of carbon dioxide to ethanol and in capturing CO. The electronic structure and Bader charge analysis demonstrated that B stabilized C<sub>2</sub> intermediates by providing both empty and occupied orbitals for CO



adsorption and activation [59]. In another study, the DFT simulations were employed to study e-CO<sub>2</sub>R using Cu-X catalysts. Thermodynamic studies linked the O affinities of dopant atom sites and the Cu site's selectivity towards C<sub>2</sub> hydrocarbons and alcohols. Doping Cu-X catalysts with strong O affinity atoms, such as the Cu-B catalyst, favored the ethylene route. Non-metal doping on Cu surfaces often improved ethane selectivity while suppressing ethanol selectivity. The effect of electrical characteristics on intermediate adsorption and inherent selectivity was also addressed [60].

In a related study, Chang and coworkers have employed DFT calculations to investigate the highly selective formation of C<sub>2</sub> during CO<sub>2</sub>RR on different copper surfaces, with a particular focus on Cu(711). The Cu(711) surface presents a unique challenge due to the presence of a high dipole-dipole repulsive force, which excludes the formation of an OC-CO intermediate via the CO-CO route. Instead, adsorbed CO undergoes protonation, leading to the creation of CHO or COH intermediates. Lowering the activation energy for C-C bond formation with adsorbed CO is achievable through the production of COH or CHO. In contrast, Cu(100) and Cu(111) surfaces are thermodynamically unfavorable for these reactions. Given the increased likelihood of COH participation in the C-C coupling processes of CO<sub>2</sub>RR, its stabilization on the Cu(711) surface is more probable [61]. Additionally, the benefits of Cu cluster-doped C<sub>3</sub>N<sub>4</sub> as a CO<sub>2</sub> reducer were investigated utilizing DFT calculations. Cu clusters were identified as ideal active sites for CO<sub>2</sub> adsorption and activation due to their structure and electrical properties, facilitating the separation and transport of photo-generated electrons and holes. The study revealed that C-O carbon atoms in gas-phase molecules could link with C-N<sub>4</sub> carbon atoms in the substrate, reducing the adsorption energy. Furthermore, it determined how the Gibbs free energy of the CO<sub>2</sub>R process to produce CO compared to that of the competing HER reaction. For C<sub>2</sub> production on Cu<sub>4</sub>-C<sub>3</sub>N<sub>4</sub>, the reaction barrier was found to be larger than the HER due to the dimerization of \*CO [62].

In addition, Xue *et al.* developed efficient and selective electrocatalysts for the e-CO<sub>2</sub>RR. Twenty-one MOF supported flexible, self-adaptive dual-metal-site pairs (DMSPs) were screened using DFT calculations. For e-CO<sub>2</sub>R to C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>5</sub>OH, the computed limiting potential is -0.87 V, while MOF-808-EDTA-FePt shows even better activity at -0.35 V for CO<sub>2</sub>R to C<sub>1</sub> products [63]. Furthermore, DFT was employed to investigate the adsorption, structural changes, energy profiles, and reaction processes caused by CO coverage on the active sites of Cu<sub>2</sub>O(111) surface. Due to the presence of unsaturated Cu atoms, the CuCUS on the



Cu<sub>2</sub>O(111) surface is shown to be highly reactive towards CO adsorption and subsequent reactions. C-C coupling is favored because the energy barrier of \*CH<sub>2</sub> dimerization is lowered at higher CO coverage, specifically between 0.13 and 0.25. The maximum barrier energy occurs in the \*CHO route, making the C-C coupling the rate-determining step [64].

Moreover, Das *et al.* modeled the CuAl<sub>2</sub>O<sub>4</sub>(111) surface for CO<sub>2</sub> conversion to DME using DFT calculations elucidates the importance of dopants (Ga and Zn) in modifying the catalyst's active center. They also reveal Ga's role in changing the acidic site of the CuAl<sub>2</sub>O<sub>4</sub>(111) surface, enabling methanol conversion to DME [65]. Furthermore, twenty bimetallic M-Cu-BTCs were subjected to DFT calculations to examine their CO<sub>2</sub> adsorption and activation properties. Linear adsorption emerged as a more effective means of interaction between CO<sub>2</sub> molecules and most bimetallic MOFs, except for Pt-Cu-BTC and Pd-Cu-BTC. CO<sub>2</sub> activation was observed on W-, Mo-, Re-, and Os-Cu-BTC complexes. While CO<sub>2</sub> adsorption was stronger on Os-Cu and Re-Cu nodes, W-Cu-BTC and Mo-Cu-BTC showed promise for investigating the underlying mechanisms due to their higher H<sub>2</sub> adsorption capacities. The study also explored both the carboxyl (COOH\*) and formate (HCOO\*) routes of CO<sub>2</sub> hydrogenation with H<sub>2</sub> molecules on W-Cu and Mo-Cu complexes. While the energy barrier for W-Cu-BTC was 1.27 eV, it was only 1.10 eV for Mo-Cu-BTC [66].

## 6. Engineering strategies in rational design of Cu-based catalysts for electrochemical CO<sub>2</sub> reduction

There are various synthesis techniques utilized to manipulate the composition, structure, and morphology of copper-based catalysts to reduce CO<sub>2</sub>. The choice of synthesis methods plays a part in determining performance and selectivity. Some strategies for synthesizing copper-based catalysts are introduced here.

### 6.1. Single crystal approach

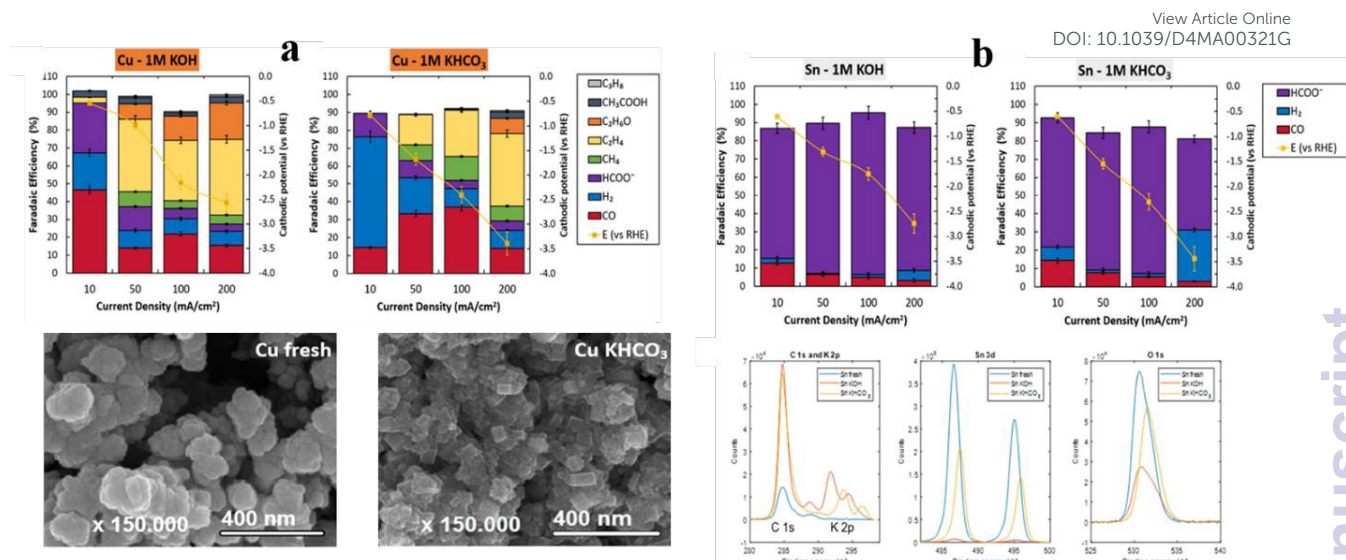
The single crystal approach included the use of single-crystal surfaces with well-defined atomic arrangements to design electrocatalysts for e-CO<sub>2</sub>RR. In this context, the key to developing and making electrocatalysts is creating catalysts with specific surfaces of single crystal. Adjusting the crystallographic orientation and atomic arrangements can provide more information about the catalytic mechanism and develop highly effective and selective catalysts. A number of different ways can be provided with this technology to create materials with the desired properties. Epitaxial growth, surface etching, atomically accurate deposition, selective



growth, template-based growth, and tip-based scanning tunnelling microscopy (STM) manipulation are all examples of this kind of technique. That is one important advantage of being able to design active sites consisting of single atoms. In this field, researchers have become interested in making electrocatalysts that can convert CO<sub>2</sub> to CH<sub>3</sub>OH using single-atom Cu. It can be seen from first-principles calculations that the Co@Cu SA catalyst has potential to catalyze CO<sub>2</sub> reactions. The d-band of the catalyst becomes narrowed and its center shifts up, making it more stable for CO<sub>2</sub>. As a result, energy barriers to the reaction are significantly reduced. This phenomenon enables us to selectively and efficiently produce CH<sub>3</sub>OH, which has a profound effect on the entire procedure. The reaction pathway, CO<sub>2</sub> → COOH\* → CO\* → COH\* → CHOH\* → CH<sub>2</sub>OH\* → CH<sub>3</sub>OH, is guided by the modified catalyst. It is significant that the SA has a small lattice mismatch, so that it is stable against a surface reconstruction. The catalyst's superiority emerges even more distinctly from the difference in activation energy for the reduction of COOH\* compared to Cu: it was not 0.22 eV and an activation energy of 0.54 eV. In addition, the reaction is exothermic, so besides the offer of a source of auxiliary energy generation in this system. In another aspect, the narrow cobalt d-band plays a vital role in the performance of this catalyst by preventing the buildup of unwanted byproducts. This feature results in a higher yield of CH<sub>3</sub>OH, further enhancing the overall sustainability and efficiency of the synthesis process. Collectively, the utilization of single-atom and the precise manipulation of crystallographic orientations hold promise for advancing the field of electrocatalysis and enabling more sustainable energy production through the selective and efficient conversion of CO<sub>2</sub> to valuable chemicals like methanol [67].

The pursuit of high-rate e-CO<sub>2</sub>RR activities, selectivity, and stability has led by Sassenburg *et al.* to investigate five distinct transition metal catalysts (Ag, Au, Pd, Sn, and Cu). Notably, Au and Pd exhibited CO-limiting current densities of 72 and 50 mAcm<sup>-2</sup>, respectively, emerging as standout contenders among the 88 diverse catalyst examinations. The study showcased the convergence of product selectivity for Cu catalysts across both neutral and alkaline environments. Additionally, the investigation highlighted Sn's susceptibility to instability under highly alkaline conditions (Figure 5). The research encompassed an assessment of catalytic selectivity at 10 and 200 mA cm<sup>-2</sup>, alongside a fundamental comparison of reaction rates [68].

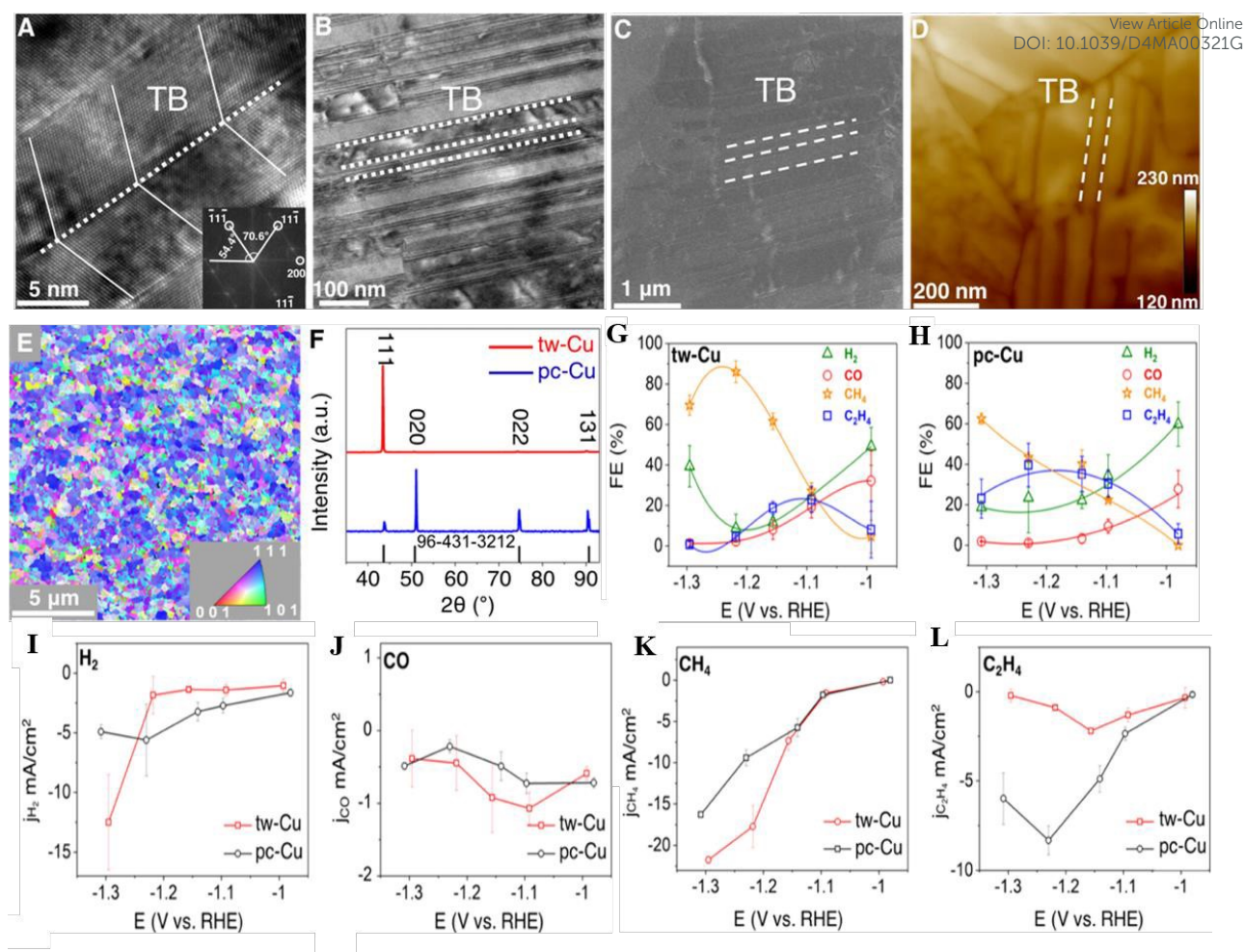




**Figure 5:** (a) Analysis of Electrodes with Copper Coating: The FE, in relation to activity, is explored across varying cathodic potentials within 1 M KOH (a) and 1 M KHCO<sub>3</sub> (b) solutions. Noteworthy, the error bars within both and panels illustrate the findings from distinct experimental runs. Employing HR-SEM, the visual depiction of fresh copper and its state after 1 hour of KHCO<sub>3</sub> electrolysis underscores the emergence of distinct cubic faceting pattern on catalyst's surface. (b) Exploring Sn-Coated Electrodes: The characterization involves the assessment of Faradaic efficiency concerning activity across cathodic potentials within 1 M KOH (a) and 1 M KHCO<sub>3</sub> (b) solutions. The error bars in both panels (a) and (b) depict the data variations from distinct experimental iterations. Further insights are gained through X-ray photoelectron spectroscopy (XPS) analyses, specifically examining C 1s and K 2p (c), Sn 3d (d), and O 1s (e) scans before and after subjecting the system to a 200 mA cm<sup>-2</sup> experiment in both electrolytes. Reproduced from Ref. [68] Open access article, American Chemical Society.

Furthermore, the evolution of a nanotwinned copper electrocatalyst specifically for e-CO<sub>2</sub>RR aimed at methane production. At a potential of  $-1.2 \pm 0.02$  V vs RHE, the catalyst exhibited impressive selectivity in generating methane, achieving a FE of  $86.1 \pm 5.3\%$ . The pivotal role of twin boundaries on Cu(111) facets in reducing the barrier for CO hydrogenation underscores their significance in the creation of CH<sub>4</sub>. Notably, the presence of these twin boundaries on Cu(111) renders the surface more predisposed to CH<sub>4</sub> selectivity than a planar copper surface (Figure 6). This multifaceted investigation and the nuanced understanding of catalyst behavior contribute to the advancement of electrocatalytic strategies for sustainable energy conversion [27].





**Figure 6:** Structural Characterization of Twin-Bound and Polycrystalline Copper Catalysts: (A) Capturing the intricate structure of tw-Cu through HRTEM. The cross-sectional image reveals the assembly of twin boundaries (TB), with an inset FFT analysis illustrating the axial direction and (111) planes expression. (B) Offering a broader perspective, a low-magnification TEM image showcases tw-Cu, where dashed white lines delineate the characteristic twin boundaries. (C) This structural insight is further corroborated by a SEM image of tw-Cu, with white dashed lines again indicating the presence of twin boundaries. (D) A detailed AFM image of tw-Cu discloses a surface roughness of 2.7 nm. (E) The crystallographic texture of the tw-Cu surface is illuminated through EBSD orientation maps. The inset highlights color-coded crystallographic vectors, vividly suggesting a robust (111) texture. (F) XRD patterns of both tw-Cu and pc-Cu reveal the strikingly high orientation toward (111) planes in tw-Cu, a sharp contrast to pc-Cu. This distinction is emphasized through a comparison with the reference sample represented by the black line with PDF number 96-431-3212. *e*-CO<sub>2</sub>RR: Demonstrating the FEs of (G) tw-Cu and (H) pc-Cu. The data points corresponding to H<sub>2</sub>, CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub> are color-coded as green, red, orange, and blue, respectively. Visualizing the





*partial current densities of (I) H<sub>2</sub>, (J) CO, (K) CH<sub>4</sub>, and (L) C<sub>2</sub>H<sub>4</sub>, where red lines signify <sup>View Article Online</sup> Cu and black lines represent pc-Cu. Each error bar emanates from three distinct <sup>DOI: 10.1039/D4MA00321G</sup> measurements, while all potentials underwent iR-correction. Reproduced from Ref. [27] Open access article, American Chemical Society.*

In contrast, the work by Lyu et al. explored into the impact of trace copper loading within N-doped graphene quantum dots (NGQDs) on both e-CORR and e-CO<sub>2</sub>RR. Interestingly, the rise of Cu loading within NGQDs exhibited the capacity to alter the selectivity of catalytic methane oxidation, shifting from primarily C<sub>1</sub> products to C<sub>2</sub> products. A notable outcome was achieved by introducing copper with an increased atomic size of 2.5 mg cm<sup>-2</sup>, resulting in a raised selectivity of up to 52% for C<sub>2</sub> products, accompanied by a reduced selectivity of 62% for CH<sub>4</sub>. Elevating the Cu loading further to 3.8 mg cm<sup>-2</sup> led to the peak of C<sub>2</sub> product production efficiency at 78%. This observation is particularly significant considering the low partial pressure of CO during e-CO<sub>2</sub>RR. The heightened copper loading becomes imperative to enhance selectivity toward C<sub>2</sub> products, thus illustrating the intricate interplay between catalyst composition and product selectivity in the context of sustainable energy conversion strategies [69]. With a shift of focus, Qai et al. carried out research experiments to probe the multifaceted role of crystalline structure and valency in oxide-derived copper (OD-Cu) catalysis as well as the mechanism and characteristics of e-CO<sub>2</sub>R. The experiment also used single crystal Cu(111) foils, enabling regulatory analysis of their intrinsic variation in morphology and crystallography. It was interesting that the overall efficiency of the OD-Cu in reducing CO<sub>2</sub>, and particularly in achieving C<sub>2</sub>H<sub>4</sub> selectivity, was shown to be significantly correlated with the initial oxidation degree of the Cu(111) foil. There is no significant effect on the catalytic activity from enhanced grain boundaries and exhibited polycrystalline structure. These findings highlight a complex web of connections among the structural features, oxidation states, and performance levels of OD-Cu, and therefore produce important contributions to the understanding of environmentally friendly energy conversion processes [70].

The study examined the catalytic activity of copper in the e-CO<sub>2</sub>RR and how it varies according to crystal phase. This was done by depositing ultra-pure Cu, which remained in the 4H and 4H/fcc phases. The study found that non-traditional crystal structures had better overall activity and selectivity in e-CO<sub>2</sub>RR than the standard fcc-Cu structure towards ethylene. The 4H phase preferentially produced C<sub>2</sub>H<sub>4</sub> according to DFT calculations, and neighbors fcc phase In case of 4H/FCC interface. This meant that different crystal phases had different C<sub>2</sub>H<sub>4</sub> selectivity



[71]. In an effort to research further, a widespread plan was drawn up by researchers. The goal was to effectively use copper-decorated through-hole carbon nanofibers (CuSAs/TCNFs) in e-CO<sub>2</sub>R for the transformation of CO<sub>2</sub> to methanol. A new method was displayed this CuSAs/TCNFs membrane, strong in the hole in a test in the first place as an e-CO<sub>2</sub>RR cathode. In the liquid state, the membrane achieved an impressive FE value of 44%.

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## 6.2 Single atom approach

The single atom approach in the design of electrocatalysts for e-CO<sub>2</sub>RR involves the dispersion of individual metal atoms on a suitable support material, often carbon-based. This method maximizes the utilization of metal atoms, ensuring that each atom acts as an active site, thereby significantly enhancing catalytic efficiency. By isolating metal atoms, this approach also allows for precise tuning of electronic properties and coordination environments, which can lead to superior selectivity and activity for specific CO<sub>2</sub>RR pathways. The unique atomic configuration of single atom catalysts (SACs) can facilitate the stabilization of key intermediates and lower energy barriers, contributing to higher overall performance in CO<sub>2</sub>RR. Chen *et al.* have aimed to increase the efficiency of converting CO<sub>2</sub> to methane by designing a Cu-based catalyst that is augmented with a Lewis acid support. For example, metal oxides like Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> can do it in this way. They can modulate the electronic structure of Cu atoms by means of the intermediate it absorbs through Lewis acid sites. The specific study explored the potential of an ultrathin porous Al<sub>2</sub>O<sub>3</sub> that was highlighted by its numerous Lewis acid sites, to bind Cu atoms at the single atom level. Remarkably, yielded a notable increase in FE for CH<sub>4</sub> synthesis, reaching 62%, operating at a potential of -1.2 V and a current density of 153 mA cm<sup>-2</sup>. This precise manipulation of individual copper atoms demonstrated a remarkable efficacy in the conversion of carbon dioxide to methane, offering a significant step towards efficient and sustainable energy conversion processes [72]. Zhao and his colleagues switched gears in their work, pursuing methanol production through electrolysis of CO<sub>2</sub>. They developed a method in which copper-monitoring MXene was made with much success. The fourth MAX phases underwent selective etching. Only aluminum and copper from the hybrid A layers were specifically targeted for removal. It makes use of the saturated vapor pressure differences between aluminum and copper products. As a result, installing a Cu single-atom catalyst attains an impressive FE of 59.1% in making CH<sub>3</sub>OH. The catalyst proved not only to have promise for electrocatalytic stability but also showed the potential of e-CO<sub>2</sub>R because of its unsaturated electronic structure at the copper atom. Because of its unique properties, the electric e-CO<sub>2</sub>RR



has a low-energy barrier in the rate-determining step. In fact, copper-immobilized MXene plays a key role in promoting the development of sustainable energy solutions [73].

Researchers considered the e-CO<sub>2</sub>RR using a carbon substrate featuring coordinated copper atoms within a unique CuN<sub>4</sub> structure. This material showed impressive rates of conversion. It converted 55% of ambient CO<sub>2</sub> with distilled water as its source into ethanol, more impressively, 80% of dissolved CO was converted to C<sub>2</sub>-products such as ethanol or ethylene. After all, the high faradaic yield in both cases proved this. Metal copper sites are exclusively ascribed to the catalytic action of separated ones, specifically. Crucially, the starting material was entirely recoverable [74]. Turning attention to another interesting study, Bao *et al.* illuminated the realm of e-CO<sub>2</sub>R, employing single copper atoms on MXene nanosheets. The researchers achieved a remarkable selectivity of 98% for multicarbon products and an impressive FE of 71% for ethylene synthesis at a potential of -0.7 V vs RHE. The process involved the combination of carbon monoxide molecules to form the \*CO-CHO species, effectively reducing the free energy barrier of the potential-determining step. This catalyst had something special about it as it continued being active all the way through the 68 hours of the electrolysis process, thereby proving that single copper atoms could produce useful compounds made up of many carbon atoms in a substantial way [75].

In a separate project, the effort to achieve e-CO<sub>2</sub>R led to the fabrication of atomically dispersed Cu catalysts on defective Ag nanowires. This innovative approach hinged upon a site-specific underpotential deposition method and an electrochemical conditioning treatment strategy, resulting in the dispersion of the Cu/Ag(S) catalyst. The integration of Cu single-atom catalysts remarkably elevated the selectivity and activity of the catalyst in CO<sub>2</sub> reduction. The alteration of the d-band structure and the facilitated interaction between Cu single-atom catalysts and the conditioned surface's defects played a pivotal role. This augmentation led to an enhanced adsorption of e-CO<sub>2</sub>RR intermediates, subsequently boosting the efficiency of the process. Impressively, at a e-CO<sub>2</sub>RR current density of 2.9 mA cm<sup>-2</sup>, the Cu/Ag(S) catalyst exhibited an outstanding FE of 93.0%, surpassing the performance of the Ag(S) catalyst lacking Cu single-atom catalysts. The presence of Cu SACs in proximity to faulty silver surfaces induced increased microstrain and a downward shift in the center of the d-band, effectively reducing the activation energy required for \*CO generation by approximately 0.5 eV. This composed interplay resulted in heightened efficiency and specificity in CO<sub>2</sub> reduction, particularly in the



production of CO and C<sub>2</sub> products, underscoring the catalytic competence of the Cu/Ag(S) catalyst [76].

In a distinct exploration by Zheng *et al.*, a catalyst consisting of a single lead atom with copper was employed to successfully convert CO<sub>2</sub> into formic acid. The catalyst's remarkable 96% FE in formate generation underscores its exceptional performance. The active copper sites regulated the first protonation step extremely accurately so that the reaction went towards formate synthesis and made that the only thing produced. The authors supported the use of this method for producing valuable liquid fuels with high purity [77]. Moreover, Song *et al.* delved into the catalytic performance of two Cu SACs with asymmetric surfaces in e-CO<sub>2</sub>RR. The CuN<sub>3</sub>O/C catalyst exhibited outstanding selectivity for e-CO<sub>2</sub>RR, boasting a CO FE of over 90% across a potential range of -0.5 to -0.9 V vs RHE. With a potential of -0.8 V, the selectivity for CO production reached an impressive 96%. In complete contrast, CuCO<sub>3</sub>/C catalyst showed terrible CO selectivity. At -0.5 V vs RHE was its only 20.0% CO FE peak. In particular, the CuN<sub>3</sub>O/C catalyst displayed a TOF of 2782.6 h<sup>-1</sup> at -0.9 V vs RHE, greatly in excess of the highest TOF recorded for CuCO<sub>3</sub>, 4.8 h<sup>-1</sup> [78].

Furthermore, the e-CO<sub>2</sub>R rate can be improved by using Cu single-atom catalysts with adjustable concentrations in addition to nitrogen attachment. In addition to facilitating water dissociation, CH<sub>4</sub> synthesis in the presence of nitrogen involves the metal assisting in the binding of hydrogen to make COOH intermediates. At a potential of -1.8 V vs RHE, CH<sub>4</sub> yield for Cu catalysts was as high as 68.2% along with an impressive CH<sub>4</sub> j of 493.1 mAcm<sup>-2</sup> [79].

So as to convert CO<sub>2</sub> into acetate and syngas more efficiently, a new tandem catalyst had to be developed. A cost-effective catalyst has copper nanoparticles that integrate nickel single atoms selectively. These single Ni atoms make CO coverages bigger, the C-C bond tends to cause an expanded interaction with adjacent Cu nanoparticles to facilitate acetate synthesis. It is worth noting that when flexibility with respect to production of syngas (H<sub>2</sub>/CO) is desired, the tandem catalyst varies from 0.06:1 to 19.5:1. The intention of this method is to supply liquid fuels more effectively by incorporating CO<sub>2</sub>RR for syngas-mediated thermocatalytic process and helping to achieve a higher selectivity. The target is single C<sub>2</sub> molecules. This is the first critical step from production in the laboratory to implementing it in industry on a large scale [80]. Based on the single crystal and single atom approach, Table 1 lists the different kinds of electrocatalysts developed and designed for e-CO<sub>2</sub>R to different products.



**Table 1:** With the single crystal/atom catalyst approach, a number of electrocatalysts have been specifically crafted for CO<sub>2</sub>R. A review of the work reveals, It reflects the selective, as well as the energetic considerations that must be made in good catalyst design in order to get good powers of efficiency.

Z	Material	electrolyte	V vs RHE	≈ FE %									Ref.
				H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	
1	Tw-Cu			39.3	1.1	69.5	0.74	0.01	0.04	--	--	--	[27]
2	Pc-Cu	0.1 M KHCO <sub>3</sub>	-1.31	18.7	1.86	62.5	23.0 2	0.01	0.04	--	--	--	[27]
3	Cu @ GDE	1 M KOH	-2.6	7	18	6	39	4	--	--	21	--	[68]
4	Cu @ GDE	1 M KHCO <sub>3</sub>	-3.4	10	17	3	46	3	--	--	8	--	[68]
5	Cu(111)-LO@ GDE			40	6	8	8	--	--	--	--	--	[70]
6	Cu(111)-MO@ GDE	1 M KOH	-1.8	32	4.8	12	20	--	--	--	--	--	[70]
7	Cu(111)-HO@ GDE			38	2.9	2.3	27.4	--	--	--	--	--	[70]
8	p-Al <sub>2</sub> O <sub>3</sub>			68	4	--	--	8	--	--	--	4	[72]
9	Cu/p-Al <sub>2</sub> O <sub>3</sub> SAC	1 M KOH	-1.4	10	10	49	1	9	--	--	1	9	[72]
10	poisoned Cu/p-Al <sub>2</sub> O <sub>3</sub> SAC			19	21	14	2	--	--	--	--	9	[72]
11	Cu NPs/p-Al <sub>2</sub> O <sub>3</sub>			10	10	39	2.5	2	--	--	12.5	13	[72]
12	SA-Cu-MXene	0.1 M KHCO <sub>3</sub>	-1.8	75.5	--	--	--	--	--	17.5	5	--	[73]
13	Cu-particles-MXene			--	--	--	--	--	--	4	--	--	[73]
14	Cu <sub>0.5</sub> NC	0.1M CsHCO <sub>3</sub>	-1.3	45	22	--	--	--	--	--	28	--	[74]
15	4H Au@Cu	0.1 M KHCO <sub>3</sub>	-1.13	22.5	17.5	2	45	8	--	--	--	--	[71]
16	4H/fcc Au@Cu			29	9	3	39	20	--	--	--	--	[71]
17	Cu SAs/TCNFs	0.1 M KHCO <sub>3</sub>	-1.2	33	45	--	--	--	--	25	--	--	[54]
18	Cu SAs/CNFs			45	33	--	--	--	--	22	--	--	[54]
19	Cu-SA/Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	1 M KOH	-0.9	18	--	--	55	--	--	--	25	--	[75]
20	Cu-NP/Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>			80	--	--	8	--	--	--	10	2	[75]
21	BNC-Cu	0.5 M KHCO <sub>3</sub> 1 M KOH	-1.46	25	1	72	2	--	--	--	2	--	[81]
22	Ag				22			2					[76]
23	Ag (S)	0.1 M KHCO <sub>3</sub>	-1.4		25			5					[76]
24	Cu/Ag(S)			--	52	4	1	6	--	--	13	--	[76]
25	Pb1Cu SAAs	0.5 M KHCO <sub>3</sub>	-1.62 (Ag/Ag Cl)	12.4	0.7	--	--	78.4	--	--	--	--	[77]
26	CuN <sub>3</sub> O/C	KHCO <sub>3</sub>	-0.9	--	96	--	--	--	--	--	--	--	[78]
	CuCO <sub>3</sub> /C			--	5	--	--	--	--	--	--	--	[78]



27	Cu SAs-0.1	KOH	-1.4	32	12	54	--	--	--	--	View Article Online DOI: 10.1039/D4MA00321G	[79]	
28	Ni SACs-Cu NPs	1 M KOH	-1.0	25	33	5	10	13	--	--	8	--	[80]

### 6.3. Oxidation state engineering

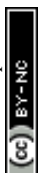
One technique to develop materials for CO<sub>2</sub> conversion involves manipulating the oxidation states of elements. Materials scientists can modify the oxidation states of elements to regulate both activity and selectivity. This way, we learn that oxidation states can change material structure, surface chemistry, and reactivity. By remaining in control of oxidation states, CO<sub>2</sub> is adsorbed and charge transfer is made possible, affecting reaction pathways. Numerous methods exist for engineering oxidation states. Through controlled changes made to a material's surface, for example the addition of groups or the creation defect, surface oxide atom can alter the oxidation states. To adjust oxidation states and improve the catalytic activity of a material, controlled doping involves introducing atoms into the lattice structure. Advanced in situ techniques, as potential modulation allows oxidation states to be manipulated in real time during catalysis and dynamic control over reaction pathways. Thanks to these techniques, researchers have a wide range of tools that can manipulate oxidation states. They can create materials that efficiently convert CO<sub>2</sub> into useful products. According to this idea, one groundbreaking study found that Cu<sub>x</sub>O-decorated graphene oxide (G-Cu<sub>x</sub>O-T) had the potential to be used as an electrocatalyst that is capable of controlling e-CO<sub>2</sub>R. It was found that the function of the electrocatalyst G-Cu<sub>x</sub>O-2h (x=1~3) can be controlled by the valency of Cu. Key to this control is the multivalence of Cu. It is Cu(I) above all that has been chosen to improve the adsorption of CO<sub>2</sub> and enable the facile desorption of HCOO<sup>-</sup>, so the catalysis process can be optimized. However, Cu(II) was important in maintaining durability thus enhancing the overall stability [82].

In a parallel avenue of investigation, another study focus shifted to the impact of the substrate (Cu<sub>2</sub>O) on the catalytic selectivity of the deposited Sn catalyst. Notably, the presence of Sn played a significant role in formate formation, with the potential to limit the HER requiring a deposition time of less than 120 seconds. Surface analysis revealed the presence of Cu<sup>+</sup> either on or beneath the surface, attributed to kinetic constraints during cathodic Sn deposition and e-CO<sub>2</sub>R. Positioned between Sn<sup>2+</sup> and Sn<sup>4+</sup> in terms of electronegativity, Cu<sup>+</sup> occupied a midrange position. The Sn-deposited electrode exhibited enhanced catalytic selectivity when the deposition time was under 120 seconds, attributed to the stabilizing influence of residual



$\text{Cu}^+$  species on the surface of Sn, maintaining it at a positive oxidation state between 2 and +4 [83]. Concurrently, a separate avenue of inquiry was pursued, leading to the discovery that a Cu/ZnO catalyst could serve as a catalyst for converting  $\text{CO}_2$  into alcohols, specifically ethanol and methanol. This was achieved through the oxidation of Cu nanoparticles at a low temperature, followed by their amalgamation with ZnO crystalline powder. Through a liquid-phase setup, the study scrutinized ZnO's influence on the restructuring of the Cu-based catalyst and its electrocatalytic efficiency in alcohol production under varying applied potentials. Enhanced carbon-carbon coupling and ethanol generation were attributed to ZnO inducing higher CO productivity on the Cu/ZnO-based electrode compared to the Cu-only counterpart. The production of ethanol within this tandem catalyst, as a precursor to further CO reduction into  $\text{C}_{2+}$  alcohols, was directly linked to the abundance of  $\text{Cu}^{1+}$  and  $\text{Cu}^0$  combinations on the CZ catalytic surface [84].

Moreover, the research revealed the catalysing role of the original copper electrodes in influencing their future activity and stability. More specifically, it was found that Cu(I) oxide would dissolve because of its low conductivity when dispersing in e- $\text{CO}_2\text{R}$ , but Cu(II) oxide would just as easily be converted into metallic copper. That is to say, when these materials were used as electrodes and maintained at above room temperature they behaved more like liquid crystals than crystalline solids. However, the high activity and selectivity reported in the literature for OD-Cu electrodes could potentially be attributed to the fact that Cu(II) dissolution, which is more prevalent in bulk electrodes like foils or single crystals, exposes the metallic surface beneath the porous Cu(II) oxide structure. The outcomes of this study demonstrated that metallic copper is an excellent electrocatalyst for e- $\text{CO}_2\text{R}$  and that the metal's intrinsic activity can be modified without compromising its conductivity. In order to maintain the stability of the metallic copper matrix phase, moderate doping levels must be used, which might influence activity and selectivity [85]. In another study, Cu-MOF/NP catalysts were made from MOF templates. More specifically, the Cu-MOF20/300 nanoparticles proved to be potent electrocatalysts for electrochemical CO generation because of their Cu/Cu<sub>2</sub>O heterogeneous structure and vast active surface area. Impressively, the Cu-MOF20/300 catalyst demonstrated a high Faradaic efficiency ( $\text{FE}_{\text{CO}}$ ) of 43.8% for CO generation. Furthermore, the electrochemical reaction performance of the flow MEA reactor displayed significant enhancements compared to the conventional H-type setup. The reactor's compact design allowed it to reach current densities in excess of  $230 \text{ mAcm}^{-2}$  at low applied potential, effectively lowering both ohmic and charge transfer resistances. The incorporation of a fillable



gas-liquid separation component made it much more sensitive to changes, thereby facilitating detection and estimation [86].

To gain deeper insights, the study explored the complex relationship between torsion and porous Cu electrode oxidation state. It turns out that substrates with high tortuosity have lower CO<sub>2</sub> content and especially in deeper layers. Amazingly high tortuosity in the network resulted in bubbles of CO traveling farther, increasing the chance of CO going back to surface catalytic surfaces. The generation of C<sub>2+</sub> products was favored by this phenomenon. The generation of CO, HCOOH, CH<sub>4</sub> and C<sub>2+</sub> products, those trends were elucidated in this study, showing that their production was influenced by CO<sub>2</sub> and CO availability and an intricate interplay between them. Cu oxidation states was used as a system of extracting selectivity insights from research on yields/efficiency for carbon dioxide reduction. This detailed analysis showed that metallic copper had more favorable C<sub>2+</sub> alcohols pathways than copper derived from Cu<sup>2+</sup> or Cu<sup>+</sup> particles [87]. In another facet of their research, scientists also succeeded in regenerating the Cu catalyst in situ for the sustainable reduction of CO<sub>2</sub> into various carbon products. Using an AC intermittent working mode, the catalysts went through periodic invigoration by the oxidizing Cu surface. When operated in this effective manner, at a constant current density of 150 mAcm<sup>-2</sup> the Cu catalyst remained active for an impressive 120 hours and maintained 40% selectivity throughout [88].

The authors demonstrated that, for better efficiency, optimizing the placement of the semiconductor sensitizer and CuO<sub>x</sub> co-catalyst was better. In addition, the research also explores the role played by thin Cu<sub>2</sub>O. The findings showed that CO<sub>2</sub> reduction was affected by the distribution of the Cu surface's oxidation states. Because of CO<sub>atop</sub> intermediate species and C<sub>1</sub> hydrocarbon-product production, electrodeposited Cu electrodes had higher Cu(I) in them. Conversely, the initially prepared electrodes' presence of Cu(0) in their oxidation state hindered hydrocarbon product development. Moreover, the coexistence of Cu(I) and Cu(0) in the CO<sub>2</sub>-reduction products yields not only CO<sub>bridge</sub> but CO<sub>atop</sub> as well, leading to the high selectivity for the C<sub>2</sub> product [89]. When using HQ-Cu or AN-Cu; both of which were electrodes comprised of mixed oxidation states, a greater selectivity for C<sub>2+</sub> products was noted. The distribution and historical development of different Cu species were characterized using FIB-TEM/EELS. Notably, during the steady state of CO<sub>2</sub>RR, the HQ-Cu electrode underwent complete reduction to metallic Cu, indicating that the observed high C<sub>2+</sub> selectivities did not rely on specific Cu oxidation states. To ensure complete reduction to Cu<sup>0</sup> prior to CO<sub>2</sub>RR, the





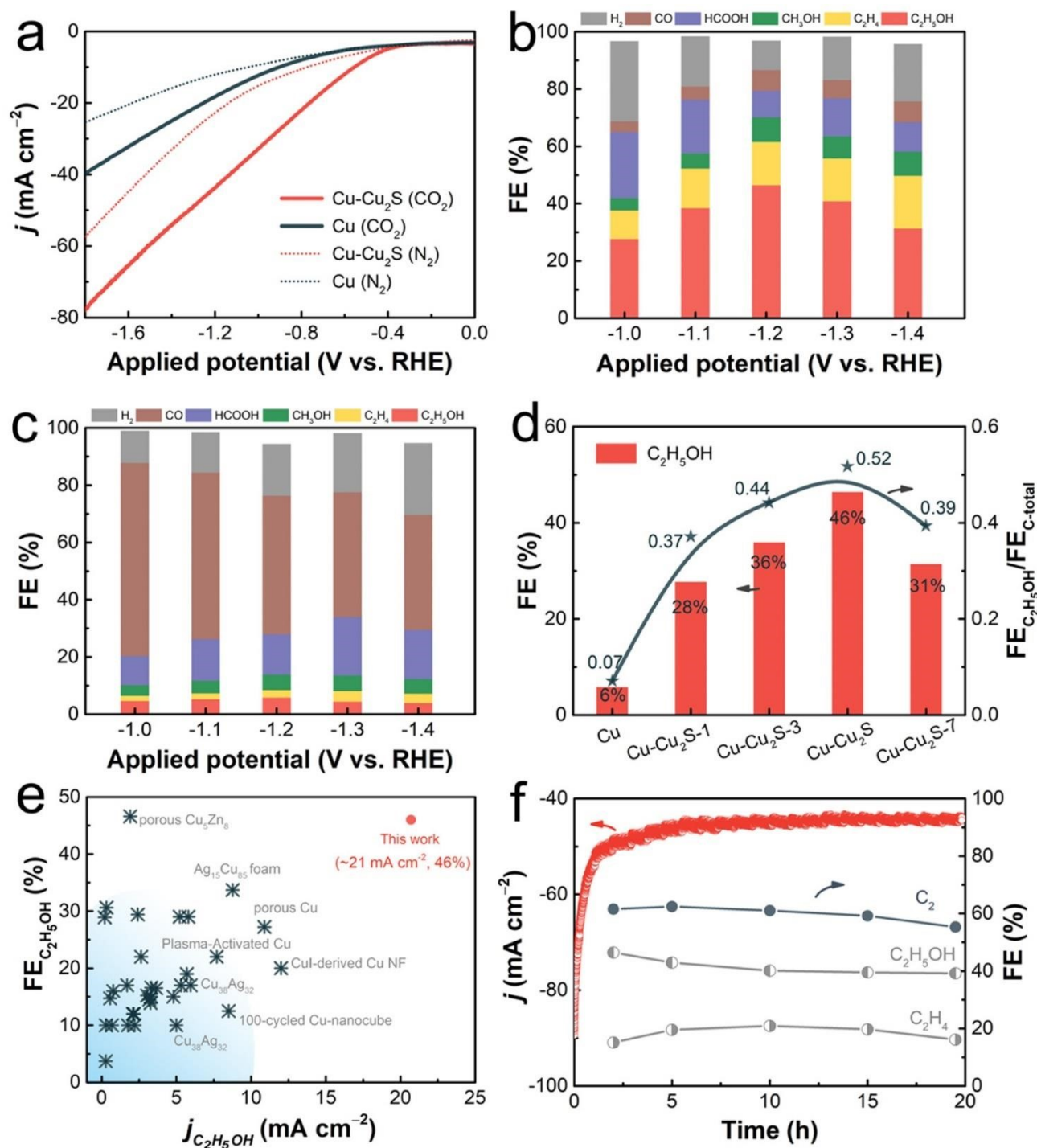
electrodes underwent electro-reduction pretreatment. Further bolstering the pivotal catalytic role of Cu<sup>0</sup> and the minimal impact of the initial oxidation state of oxidized Cu, the pretreated electrodes exhibited slightly enhanced selectivity toward C<sub>2+</sub> products. Notably, an oxidation-reduction cycle led to crystal fragmentation, observed when oxide crystals in HQ-Cu and AN-Cu were reduced and fragmented into small irregular Cu grains under the negative potential of electro-reduction pretreatment or CO<sub>2</sub>RR [90].

In the pursuit of exceptional CO<sub>2</sub>RR performance, a 1D composite SnCu-CNS was resourcefully developed, boasting a hierarchical structure of nanotubes and loaded nanorods. This composite showcased remarkable trait, achieving a partial current density of 205.1 mA cm<sup>-2</sup> for formate at a 1.0 V vs RHE cathode potential, and reaching an impressive peak FE of 95.1% within an H-type cell [91]. Another study's findings unveiled a synergistic connection between the structural evolution of Cu<sub>2</sub>O and the surface-interface CO<sub>2</sub> reaction. During the cathodic scanning phase of CV, CO\* derived from CO<sub>2</sub>R assumed the role of a stabilizer, effectively preventing the oxidation of metallic Cu. This stabilization process expedited the shift from inert Cu<sub>2</sub>O to the more dynamic Cu/Cu<sub>2</sub>O under regular operational conditions. Importantly, the incorporation of Cu/Cu<sub>2</sub>O led to a substantial increase in FE for ethanol, elevating it from 5.15% to an impressive 56.56%, and significantly fostering the generation of C<sub>2</sub> products [92].

To ensure the stability of Cu<sup>+</sup> sites during the CO<sub>2</sub>RR reaction, the researchers designed PdCu<sub>3</sub>N, a catalyst built upon the antiperovskite type Cu<sub>3</sub>N. Remarkably, the incorporation of negative-valence Pd into the catalyst significantly augmented the synthesis of C<sub>2</sub> products, resulting in a substantial increase in the FE of C<sub>2</sub> (78.2%) compared to the Cu<sub>3</sub>N catalyst with only single Cu<sup>+</sup> sites (5.6%) [93]. Concurrently, another study delved into the utilization of Cu nanosheets decorated with small Cu<sub>2</sub>S nanocrystals as catalysts for the e-CO<sub>2</sub>R into C<sub>2</sub>H<sub>5</sub>OH (Figure 7). The investigation showcased that in an H-cell containing 0.1 M KHCO<sub>3</sub>, the total current density reached 45 mA cm<sup>-2</sup>, accompanied by a substantial J<sub>C<sub>2</sub>H<sub>5</sub>OH</sub> of approximately 20.7 mA cm<sup>-2</sup>. The advantageous attributes of decorating Cu nanosheets with nanocrystals encompassed a non-flat, stepped surface, a high localized positive charge of Cu<sup>+</sup>, and well-established interfaces between Cu<sup>+</sup> and Cu<sup>0</sup>. These attributes collectively enhanced CO<sub>2</sub> adsorption, facilitated charge transfer for CO<sub>2</sub>RR kinetics, facilitated the dissociation of the \*COOH intermediate into \*CO, heightened the affinity of \*CO on the catalyst, reduced the



energy barrier of CC coupling, created favorable spatial conditions for  $C_2H_5OH$  production, and facilitated the spontaneous hydrogenation of  $*CH_2CHO$  to  $*CH_3CHO$  [94].



**Figure 7:** Electrochemical activity of the manufactured catalysts for CO<sub>2</sub>R. In a N<sub>2</sub> and CO<sub>2</sub> saturated 0.1 M KHCO<sub>3</sub> aqueous electrolyte (a), the LSV curves of pure Cu and CuCu<sub>2</sub>S are shown. Distributions of the products of the catalyzed CO<sub>2</sub>RR for (b) CuCu<sub>2</sub>S nanosheets and (c) pure Cu nanosheets at various applied potentials. At 1.2 V (against RHE), FE<sub>C<sub>2</sub>H<sub>5</sub>OH</sub> and



$FE_{C_2H_5OH/FEC}$  products for  $CuCu_2S$ , pure  $Cu$ , and  $CuCu_2S-1,3,7$  in an  $H$ -cell containing  $0.1 M$   $KHCO_3$  solution (d), The comparison of partial current density for  $C_2H_5OH$  and the  $FE_{C_2H_5OH}$  of  $CuCu_2S$  to those of previously reported catalysts. Some examples of these catalysts are copper nanocubes, copper nanofibrils, nanofibrils generated from copper ions, copper alloys, copper activated in plasma, copper foam, and porous copper (e). 20 hours of stability at 1.2 V (against RHE) in terms of geometrical current density and field strength for carbonaceous compounds catalyzed by  $Cu$  and  $Cu_2S$  (f). Reproduced with permission from Ref. [94] Copyright 2023, American Chemical Society.

In a related investigation, the selective production of  $CH_4$  and  $C_2H_4$  in the  $CO_2RR$  process took center stage as  $CuO_x$  catalysts with varying oxidation states and reductant agents. The study identified the optimal oxidation state of the copper catalyst, leading to the highest selectivity for  $C_2H_4$  (FE = 53 %). The study explored several potential reaction pathways, including CC coupling, hydrogenation of CO to produce CHO, direct dimerization of CO to produce  $C_2H_4$ , and hydrogenation of CO to yield CHO or COH [95]. Table 2 presents an overview of different electrocatalysts designed by following oxidation state engineering approach for  $e-CO_2R$  to a number of fuels.

**Table 2:** By investigating materials synthesized through oxidation state engineering this table explores the landscape of  $CO_2R$ . Specifically tailored catalysts show promise in energy production through their performance in  $CO_2RR$ , which involves generating hydrogen, carbon monoxide, methane and other compounds.

Material	electrolyte	V vs RHE	≈ FE %									Ref.
			H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	
G-Cu <sub>x</sub> OT	0.5 M KHCO <sub>3</sub>	-0.8	64	--	--	--	9	--	2	--	--	[82]
Cu foil			25	22	--	--	20	--	--	--	--	
3 Soaked Cu 0 s	0.5 M KHCO <sub>3</sub>	-1.2	24	31	--	--	37	--	--	--	--	[83]
4 Sn foi			30	7	--	--	68	--	--	--	--	
5 S Sn			22	8	--	--	73	--	--	--	--	
6 Cu calc			68	3	2	--	9	--	--	5	--	
7 CZ calc		-1.4	78	5	1	--	4	--	1	7	--	[84]
8 PVD Cu films @ 25°C	100 mM	-1.8	76	2	9	9	3	--	--	1	--	
9 PVD Cu films @ 150°C	KHCO <sub>3</sub>	Ag/Ag Cl	67	1	13	12	1	--	--	6	--	[85]
10 Cu/MOF 20/300	0.5 M KHCO <sub>3</sub>	-0.66	62	35	--	--	--	--	--	--	--	[86]
11 OD-Cu-16			--	22	2	15	23	--	--	--	--	
12 OD-Cu-32	0.1 m KHCO <sub>3</sub>	-1.0	--	23	3	21	21	--	--	--	--	
13 OD-Cu-45			--	5	4	31	14	--	--	--	--	[87]
14 OD-Cu-70			--	3	6	28	17	--	--	--	--	
15 Cu/PTFE 200 nm	1 M KHCO <sub>3</sub>		17	4	16	38	4	--	--	10	--	
16 Cu/PTFE 700 nm			19	7	1	42	8	--	--	17	--	[88]



			100									
17	Cu/PTFE 1000 nm		mAcm <sup>-2</sup>	18	9	1	42	10	--	--	37	--
18	Electrodeposited-Cu			53	--	32	--	9	--	--	--	--
19	As-prepared-Cu	0.1 M KHCO <sub>3</sub>	-1.0	49	3	--	--	14	--	--	--	--
20	CV-treated Cu			10	5	38	42	8	--	--	--	--
	Electropolished-Cu			70	11	2	15	--	--	--	--	--
	HQ-Cu	0.1 M KHCO <sub>3</sub>	-1.0	30	2	5	27	--	--	--	--	--
	AN-Cu			29	3	3	23	--	--	--	--	--
	SnCu-CNS	0.1 M KHCO <sub>3</sub>	-1.0	9	28	--	--	63	--	--	--	--
	o-Cu <sub>2</sub> O	0.1 M KHCO <sub>3</sub>	-1.06	30	22	--	13	12	--	--	5	--
	Cu/Cu <sub>2</sub> O-CV			9	8	--	9	14	--	5	58	5
	Ce-Cu <sub>2</sub> O	0.5 M KHCO <sub>3</sub>	-1.1	--	8	--	11	--	--	--	--	--
	Cu <sub>2</sub> O			--	4	--	8	--	--	--	--	--
	Cu <sub>3</sub> N	1 M KOH	-1.1	19	43	--	2	36	--	--	--	--
	Pd <sub>0.1</sub> -Cu <sub>3</sub> N			9	10	--	39	4	--	--	32	--
	Pd <sub>0.1</sub>			--	90	1	--	--	--	9	--	--
	Cu			--	89	--	--	--	--	11	--	--
	CuPd <sub>0.05</sub>			--	65	--	--	--	--	35	--	--
	CuPd <sub>0.1</sub>			--	93	--	--	--	--	7	--	--
	CuPd <sub>0.5</sub>			--	87	--	--	--	--	13	--	--
	CuPd <sub>2</sub>			--	89	1	--	--	--	10	--	--
	CuPd <sub>5.7</sub>			--	91	1	--	--	--	8	--	--
	Cu-Cu <sub>2</sub> S	0.1 M KHCO <sub>3</sub>	-1.1	18	3	--	14	19	--	6	38	--
	Pristine Cu nanosheets	0.1 M KHCO <sub>3</sub>	-1.5	15	57	--	3	15	--	3	5	--
	CuO <sub>x-1</sub>	0.1 M KHCO <sub>3</sub>	-1.5	--	--	40	20	--	--	--	--	--

## 6.4. Alloying approach

The use of alloying is a versatile strategy, in designing electrocatalysts for CO<sub>2</sub>R. By combining metals catalysts with customized properties can be created to enhance efficiency and selectivity in converting CO<sub>2</sub> into products. This approach plays a role in tackling challenges related to clean energy conversion. Researchers carefully. Mix metals to optimize the binding strength for CO<sub>2</sub> and its byproducts minimize overpotentials and improve catalytic performance. Importantly alloying can result in effects where the resulting alloys properties surpass those of metals making it an invaluable tool in the pursuit of sustainable CO<sub>2</sub>R.

There are two primary types of alloying approaches used in electrocatalysis; pure metallic alloys and compound alloys. Pure metallic alloys involve blending metals to create alloys with enhanced catalytic activity and selectivity. Metals are selected based on their characteristics. Desired catalytic outcomes. On the hand compound alloys combine a metal with a metal element or compound. This approach introduces sites and modifies the electronic structure of the alloy leading to improved performance, in CO<sub>2</sub>R.



### 6.4.1. Pure metallic alloys

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The use of metal alloys, as a strategy for designing e-CO<sub>2</sub>R shows potential in the field of sustainable energy conversion. This approach involves creating catalysts by combining metals to take advantage of their unique electronic and structural properties resulting in synergistic effects. Pure metal alloys are valuable because they can enhance activity, selectivity and stability for CO<sub>2</sub>RR. Researchers can carefully. Combine metals to create catalysts with customized behaviors enabling conversion of CO<sub>2</sub> into valuable chemicals and fuels. The significance of this strategy lies in its ability to promote the use of materials found on Earth reducing reliance on precious metals like platinum and palladium. There are different methods used to obtain metal alloys for e-CO<sub>2</sub>R. One common approach is controlled electrodeposition, where different metal precursors are deposited together onto a conductive surface, under specific electrochemical conditions. Alloying can also be achieved through treatment by mixing metal precursors and heating them to encourage solid state diffusion and alloy formation. These resulting alloys exhibit effects that improve the binding of CO<sub>2</sub> intermediates and facilitate their conversion into desired products. Pure metallic alloys, in essence provide an eco-friendly approach, to creating electrocatalysts. This significantly contributes to the progress of energy technologies. Helps curb the release of greenhouse gases.

Gunji *et al.* have explored the electrocatalytic selectivity of Pd-based bimetallic nanoparticles for CO<sub>2</sub> reduction. PdZn NPs/CB and PdCu NPs/CB exhibited selectivity for HCOO<sup>-</sup> production, while PdSn NPs/CB and PdAg<sub>3</sub> NPs/CB favored CO generation. Notably, PdZn NPs/CB displayed a higher selectivity for HCOO<sup>-</sup>, achieving approximately 100% Faradaic efficiency for HCOO<sup>-</sup> generation at -0.1 V. The presence of PdSn NPs and PdAg<sub>3</sub> NPs/CB suppressed HCOO<sup>-</sup> production, leading to CO selectivity. The underlying mechanism driving this selectivity is currently undergoing further theoretical investigation [97]. Additionally, CuZn catalysts with varying Zn contents were developed to enhance CO<sub>2</sub>R into various products, particularly HCOOH. These catalysts were used as cathodes in PEC reactions and electrodes in electrochemical CO<sub>2</sub> reduction. The CuZn-0.5 catalyst exhibited significantly higher current density compared to Cu-foil, with a FE of 60 %. The synergistic interaction between Cu and Zn sites played a crucial role in increasing the selectivity for HCOOH during CO<sub>2</sub>R [98].

In comparison to an electrodeposited Cu electrode, the Cu<sub>76</sub>Sn<sub>24</sub> alloy, composed of Cu<sub>3</sub>Sn, demonstrated reduced H<sub>2</sub> and hydrocarbon formation during CO<sub>2</sub>R. The alloys exhibited selectivity for CO generation across all applied potentials, with an increase in HCOOH



production as the potential was raised. Furthermore, another study highlights that by analyzing the structure of the active site, Cu-Sn binary catalysts have shown improved selectivity. To mitigate hydrogen generation in electrochemical operations, Sn single atoms should replace nearby terrace Cu atoms. The active Cu edge atoms are responsible for this mechanism. These structures maintain thermodynamic stability under reducing conditions. It is advisable to avoid creating competing structures during material preparation. Substituting Sn prevents the HER process by disrupting the local 3-fold symmetry required for efficient H adsorption at Cu edges. By facilitating CO formation from CO<sub>2</sub> through charge transfer from the Sn atom to the Cu edge atoms, increased selectivity for CO is achieved [99]. Similarly, Yoo *et al.* have fabricated 3D-h CuSn in order to examine the impact of composition and geometry on CO<sub>2</sub>R. Remarkably, the FE<sub>CO</sub> was significantly increased to 98.6% at -0.45 V vs RHE when tiny Sn NPs partially covered the Cu surface. Effective CO production was demonstrated at this low Cu/Sn ratio. This change in the FE landscape for the CO<sub>2</sub>R is attributed to the hierarchical nanoscale architecture, which generates a strong localized electric field, resulting in K<sup>+</sup> accumulation near the catalyst surfaces [100].

Using a co-reduction strategy, the Tang *et al.* have developed a Cu-decorated Cu<sub>2</sub>O catalyst with tunable activity by adjusting the amount of Ag. The modified CuAg-0.75% catalyst displayed enhanced catalytic performance in producing liquid multi-carbon compounds, particularly ethanol. It achieved a maximum  $J_{liquid\ C_{2+}}$  of 288 mA cm<sup>-2</sup> and a  $j_{ethanol}$  of 214 mA cm<sup>-2</sup> at a low overpotential. DFT simulations suggested that the CC coupling process might benefit from the overflow of CO from sites with strong CO adsorption on Cu sites [101]. In another experiment, a CuNiZn alloy was also served as the electrocatalyst for the e-CO<sub>2</sub>R and e-COR. The primary hydrocarbons produced were alkenes, while formate, carbon monoxide, and methane were byproducts of the initial CO<sub>2</sub>R [102]. An-other study highlighted the ability to manipulate bimetallic Cu-Pd nanoalloys to achieve specific morphologies and compositions. Spherical Cu-Pd nanoalloys with a Cu/Pd molar ratio of 1/0.3 exhibited the highest FE for CO conversion, while dendritic Cu-Pd nanoalloys were efficient for H<sub>2</sub> synthesis via HER (65.2% at a polarized potential of -0.87 V) [103].

In addition, the Liu *et al.* investigated the electrical and nano/mesostructural effects of uniformly produced Au-Cu bimetallic films, with an emphasis on their utilization in e-CO<sub>2</sub>R. The introduction of Au drastically altered the d-band electronic structure, leading to a reduction in the binding strength of CO. The binding energy in the d-band could be tuned by varying the



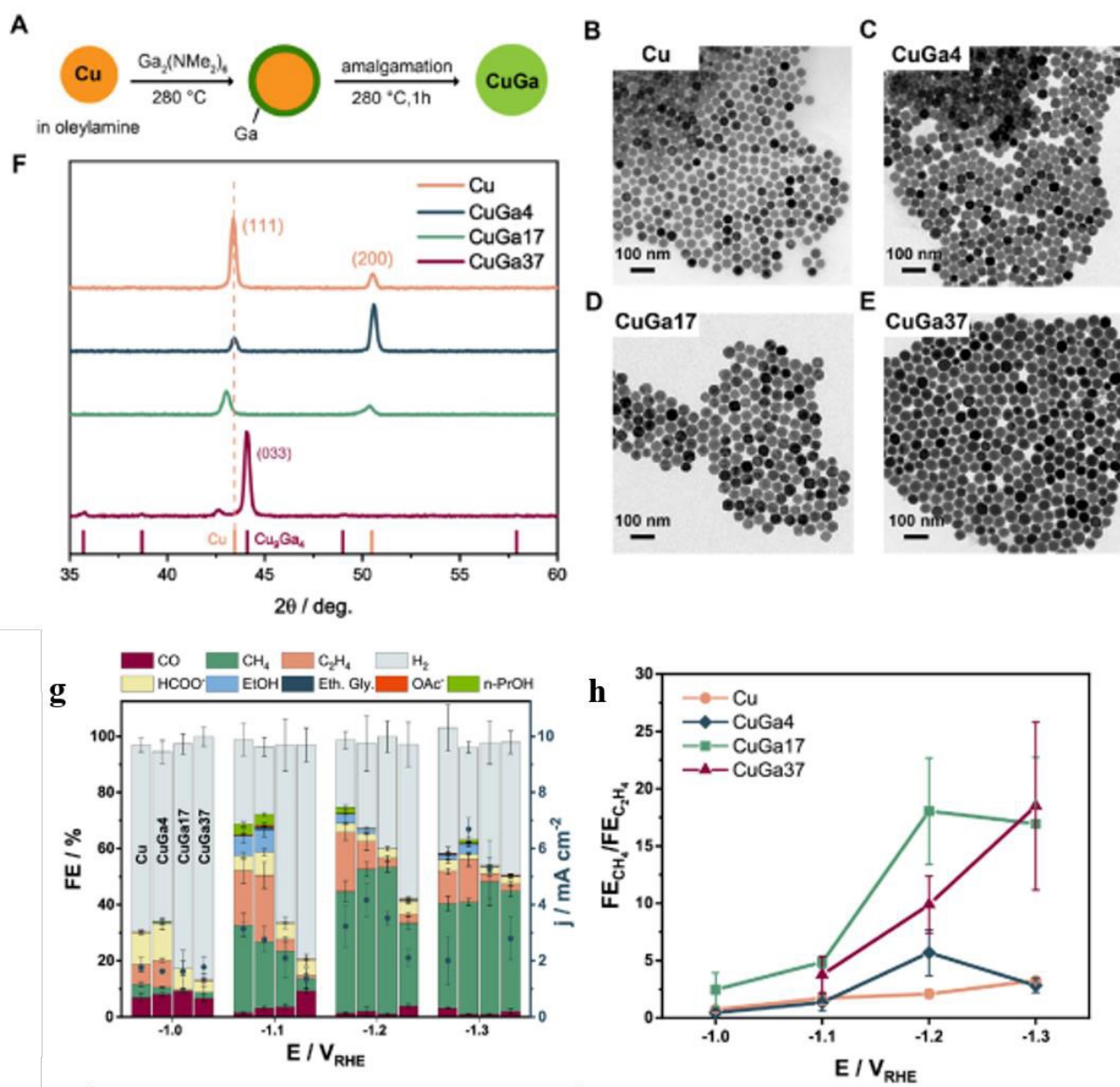
composition of the alloy. Increasing the Au content was found to enhance e-CO<sub>2</sub>R activity and selectivity, demonstrating that the electronic effect alone was not sufficient to overcome the linear scaling relationship. Interestingly, copper oxide/hydroxide species on Au-Cu surfaces were less stable compared to those on pure copper, despite the presence of gold. Alloying Cu with Au could prevent the formation of HCOO<sup>-</sup> by reducing the adsorption energy of \*OCHO. The generation of HCOO<sup>-</sup> was profoundly affected by the electrical effect and d-band structure, although the activity did not scale linearly with changes in composition [104].

Again, for e-CO<sub>2</sub>R, Cu-Co bimetallic nanoparticles were synthesized on porous carbon using a process adapted from ZIF by Guo et al. These catalysts achieved current densities as high as 62.1 mA cm<sup>-2</sup> in an electrolyte containing 0.5 M [Bmim]PF<sub>6</sub> in MeCN, resulting in a FE<sub>CO</sub> of 97.4%. Catalytic activity was increased due to the interaction between Cu and Co, which increased the electrochemical surface area and CO<sub>2</sub> adsorption capacity [105]. However, the Velasco-Vélez et al. have discovered that adding Zn heteroatoms to a copper metal lattice did not significantly boost the creation of profitable multi-carbon species during the e-CO<sub>2</sub>RR. The presence of Cu<sup>+</sup> species in the reaction pathway had little effect on these species [106]. Further, the impact of metal content and particle size on CuCo nanoparticles generated via inverse micellar encapsulation on e-CO<sub>2</sub>RR activity was investigated. The results demonstrated that initially, both metals oxidized, and even a small amount of Co significantly enhanced the activity of CuCo nanoparticles. As particle size increased, e-CO<sub>2</sub>RR outperformed HER [107].

Furthermore, the pulsed laser ablation in liquids (PLALs) was used to produce noble metal-free multi-principal element alloy nanoparticles (MPEA-NPs) for the e-CO<sub>2</sub>R. The electrochemical testing confirmed the unique activity of MPEA-NPs stabilized with poly-(diallyldimethylammonium chloride) (PDADMAC) for CO<sub>2</sub>R. It was discovered that Al<sub>8</sub>Cr<sub>17</sub>Co<sub>17</sub>Cu<sub>8</sub>Fe<sub>17</sub>Ni<sub>33</sub> MPEA-NPs exhibited highly efficient catalysis for CO<sub>2</sub>R, potentially replacing costly noble metal electrocatalysts [108]. Okatenko *et al.* had shown that the stability of Cu nanoparticles under CO<sub>2</sub>RR had been significantly enhanced by the addition of Ga. Ga-added nanoparticles had remained stable for up to 20 hours, whereas the parent Cu nanoparticles had decayed quickly (Figure 8). Employing various experimental and theoretical methods based on the known reconstruction mechanism of Cu nanoparticles under CO<sub>2</sub>RR, the researchers had provided an explanation for this observation. They had hoped that their findings would overlay the way for the development of alloyed Cu-based nano-catalysts that could withstand CO<sub>2</sub>RR and other reducing reaction conditions. Similar mechanisms to prevent



Cu reconstruction and produce more stable nanoparticles had been found in the study for metals with higher oxophilicity and strong M-Cu bonding energies [109].



**Figure 8:** CuGa NPs were synthesized and characterized. (A) A streamlined approach to synthesis. Bright field TEM images of Cu, CuGa<sub>4</sub>, CuGa<sub>17</sub>, and CuGa<sub>37</sub> NPs (B–E) and their matching XRD patterns (F). These results point to the synthesis of CuGa NPs with a consistent shape, extremely similar diameters, and varying Ga concentrations. how well the CuGa NPs electrocatalyze CO<sub>2</sub>RR. (g) Mean FE (left axis) and geometric current density (right axis) for Cu, CuGa<sub>4</sub>, CuGa<sub>17</sub>, and CuGa<sub>37</sub> NPs at various applied potentials (NP loading was held constant at 15 g on glassy carbon with a geometric area of 1.33 cm<sup>2</sup>) during 45 min CO<sub>2</sub>RR in CO<sub>2</sub>-saturated 0.1 M KHCO<sub>3</sub>. CH<sub>4</sub> preferment in CuGa NPs is indicated by the ratio of the FE





for  $CH_4$  and  $C_2H_4$  across the same potential range (h). Reproduced with permission from Ref. [109] Copyright 2023, American Chemical Society.

Foucher et al. have presented a strategy for the synthesis of Cu-Pt nanocrystals of varying sizes and crystal shapes. A Cu-rich core had been found to be enclosed in a Pt-rich layer, as determined by a thorough STEM-EDS study. Cu-Pt particles had been stable as catalysts because, after being annealed at 800°C, they had become intermetallic CuPt particles. Non-intermetallic CuPt had been found to be stable at 400°C in  $H_2$  or  $O_2$  using in-situ STEM analysis. The production of a Cu oxide layer, which would cover and render Pt inactive, had been prevented by the intermetallic CuPt phase. They had shown that copper alloys didn't always oxidize and decay as quickly as feared, and that nanoscale CuPt structures could help conserve otherwise costly Pt. CuPt particle stability had been of significant interest and may be useful in a number of different chemical processes [110]. In a related context, another study delved into bimetallic CuAg electrodes. These electrodes had bulk compositions closely matching their surface compositions, primarily consisting of Cu and Ag crystallites. During  $CO_2RR$ , the presence of CO adsorbates induced the segregation of initially dissolved Cu in the Ag phase, resulting in Cu surface enrichment on the Ag-rich bimetallic electrodes. CO formation primarily occurred on the surface of the Ag domains, while CO reduction was exclusive to the Cu domains. The distribution of products changes when they are produced on a stable CuAg electrode. Changing from pure Cu electrodes significantly decreases hydrogen generation and favors carbonyl compounds [111].

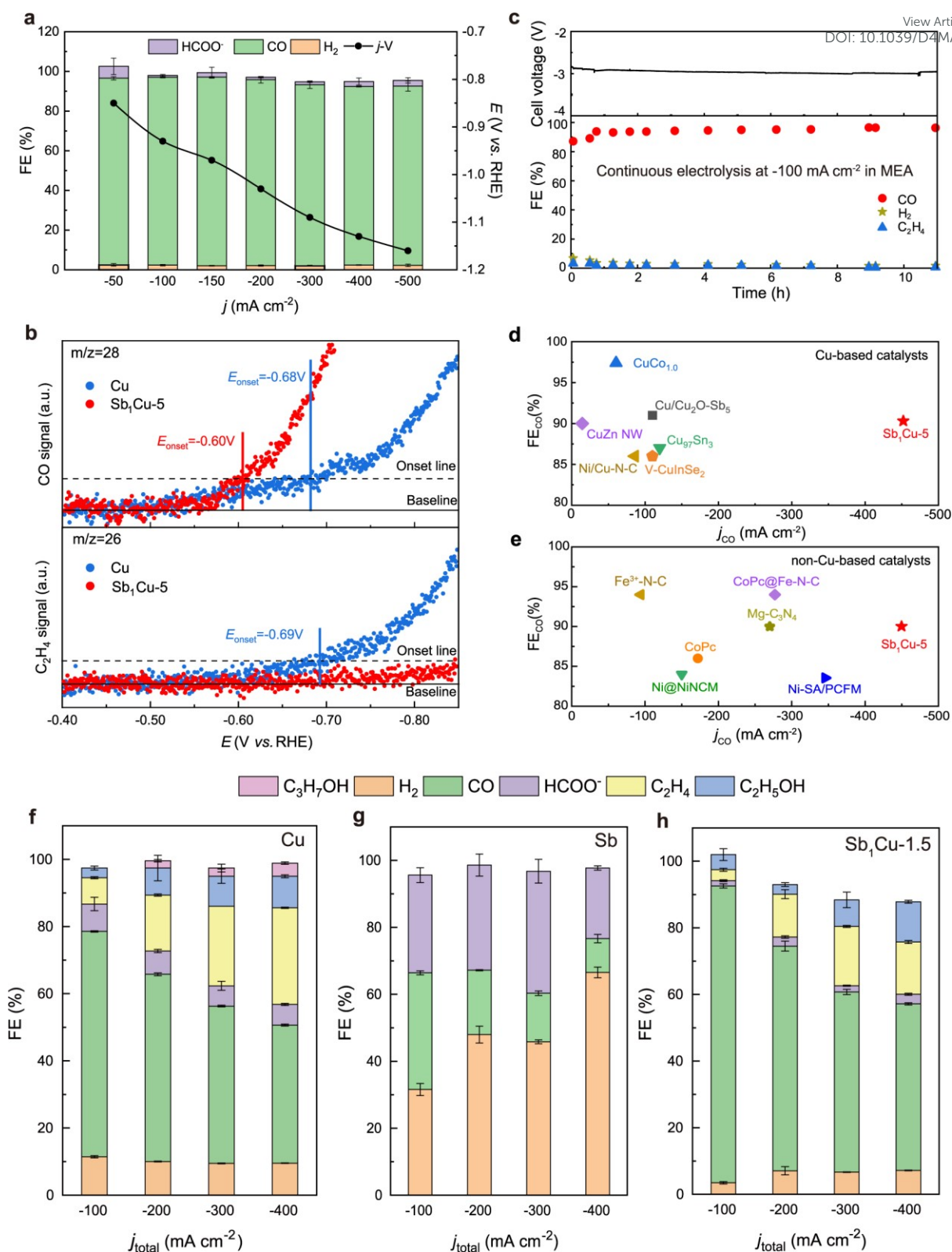
The study proposed an alternate route, using the chemical named DAT to co-electrodeposit high-surface-area CuAg alloys. Instead of nucleus formation the way this method worked merely prevents nucleation, producing more evenly distributed samples of Cu and Ag atoms in CuAg-wire. Using a flow electrolyzer, we found that CuAg-wire samples were more active and cordant in terms of selectivity compared to CuAg-poly and Cu-wire in the e- $CO_2R$ . Products such as  $C_2H_4$  and  $C_2H_5OH$  were detected [112]. Seeking a different avenue of study, Pd@Au nanoparticles were developed by impregnating Au nanoparticles with specified amounts of Pd. Intriguingly, it was shown that at varying Pd loadings the catalytic activity for  $CO_2R$  was non-linear. In addition, the bimetallic Pd-Au surfaces with isolated Pd presented lower energy barriers for  $CO_2$  activation and were less prone to poisoning by strongly binding \*CO intermediates [113].



Moreover, the research delved into the impact of the starting Cu/Zn ratio and the extent of alloying between Cu and Zn components on the product selectivity of CuZn nanoparticles. Under CO<sub>2</sub>R conditions, CH<sub>4</sub> was predominantly generated near the metallic Cu in proximity to ZnO, while the exclusive production of CO and H<sub>2</sub> resulted from the reduction of ZnO species and the enhanced Cu-Zn contact [114]. Additionally, Li *et al.* have attained FE exceeding 95% in industrial-scale CO<sub>2</sub> reduction to CO, by a novel antimony-copper single-atom alloy catalyst (Sb<sub>1</sub>Cu). This catalyst offered improved selectivity and throughput due to the atomic-level SbCu interface, which facilitated CO<sub>2</sub> adsorption while reducing CO\* binding (Figure 9) [9].

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**Figure 9:**  $\text{CO}_2\text{RR}$  performance over  $\text{Sb}_1\text{Cu}$  catalysts and  $\text{Cu}$ . FEs of all  $\text{CO}_2\text{RR}$  products at different current densities and the associated  $j$ - $V$  curve for  $\text{Sb}_1\text{Cu-5}$  (a). In situ DEMS measurement of the production of (up)  $\text{CO}$  and (down)  $\text{C}_2\text{H}_4$  during  $\text{CO}_2\text{RR}$  on  $\text{Cu}$  and  $\text{Sb}_1\text{Cu-}$

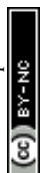


5 catalysts (b). Stability test at  $100 \text{ mA cm}^{-2}$  current density in MEA for more than 10 hours. GC analysis shows an average  $FE_{CO}$  of about 95% (c). Different reported  $CO_2RR$ -to-CO (d) Cu-based and (e) non-Cu-based catalysts' performance measures. Product FEs on (f) Cu, (g) Sb, and (h)  $Sb_1Cu_{1.5}$  compared. The error bars show the average difference between three different readings. Reproduced from Ref. [9] Open access article, Nature.

In a different facet of the research, bimetallic  $Au_{0.5}Cu_{0.5}$  NPs with a narrow size distribution were synthesized using inverse micelle encapsulation. Smaller NPs exhibited higher current density during e- $CO_2R$  due to their larger population of low-coordinated sites, as confirmed by X-ray spectroscopy. While Faradaic selectivity showed less size dependence, with  $H_2$  being the predominant product at approximately 80% selectivity, larger NPs yielded a 7% increase in CO output and a 7% decrease in  $H_2$  production [115]. Table 3 provide a comprehensive overview of different designed electrocatalysts for e- $CO_2RR$  following pure metallic approach on Cu-based materials.

**Table 3:** Delving into the realm of pure metallic alloys approach, this comprehensive table evaluates electrocatalytic materials designed for  $CO_2R$ . It sheds light on the behavior of these materials and highlights how metallic alloys significantly influence product selectivity under different reaction conditions.

N	Material	electrolyte	V vs RHE	≈ FE %									
				$H_2$	CO	$CH_4$	$C_2H_4$	$HCOO^-$	$C_2H_5^+$	CH <sub>3</sub> OH	$C_2H_5OH$	$C_2H_3O_2^-$	
1	Pd NPs/CB	0.1 M $KHCO_3$	-1.0	63	38	--	--	3	--	--	--	--	
2	Ag NPs/C			43	63	--	--	3	--	--	--	--	
3	PdZn NPs/CB			44	17	--	--	42	--	--	--	--	
4	PdCu NPs/CB			53	57	--	--	1	--	--	--	--	
5	PdSn NPs/CB			62	15	--	--	1	--	--	--	--	
6	PdAg <sub>3</sub> NPs/CB			18	84	--	--	1	--	--	--	--	
7	Cu	0.1 M $KHCO_3$	-1.09	18	5	--	--	10	--	--	--	--	
8	$Cu_3Sn$ ( $Cu_{76}Sn_{24}$ )			5	38	--	--	43	--	--	--	--	
9	Sn			5	3	--	--	89	--	--	--	--	
10	Cu			45	4	--	--	19	--	--	--	--	
11	CuZn-0.1			40	5	--	--	33	--	--	--	--	
12	CuZn-0.5			26	7	--	--	60	--	--	--	--	
13	CuZn-1	0.1 M $KHCO_3$	-1.1	28	10	--	16	31	--	--	--	--	
14	Zn			20	55	--	--	15	--	--	--	--	
15	Flat Cu-Sn			-1.0	--	77	--	--	--	--	--	--	
16	3D-h- Cu-Sn			-0.4	--	91	--	--	--	--	--	--	
17	Cu <sub>2</sub> O			-0.75	20	22	7	28	4	--	--	13	--
18	CuAg-0.25%			19	18	8	34	1	--	--	--	16	--
19	CuAg-0.75%	16	19	5	37	1	--	--	--	17	--		
20	CuAg-2%	14	19	2	45	1	--	--	--	15	--		



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21	CuNiZn	0.1 M KHCO <sub>3</sub>	-1.2	68	4	2	2	38	--	--	--	--	[1 02 ]
22	Cu-Pd-D			65	30	--	--	--	--	--	--	--	
23	Cu-Pd-0.8			9	86	--	--	--	--	--	--	--	
24	Cu-Pd-C			71	48	--	--	--	--	--	--	--	[1
25	Cu-Pd-0.3	0.5 M KHCO <sub>3</sub>	-0.87	5	92	--	--	--	--	--	--	--	03
26	Cu-Pd-S			25	55	--	--	--	--	--	--	--	]
27	Cu-Pd-0.1			40	53	--	--	--	--	--	--	--	
28	Pd/C			68	37	--	--	--	--	--	--	--	
29	Au			22	78	--	--	1	--	--	--	--	
30	Au <sub>75</sub> Cu <sub>25</sub>			42	66	--	--	2	--	--	--	--	
31	Au <sub>50</sub> Cu <sub>50</sub>	0.1 M KHCO <sub>3</sub>	-0.8	58	49	--	--	3	--	--	--	--	[4
32	Au <sub>25</sub> Cu <sub>75</sub>			63	29	--	--	4	--	--	--	--	]
33	Cu			59	12	--	--	13	--	--	--	--	
34	Cu			77	23	--	--	--	--	--	--	--	
35	CuCo <sub>0.4</sub>			50	50	--	--	--	--	--	--	--	
36	CuCo <sub>0.6</sub>	0.5 M		12	88	--	--	--	--	--	--	--	[1
37	CuCo <sub>1.0</sub>	[Bmim]PF <sub>6</sub>	-2.1	2	99	--	--	--	--	--	--	--	05
38	CuCo <sub>1.9</sub>			22	79	--	--	--	--	--	--	--	]
39	Co			66	22	--	--	--	--	--	--	--	
40	Cu:Zn 100:0			38	2	3	30	--	--	--	--	--	
41	Cu:Zn 91:9		-1.8	32	5	7	31	--	--	--	--	--	
42	Cu:Zn 83:17	100 mm	Ag/	30	8	5	35	--	--	--	--	--	[1
43	Cu:Zn 50:50	KHCO <sub>3</sub>	AgC	23	10	17	28	--	--	--	--	--	06
44	Cu:Zn 9:91		1	67	20	18	4	--	--	--	--	--	]
45	Cu:Zn 0:100			70	25	28	1	--	--	--	--	--	
46	Co			98	1	--	--	1	--	--	--	--	
47	Cu <sub>30</sub> Co <sub>70</sub>			93	2	--	--	6	--	--	--	--	
48	Cu <sub>50</sub> Co <sub>50</sub>		-1.1	92	3	--	--	5	--	--	--	--	[1
49	Cu <sub>70</sub> Co <sub>30</sub>	0.1 M KHCO <sub>3</sub>	V	92	4	--	--	5	--	--	--	--	07
50	Cu <sub>90</sub> Co <sub>10</sub>			82	5	--	--	13	--	--	--	--	]
51	Cu			87	8	--	--	8	--	--	--	--	
52	Cu			67	7	6	7	11	--	--	--	--	
53	CuGa <sub>4</sub>	0.1 M KHCO <sub>3</sub>	-1.0	58	8	3	9	14	--	--	--	--	[1
54	CuGa <sub>17</sub>			80	6	2	1	3	--	--	--	--	09
55	CuGa <sub>37</sub>			85	6	2		3	--	--	--	--	]
56	Cu wire			--	15	--	35	--	--	--	--	28	
57	Cu-Ag poly	0.1 M KHCO <sub>3</sub>	-0.8		8	--	27	--	--	--	--	16	[1
58	Cu-Ag wire				7	--	55	--	--	--	--	26	]
59	Cu				58	--	--	--	--	--	--	--	
60	Pd <sub>2</sub> @Cu <sub>98</sub>				48	--	--	--	--	--	--	--	
61	Pd <sub>5</sub> @Cu <sub>95</sub>			30	58	--	--	7	--	--	--	--	[1
62	Pd <sub>10</sub> @Cu <sub>90</sub>	0.1 M KHCO <sub>3</sub>	-0.8		41	--	--	10	--	--	--	--	13
63	Pd <sub>20</sub> @Cu <sub>80</sub>				40	--	--	22	--	--	--	--	]
64	Pd				9	--	--	38	--	--	--	--	
65	Cu			52	1	40	3	2	--	--	--	--	
66	Cu <sub>90</sub> Zn <sub>10</sub>	0.1 M KHCO <sub>3</sub>	-1.3	32	2	62	1	2	--	--	--	--	[1
67	Cu <sub>70</sub> Zn <sub>30</sub>		5	25	4	70	2	3	--	--	--	--	14
68	Cu <sub>50</sub> Zn <sub>50</sub>			50	5	68	2	4	--	--	--	--	]

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69	Cu <sub>30</sub> Zn <sub>70</sub>			51	38	9	1	5	--	--	--	--	<a href="#">View Article Online DOI: 10.1039/D4MA00321G</a>
70	Cu <sub>10</sub> Zn <sub>90</sub>			52	42	2	1	1	--	--	--	--	--
71	Zn <sub>10</sub>			53	43	1	1	1	--	--	--	--	--
72	Ni-N-C			--	70	--	--	--	--	--	--	--	[1
73	Cu-Ni-C	0.5 M KHCO <sub>3</sub>	-1.0	--	12	--	--	--	--	--	--	--	16
74	Ni/Cu-N-C			--	92	--	--	--	--	--	--	--	]
75	Cu			11	68	--	7	9	--	--	3	--	--
76	Sn	0.5 M KHCO <sub>3</sub>	-100	31	34	--		30	--	--	--	--	[9
77	Sb <sub>1</sub> -Cu-1.5			3	80	--	3	2	--	--	4	--	--
78	Sb <sub>1</sub> -Cu-5			2	96	--	--	1	--	--	--	--	--
79	AuCu-5 nm	0.1 M KHCO <sub>3</sub>	-1.2	83	13	3	--	--	--	--	--	--	5
80	Cu <sub>100</sub> Bi			50	8	--	--	--	--	--	--	--	--
81	Cu <sub>50</sub> Bi		50	70	14	3	2	--	--	--	--	--	--
82	Cu <sub>10</sub> Bi		mA	20	44	--	--	--	--	--	--	--	--
83	Cu <sub>5</sub> Bi		cm <sup>-2</sup>	19	31	--	--	42	--	--	--	--	--

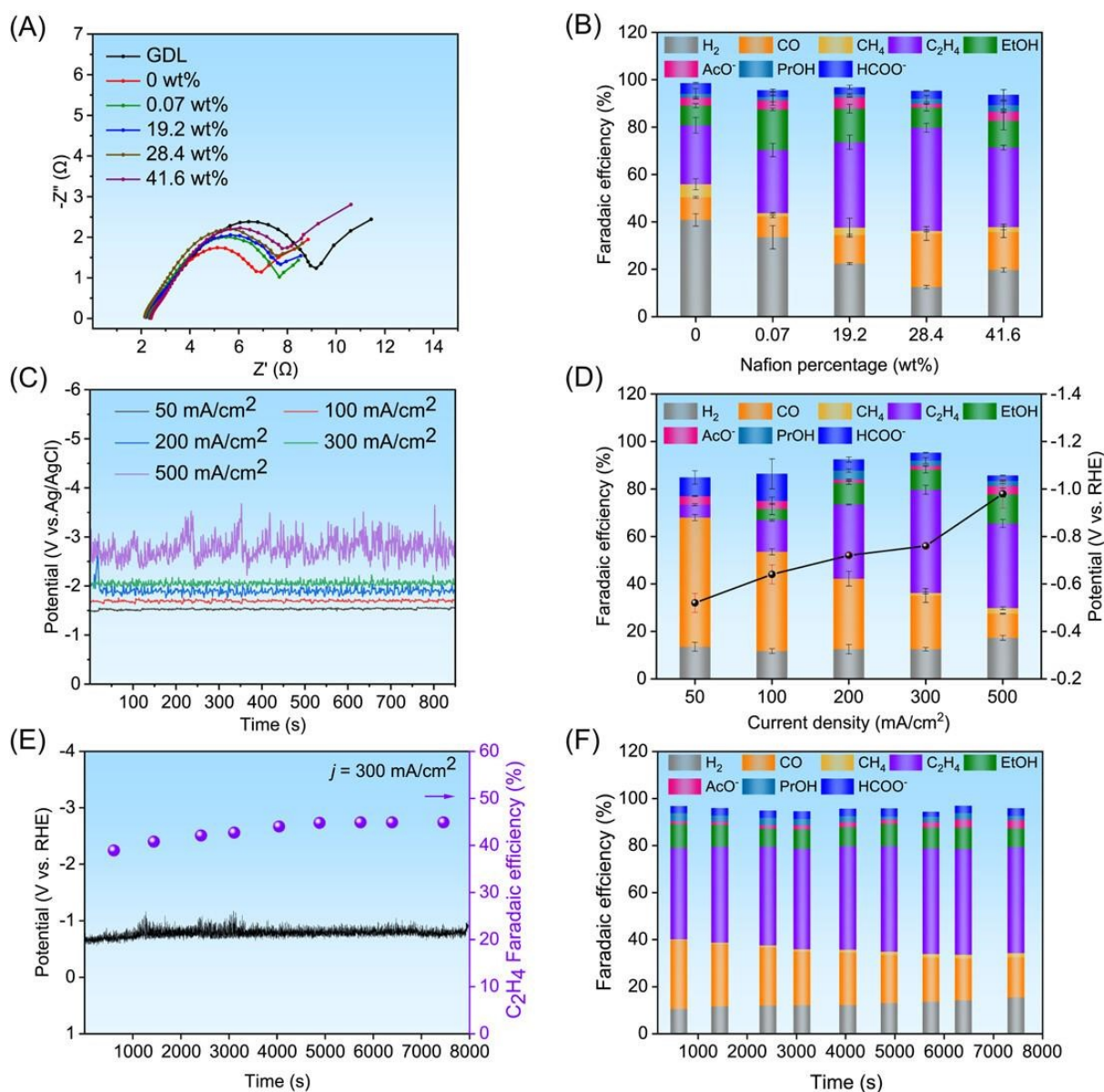
### 6.4.2. Compound alloys

The strategy of combining elements to create alloys plays a role, in designing electrocatalysts for e-CO<sub>2</sub>R. This approach has the potential to enhance the catalytic performance and selectivity of these materials. When two or more elements with properties are combined their synergy can result in catalytic activity. By selecting elements with electronegativities, electronic structures and atomic sizes researchers can customize the surface properties and reactivity of the alloy, which in turn affects its ability to convert CO<sub>2</sub>. Compound alloying is crucial because it allows for optimization of the binding energies between CO<sub>2</sub> and reaction intermediates. This optimization promotes selective conversion of CO<sub>2</sub>. Additionally alloying helps address issues such as catalyst deactivation and unwanted byproduct formation thus contributing to the development of economically viable technologies for CO<sub>2</sub> conversion. There are methods to achieve compound alloying, including wet chemistry synthesis, electrodeposition and physical vapor deposition. Each method offers control over the composition and structure of the alloy. Through these techniques researchers can explore a range of combinations to discover new electrocatalysts with exceptional performance. This research brings us closer, to achieving CO<sub>2</sub> conversion and advancing energy production.

Lai et al. have presented the inclusion of the organic additive 1-Br<sub>2</sub> can enhance CO<sub>2</sub>R activity and selectivity in Cu alloys containing Co, In, Mn, and Zn. This covered the way for the development of hybrid electrocatalysts with improved performance in CO<sub>2</sub>R to higher-order products. It was noteworthy that these compounds displayed strong correlations with CH<sub>4</sub> and C<sub>2+</sub>, underscoring a fundamental limitation in selectivity tuning through alloying. The hybrid



organic-inorganic catalysts demonstrated the potential to exert control over branching ratios within the CO<sub>2</sub>R reaction network [118]. Further, a novel activation approach by Nafion on Cu(OH)<sub>2</sub>-derived Cu was applied for transforming this material into an effective e-CO<sub>2</sub>RR for flow cell applications (Figure 10). Notably, under optimized conditions, a  $FE_{C_2H_4}$  of 44% and a total CO<sub>2</sub> reduction FE of 83% were achieved at 300 mA cm<sup>-2</sup>, showcasing exceptional performance. This activation strategy showcased its efficacy by promoting C<sub>2</sub>H<sub>4</sub> production and simultaneously mitigating the occurrence of hydrogen evolution reactions [119].

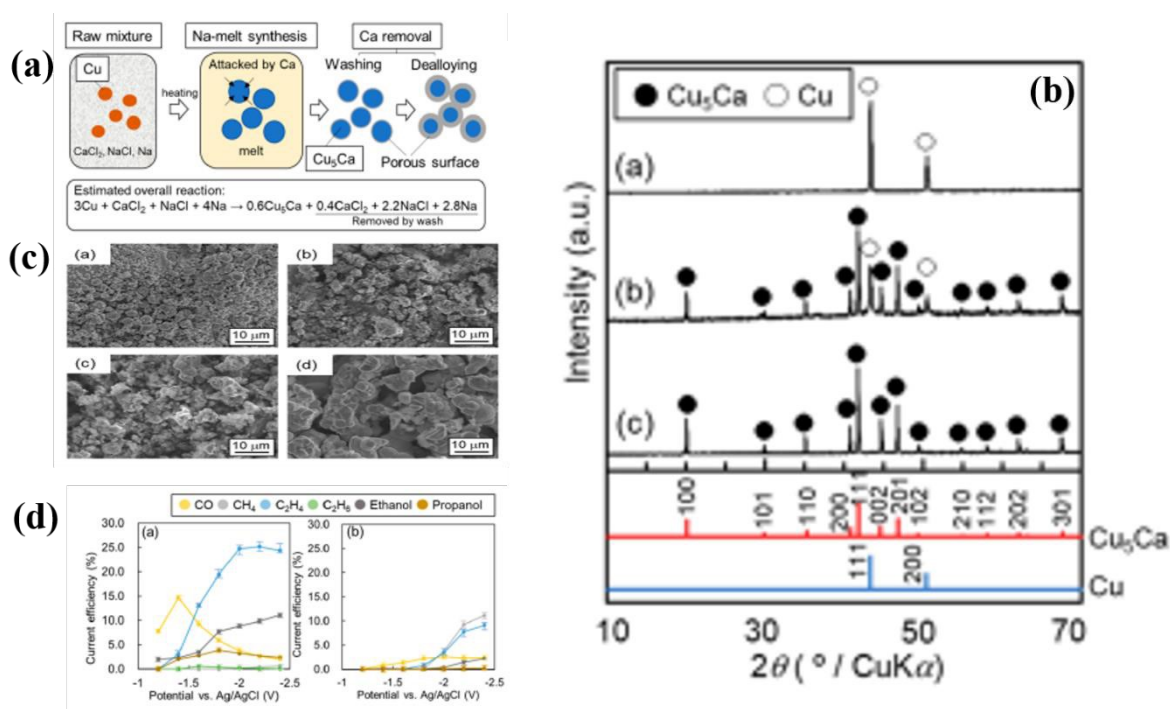


**Figure 10:** ANCu@Nafion catalysts with varying Nafion percentages were fabricated at 0.1 V, and their Nyquist plots from 0.01 Hz to 100 kHz (A) and their product distribution FEs at 300 mA cm<sup>-2</sup> (B) were plotted. The CO<sub>2</sub> reduction kinetics of ANCu@Nafion-28.4 wt% in 1 M KOH electrolyte (C) along with the corresponding current density versus product distribution



kinetics (D), voltage profile and  $C_2H_4$  kinetics (E), and product distribution kinetics (F) over the course of an 8000-second test. Reproduced from Ref. [119] Open access article, Wiley.

Further, Chang et al. have investigated structural changes,  $CO_2RR$  activity, and selectivity from Ag@Cu core-shell system. Employing a straightforward polyol reduction strategy, researchers manipulated the compositions and structures of nanoparticles (NPs). The significance of synergistic interactions between Ag and Cu emerged, leading to elevated CO or hydrocarbon production within specific NP configurations, such as Ag@Cu-5 or Ag@Cu-20 [120]. Additionally, the synthesis of granular particles featuring a Cu-based nanostructure and approximately 10 nm nanopores was undertaken using a Na-melt technique (Figure 11). The process involved the electrochemical extraction of calcium from  $Cu_5Ca$ , facilitating the further evolution of these nanostructures. The application of a large negative voltage to the  $Cu_5Ca$  particles resulted in the generation of platelet Cu particles with comparable nanopores [121].



**Figure 11:** (a) Schematic Representation of the  $Cu_5Ca$  and its Derivatives Synthesis Process, (b) The P-XRD patterns for the  $Cu_5Ca$  (PDF 04-007-1585) and Cu (PDF 00-004-0836) synthesized at 400, 600, and 750 °C from a Na melt-synthesized sample with a nominal molar ratio of  $Cu/Ca = 3/1$ , (c) Micrographs taken with a SEM of (a) raw Cu powder and (b) 400, 600, and 750 °C Na-melt-synthesized samples, (d) Current efficiencies for  $CO_2R$  products at different potentials for (a)  $Cu_5Ca$  and (b) Cu samples. Each applied potential lasted for 1 hour. Reproduced with permission from Ref. [121] Copyright 2022, American Chemical Society.

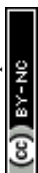




Remarkable exposures emerged from the study of bimetallic Cu-Sn catalysts, unveiling spontaneous surface transformations driven by local galvanic corrosion during CO<sub>2</sub>RR. The distinct oxidation potential gap between Cu and Sn induced accelerated corrosion of the thin Sn layer on Cu foil, prompting the emergence of finer Sn patterns and outward Sn migration. This intriguing redox interplay fostered thinner Sn patterns and showcased the novel Cu/p-Sn 3-nm catalysts, boasting exceptional catalytic selectivity of 58.1% at -1.0 VRHE [122]. Further, in the pursuit of effective ethylene synthesis via CO<sub>2</sub>RR, a groundbreaking CeO<sub>2</sub>/CuO electrocatalyst was synthesized. Innovatively integrating CeO<sub>2</sub> quantum dots, this catalyst harnessed heterointerfaces to enhance CO<sub>2</sub> and CO adsorption, while stabilizing Cu<sup>+</sup> for CO<sub>2</sub>RR. Remarkably surpassing both CuO and CuO-CeO<sub>2</sub> hybrid counterparts [123].

Moreover, the electrochemical narrative unraveled the potential of CuWO<sub>4</sub> to shine as an exceptional electrocatalyst for CO<sub>2</sub>R, surpassing conventional CuO [124]. Further, the synthesis of a new composite by combining Cu-BTC with GrO yielded a transformative breakthrough, showcasing augmented adsorption capabilities. With the infusion of GrO, the composite's BET surface area and pore volume were elevated compared to its Cu-BTC precursor. This composite displayed a significantly elevated capacity for CO<sub>2</sub> adsorption, while the CH<sub>4</sub> adsorption remained essentially unaltered [125]. Embracing innovative methodologies, Huang *et al.* harnessed a unique seeded-growth colloidal technique to synthesize AgCu NDs, unraveling intricate interplays between varying Cu domain sizes. This approach, indicating dimer systems such as CuRu, CuRh, and CuIr, presented a gateway to synthetic control over Cu and Ag nanoparticle counterparts. Remarkably, Ag<sub>1</sub>Cu<sub>1.1</sub> NDs exhibited a transformative 3.4-fold surge in FE toward C<sub>2</sub>H<sub>4</sub>, alongside a twofold increase in total CO<sub>2</sub>RR activity compared to similar-sized Cu NPs [126]. A meticulous approach involving the electrodeposition of Sn onto porous Cu hollow fibers illuminated pathways to enhancing current density and reaction selectivity in electrochemical CO<sub>2</sub>R. Skilled optimization of the Sn<sup>2+</sup>/Sn<sup>4+</sup> ratio on the HFGDE surface yielded substantial enhancements in FE of formate [127]. Unveiling a pathway to dual-loop CO<sub>2</sub> capture during gasification, Rahman *et al.* showcased the potential of pellets merging CuO and limestone. Intriguingly, core-in-shell Ca<sub>50</sub>Cu<sub>40</sub>Cem10 pellets exhibited rapid CuO reduction in the presence of CO and H<sub>2</sub> [128].

Continuing this scientific journey, elevated-temperature pyrolysis in a reducing atmosphere was harnessed to successfully produce monometallic Cu/C, Ni/C, and intermetallic Cu<sub>0.85</sub>Ni<sub>0.15</sub>/C nanomaterials from phase-pure MOFs Cu-BTC, Ni-BTC, and Cu<sub>0.85</sub>Ni<sub>0.15</sub>-BTC.



Structural analyses unveiled the creation of a substitutional solid solution, the Cu<sub>0.85</sub>Ni<sub>0.15</sub>/C nanoalloy, within these MOF-derived nanomaterials, showcasing a significant dispersion of active metal sites on the carbonaceous substrate. With an impressive selectivity for CH<sub>3</sub>OH and a high FE reaching up to 60% at 0.40 V, the intermetallic nanoalloy outperformed conventional monometallic catalysts in enhancing the efficiency of CO<sub>2</sub>RR [129]. In a parallel exploration, Wannakao *et al.* expressed realm of e-CO<sub>2</sub>R on metal/WC surfaces, employing density functional theory simulations to unravel activity and selectivity trends involving 13 different metal species. The findings revealed that metals such as Zn/WC, Ag/WC, and Au/WC, known for their limited interactions with reaction intermediates, produced CO as a significant product with a limiting potential similar to their pristine metal surfaces. These core-shell M/WC systems showcased potential to reduce the demand for costly metals in contemporary catalytic processes. Conversely, Cu/WC and Pd/WC surfaces exhibited a comparatively low capability for reducing CO<sub>2</sub> to CO [130]. In another facet of investigations, Zhang *et al.* explored the functions of Cu and Sn in selective e-CO<sub>2</sub>R by designing a series of Cu-Sn-based composites as model catalysts. By varying the ratio of copper to silver, e-CO<sub>2</sub>RR's products can be adjusted to produce either formate or carbon monoxide. Remarkably, both Cu<sub>1</sub>Sn<sub>1</sub> and Cu<sub>20</sub>Sn<sub>1</sub> emerged as excellent catalysts for formate and CO oxidation, exhibiting high selectivity and partial current density. While Cu<sub>20</sub>Sn<sub>1</sub> featured a structure consisting of a single Sn atom doped into a Cu atom, characterizations of Cu<sub>1</sub>Sn<sub>1</sub> unveiled a CuSn alloy core with a minimal quantity of a Cu-doped SnO shell [131]. Table 4 provide a complete summary of different designed electrocatalysts for e-CO<sub>2</sub>RR following compound alloying approach on Cu-based materials.

**Table 4:** This table provides a summary of compound alloys strategy employed for developing electrocatalysts and their corresponding electrochemical efficiency. It offers information on approaches for environmentally sustainable conversion of CO<sub>2</sub>.

N	Material	electrolyte	V vs RHE	≈ FE %									Ref.
				H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	
1	Cu-Raw			48	7	12	--	--	--	--	--	--	
2	Cu-50			38	11	11	--	--	--	--	--	--	[132
3	Cu-100	0.1 M KHCO <sub>3</sub>	-1.0	33	10	8	--	--	--	--	--	--	]
4	Cu-200			37	7	6	--	--	--	--	--	--	
5	Flat-Cu-Sn				75	--	--	--	--	--	--	--	
6	Cu-Sn rod	0.1 M KHCO <sub>3</sub>	-1.0		51	--	--	--	--	--	--	--	[100
7	3D-h Cu-Sn				68	--	--	--	--	--	--	--	]



8	AN-Cu			41	9	6	24	3	--	--	10	[119
9	AN-Cu@Nafion (0.07)	1 M KOH	-0.1	35	8	1	26	2	--	--	17	]
10	Ah NPs			29	63	--	--	--	--	--	--	
11	Ag@Cu-5			29	68	--	--	--	--	--	--	
12	Ag@Cu-7			29	70	2	--	--	--	--	--	
13	Ag@Cu-10	0.1 M KHCO <sub>3</sub>	-1.16	53	21	13	4	--	--	--	--	[120
14	Ag@Cu-15			53	10	20	13	--	--	--	--	]
15	Ag@Cu-20			45	5	23	16	--	--	--	--	
16	Ag@Cu-25			44	5	21	17	--	--	--	--	
17	Cu NPs			58	7	17	19	--	--	--	--	
18	Cu <sub>5</sub> Ca		-2.5	--	3	1	24	--	--	--	11	--
19	Cu samples	0.5 M KHCO <sub>3</sub>	Ag/ AgC	--	3	11	8	--	--	--	3	--
20	Cu		1	--	2	--	--	8	--	--	--	--
21	Cu/p-Sn 3nm			--	52	--	--	12	--	--	--	--
22	Cu/p-Sn 20nm	0.1 M KHCO <sub>3</sub>	-1.2	--	36	--	--	62	--	--	--	--
23	Cu/p-Sn 30nm			--	3	--	--	98	--	--	--	--
24	CeO <sub>2</sub> /CuO-50%			--	--	--	--	42	--	--	--	--
25	CuO			--	--	--	--	2	--	--	--	--
26	CeO <sub>2</sub> /CuO-50%-PM			--	--	--	--	1	--	--	--	--
27	CeO <sub>2</sub> /CuO-50%-Bulk	1 M KOH	250 mA	--	--	--	--	14	--	--	--	--
28	CeO <sub>2</sub> /CuO-20%		cm <sup>-2</sup>	--	--	--	--	32	--	--	--	--
29	CeO <sub>2</sub> /CuO-37.5%			--	--	--	--	38	--	--	--	--
30	CeO <sub>2</sub> /CuO-50%			--	--	--	--	42	--	--	--	--
31	CeO <sub>2</sub> /CuO-70%			--	--	--	--	28	--	--	--	--
32	Ag NPs			45	68		1	--	--	--	--	--
33	Cu NPs	0.1 M KHCO <sub>3</sub>	-1.1	52	13	8	12	12	--	--	--	--
34	Ag <sub>1</sub> -Cu <sub>1.1</sub> NDs			34	18	19	41	19	--	--	--	--
35	CuSn (50 s) HFGDEs	0.5 M KHCO <sub>3</sub>	-1.4	--	--	--	--	50	--	--	--	--
36	CeO <sub>2</sub>			78	3	--	--	2	--	--	2	--
37	5-CuO/CeO <sub>2</sub>	0.1 M KHCO <sub>3</sub>	-1.4	57	17	2	3	1	--	2	9	--
38	60-CuO/CeO <sub>2</sub>			45	2	27	55	1	--	2	3	--
39	CuO			39	2	10	21	5	--	--	16	--
40	Cu/C			--	10	10	--	--	--	13	--	--
41	Cu <sub>0.85</sub> Ni <sub>0.15</sub> /C		-1.0	--	3	4	--	--	--	2	--	--
42	Ni/C			--	16	--	--	--	--	2	--	--
43	pure Sn			9	15	--	--	70	--	--	--	--
44	pure Cu	0.5 M KHCO <sub>3</sub>	-1.1	41	41	--	--	16	--	--	--	--
45	Cu <sub>1</sub> Sn <sub>1</sub>			4	9	--	--	87	--	--	--	--
46	Cu <sub>20</sub> Sn <sub>1</sub>			5	78	--	--	25	--	--	--	--

## 6.5. Composite engineering approach

The strategy of engineering is an approach when designing electrocatalysts for e-CO<sub>2</sub>R providing adaptable solutions to improve catalytic performance. This approach involves integrating materials or phases with functionalities into one catalyst system. By selecting and



combining these components researchers can optimize the activity, selectivity and stability of catalysis effectively addressing the challenges associated with CO<sub>2</sub>R. The significance of composite engineering lies in its ability to harness the strengths of various materials to create synergistic effects. For instance, a composite catalyst may include supports, active catalytic sites and promoters to enhance CO<sub>2</sub> adsorption, electron transfer and intermediate binding. This tailored approach enables adjustment of catalyst properties to meet requirements, for reducing CO<sub>2</sub>R. Different methods such as co precipitation, sol gel synthesis and chemical vapor deposition can be employed to produce composite catalysts with controlled structures. Overall composite engineering plays a role in advancing electrocatalysis by providing pathways for developing sustainable technologies for converting CO<sub>2</sub> that are essential, in combating climate change and transitioning towards a greener energy future.

The research group of Cao and co have utilized microporous nitrogen-rich MOFs known as Cu-BTT to serve as precursors for the synthesis of Fe-Cu-BTT. Through a meticulously controlled pyrolysis process, this endeavor yielded Fe<sub>x</sub>Cu-N-C compounds specialized by a diverse array of Fe-N<sub>x</sub> sites. The introduction of Fe induced notable structural alterations, including an increase in the BET surface area and total pore volume, a reduction in Cu nanoparticle density, and an augmentation of Fe-N<sub>x</sub> sites within the carbon matrix. This structural evolution resulted in an enhanced CO generation, with Fe<sub>0.07</sub>Cu-N-C800 exhibiting the highest CO<sub>2</sub> transfer efficiency at 48.5% [134]. In the context of e-CO<sub>2</sub>RR conducted in neutral aqueous solutions, a novel organic-inorganic composite was crafted by Li *et al.* via a hydrothermal synthesis method. Remarkably, this composite demonstrated sustained performance without degradation even after 24 hours of continuous e-CO<sub>2</sub>R. It comprised a 3D g-C<sub>3</sub>N<sub>4</sub> nanosheet-CNT interconnected framework adorned with a polymeric CoPc layer. This reported innovative method have offered several advantages, including an increased electrochemically active surface area with numerous active sites, improved homogenous immobilization at high catalyst loading, and reinforced contacts between the molecular catalyst and the conductive support [135]. Furthermore, CoPc-based and O-linked MOFs were predicted to exhibit reduced activation energies in the synthesis of the carboxyl intermediate, as evidenced by density functional theory calculations. This reduction in activation energy translated into improved catalytic activity and selectivity. These findings underscored the potential for fine-tuning MOFs' activity and selectivity in catalysis through the meticulous design and selection of functional ligands, offering a significant degree of modular tunability. Notably, for the e-CO<sub>2</sub>R to CO using reticular framework materials, it was demonstrated that



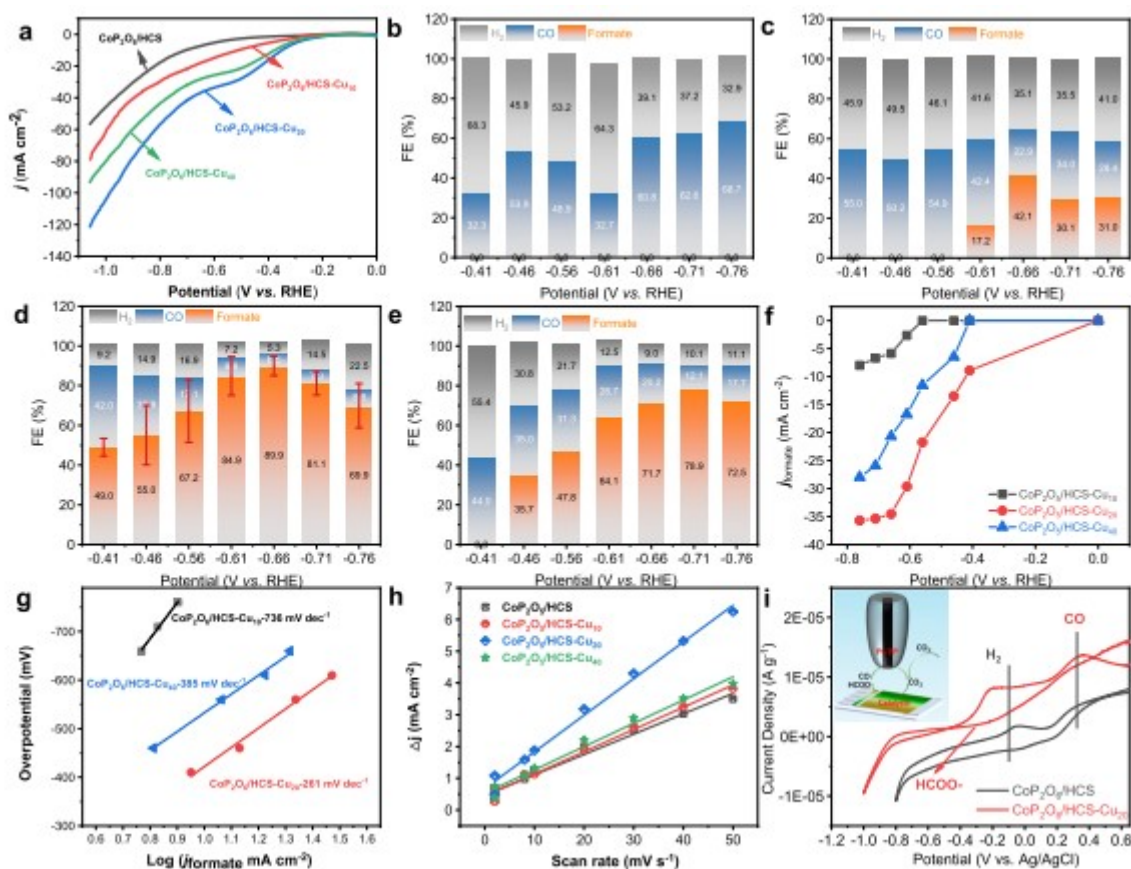
these materials served as exceptional cathode materials, boasting high current density and excellent selectivity toward the CO product at a relatively low overpotential of 0.63 V [136].

To optimize support connections and catalytic efficiency, He *et al.* have developed the dimer catalyst, a minimal bimetallic catalyst structure. This innovation opened up the possibility of breaking scaling relationships by expanding the parameter space for optimizing attributes while retaining non-monotonic property correlations. The dimers, formed from Group 10 (Ni, Pd, Pt) and Group 11 (Cu, Ag, Au) elements, were supported at single vacancy sites of graphene. These dimers featured an anchoring atom that transferred a large number of electrons to the graphene and an antenna atom that was much less positively charged and protruded from the graphene surface. All clusters exhibited strong binding energies to the defective graphene, indicating their stability. Notably, the stability of the alloy dimers, such as Cu<sub>2</sub>, Ag<sub>2</sub>, and Au<sub>2</sub>, was significantly improved compared to their monometallic forms. These dimers were selected for further investigation as potential candidates for the e-CO<sub>2</sub>R to CH<sub>4</sub> using a first-principles approach and the computational hydrogen electrode model. Among the options studied, Pt<sub>2</sub>, AgNi, Pd<sub>2</sub>, and AgPt showed the lowest overpotential values when compared to standard Cu electrodes. While the oxygen binding strength of the catalytic dimer provided a semi-quantitative description of the reactivity of the supported dimers, the free energies of OCHO\* and OH\* correlated well with O\*, whereas the free energies of CHO\* and HCOOH\* exhibited significant variations in their reactivity [137].

Further, for the e-CO<sub>2</sub>R to carbon, an inexpensive and robust Cu-based hybrid catalyst was created. The catalyst, a polymer of Cu phthalocyanine coated on carbon nanotubes, showed 80% faradaic yield for CO synthesis at low overpotentials and was selective for CO production. Since Cu phthalocyanine polymerization was selective for proton reduction under the same conditions, this resulted in a marked increase in reaction selectivity. Although the material initially displayed isolated Cu sites in phthalocyanine-like CuN<sub>4</sub> coordination, the Cu atoms were transformed to Cu nanoparticles under operational conditions [138]. In addition, the research findings showed that CoP<sub>2</sub>O<sub>6</sub> played a crucial role in enhancing the efficiency of the Cu/C catalyst for formate production through e-CO<sub>2</sub>R (Figure 12). Utilizing ZIF-67 as the carbon precursor, the resulting CoP<sub>2</sub>O<sub>6</sub>/HCS-Cu catalyst not only increased current density but also reduced overpotential. Importantly, the catalyst's efficiency in e-CO<sub>2</sub>R was found to be modulated by the Cu/Co ratio. Impressively, this catalyst exhibited the most negative overpotential (-0.4 mV) and achieved the highest current density (34.5 mA cm<sup>-2</sup>) for formate



production during e-CO<sub>2</sub>R. Furthermore, at -0.66 V vs. RHE, formate was generated with an exceptional FE of 89.9% [139].



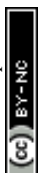
**Figure 12:** The LSV curves were generated through experiments conducted in a CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> electrolyte using a scan rate of 10 mV s<sup>-1</sup> (a). The formate, CO, and H<sub>2</sub> FEs were determined at a specific potential for the CoP<sub>2</sub>O<sub>6</sub>/HCS and CoP<sub>2</sub>O<sub>6</sub>/HCS-Cu catalysts (b-e). The current density (f), Tafel slopes (g), and electrochemically active surface area were determined for the CoP<sub>2</sub>O<sub>6</sub>/HCS and CoP<sub>2</sub>O<sub>6</sub>/HCS-Cu catalysts. The detection of products resulting from e-CO<sub>2</sub>R on the CoP<sub>2</sub>O<sub>6</sub>/HCS and CoP<sub>2</sub>O<sub>6</sub>/HCS-Cu20 catalysts was carried out in situ. This was achieved by utilizing a Pt UME tip CV response, with a scan rate of 10 mV s<sup>-1</sup>, at substrate potentials of -1.1 vs Ag/AgCl. The electrolyte employed was a 0.5 M solution of KHCO<sub>3</sub> that was saturated with CO<sub>2</sub> under atmospheric pressure. The experiments were carried out at a temperature of 293 K. Reproduced with permission from Ref. [139] Copyright 2023, American Chemical Society.

In a separate study, solvothermal processing was employed to vulcanize copper hydroxide nanowire arrays (S-CNWs) with a specific amount of cuprous sulfide. These S-CNWs were subsequently investigated for their e-CO<sub>2</sub>R under neutral conditions. The research revealed a



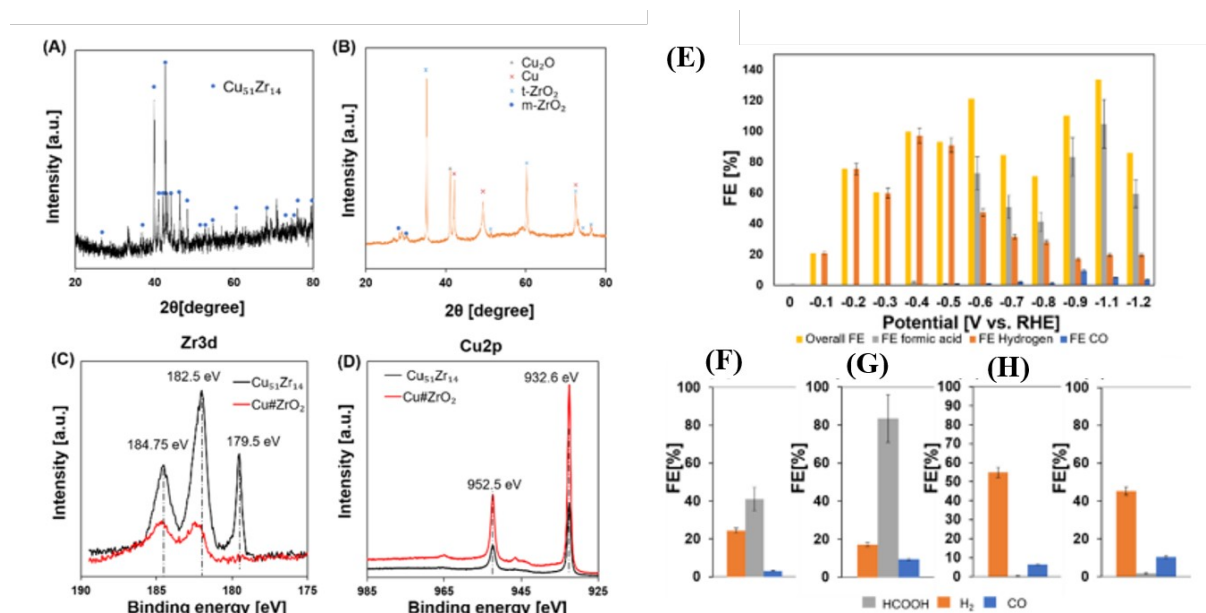
strong correlation between the degree of vulcanization of the catalyst and formate selectivity. When vulcanized to an optimal extent, the FE could exceed 60%, with almost no generation of additional e-CO<sub>2</sub>RR products. Further, the introduction of a small quantity of sulfur was found to facilitate the formation of formate by lowering the energy barrier associated with generating the OCHO intermediate [140]. In a related endeavor, hydrothermal processing followed by pyrolysis was employed to synthesize various Cu-Ni alloys tailored for e-CO<sub>2</sub>R. Within the 0.5 M KHCO<sub>3</sub> electrolyte, the optimized CuNi/NCNT catalyst exhibited a remarkable FE<sub>CO</sub> of 94.8% for CO<sub>2</sub>R and a substantial current density of 26.6 mA cm<sup>-2</sup>. The addition of nickel to copper facilitated the formation of a crucial intermediate, COOH\*, which played a pivotal role in boosting e-CO<sub>2</sub>RR activity. Promisingly, the current density further increased to 124.6 mA cm<sup>-2</sup> with an FE<sub>CO</sub> of 92.8% at 1.1 V versus RHE [141].

Additionally, the Daiyan *et al.* created metal-carbon composites with dual active sites to produce H<sub>2</sub> and CO during e-CO<sub>2</sub>RR. Co@CoNC-900 composites exhibited a wide potential window within which they could produce a tunable syngas ratio of 1:1. By adjusting the HER active sites, this syngas ratio could be shifted from 1:1 to 3:2, unlocking new possibilities for the production of a diverse range of fuels and chemicals using the well-established FT process in the industry [142]. In a separate research effort, the impact of Nafion/solvent formulation on CO<sub>2</sub> electrolysis employing a CuO as a model catalyst was examined. The composition of Nafion/solvent exerted a significant influence on the activity, selectivity, and stability of e-CO<sub>2</sub>RR. The effects of Nafion/solvent formulation on CO<sub>2</sub> electrolysis were attributed to three primary factors: the evolution of catalyst structure, alteration of the local microenvironment, and accumulation of surface adsorbates. Nafion played a stabilizing role in preserving product distributions by preventing morphological rearrangement and delamination of weakly bound catalysts. The surface coverage of CO and local concentrations of CO<sub>2</sub> and H<sub>2</sub>O in the reaction microenvironment were influenced by adjusting the thickness of Nafion coatings and the connectivity of their inner networks via modifications to the catalyst ink formulations [143]. Furthermore, researchers produced catalysts derived from CuO for e-CO<sub>2</sub>RR, which exhibited resistance to a single thermal treatment but could be removed in two steps. g-C<sub>3</sub>N<sub>4</sub>-supported CuO catalysts favored the production of CH<sub>4</sub>, whereas CuO displayed the highest selectivity toward C<sub>2</sub>H<sub>4</sub>. Various factors, including particle growth, the ensemble effect due to varying catalyst loading densities, and hybridization and stabilization of the catalyst-support relationship, contributed to this disparity. Scientists aimed to design catalyst systems that



would result in a more tightly regulated product distribution of hydrocarbons over  $H_2$  or  $CO$  by carefully controlling experimental conditions [144].

Another research reports metal precursor underwent reaction with the nitrogen-doped carbon support to generate (sub)nanosized metal oxide clusters in ex situ conditions. The study encompassed a variety of M/NC catalysts. The results indicated that the catalytic activity increased in CO formation with respect to the transition metal family. Co/NC exhibited the highest activity at 0.5 V vs. RHE, while Ni/NC demonstrated good activity and selectivity. Fe/NC, Co/NC, and Ni/NC outperformed other metal hydroxides due to phase contraction and  $HCO_3^-$  insertion into the layered structure of metal hydroxides [145]. Furthermore, nanophase-separated  $Cu\#ZrO_2$  was successfully produced through the internal oxidation of the  $Cu_{51}Zr_{14}$  precursor composite alloy (Figure 13). The material featured nanoscale lamellae of Cu metal and tetragonal  $ZrO_2$ , creating a stable Cu- $ZrO_2$  interface. Its uniformly dispersed catalytic sites and abundant metal-oxide interface contributed to increased selectivity for  $e-CO_2RR$  to-FA conversion.  $CO_2$  adsorption led to protonation over the nearby Cu sites, generating FA through the formation of  $O(CH)O$  [146].



**Figure 13:** The p-XRD patterns of the  $Cu_{51}Zr_{14}$  composite alloy (A) and  $Cu\#ZrO_2$  (B) were analyzed. The HAXPES profiles of the  $Cu_{51}Zr_{14}$  precursor alloy (black) and  $Cu\#ZrO_2$  (red) were analyzed in the Zr 3d region (C) and the Cu 2p region (D). The product distribution of  $e-CO_2RR$  over  $Cu\#ZrO_2$  was quantified after 3 hours of electrolysis at a potential of -0.9 V vs RHE. The  $e-CO_2RR$  performance was evaluated for different catalysts, including a mixture of



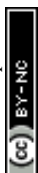


*Cu and YSZ (B), Cu#ZrO<sub>2</sub> (F), commercial Cu (G), and Cu<sub>2</sub>O (H). Reproduced from Ref. [146] Open access article, American Chemical Society.*

Furthermore, another research explored the use of a triphenylene-cored porous structure as a means to modify the performance of Cu atomic catalysts in e-CO<sub>2</sub>RR. The triangular pores within this structure served as anchoring sites for Cu atoms, forming complexes that facilitated the hydrogenation of CO<sub>2</sub>, a rate-limiting step in e-CO<sub>2</sub>RR. Functionalization of these structures with oxygen and nitrogen resulted in reduced overpotentials for e-CO<sub>2</sub>RR on Cu@TPGDY, which decreased from 0.26 V to 0.16 V and 0.08 V, respectively [147]. In another facet of e-CO<sub>2</sub>RR research, scientists devised a novel catalyst model using a Cu nanosheet coated with a thin layer of carbon. This carbon coating acted as a barrier, inhibiting surface reconstruction at high reducing potentials and preventing the surface oxidation of metallic Cu. Operating at 1.0 V and a current density of 20.3 mA cm<sup>-2</sup>, the C/Cu/C nanosheet exhibited remarkable stability and a high FE of 47.8% for the production of CH<sub>4</sub>. The carbon layers not only enhanced the catalyst's electrical conductivity but also facilitated streamlined electron transport [148]. Furthermore, another research showcased the synthesis and application of ultrasmall Cu nanocrystals uniformly distributed in nitrogen-doped carbon as catalysts for e-CO<sub>2</sub>RR to produce ethanol and formate. These compounds' selective production necessitated specific potentials. At a low potential, the FE for ethanol reached 43.7%, while that for formate was 63.5%. The electronic environment of Cu was influenced by the nitrogen-doped carbon, facilitating proton-electron transport [149]. The overview of composite engineering strategy utilized to create a number of electrocatalysts for e-CO<sub>2</sub>RR to different sustainable products is given in Table 5.

**Table 5:** Composite engineering is a technique used to create catalysts, for CO<sub>2</sub>R. The table presents an analysis of electrocatalyst materials specifically designed for this process. It thoroughly examines the properties of these materials and investigates how metal doping affects the distribution of products under different reaction conditions.

N	Material	electrolyte	V vs RHE	≈ FE %								
				H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub>
1	Cu-N-C800		-1.2	58	11	--	--	22	--	--	--	--
2	Fe <sub>0.01</sub> Cu-N-C800	0.1 M KHCO <sub>3</sub>	Ag/A gCl	49	27	--	--	20	--	--	--	--
3	Fe <sub>0.07</sub> Cu-N-C800			44	48	--	--	4	--	--	--	--
4	Fe <sub>0.13</sub> Cu-N-C800			41	46	--	--	5	--	--	--	--
5	CoPPc@g-C <sub>3</sub> N <sub>4</sub> -CNTs			0.5 M KHCO <sub>3</sub>	-0.55	35	43	--	--	--	--	--
6	CoPc-Cu-NH	KHCO <sub>3</sub>	-0.95	41	59	--	--	--	--	--	--	



7	CoPc-Cu-O			42	59	--	--	--	--	--	--	--	View Article Online DOI: 10.1039/D4MA00321G	[136
8	NiPc-Cu-NH			62	37	--	--	--	--	--	--	--	--	]
9	NiPc-Cu-O			50	48	--	--	--	--	--	--	--	--	]
10	CuPolyPc@CNT	0.1m CsHCO <sub>3</sub>	-1.1	42	53	--	--	--	--	--	--	--	--	[138
11	CoP <sub>2</sub> O <sub>6</sub> /HCS			68	32	--	--	--	--	--	--	--	--	]
12	CoP <sub>2</sub> O <sub>6</sub> /HCS-Cu10	0.5 M KHCO <sub>3</sub>	-0.76	41	28	--	--	31	--	--	--	--	--	[139
13	CoP <sub>2</sub> O <sub>6</sub> /HCS-Cu20			25	9	--	--	70	--	--	--	--	--	]
14	CoP <sub>2</sub> O <sub>6</sub> /HCS-Cu40			11	18	--	--	73	--	--	--	--	--	]
15	CF			62	1	--	--	3	--	--	--	2	--	[140
16	CNWs	KHCO <sub>3</sub>	-1.1	62		--	1	22	--	--	--	3	--	]
17	S-CNWs-2			23	1	--	--	60	--	--	--	--	--	]
18	Cu <sub>2.4</sub> Ni/NCNT			8	92	--	--	--	--	--	--	--	--	]
19	CuNi/NCNT			5	95	--	--	--	--	--	--	--	--	]
20	Cu <sub>0.36</sub> Ni/ NCNT	0.5 M KHCO <sub>3</sub>	-0.9 V	25	75	--	--	--	--	--	--	--	--	[141
21	Cu/NCNT			16	84	--	--	--	--	--	--	--	--	]
22	Ni/NCNT			16	84	--	--	--	--	--	--	--	--	]
23	NCNT			6	92	--	--	--	--	--	--	--	--	]
24	Co-N-C			76	19	--	--	--	--	--	--	--	--	]
25	Co@ CoNC-800	0.1 M KHCO <sub>3</sub>	-0.8	61	38	--	--	--	--	--	--	--	--	[142
26	Co@ CoNC-900			48	43	--	--	--	--	--	--	--	--	]
27	Co@ CoNC-1000			38	59	--	--	--	--	--	--	--	--	]
28	CuO/ Nafion/solvent formulations (0.5:75 Vol.)	0.1 M K <sub>2</sub> SO <sub>4</sub>	-50 mA cm <sup>-2</sup>	28	10	1	39	7	--	--	--	6	--	[143
29	g-C <sub>3</sub> N <sub>4</sub>			92	--	--	--	--	--	--	--	--	--	]
30	as-syn CuO			65	4	6	11	--	--	--	--	--	--	[144
31	as-syn CuO/C <sub>3</sub> N <sub>4</sub>		-1.2	78	4	6	2	--	--	--	--	--	--	]
32	as-syn Cu/C <sub>3</sub> N			77	5	11	2	--	--	--	--	--	--	]
33	Mn/N-C			82	18	--	--	--	--	--	--	--	--	]
34	Fe/N-C			79	19	--	--	--	--	--	--	--	--	]
35	Co/N-C	20		70	25	--	--	--	--	--	--	--	--	[145
36	Ni/N-C	1 M KHCO <sub>3</sub>	mA	90	10	--	--	--	--	--	--	--	--	]
37	Cu/N-C		cm <sup>-2</sup>	79	26	--	--	--	--	--	--	--	--	]
38	Zn/N-C			71	19	--	--	--	--	--	--	--	--	]
39	Cu + YSZ			21	2	--	--	42	--	--	--	--	--	]
40	Cu#ZrO <sub>2</sub>		-0.9	19	8	--	--	82	--	--	--	--	--	[146
41	Commercial Cu	0.1 M KHCO <sub>3</sub>	Ag/A	55	5	--	--	--	--	--	--	--	--	]
42	Cu <sub>2</sub> O		gCl	43	1	--	--	8	--	--	--	--	--	]
43	CuNCs@p-Cu/g-Cu	0.1 M KHCO <sub>3</sub>	-1.15	45	1	9	41	5	--	--	--	--	--	[147
44	Cu nanosheet	0.5 M KHCO <sub>3</sub>	-1.0	--	--	27	24	--	--	--	--	--	--	[148
45	C/Cu/C nanosheet			--	--	48	10	--	--	--	--	--	--	]
46	Cu/NC-NSs	KOH	-0.37	--	--	--	--	3	--	--	--	45	--	[149

## 6.6. Surface engineering approach

Surface engineering is a multifaceted strategy employed in the design of electrocatalysts for e-CO<sub>2</sub>R. Its importance stems from the critical role of catalyst surfaces in dictating reaction



pathways and kinetics during electrochemical CO<sub>2</sub> conversion. Surface engineering encompasses various techniques aimed at tailoring the catalyst's surface properties to enhance its activity, selectivity, and stability. Among these techniques, surface anchoring, Molecular surface functionalization, interfacial engineering and speciation of Cu surface involves the precise attachment of catalytic sites, often metal nanoparticles, onto a support material.

### 6.6.1 Surface anchoring

The strategy of anchoring the surface plays a role, in designing electrocatalysts for CO<sub>2</sub>R. It has implications for improving the performance and selectivity of these catalysts. The main idea behind this approach is to attach sites, such as metal nanoparticles or single atoms to support materials like graphene or metal oxides. This prevents their detachment during the process. Enhances the stability of the catalysts, which is essential for long term and efficient CO<sub>2</sub>R. Various techniques, such as chemical binding, physical adsorption or covalent bonding are used to achieve surface anchoring. By controlling the strength and density of anchoring researchers can customize the behavior of catalysts for CO<sub>2</sub>R reduction reactions. Surface anchoring not enhances activity but also addresses challenges, in sustainable energy conversion. It leads to efficiencies by preventing aggregation or dissolution of active sites during reactions. This ensures that target fuels or chemicals are produced with by products. Furthermore, surface anchoring offers the advantage of using affordable materials as catalysts. This is because the support provides stability to sites that may be less stable, on their own. Another benefit is that it allows for the integration of sites, onto a single support, which encourages cooperative catalysis and enhances reaction kinetics.

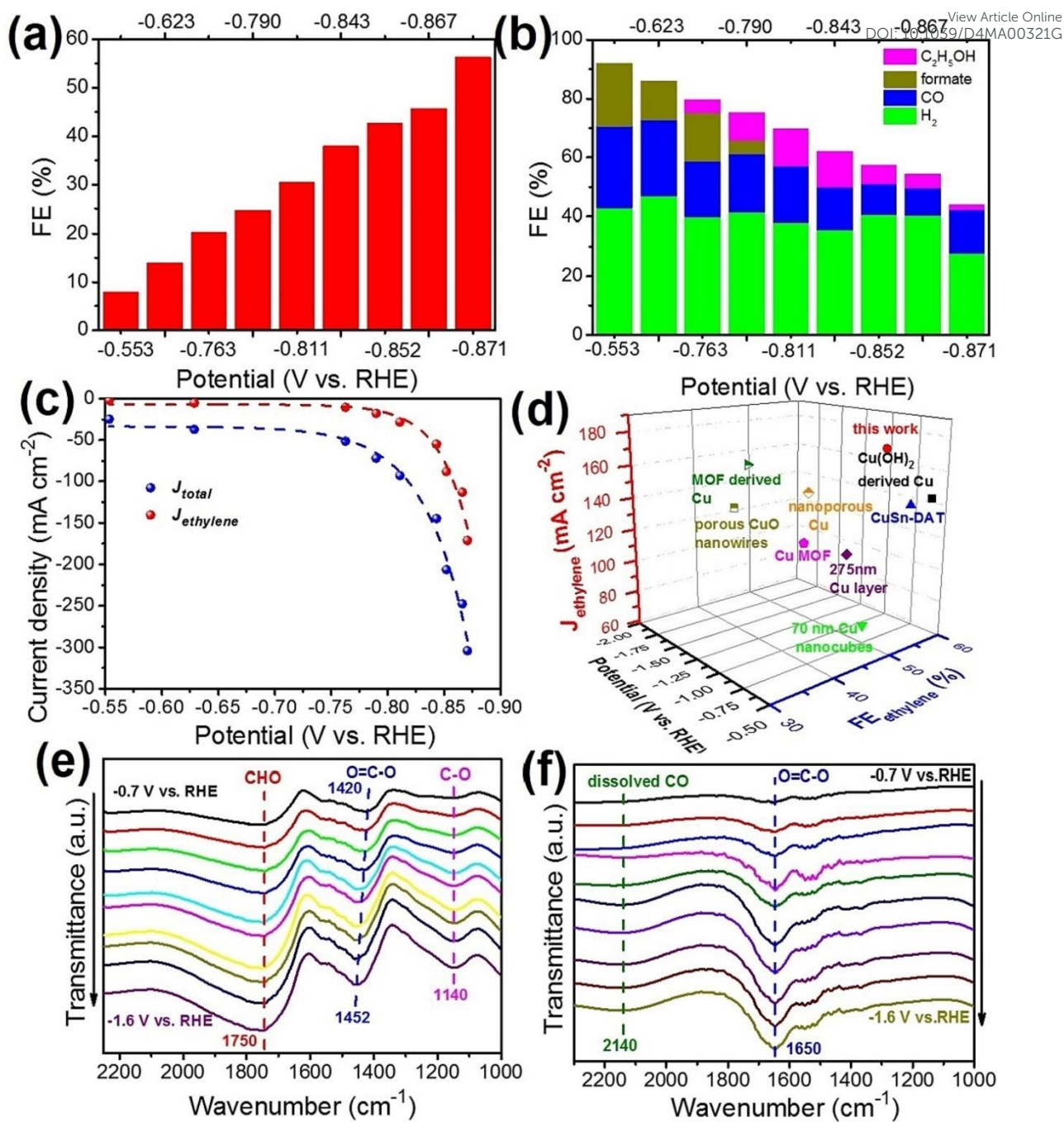
A comparison of CO<sub>2</sub>RR performance between blank Cu, Cu modified with PPT (Cu-PPT), and Cu modified with QAPPT (Cu-QAPPT) revealed that attaching Pip<sup>+</sup> cations onto the Cu electrode reduced competing HER and enhanced CO<sub>2</sub>RR selectivity. This enhancement was attributed to reduced interfacial water concentration, an increase in "ice-like" water, and the presence of \*CO<sub>atop</sub>, \*CO<sub>bridge</sub>, and CO-CO dimer species at the Cu/QAPPT interface [150]. Additionally, Ye *et al.* successfully engineered a bi-phasic p-Cu@Cu<sub>2</sub>O nanosphere, comprising a Cu nanocrystal core and a Cu<sub>2</sub>O nanoprism shell. These nanospheres exhibited exceptional e-CO<sub>2</sub>R, with a maximum  $FE_{C_2H_4}$  of 79% at -1.18 V vs RHE. Phase engineering facilitated synergistic control of CO<sub>2</sub> reactant and \*CO intermediate adsorption behaviors, resulting in improved CO-CO coupling and increased production of C<sub>2+</sub> products. During e-CO<sub>2</sub>R, CO<sub>2</sub> molecules were absorbed by the faceted Cu<sub>2</sub>O shell, where they underwent reduction to \*CO intermediates capable of escaping [151].



In another study, Cu dendrites were coated with PTFE at varying concentrations to create a hydrophobic structure with a stable WCC wetting state. This hydrophobic coating enabled the catalyst surface to efficiently take in gas, increasing the number of triphase contacts for gas diffusion. Consequently, the reaction of  $^*CO$  was enhanced, with an increase in  $CO_2$  and intermediate  $^*CO$  on the catalyst surface. Hydrophobic Cu dendrites exhibited a twofold increase in the intrinsic electrochemical activity of their active sites compared to untreated Cu dendrites, leading to more efficient conversion of  $CO_2$  into liquid fuel products such as  $CH_3OH$  and  $C_2H_5OH$  [152]. Xie *et al.* also unveiled that increased activity and selectivity for  $C_2H_4$  generation were achieved by creating C-Cu nanosheets through the in-situ reduction of C-CuO nanosheets during e- $CO_2RR$  (Figure 14). In a gas diffusion flow cell,  $FE_{C_2H_4}$  reached 56.2%, and its partial current density reached  $171.0 \text{ mA cm}^{-2}$ . Both electrochemical measurements and XAS spectra confirmed the presence of uncoordinated edge sites in the nanosheets. C-Cu nanosheets displayed exceptional activity and selectivity for e- $CO_2RR$  with  $C_2H_4$ . They disclosed that Cu atoms with a coordination number of around 5 played a crucial role in assisting the development of a  $^*CHO$  intermediate, thereby enhancing the coupling reaction of  $^*CO$  and  $^*CHO$  intermediates [153].

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**Figure 14:** Gas diffusion flow cell with 1.0 M KOH electrolyte with FEs of  $C_2H_4$  (a) and  $H_2$  (b) CO,  $C_6H_5OH$ , and formate on C-Cu nanosheets. In a gas diffusion flow cell with an Ar-saturated 1.0 M KOH electrolyte, the corresponding total and ethylene currents ( $J_{total}$  and  $J_{ethylene}$ ) are measured at varying potentials and the differences between them are  $iR$  compensated (c). When utilizing a gas diffusion flow cell and an electrolyte of 1.0 M KOH, a summary of the performance of Cu-based electrocatalysts for the formation of  $C_2H_4$  is provided (d). ATR-FTIR spectra of (e) C-Cu nanosheets (e) and Cu powder (f) taken in situ during e-



*CO<sub>2</sub>RR at varying potentials in a CO<sub>2</sub>-saturated 0.1 M KHCO<sub>3</sub> electrolyte. Reproduced with permission from Ref. [153] Copyright 2023, Elsevier.*

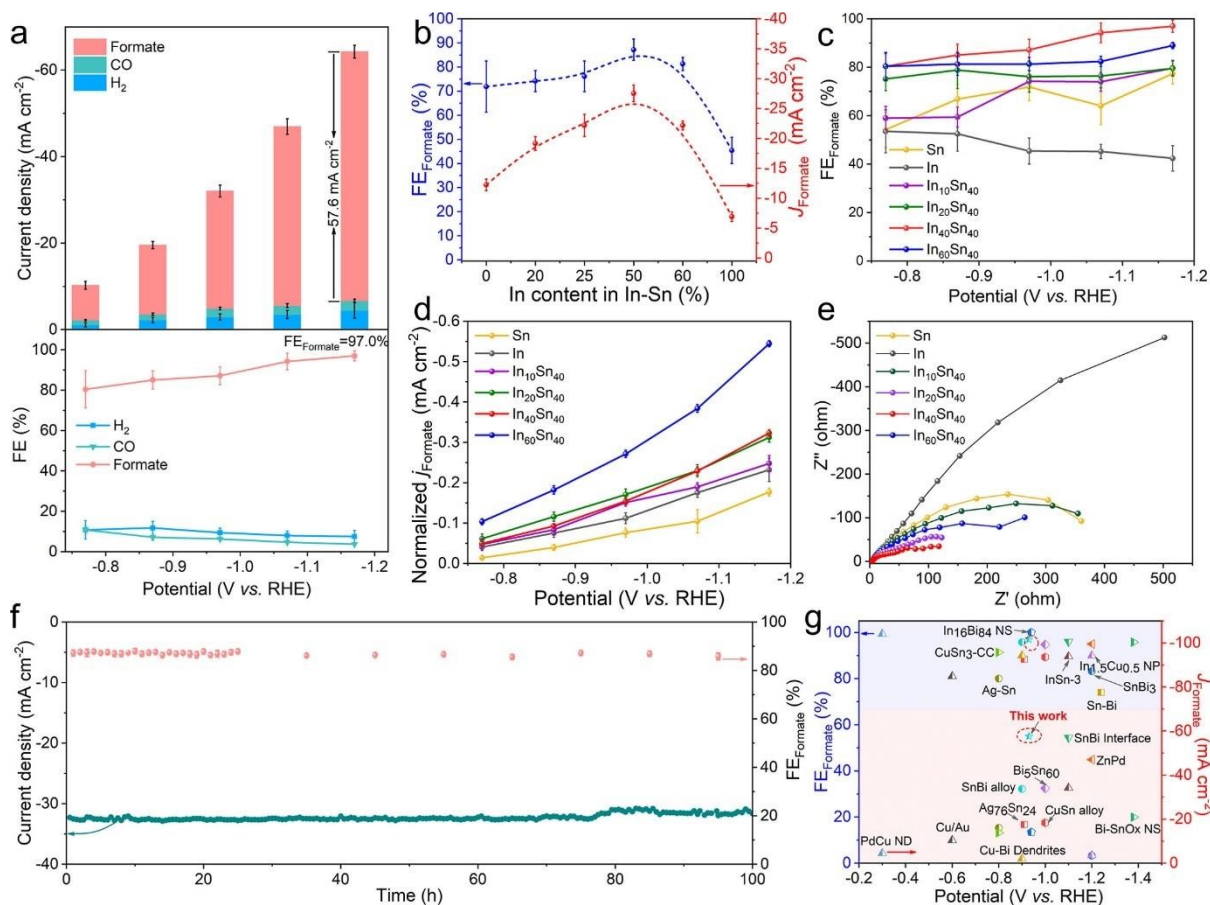
In a separate development, researchers devised a method to modify Cu<sub>2</sub>O nanocubes to encapsulate carbon dioxide and reduce its concentration. This molecular-scale wrapping was made possible by the CuAAC layer development, transitioning from surface-confined to random as a function of temperature. As a result of this modification, the increased hydrophobicity of the nanocubes dampened hydrogen evolution, making self-controlled modification the optimal condition for CO<sub>2</sub> reduction electrocatalysis [154]. In a different study, Cu nanocubes had been synthesized with rGO modifications through a straightforward electrochemical method. This modification had shifted the post-C-C coupling selectivity from ethylene to ethanol, enhancing local CO concentration on Cu sites. The tandem electrocatalysis approach had led to reduced formate synthesis, increased selectivity, and intrinsic activity towards C<sub>2+</sub> products during e-CO<sub>2</sub>R. Notably, at 0.9 V, the Cu NCbs rGO-60 catalyst had exhibited the highest C-C bond coupling efficiency, favoring ethanol with a 76.84% FE. NCbs rGO-120 and NCbs rGO-60 catalysts had achieved selectivity ratios of approximately 107 and 85.34 for C<sub>2+</sub> oxygenates/C<sub>2+</sub> hydrocarbon (ethylene) products, respectively [155].

In an overarching overview, the utilization of organic chemicals to modify the Cu surface for e-CO<sub>2</sub> conversion had been explored. Catalytic activity had been found to be heavily influenced by the local microenvironment of the electrode surface, encompassing factors like hydrophobicity, electric field, pH, and intermediate coverage. The tunability and designability of organic compounds had offered numerous avenues for enhancing the catalytic activity of Cu-based catalysts. However, challenges remained, such as improving the conductivity and stability of organic compounds. The enhancement of catalytic activity for organic/inorganic hybrid catalysts would benefit from the design and synthesis of well-defined organic molecules or polymers with excellent conductivity and durability. Machine learning with artificial intelligence had the potential to expedite catalyst manufacturing by anticipating crucial reaction parameters, ultimately leading to Cu-based catalysts with high activity, selectivity, and stability for CO<sub>2</sub>RR [156]. In the meantime, the discussion also underscored the need to move beyond single-crystal studies and design Cu nanocrystals (NCs) in order to better understand the structural dependence of CO<sub>2</sub>RR. The view of NCs is a necessary tool, elucidating the reaction pathway and identifying size-dependent selectivity trends for C<sub>2</sub> products. Most studies have focused on shapes exposing high-index facets. Therefore, it is extremely important to enrich the family of Cu NC shapes. The steps for rebuilding the catalyst, primarily driven by a



dissolution-redeposition cycle, can be better understood by using NCs to identify the transient species involved [157].

In another study, rough-edged Ag NPs/CuO MNSs were synthesized on a Cu foil for e-CO<sub>2</sub>R to CO synthesis. The heterostructure exhibited high electrical conductivity, abundant active sites, and a superior electronic structure, leading to enhanced CO<sub>2</sub> adsorption and activation. The critical COOH intermediate in the pathway from e-CO<sub>2</sub>R to CO was stabilized at the Ag-CuO contact. The best Ag1.01%/CuO catalyst achieved a maximum FE<sub>CO</sub> of 91.2% at a partial current density of 10.5 mA cm<sup>-2</sup> and 0.7 V in 0.1 M KHCO<sub>3</sub>. The catalyst demonstrated good catalytic stability, maintaining a FE<sub>CO</sub> of over 80% in the potential region [158]. Additionally, a novel bimetallic InSn catalyst was developed using a potential-driven volume diffusion approach at room temperature (Figure 15). This catalyst effectively increased current density by selectively reducing CO<sub>2</sub> to formate. The catalyst featured an InSn hybrid core, nanoshell structures with multiple interfaces, a multicomponent core-shell heterostructure, and a novel configuration that potentially accelerated CO<sub>2</sub> and HCO<sub>3</sub> equilibrium on the InSn interface [159].



**Figure 15:** *CO<sub>2</sub>RR effectiveness. Formation of CO, H<sub>2</sub>, and format) on In<sub>40</sub>Sn<sub>40</sub> at different applied potentials current densities (top) and FE (a). Formate production FE values and partial current densities for In, Sn, and InSn catalysts vs various In concentrations at 0.97 V vs RHE (b). Each catalyst's FE<sub>formate</sub> at varying potentials (c). Partial current densities of each catalyst, expressed in a formate (d). EIS plots of all the produced samples were analyzed (e). Electrolysis of In<sub>40</sub>Sn<sub>40</sub> for 100 hours at 0.97 V vs RHE (f). Formate current density and FE<sub>formate</sub> with 90% iR-correction are examples of how this work compares to cutting-edge bimetallic electrocatalysts (g). Standard deviations from at least three separate measurements of the sample are used to create the error bars. Reproduced with permission from Ref. [159] Copyright 2023, American Chemical Society.*

In addition, the effectiveness of GDEs loaded with copper nanocubes for e-CO<sub>2</sub>R in a zero-gap, MEA-type electrolyzer was investigated. These GDEs produced ethylene ( $j_{C_2H_4}$  up to about 80 mA cm<sup>-2</sup>) and propylene, a valuable industrial product, at higher rates compared to nanocube and sputtered Cu catalysts. Although flooding occurred in nanocube GDEs at current densities exceeding 150 mA cm<sup>-2</sup>, they maintained high ethylene production rates even during flooded operation. Researchers are currently focusing on optimizing mass loading and developing mitigation methods to prevent the loss of ethylene selectivity in Cu nanocube-loaded electrodes due to flooding [160]. In a separate study, electrocatalytic TDPA-capped CuAg NCs were synthesized using a novel approach that involved investigating near-stoichiometric ligand-to-copper (P/Cu) ratios and utilizing Cu(II) acetate monohydrate. Depending on the diameter of the Cu NC precursor, one or two galvanic replacement steps were employed to form sub-10 nm Cu@Ag core-shells and Cu/Ag nanodimers, as confirmed through HRTEM and spectroscopy. The relationship between composition and selectivity was explored in the range of 14 to 41% Ag by spreading the nanocrystals on carbon black at high packing densities. The CO<sub>2</sub>RR selectivity transitioned from ethylene to ethanol production between CuNCs/C and CuAg/C-based electrodes, resulting in a 2-to-3-fold increase in the oxygenate-to-hydrocarbon ratio at moderate Ag atom %age levels. Cu/Ag<sub>0.14</sub>/C nanodimers and Cu@Ag<sub>0.17</sub>/C core-shells achieved a total C<sub>2</sub> & C<sub>3</sub> selectivity of 50% at neutral bulk pH and 0.1 A cm<sup>-2</sup>, suggesting a substantial impact from local CO concentration and CO-spillover on catalytic patterns at high CO<sub>2</sub>RR rates [161].

Moreover, another research endeavor proposed that the e-CO<sub>2</sub>R to ethylene can be significantly improved by utilizing an ionic liquid (IL) in combination with a Cu electrocatalyst. The IL was





demonstrated to alter the electronic structure of the Cu catalyst, facilitating \*CO dimerization and enhancing ethylene generation. This method achieved a remarkably high 77.3%  $FE_{\text{ethylene}}$  in a water-based electrolyte and a standard H-type cell [162]. Additionally, researchers have coated a layer of PTFE that conforms itself to a Cu nanoneedle (NN). By increasing the amount of PTFE at the end of a nanoneedles, the electric and thermal field strength rapidly varies. This in turn accelerates the C-C coupling of  $C_2$  and CO intermediates production. This method also enabled  $C_2$  generation at a TOF of  $11.5 \pm 0.3 \text{ s}^{-1} \text{ Cu\_site}^{-1}$  and a  $FE_{C_2}$  of  $85.4 \pm 1.5\%$  under partial currents exceeding  $250 \text{ mAcm}^{-2}$  [163]. The effect of plasma pretreatment of the Cu surface on the overall surface was unusual. This, in turn, caused huge differences in the way the  $CO_2RR$  products distributed. The observed differences in  $CO_2RR$  activity seen across the series are related to changes in the electrochemically active surface area. The roughened surface has a stronger inclination to CO formed through e- $CO_2R$  than does the electrochemically polished surface. This phenomenon implies that as the size of the surface increases, the percentage of the adsorbed H to CO showed a decreasing trend. Also, as surface roughness increased, the fractions of products containing two or more carbons design. The ratio of current densities for  $C_{2+}$  to  $C_1$  products displayed an increasing trend with increasing surface roughness, mainly due to the production of  $CH_4$  increasing on substrates with roughness levels above 3 [164].

Meanwhile, during the course of e- $CO_2R$ , the selectivity to  $C_2H_4$  was greatly improved through the formation of Cu nanoparticle substructure from spheres to cubes. The development was initiated by a weak adhesion of Cu NPs to graphene oxide substrate. However, with time these Cu nanocubes turned into smaller, less organized nanoparticles, thus reducing the tendency to select for  $C_2H_4$ . To meet this challenge, an innovative approach appeared in which 2D-or "flat"-graphene with nitrogen doping served as an anchoring framework for Cu nanocubes. This relied on the strong interactions between Cu NPs and the pyridinic nitrogen atoms that covered the surface of 2D graphene [165]. Simultaneously,  $Cu_2O$  nanostructures with precisely controlled crystal facets were synthesized through a hydrothermal methodology. The catalytic ability and alcohol selectivity of these catalysts were intrinsically secured to the exposed crystal facets, ultimately dictating their performance in e- $CO_2R$ . The electrochemical evaluation of the  $Cu_2O$ -o catalyst, decorated with (111) crystal facets, revealed an impressive high partial current density and a 35.4% selectivity for alcohol generation at 0.3 V vs RHE [166]. Transitioning to the TB catalyst, the most elongated among the examined 1D active sites, it was synthesized with density adjustments ranging from 0 to  $105 \text{ cm}^{-1}$ . Research findings illuminated TB's



remarkable electrocatalytic ability, characterized by an exceedingly high local  $j_{CH_4}$  of 1294 mA cm<sup>-2</sup>, accompanied by inherent CH<sub>4</sub> selectivity fixed at 92%. Computational simulations, in alignment with DFT, affirmed that TB atoms outpaced flat atoms by a staggering factor of 104 in protonating CO\* [167].

In a comprehensive comparative analysis deploying gas-diffusion electrodes and flowing alkaline catholytes, researchers meticulously scrutinized the electrocatalytic performance of Cu nanocubes and nanospheres in CO<sub>2</sub>R. While an uptick in catalytic efficiency ensued with the use of more concentrated alkaline catholyte, it became evidently clear that Cu nanocubes surpassed their nanospheric counterparts when catalyzing CO<sub>2</sub>R toward ethylene [168]. Furthermore, the research unveiled that liquid C<sub>2+</sub> products could be produced at a significantly accelerated rate due to the synergistic interplay of Cu and Pb within Cu/Pb core/shell nanocrystals. The partial current density for CO<sub>2</sub>RR in a flow cell system over CuPb-0.7/C reached an impressive 294.4 mA cm<sup>-2</sup>, and the total free energy associated with C<sub>2+</sub> products stood at 73.5 kJ mol<sup>-1</sup>. Notably, in terms of generating C<sub>2+</sub> liquid products, the total free energy achieved an outstanding 49.5%, accompanied by a partial current density of 196.8 mA cm<sup>-2</sup>. These results surpassed the performance of most reported Cu-based catalysts for CO<sub>2</sub>RR. When CuPb-0.7/C was used as a catalyst for the CO<sub>2</sub> reduction, the cooperation between Cu and Pb made it easier to pass through the intermediate product of COOH, and then into C<sub>2+</sub> products through the production of \*OCCOH [169].

In the search for affordable and environmentally friendly e-CO<sub>2</sub>R catalysts, research teams have developed a new bimetallic alloy/oxide nanowire catalyst with a core-shell structure. The core of this catalyst boasts high electrical conductivity, while the catalytic activity and selectivity are guaranteed by the amorphous Cu-doped SnO<sub>2</sub> shell. Computational analyses underscored the pivotal role of the Cu-doped SnO<sub>2</sub> layer in curbing the electrocatalytic generation of formate and hydrogen. Remarkably, when operating at 0.9 V versus RHE, this electrocatalyst achieved an impressive FE of 78% for formate production at a partial current density of 30 mA cm<sup>-2</sup> [170]. Another noteworthy development in the field of CO<sub>2</sub>R was the monodisperse core/shell Cu/In<sub>2</sub>O<sub>3</sub> nanoparticles, concluding in the effective production of syngas. The H<sub>2</sub>/CO ratios in syngas could be finely tuned over a broad range, with a FE for syngas generation exceeding 90% through adjustments in the thickness of the In<sub>2</sub>O<sub>3</sub> shell and applied voltage. Compared to other reported electrocatalysts for syngas production, the Cu/In<sub>2</sub>O<sub>3</sub>-0.4 catalyst emerged as the top performer, delivering high current densities at



remarkably low overpotentials. The incorporation of compression strain alongside Cu doping in the In<sub>2</sub>O<sub>3</sub> shell was identified as a key factor responsible for elevating CO production activity and enhancing the H<sub>2</sub>/CO ratio [171]. Table 6 showed properties of different electrocatalysts for e-CO<sub>2</sub>R to sustainable products designed by following surface anchoring strategy.

**Table 6:** The table serves as an overview of electrocatalyst materials used in CO<sub>2</sub>R making it a valuable resource for navigating this field. It presents an analysis of the properties of these materials with an emphasis on how surface anchoring influences the distribution of reaction products under different conditions.

	Material	electrolyte	V		≈ FE %								Ref.
			vs RHE	H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> <sup>-</sup>	
1	blank Cu			1	83	--	--	--	--	--	--	--	
2	Cu-PPT	0.1 M	-1.0	1	87	--	--	--	--	--	--	--	[150]
3	Cu-QAPPT	KHCO <sub>3</sub>		42	16	--	--	20	--	--	--	--	]
4	p-Cu@Cu <sub>2</sub> O			18	18	1	35	3	--	--	13	--	
5	i-Cu@Cu <sub>2</sub> O	0.1 M	-0.98	--	--	--	4	--	--	--	--	--	[151]
6	r-Cu@Cu <sub>2</sub> O	KHCO <sub>3</sub>		--	--	--	2	--	--	--	--	--	]
7	Untreated Cu dendrite	0.1 M		--	--	--	--	3.5	--	3	2	--	[152]
8	hydrophobic Cu dendrite	KHCO <sub>3</sub>	-1.0	--	--	--	--	--	--	4.5	2.8	--	]
9	C-Cu nanosheets	0.1 M		25	22	1	31	--	--	--	--	--	[153]
10	Cu powder	KHCO <sub>3</sub>	-1.0	62	2	1	10	--	--	--	--	--	]
11	@3AZ rt-1h			65	1	28	2	--	--	--	--	--	
12	@3AZ rt-20h			37	1	43	2	--	--	--	--	--	
13	@3AZ 80°C 1h	0.1 M	-1.4	37	1	40	4	--	--	--	--	--	[154]
14	@3AZ 80°C 20h	KHCO <sub>3</sub>		33	1	43	1	--	--	--	--	--	]
15	@2AZ r-t 20h			41	1	35	2	--	--	--	--	--	
16	Cu NCbs			--	--	20	33	--	--	13	34	--	[155]
17	Cu NCbs-rGO/60	0.1 M	-1.1	--	--	10	32	4	--	2	35	--	]
18	Cu NCbs-rGO/120	KHCO <sub>3</sub>		--	--	18	55	1	--	--	45	--	
19	Ag1.55%/CuO			59	40	--	--	--	--	--	--	--	
20	Ag0.68%/CuO	0.1 M		32	63	--	--	--	--	--	--	--	[158]
21	Ag1.01%/CuO	KHCO <sub>3</sub>	-0.4	41	56	--	--	--	--	--	--	--	]
22	CuO			40	53	--	--	--	--	--	--	--	
23	Sn			--	--	--	--	65	--	--	--	--	
24	In			--	--	--	--	44	--	--	--	--	
25	In <sub>10</sub> Sn <sub>40</sub>	0.5 M		--	--	--	--	72	--	--	--	--	[159]
26	In <sub>20</sub> Sn <sub>40</sub>	KHCO <sub>3</sub>	-1.1	--	--	--	--	73	--	--	--	--	]
27	In <sub>40</sub> Sn <sub>40</sub>			5	3	--	--	86	--	--	--	--	
28	In <sub>60</sub> Sn <sub>40</sub>			--	--	--	--	80	--	--	--	--	
29	Cu-Cubes GDE (loading 440 μg cm <sup>-2</sup> )	0.1 M	100										[160]
		KHCO <sub>3</sub>	mA	--	62	--	10	--	--	--	--	--	]
			cm <sup>-2</sup>										
30	Cu/Ag <sub>0.14</sub>	0.1M	0.1	11	50	6	18	2	--	--	15	--	[161]
31	Cu/Ag <sub>0.17</sub>		A	8	83	1	1	2	--	--	3	--	]
32	Cu/Ag <sub>0.41</sub>	CsHCO <sub>3</sub>	cm <sup>-2</sup>	13	84	--	--	2	--	--	--	--	
33	IL@Cu	0.1 M		49	10	1	40	--	--	--	--	--	[162]
34	Cu	KHCO <sub>3</sub>	-1.19	62	8	2	22	--	--	--	--	--	]



35	Cu-NP			43	2	3	16	20	--	--	6	View Article Online DOI: 10.1039/D4MA00321G	
36	Cu-NN			43	4	4	24	4	--	--	21		
37	Cu-PTFE NNs (70%)	0.1 M	-1.5	25	2	3	37	2	--	--	33		[163
38	Cu-PTFE NNs (90%)	KHCO <sub>3</sub>		18	2	2	34	2	--	--	43		]
39	Cu-PTFE NNs (99%)			10	1	1	55	1	--	--	41		
40	EC polished Cu			34	17	4	25	7	--	--	5		
41	After N <sub>2</sub> plasma	0.1 M	-1.0	30	8	4	34	6	--	--	5		[164
42	After Ar plasma	CsHCO <sub>3</sub>		28	3	2	43	4	--	--	10		]
43	After O <sub>2</sub> plasma			33	3	3	42	3	--	--	11		
44	20 wt % Cu/GO			66	3	2	10	10	--	--	2		
45	40 wt % Cu/GO			53	4	4	8	20	--	--	--		[165
46	60 wt % Cu/GO			45	12	9	22	5	--	--	--		]
47	80 wt % Cu/GO			51	10		8	25	--	--	--		
48	Cu <sub>2</sub> O-c			2	21	28	--	2	--	5	--		
49	Cu <sub>2</sub> O-o			11	40	5	--	5	--	6	--		
50	Cu <sub>2</sub> O-t	0.5 M	-0.3	5	37	1	--	4	--	11	--		[166
51	Cu <sub>2</sub> O-u	KHCO <sub>3</sub>		4	10	16	--	--	--	2	--		]
52	Cu			1	25	--	--	--	--	20	--		
53	CuO			1	--	--	--	--	--	4	--		
54	Nt-16			20	1.9	59	3.6	19	--	--	--		
55	Nt-43	0.2 M	-1.6	26	1.6	49	1.4	16	--	--	--		[167
56	Nt-77	KHCO <sub>3</sub>		40	1.5	38	1.2	15	--	--	--		]
57	Nt-265			42	0.8	32	1.8	18	--	--	--		
58	Ut-Cu			47	0.38	28	1.5	20	--	--	--		
59	Cu nano-cubes	0.1 M	-0.8	5	24		51	5	--	--	--		[168
	Cu nano-spheres	KHCO <sub>3</sub>		5	34	1	20	22	--	--	--		]
60	CuPd <sub>0.5</sub> /C	1 M KOH	100 mA cm <sup>-2</sup>	10	20	--	34	--	--	--	18		[169
													]
61	Cu <sub>3</sub> Sn/CF	0.5 M KHCO <sub>3</sub>	-0.9	64	4	--	--	37	--	--	--		[170
													]
62	C-Cu			64	4	--	--	32	--	--	--		
63	C-Cu/In <sub>2</sub> O <sub>3</sub> -0.4	0.5 M		38	52	--	--	10	--	--	--		[171
64	C-Cu/In <sub>2</sub> O <sub>3</sub> -0.8	KHCO <sub>3</sub>	-0.9	42	48	--	--	10	--	--	--		]
65	C-Cu/In <sub>2</sub> O <sub>3</sub> -1.5			34	21	--	--	40	--	--	--		
66	Acid-treated In foil			88	--	--	--	17	--	--	--		

### 6.6.2. Molecular Surface Functionalization

The strategy of modifying the surface of electrocatalysts at the level is a technique that offers precise control, over the catalyst's properties. By attaching groups or molecules to the catalysts surface researchers can finely tune its reactivity and selectivity towards converting CO<sub>2</sub>. This method can produce high performance, selective catalysts, which might help turn carbon dioxide into valuable chemicals or fuels. Precise engineering at atomic levels reduces back or side reactions, and improves the overall performance of CO<sub>2</sub> conversion. It is conceptually equal to addressing main difficulties in clean energy conversion and controlling greenhouse



gas emissions. The importance of molecular surface functionalization is found in its capacity to regulate sites and bond strengths for CO<sub>2</sub> and its beginning chemicals. It helps facilitate binding. Self-assembly, chemical modification, and atomic layer deposition are techniques that allow amines, carboxylates, or imidazoles to be introduced onto the catalysts surface. These catalytic methods use these functional groups as adsorption sites for CO<sub>2</sub>. By facilitating its conversion reaction pathways can be optimized to bring about the desired products, such as methane and ethylene. This approach lays the groundwork for creating tandem reactions through the catalyst it employs, which will take us beyond just one molecule to whatever other valuable chemicals can be derived from CO<sub>2</sub>.

The e-CO<sub>2</sub>R into enantiomeric amino acids had represented one of the earliest instances of producing complex C<sub>3+</sub> products with C-N bonds. This achievement was made possible by reducing reaction barriers in the synthesis of C<sub>3+</sub> compounds through the utilization of chiral twist sites on catalyst surfaces. This discovery underscored the viability of a universal strategy aimed at enhancing the intrinsic catalytic activities of materials for the production of C<sub>3+</sub> species, while also showcasing the potential of chiral twist sites for generating specific biomolecules starting from CO<sub>2</sub> and ammonium bicarbonate [172]. In a significant development, inorganic CuNCs underwent functionalization with an imidazolium ligand, resulting in the creation of hybrid CO<sub>2</sub>RR catalysts that were subject to comprehensive investigation. The findings revealed that, at higher applied potentials, the ImPF<sub>6</sub> ligand exhibited a preference for CO<sub>2</sub>RR over HER and formates over ethylene across the studied potential range. The structural stability of cubic CuNCs and their strong interactions with the ligands facilitated surface modification experiments. However, it was noteworthy that the promoter effect of the imidazolium ligand dissipated during the reconstruction of spherical CuNCs. These insights highlighted the pressing need for hybrid catalysts characterized by either ligands impeding the rebuilding processes or stable NC morphologies [173].

In a stunning revelation of scientific achievement, previous researches unveiled the remarkable enhancement of copper catalytic activity through the application of various imidazolium salts. These chemical modifications yielded impressive improvements in ethylene selectivity, all while effectively suppressing the production of H<sub>2</sub>, CH<sub>4</sub>, and ethanol by skillfully manipulating substituents in organic modifiers. Amazingly, the modified electrodes exhibited ethylene selectivities of up to 73%, with C<sub>2</sub> product selectivities rising as high as 82%. Even after a demanding 19 hours of continuous use, the total current densities remained virtually

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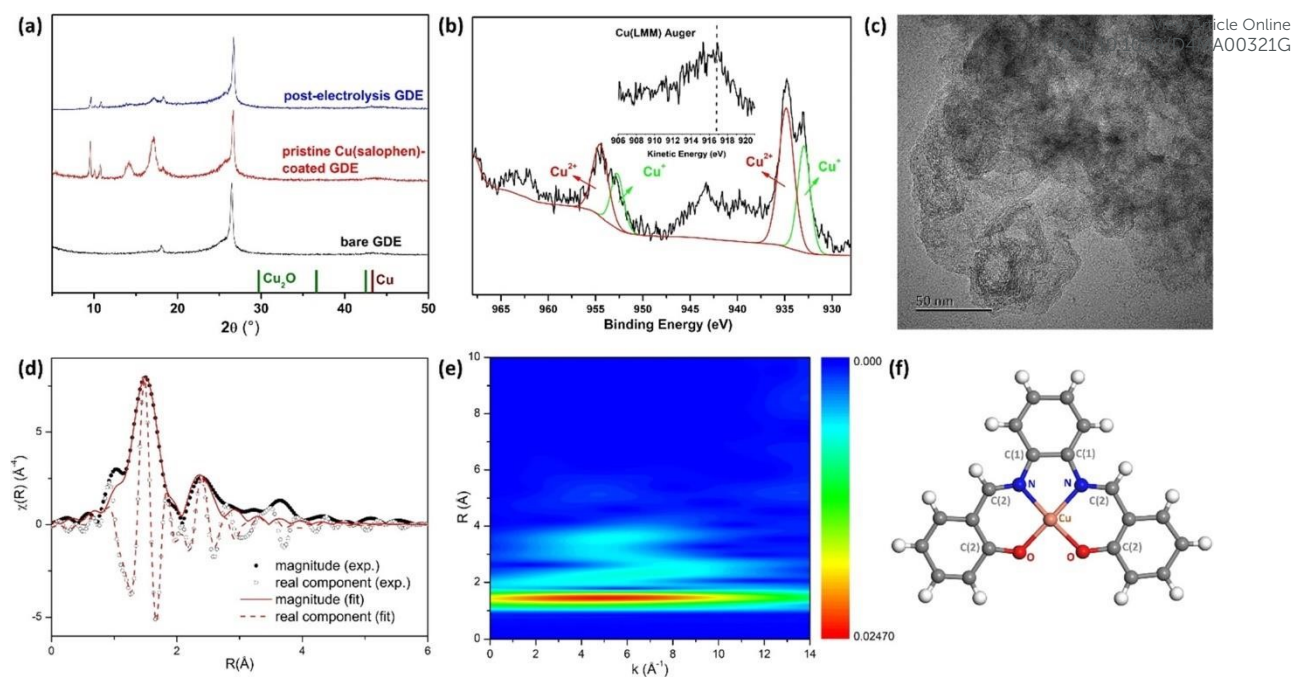


indistinguishable between the modified electrodes and their bare copper counterparts. The nuanced steric and electronic characteristics of substituents on imidazolium nitrogen atoms took center stage, dictating product distribution with the finesse to fine-tune selectivity through adjustments in film deposition potential and alkyl chain length [174].

To explore this further, researchers entered the e-CO<sub>2</sub>R process excitedly in a novel way using Cu/SnO<sub>x</sub> heterostructured nanoparticles combined with CNTs. As the ratio of Cu/SnO<sub>x</sub> was carefully adjusted, the potential for modulating the primary product was revealed-intermediate hydrocarbons, CO<sub>2</sub>-formaldehyde or formic acid [175]. Further, the addition of CTAB to an electrolyte was found to significantly change the selectivity of unmodified Cu for formate production during e-CO<sub>2</sub>R. In near-neutral aqueous electrolytes, this produced a remarkable 82% selectivity and 56-fold increase in partial current density [176].

Moreover, an innovative technique was described for manufacturing a catalyst containing Ni/Cu dual sites on MOF-templated porous carbon. This approach facilitated uniform dispersion of dual sites with adjacent NiN<sub>4</sub> and CuN<sub>4</sub> moieties. The presence of Cu sites was found to lower the formation barrier of \*COOH on surrounding Ni sites, making the rate-limiting step more accessible. As a result, the Ni/CuNC catalyst with N<sub>4</sub>Ni/CuN<sub>4</sub> moieties exhibited an exceptionally high intrinsic activity and achieved impressive FE<sub>CO</sub> values (99.2% at 0.79 V versus RHE and greater than 95% from 0.39 to 1.09 V vs RHE) [177]. In addition to these findings, Zhu *et al.* shed light on the role of metal-supramolecular couples constructed via stacking interactions in facilitating a pivotal phase of C<sub>2+</sub> product production, specifically C-C coupling (Figure 16). The selectivity towards C<sub>2+</sub> products was attributed to the paired structure of metal sites and the van der Waals interaction between the secondary coordination sphere and the adsorbed intermediates. Remarkably, they marked the first detailed exploration of engineering metal-supramolecular couples capable with catalytic activity for multicarbon-selective electrochemical reduction [178].





**Figure 16:** The P-XRD patterns of the GDE without any modification and the GDEs with the Cu(salophen)-carbon composite catalyst were analyzed before and after electrolysis (a). The Cu 2p XPS spectrum was examined, and the Cu LMM Auger spectrum was included as an inset (b). A TEM image was taken to visualize the structure of the catalyst (c). The Cu K-edge EXAFS spectrum was analyzed, and the fit in R-space was determined (d). The Cauchy wavelet transform of the Cu K-edge X-ray absorption spectrum was studied for the post-electrolysis Cu(salophen)-carbon composite catalyst (e). A structural model was used for EXAFS fitting (f). Reproduced with permission from Ref. [178] Copyright 2023, American Chemical Society.

Moreover, the research proposed an approach aimed at enhancing the selectivity of e-CO<sub>2</sub>R, with a specific focus on C<sub>2</sub> products, notably ethanol. Impressively, CuBr treated with DDT molecules yielded remarkable results, a high ethanol-to-ethylene ratio and an impressive FE of 72%. This achievement stemmed from the inhibition of Br migration and the complete reduction of CuBr through DDT adsorption onto CuBr, leading to the formation of a novel and highly stable Br-doped Cu-thiol interface during the catalytic process. Additionally, the incorporation of Br species into Cu was hypothesized to stabilize high-valence Cu species and direct selectivity towards C<sub>2</sub> products, particularly ethanol, as evidenced in the study [179]. In parallel, another research findings unveiled a significant breakthrough in the realm of e-CO<sub>2</sub>R. The incorporation of ZrO<sub>2</sub> and the meticulous tuning of nanocavities within CuO were identified as critical factors that facilitated the dimerization and protonation of CO, ultimately yielding C<sub>2</sub>H<sub>4</sub>. Notably, this approach also acted as an impediment to the antagonistic HER.



The capacity for rational manipulation of e-CO<sub>2</sub>R performance was established through the modulation of ZrO<sub>2</sub> incorporation levels and the control of flaws in CuO. Notably, over CuO@ZrO<sub>2</sub> in an H-cell configuration, the FE and cathodic energy efficiency (EE) for C<sub>2</sub>H<sub>4</sub> generation witnessed substantial enhancements compared to bare CuO, with FE increasing from 19.7% to 1.5% and cathodic EE from 11% to 1.9%. Furthermore, with a flow cell architecture operating at a high current density of 250 mA cm<sup>-2</sup>, the overall FE and EE for C<sub>2</sub>H<sub>4</sub> were significantly boosted to 84.3% and 54.7%, respectively [180].

In a related domain, the e-CO<sub>2</sub>R to CO in an aqueous environment, utilizing metal nanoparticle catalysts such as Au nanoparticles, witnessed significant advancement through the implementation of a molecular surface functionalization strategy [181]. Concurrently, the research delved into the utilization of a one-step solvothermal methodology for the synthesis of copper hydroxyphosphate catalysts tailored for deployment in e-CO<sub>2</sub>RR. Electrochemical investigations brought to light the remarkable component-specific efficiency of these catalysts. The FE exhibited by polyhydroxyl Cu<sub>5</sub>(OH)<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub> reached 37.4% at -1.6 V, surpassing that of Cu<sub>2</sub>(OH)PO<sub>4</sub> by over 100% in terms of current density [182].

In a parallel research avenue, an innovative strategy revolves around surface molecule functionalization, presenting a potential breakthrough for catalytic applications. Specifically, the 4H/fcc Au-MMT configuration outperformed its counterpart, 4H/fcc Au-OAm, by a significant margin in terms of e-CO<sub>2</sub>RR performance within H-type cells. This surface functionalization strategy also exhibited the capacity to enhance the selectivity of the flow cell for CO. DFT simulations conducted on 4H/fcc Au nanorods functionalized with OAm and MMT ligands revealed opposing modulation effects. In both the fcc and 4H phases, surface MMT activation of Au was observed, resulting in a e-CO<sub>2</sub>RR process characterized by minimal reaction barriers. In contrast, OAm exerted effects such as reduced electroactivity and the introduction of spatial barriers for intermediate adsorptions on the surface [183]. The review for electrocatalysts designed by following molecular surface functionalization approach is also tabulated in table 7.





**Table 7:** The table offers an overview of electrocatalysts specifically designed for CO<sub>2</sub>R focusing on the approach of molecular surface functionalization. It highlights the range of materials used in electrocatalysis for CO<sub>2</sub>R. Provides a review of their electrochemical behavior, product selectivity and efficiency. This information provides insights, across variable reaction conditions.

Material	electrolyte	V vs RHE	≈ FE %										Ref.
			H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> <sup>-</sup>		
L-CCFs	0.25 M		--	--	--	--	1	--	--	10	--	[172]	
ACFs	NH <sub>3</sub> , H <sub>2</sub> O		--	--	--	--	1	--	--	4	--	]	
Cu <sub>cub</sub>	0.1 M KHCO <sub>3</sub>	-1.05	65	7	2	20	3	--	--	1	--	[173]	
Cu <sub>cub</sub> -ImPF <sub>6</sub>			67	7	1	14	10	--	--		--	]	
Modified polycrystalline copper (12)	0.1 M KHCO <sub>3</sub>	-1.1	39	5	10	20	21	--	--	3	--	[174]	
CuO <sub>y</sub> -CNT-#1			46	4	35	10	6	--	--	--	--	]	
CuO <sub>y</sub> /SnO <sub>x</sub> -CNT-#2			50	5	25	10	10	--	--	--	--	[175]	
CuO <sub>y</sub> /SnO <sub>x</sub> -CNT-#7	0.1 M KHCO <sub>3</sub>	-1.09	12	76	--	--	12	--	--	--	--	]	
CuO <sub>y</sub> /SnO <sub>x</sub> -CNT- #12			14	13	--	--	80	--	--	--	--	]	
SnO <sub>x</sub> -CNT- #13			23	25	--	--	52	--	--	--	--	[176]	
oxide-derived Cu	0.5 M KHCO <sub>3</sub>	-0.9	45	2	2	1	50	--	--	--	--	]	
Cu-CTAB			48	1	--	--	54	--	--	--	--	]	
N/C			--	25	--	--	--	--	--	--	--	[177]	
Cu-N-C			--	50	--	--	--	--	--	--	--	]	
Ni-N-C			--	51	--	--	--	--	--	--	--	[178]	
Ni/Cu-N-C			--	85	--	--	--	--	--	--	--	]	
Cu(salophen)-coated GDE	1 M KOH	-1.0	30	20	3	38	6	--	--	3	--	[179]	
CuBr	--	-1.10	24	4		25	--	--	--	--	--	]	
CuBr-DDT			18	20		18	--	--	--	--	--	[180]	
CuO@ZrO <sub>2</sub>			--	9	7	48	7	--	--	--	--	]	
CuO	0.1 M KHCO <sub>3</sub>	-1.1	--	2	2	25	9	--	--	--	--	[182]	
ZrO <sub>2</sub>			--	--	--	--	7	--	--	--	--	]	
Cu <sub>2</sub> (OH)PO <sub>4</sub>	0.1 M KHCO <sub>3</sub>	-1.0	38	8	--	--	--	--	--	--	--	[183]	
Cu <sub>5</sub> (OH) <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub>			46	8	--	9	--	--	--	--	--	]	
4H/fcc Au-MMT	1.0 M KHCO <sub>3</sub>	-1.0		70	--	--	--	--	--	--	--	[183]	
4H/fcc Au-OAm				53	--	--	--	--	--	--	--	]	

### 6.6.3. Interfacial engineering

Interfacial engineering represents an innovative strategy when it comes to designing electrocatalysts, for CO<sub>2</sub>R. Its main focus is on manipulating and optimizing the interface between the catalyst and the electrolyte. The significance of this approach lies in its ability to enhance activity, selectivity and stability all of which are factors in efficiently converting CO<sub>2</sub> into valuable products. By adjusting the properties of this interface researchers can influence how CO<sub>2</sub> and its intermediates are adsorbed, thereby controlling the reaction pathways. This level of control is vital in addressing the challenges associated with CO<sub>2</sub>R. Contribute to the

production of fuels and chemicals sustainably. There are various techniques that can be utilized for engineering in catalyst design. For example, using molecules to modify a surface, such as with electrodes, allows for the introduction of specific binding sites and active groups that help CO<sub>2</sub> capture or conversion. The choice among various support materials and catalyst substrates can also play a role in property determinants. Nanostructuring roughened surfaces or producing heterojunctions is among the ways to engineer the interface between the cathode material and the electrolyte leading to increased catalytic performance. Engineering's importance is that it may allow electrocatalysts to be tailored for CO<sub>2</sub>R reactions like methane production or ethylene on one side focusing on practical applications the other side towards sustainability energy solutions. And it reduces CO<sub>2</sub> emissions, mitigating climate change.

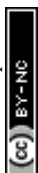
Zhang *et al.* Designed a Cu-Zn alloy/Cu-Zn aluminate oxide composite system for the e-CO<sub>2</sub>R to valuable C<sub>2+</sub> products. Decomposing the Cu-Zn-Al-LDH precursor signals the beginning of this novel composite system. Following this, the precursory catalyst was transformed into a composite catalyst consisting of Cu-Zn alloy and Cu-Zn aluminate oxide. Under side-scene, these two components were replicated in a lattice, while interface after interface crisscrossed through the structure. An optimized Cu<sub>9</sub>Zn<sub>1</sub>/Cu<sub>0.8</sub>Zn<sub>0.2</sub>Al<sub>2</sub>O<sub>4</sub> catalyst displayed massive current and atom-light effects (though only for C<sub>2+</sub> products): 88.5% FE at 400 mAcm<sup>-2</sup> when operating on 1.15 V vs RHE [184]. Simultaneously, another study delved into the e-CO<sub>2</sub>R into methane, leveraging a Cu foil modified with ZnO<sub>x</sub> nanoparticles. Notably, the peak FE for methane production was achieved at 1.1 V, reaching approximately 36%, and it exhibited no significant deterioration over time. This catalytic activity was attributed to the induction of active sites for methane production, identified as cupric ions, at the Cu/ZnO<sub>x</sub> interface. The interaction between Cu and ZnO<sub>x</sub> provided stability to these active species, prolonging their catalytic lifespan. Importantly, the synthesis process for this system was characterized by its swiftness, simplicity, cost-effectiveness, and straightforwardness. Furthermore, the scalability of methane production was achieved by expanding the surface area of the Cu foil [185].

Furthermore, in the pursuit of achieving exceptional selectivity and stability in the e-CO<sub>2</sub>R to C<sub>2+</sub> products, Liu *et al.* developed a heterostructured catalyst comprising 2D Cu MOFs and Cu<sub>2</sub>O nanoparticles (Cu<sub>2</sub>O@Cu-BDC). This catalyst consistently generated stable C<sub>2+</sub> products with remarkable FE of 72.1% in an H-type cell and 58.2% in a flow cell setup. The key to its success lay in the stabilization of Cu<sup>+</sup> active sites at the interfaces formed between Cu<sub>2</sub>O and Cu-BDC within the 2D Cu MOFs. This stabilization, in turn, enhanced C-C coupling reactions and improved the adsorption of critical intermediates involved in the production of C<sub>2+</sub>



products [186]. Additionally, a one-step reduction technique had been employed to create a bimetallic Cu and SnO<sub>x</sub> nanocomposite on amorphous rGO support, aiming to enhance formate synthesis through the interplay between the materials, heterointerfaces, high oxophilicity, and electrochemical surface area. The production of SnO<sub>x</sub> nanoparticles had hindered C-C coupling and had reduced H<sub>2</sub> and CO generation, ultimately leading to enhanced formate selectivity and endurance. Remarkably, even after 6 hours of electrolysis, the nanocomposite had maintained 85% of its original current density [187]. In the quest to improve C<sub>2+</sub> selectivity in e-CO<sub>2</sub>R, researchers had devised a method for in situ modification of the Cu<sup>+</sup>/Cu<sup>0</sup> interface within oxide-derived Cu catalysts. Tests of the RCu with Br catalyst's performance in e-CO<sub>2</sub>R had unveiled outstanding stability, complemented by its excellent activity and selectivity in producing C<sub>2+</sub> products. The cooperative Cu<sup>+</sup>/Cu<sup>0</sup> interface, which played a pivotal role in conferring remarkable selectivity for C<sub>2+</sub> products, had substantially lowered the energy barrier for CO-CO coupling and had repressed the HER, thereby enhancing the efficiency of CO-CO coupling [188].

In a related context, the interactions between Cu and the electrolyte were found to be of paramount importance in the context of CO<sub>2</sub>R in aqueous solutions. When CuO electrodes were modified with various polymers such as PVDF, PE, PVA, and PVP, the FE for C<sub>2</sub>H<sub>4</sub> generation doubled, and the partial current density nearly tripled. This advantageous effect was primarily governed by the hydrophobic environments created by PVDF and PE polymers on the Cu surface. Hydrophobic polymer coatings resulted in a higher surface pH, inhibiting HER and promoting the reduction of CO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> [189]. To illustrate uniform Cu dispersion onto the CeO<sub>2</sub> support and the fine-tuning of interfacial characteristics, the Yin *et al.* had demonstrated the fabrication of heterostructured Cu<sub>y</sub>/CeO<sub>2</sub> nanorods through chemical pre-lithiation and galvanic displacement. The Cu decoration had facilitated the activation of CO<sub>2</sub> and its subsequent conversion to the \*CO intermediate on the surrounding Cu surface, generating a new strong-binding site at the Cu and CeO<sub>2</sub> interface. The trends in the production of C<sub>1</sub> and C<sub>2+</sub> products in e-CO<sub>2</sub>R had exhibited a decreasing and volcano-shaped pattern as the extent of Cu decoration had increased. Through in situ ATR-SEIRAS and Raman measurements, it had been found that the Cu surface had generated two distinct types of \*COLFB and \*COHFB intermediates, with a high coverage of the \*COHFB promoting the creation of C<sub>1</sub> products and a high coverage of the \*COLFB contributing to the formation of C<sub>2+</sub> products [190]. Moreover, it was found that during e-CO<sub>2</sub>RR the S-CuSn catalyst goes through dynamic changes. There are five stages in this complicated process: CuS reduction; S

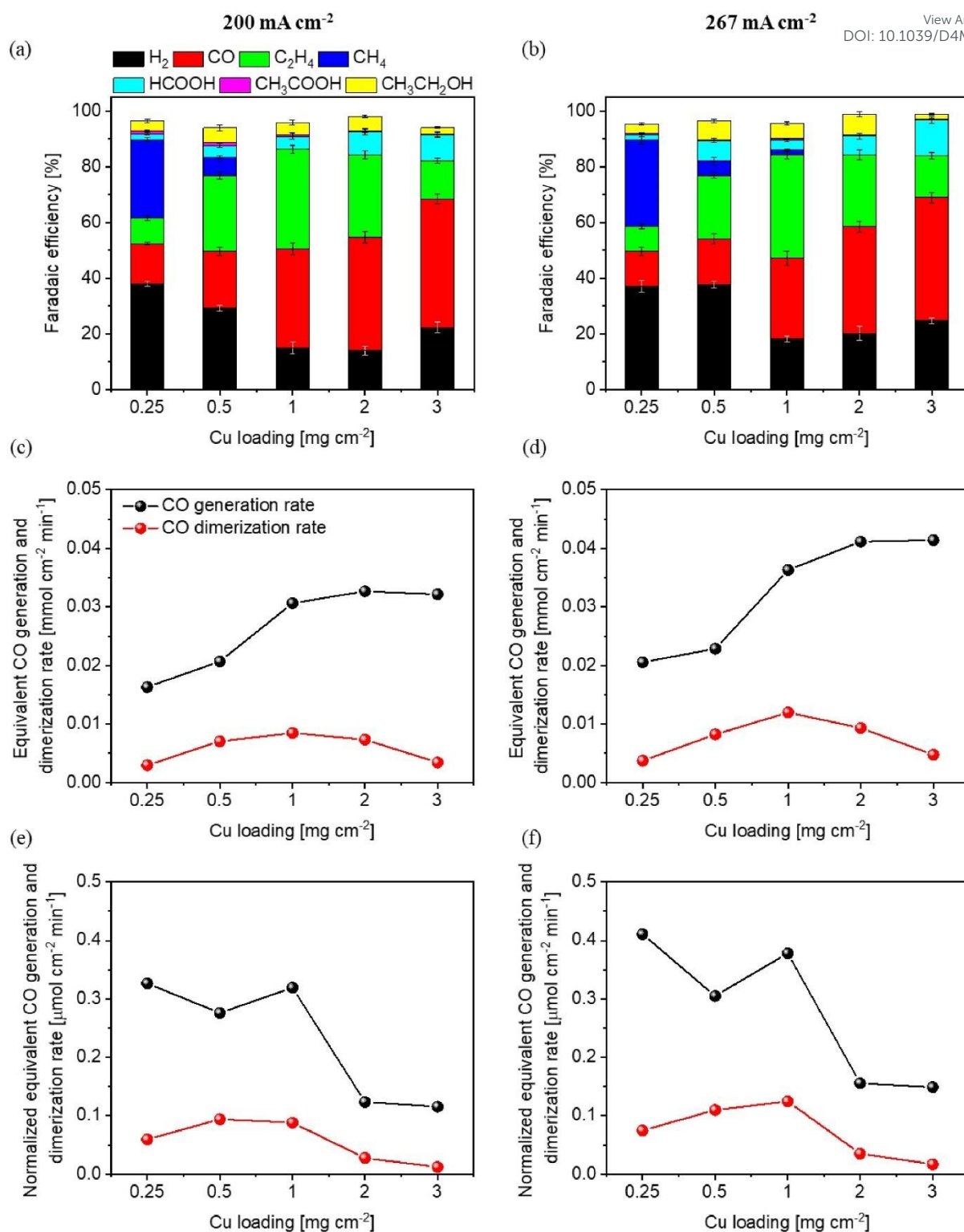


leaching from  $\text{Cu}_2\text{SnS}_3$ ;  $\text{Cu}_{24}\text{Sn}_{20}$  alloy generation; Sn metal formation; and the constitution of a stable structure in the form of co-doped  $\text{Cu}_{24}\text{Sn}_{20}$  alloys with S/Sn. This reconstructed S-CuSn catalyst gave a maximum  $\text{CO}_2$  FE of 91.5% and formate FE of 96.4%, indeed homage to its exemplary activity in the e- $\text{CO}_2\text{R}$  toward formate [191].

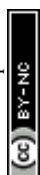
Furthermore, metallurgy-dealloying techniques were employed to craft a novel  $\text{CeO}_2\text{Cu}$  amorphous heterostructure. This catalyst, through its interfacial sites, increased the adsorption strength of CO and stabilized  $\text{CH}_2\text{CHO}$ , guiding the reaction toward  $\text{C}_{2+}$  alcohol production. The catalyst significantly enhanced the inherent activity and selectivity of Cu-based catalysts in the synthesis of  $\text{C}_{2+}$  alcohols, achieving a remarkable FE of 32.9% at a low potential [192]. Besides, Rudd *et al.* investigated the creation of foams, their morphology, crystal structure, and catalytic efficiency under varying conditions. They also studied how foams reacted to  $\text{CO}_2$  electrolysis and examined the potential impact of urea as an additive. Both the unmodified and urea-treated foam electrodes exhibited a variety of cub-octahedra and dendrites. However, changes in the shape, crystallinity, and surface content of the copper foams after 35 minutes of electrolysis resulted in their deactivation as catalytic materials [193].

Additionally, the study examined two electrode families comprised of Cu NPs loaded at varying concentrations (ranging from 0.25 to 2.0  $\text{mg}/\text{cm}^2$ ) as e- $\text{CO}_2\text{RR}$  catalysts (Figure 17). At low loadings, the predominant reduction product at the electrodes was  $\text{CH}_4$ , while at higher loadings, CO became the dominant product. Interestingly, at moderate concentrations (0.5 to 1.0  $\text{mg}/\text{cm}^2$ ),  $\text{C}_2\text{H}_4$  selectivity was maximized. This behavior was attributed to the presence of low-density NPs, which reduced the likelihood of CO dimerization, ultimately leading to increased  $\text{CH}_4$  generation. Bulk CO generation increased with higher loading, increasing the probability of dimerization and thus favoring  $\text{C}_2\text{H}_4$  synthesis. Additionally, capacitance was found to slow the outward flow of charges from the electrode as NP loading increased further [194].





**Figure 17:** Comparison of electrodes consisting of 25 nm nanoparticles (NPs) with varying loadings: at 200 mA cm<sup>-2</sup>, (a) assessing selectivity, (c) evaluating equivalent bulk CO generation and dimerization rates, and (e) normalizing equivalent CO generation and dimerization rates to the electrode's electrochemically active surface area (ECSA); at 267 mA cm<sup>-2</sup>, (b) analyzing selectivity, (d) calculating equivalent bulk CO generation and dimerization



rates, and (f) ECSA-normalized equivalent CO generation and dimerization rates. Each electrode underwent testing on multiple occasions. The bulk and ECSA-normalized equivalent CO generation and dimerization rates in (c-f) were computed based on the average selectivity values from at least two sets of experiments conducted at different catalyst loadings and current densities. Reproduced with permission from Ref. [194] Copyright 2023, Elsevier.

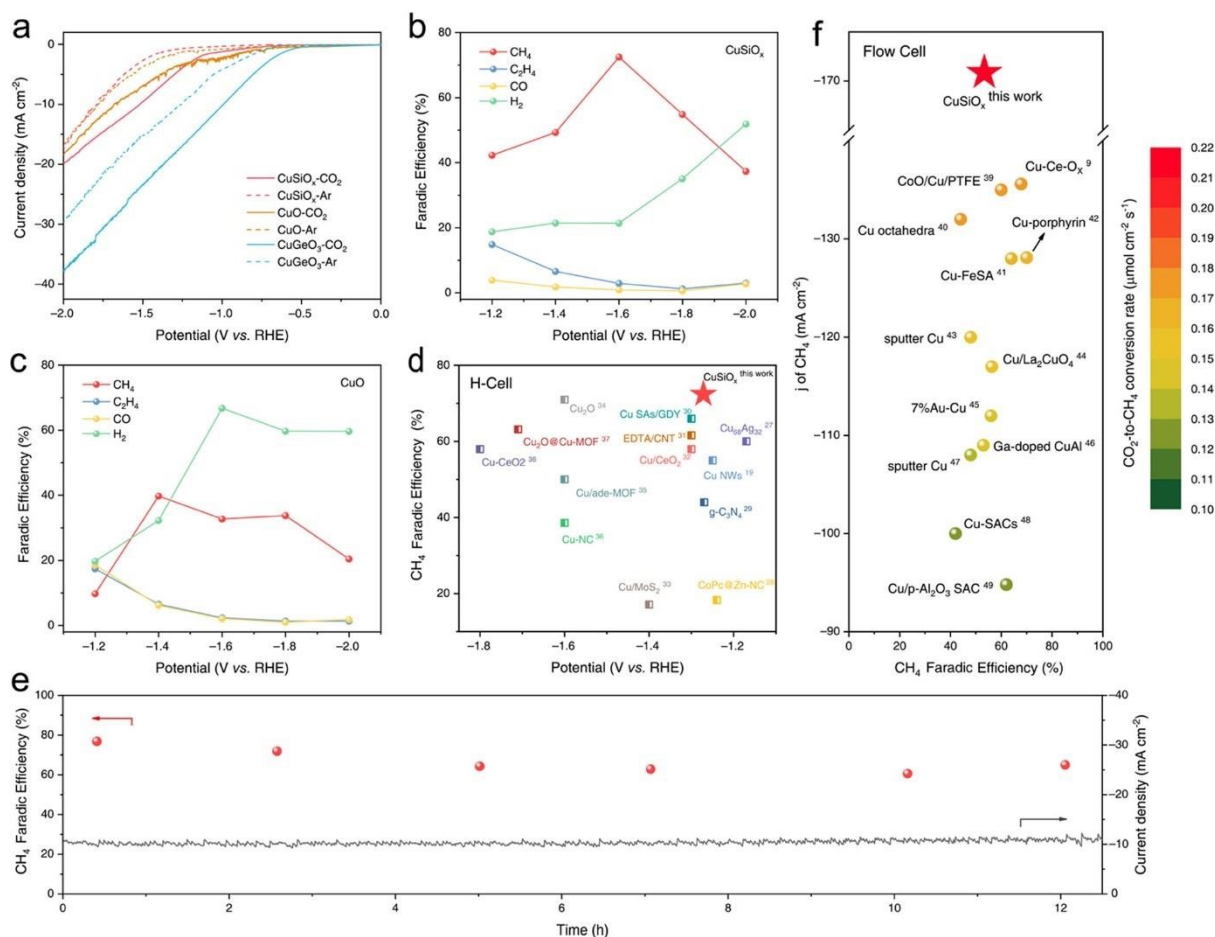
Likewise, the Tafazoli *et al.* highlighted a substantial difference in the FEs of C<sub>2</sub> products between low and high current density electrodeposited Cu oxides. In-situ SERS was employed to monitor changes in surface chemistry under CO<sub>2</sub>RR conditions, revealing rapid shifts in Cu oxidation states on porous high current density electrodes but not on low current density electrodes. The formation of Cu<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>2</sub> was linked to Cu oxidation states, surface intermediates, and product analyses, affecting adsorbed intermediates and C<sub>2</sub> products based on local HCO<sup>3-</sup> concentration and pH during Cu<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>2</sub> production. The high current density surface was easily terminated by Cu<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>2</sub>, inhibiting further CO<sub>2</sub>RR. As a result, HER was enhanced at the expense of C<sub>2</sub> products due to decreased CO<sub>2</sub> concentration near the surface, driven by HCO<sup>3-</sup> consumption and resulting in higher alkalinity over the electrode. The strong adsorption of CO molecules over the high current density electrode terminated by Cu<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>2</sub> might account for the removal of the C<sub>2</sub> pathway [195].

In addition, Yang *et al.* demonstrated increased selective adsorption of Cl at dual-phase interfaces using a Cu-based catalyst with abundant Cu<sup>+</sup> species. This facilitated CO<sub>2</sub>-to-C<sub>2+</sub> conversion in neutral fluids by providing local \*CO coverage, which favored energetically advantageous CO dimerization. The employment of the dual-phase method to enhance \*CO intermediates' coverage has broader implications for improving CO<sub>2</sub>R catalysis in various electrolytes and other electrochemical processes [196]. Also, Single-atom-thick Cu-Sn surface alloys (Cu<sub>97</sub>Sn<sub>3</sub> and Cu<sub>99</sub>Sn<sub>1</sub>) were created for effective e-CO<sub>2</sub>R. These alloys exhibited different catalytic selectivity compared to pure Cu<sub>100</sub> and Cu<sub>70</sub>Sn<sub>30</sub> bulk alloys due to their distinct geometric and electronic structures. The Cu<sub>97</sub>Sn<sub>3</sub> catalyst achieved 98% FE<sub>CO</sub> at low overpotential, showcasing the influence of the local coordinating environment in isolated Cu-Sn bonding, as demonstrated by density functional theory simulations [197].

Additionally, a practical method for stabilizing copper with silica and producing CuSiO<sub>x</sub> amorphous nanotube catalysts that are resistant to rebuilding were introduced by Tan *et al.* The Cu-O-Si interfacial sites are ultra-stable in the CO<sub>2</sub>RR without evident reconstruction due to the strong interfacial connection between Cu and silica, resulting in high CO<sub>2</sub>-to-CH<sub>4</sub>



selectivity (72.5% after 12 hours of testing) and stability ( $FE_{CH_4}$  remains over 60% after 12 hours of testing) (Figure 18). In a flow cell device, an impressive  $CO_2$ -to- $CH_4$  conversion rate of  $0.22 \text{ mol cm}^{-2}\text{s}^{-1}$  was also attained, suggesting a viable path toward the development of highly active and stable Cu-based  $CO_2$ R catalysts [198]. Table 8 shows a comparative overview of different electrocatalyst synthesized by interfacial engineering approach for e- $CO_2$ R to sustainable products.



**Figure 18:** e- $CO_2$ R performance: LSV curves of  $CuSiO_x$ ,  $CuGeO_3$ , and  $CuO$  under  $CO_2$  or Ar purging conditions (a). FEs of  $CO_2$ R products at varying potentials (b, c). FE for  $CH_4$  production by  $CuSiO_x$  compared with other catalysts from previous studies after iR corrections (d). Time-dependent total current density and  $FE_{CH_4}$  generated by  $CuSiO_x$  measured at  $-1.6 \text{ V}$  vs RHE over a 12-hour period (e). A comparative analysis of this research with prior investigations regarding electrocatalytic  $CO_2$ -to- $CH_4$  conversion, conducted in a flow cell device (f). Reproduced with permission from Ref. [198] Copyright 2023, American Chemical Society.



**Table 8:** The presented table showcases the performance of materials in terms of their properties. It specifically focuses on how an interfacial engineering approach affects the selectivity and efficiency of the resulting products. The findings, from this table provide insights for advancing sustainable solutions in the field of energy conversion technologies.

Material	electrolyte	V vs RHE	≈ FE %										Ref.
			H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> <sup>-</sup>		
CuZn/CuZnAl <sub>2</sub> O <sub>4</sub>			4	4	--	38	2	--	--	34	--		
Cu/CuAl <sub>2</sub> O <sub>4</sub>	2 M KOH	-1.1	18	4	--	35	4	--	--	25	--	[184]	
CuZn			17	18	2	17	2	--	--	21	--	]	
0D-CuZn			--	--	35	18	--	--	--	--	--		
0D-Cu	0.1 M KHCO <sub>3</sub>	-1.1	--	--	8	30	--	--	--	--	--	[185]	
Cu			--	--	6	2	--	--	--	--	--	]	
Cu <sub>2</sub> O@Cu-BDC			17	21	2	25	6	--	--	--	--		
Cu-BDC	0.1 M KBr	-1.1	38	6	5	14	2	--	--	--	--	[186]	
Cu <sub>2</sub> O			40	5	8	26	5	--	--	--	--	]	
Ni-N-C@900°C			93	12	--	--	--	--	--	--	--		
Ni-N-C@700°C	0.1 M KHCO <sub>3</sub>	-1.1	77	8	--	--	--	--	--	--	--	[199]	
NiNPs-N-C			94	7	--	--	--	--	--	--	--	]	
N-C			85	6	--	--	--	--	--	--	--		
CuSnO <sub>x</sub> /rGO			2	21	--	--	22	--	--	--	--		
Cu <sub>3</sub> SnO <sub>x</sub> /rGO	0.5 M KHCO <sub>3</sub>	-0.99	3	28	--	--	28	--	--	--	--	[187]	
Cu <sub>0.33</sub> SnO <sub>x</sub> /rGO			3	27	--	--	69	--	--	--	--	]	
R-Cu	0.1 M KHCO <sub>3</sub>	1.0	18	1	1	52	2	--	--	12	--	[188]	
R-Cu-Br			38	1	8	38	1	--	--	5	--	]	
CuO	0.5 M KHCO <sub>3</sub>	-1.02	51	12	2	18	--	--	--	--	--	[189]	
CuO-PVDF			40	10	2	25	--	--	--	--	--	]	
Cu <sub>0.04</sub> /CeO <sub>2</sub>			23	32	--	2	33	--	--	--	--		
Cu <sub>0.12</sub> /CeO <sub>2</sub>			31	17	--	24	22	--	--	--	--		
Cu <sub>0.32</sub> /CeO <sub>2</sub>	0.1 M KHCO <sub>3</sub>	-1.0	25	20	--	20	23	--	--	7	--	[190]	
Cu <sub>0.4</sub> /CeO <sub>2</sub>			24	10	4	23	24	--	--	7	--	]	
Cu <sub>0.6</sub> /CeO <sub>2</sub>			29	18	--	13	38	--	--	--	--		
S-CuSn			-0.8	8	10	--	--	50	--	--	--		
S-Cu	0.5 M KHCO <sub>3</sub>	-0.65	66	--	--	--	3	--	--	--	--	[191]	
S-Sn			-0.99	9	9	--	--	41	--	--	--	]	
CeO <sub>2</sub> -Cu			-0.6	--	--	--	--	--	--	30	--		
CuZn			-0.7	--	--	--	--	--	--	38	--		
Grain Boundary rich Cu			-0.8	--	--	--	--	--	--	17	--		
CuAg			-0.8	--	--	--	--	--	--	19	--		
Cu <sub>2</sub> S-Cu-V	1.0 M KOH	-1.0	--	--	--	--	--	--	--	19	--	[192]	
Nanoporous Cu			-0.7	--	--	--	--	--	--	10	--	]	
CuAg Wires			-0.7	--	--	--	--	--	--	10	--		
Cu nanoparticles			-0.8	--	--	--	--	--	--	15	--		
Porous Cu			-0.8	--	--	--	--	--	--	15	--		
CuAu			-1.0	--	--	--	--	--	--	25	--		
CF-18H	0.1 M KHCO <sub>3</sub>	-1.05	74.3	1.7	0.3	11.6	2.6	--	--	2.5	--	[193]	
CF-18H-100U			90.9	0.8	0.7	8	2.4	--	--	1.5	--	]	
CuZn/CuZnAl <sub>2</sub> O <sub>4</sub>	2 M KOH	-1.1	4	6	--	38	2	--	--	34	--		





42	Cu/CuAl <sub>2</sub> O <sub>4</sub>			26	4	--	33	4	--	--	27	View Article Online DOI: 10.1039/D4MA00321G	184
43	CuZn			17	20	4	16	--	--	--	21	--	]
44	Cu NPs (3 mgcm <sup>-2</sup> )	1.0 M KOH	200 mA cm <sup>-2</sup>	22	44	--	16	10	--	--	--	--	[194 ]
45	S-ZnO			38	30	--	--	8	--	--	--	--	--
46	S-CuO	1 M KOH	-1.06	21	5	3	40	--	--	--	12	--	[50]
47	S-Cu <sub>5</sub> Zn <sub>1</sub> O <sub>x</sub>			48	12	2	18	--	--	--	6	--	--
48	S-Cu <sub>1</sub> Zn <sub>3</sub> O <sub>x</sub>			28	14	3	16	--	--	--	7	--	--
49	CuSiO <sub>x</sub>	1 M KOH	-1.3	19	4	43	16	--	--	--	--	--	[198 ]
50	CuO			20	18	10	18	--	--	--	--	--	--
51	Cu <sub>100</sub>			22	18	--	28	28	--	--	--	--	--
52	Cu <sub>97</sub> Sn <sub>3</sub>	0.5 M KHCO <sub>3</sub>	-1.0	5	84	--	--	9	--	--	--	--	[197 ]
53	Cu <sub>70</sub> Sn <sub>30</sub>			2	5	--	--	90	--	--	--	--	--

#### 6.6.4. Speciation of Cu surface

In the design of catalysts for e-CO<sub>2</sub>R, the arrangement of copper surfaces completely different. Since the selectivity, activity, and stability of the catalyst in converting CO<sub>2</sub> into useful chemicals and fuels are directly influenced by the surface configuration of Cu, it is important to understand and control this. The key to this approach lies in the fact that through it we can tailor the properties of Cu surfaces allowing us to control the reaction pathways and sideline reactions. By manipulating the surface configuration researchers can enhance the performance of the catalyst making it more energy efficient and economically viable for large scale CO<sub>2</sub>RR applications. Additionally, by modifying the configuration of the Cu surface, it can be made into a selectivity catalyst, demonstrated through catalysts that can convert C<sub>2</sub> into ethylene or ethanol, and suppress the production of competing by-products. To design CO<sub>2</sub>RR catalysts, a variety of methods are available to control and manipulate Cu's surface configuration. One way is to use electrodeposition techniques create thin films or nanostructured Cu surfaces having controlled crystallographic orientations, grain size and defect types. In addition, adding foreign elements/molecules, such as in atomic layer deposition of metal oxide or the forming of surface alloys, can change Cu's electronic structure and coordination environments to change its responsiveness to CO<sub>2</sub>. One possible approach is to use electrochemical potential control and pH adjustment as a way to synthesize and operate Cu-based catalysts. This can mediate specific surface speciation and stabilize reactive intermediates.

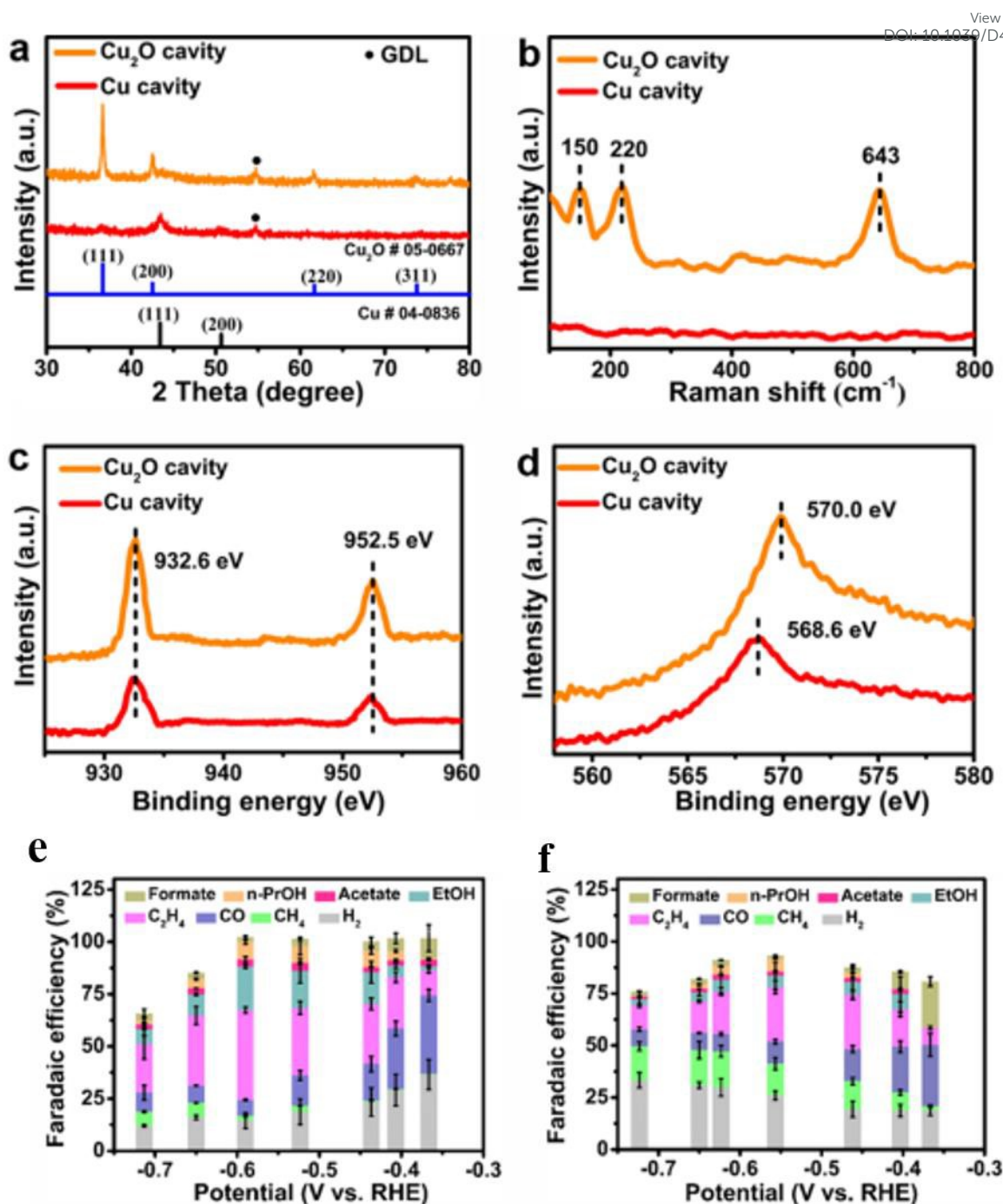
Continuing with this line of investigation, tin doped CuO NSs were prepared and the catalyst activity of them was higher than that of pure CuO catalysts. The excellent performance of the



NS's was mainly attributed to the increased  $\text{CO}_2$  adsorption. The synergistic relationships between  $\text{SnO}_2$  and  $\text{CuO}$  were found to be beneficial for e- $\text{CO}_2\text{R}$  [200]. In another facet of research,  $\text{La}_2\text{CuO}_4$  perovskites with engineered grain boundaries (GBs) were developed as effective electrocatalysts for e- $\text{CO}_2\text{RR}$ . These tailored nanoparticles exhibited a strong FE toward  $\text{C}_2\text{H}_4$ , a desirable product of  $\text{CO}_2\text{R}$ . The enhanced selectivity for the  $\text{C}_2$  product was attributed to their high adsorption affinity for CO intermediates. The introduction of strain generated by the twin boundaries (TBs) in  $\text{La}_2\text{CuO}_4$  nanoparticles led to increased CuO and CuLa bond lengths, further improving  $FE_{\text{C}_2\text{H}_4}$  [201]. Advancing this research, a microfluidic flow cell was utilized to reduce  $\text{Cu}_2\text{O}$  precursors under  $\text{CO}_2\text{RR}$  conditions, resulting in the formation of a porous Cu cavity (Figure 19). These catalysts exhibited a Cu (111) faceted cavity with dimensions of approximately  $108 \pm 23$  nm. Remarkably, these structures led to an increase in both the FE for  $\text{C}_{2+}$  products and the partial current density, all achieved at a low applied voltage. This was attributed to the entrapment of numerous \*CO intermediates within the cavities, preventing their easy migration between cavities. DFT calculations and electrochemical Raman spectra suggested that C-C coupling primarily occurred via the CO-CHO coupling mechanism [202].

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DOI: 10.1039/D1MA00321G





**Figure 19:** The study focuses on characterizing the synthesized Cu<sub>2</sub>O pre-catalyst and the Cu cavity catalysts. The XRD pattern (a), Raman spectra (b), and XPS of Cu 2P (c) and Cu LMM (d) were obtained for the synthesized Cu<sub>2</sub>O precatalyst and the Cu cavity catalysts. "GDL" refers to the commercial gas diffusion layer. The performance of e-CO<sub>2</sub>RR in a flow cell reactor. The major products of the e-CO<sub>2</sub>RR were studied on both cavity Cu and solid Cu surfaces at various applied potentials in a 1 M KOH solution. Reproduced with permission from Ref. [202] Copyright 2023, American Chemical Society.



In the realm of catalytic advancements, a groundbreaking achievement was made by immobilizing  $\text{OH}_{\text{ad}}$ -introduced noncovalent interactions (NCI) in the reduction of  $\text{CO}_2$  on SnO nanosheet catalysts. This innovative approach yielded remarkable results, including a high FE of 90.5% and a substantial partial current density of  $61.8 \text{ mA cm}^{-2}$ . The catalytic mechanism revolved around the rapid protonation of  $\text{CO}_2$  into formate on the SnO(001) surface through activation. The introduction of NCI by  $\text{O}_{\text{Had}}$ , coupled with its role in enhancing hydrogen adsorption, facilitated efficient regeneration, enabling continuous operation. Notably,  $\text{O}_{\text{Had}}$ -induced NCIs outperformed their  $\text{H}_2$ -annealed counterparts in promoting formate reduction across various catalysts, including CuO,  $\text{Bi}_2\text{O}_3$ , and  $\text{TiO}_2$  [203]. Another notable advancement in catalytic science involved the creation of a  $\text{Cu}_2\text{O}(\text{CO})$  nanocubic catalyst through controlled thermal topological transformation of  $\text{Cu}_2\text{O}$  nanocubes under a CO atmosphere at  $275^\circ\text{C}$ . This catalyst exhibited a unique structural configuration characterized by high-density nanograin boundaries, which exposed Cu(100) facets,  $\text{Cu}[n(100)\times(110)]$  step sites, and  $\text{Cu}^0/\text{Cu}^+$  interfaces. During the  $\text{CO}_2\text{RR}$  process, it demonstrated exceptional performance, achieving a  $FE_{\text{C}_{2+}}$  of 77.4%, and showcased remarkable stability even under high polarization and current densities. The abundance of  $\text{Cu}^0/\text{Cu}^+$  interfaces played a pivotal role in increasing the adsorption density of  $^*\text{CO}$  intermediates, thereby contributing to the high selectivity for  $\text{C}_{2+}$  products. Furthermore, the presence of rich nanograin boundaries significantly improved the catalytic stability, underscoring the critical importance of surface structures in Cu-based catalysts for achieving high  $\text{C}_{2+}$  selectivities during  $\text{CO}_2\text{RR}$ , especially under industrially relevant current densities [204].

Synthesis of methanol using Cu/ZnO/ $\text{Al}_2\text{O}_3$  catalysts on an industrial level has long been a mystery, and it is mainly because we are not certain of where the active sites are located or of how high up in  $\text{FeO}^*(z=1.0)$  exposed under these conditions with CaO (0001) facets could be for unit cell faceted Cu-Zn-like structures. A large-scale machine learning atomic simulation was harnessed to investigate thousands of reaction paths connected to both  $\text{CO}_2$  and CO hydrogenations on Cu-Zn surfaces predicted by thermodynamic calculations to be stable. This extensive study revealed several key insights. Firstly, under reaction conditions, Zn decorates at the step-edge of Cu(211) up to 0.22 monolayers (ML), indicating a dynamic surface modification process. Additionally, the investigation highlighted that  $\text{CO}_2$  hydrogenation overwhelmingly governs the methanol synthesis process. Moreover, the formation of  $[-\text{Zn}-\text{OH}-\text{Zn}-]$  chains on Cu(111) surfaces was observed under reaction conditions, suggesting the pivotal role of CO in the mixed gas environment [205]. Transitioning to the



selectivity of the carbon reduction reaction (CRR) aimed at producing  $C_{2+}$  products on oxidized Cu-based catalysts, it was discovered that the oxidation state of the surface Cu active site plays a pivotal role. At lower oxidation states, weak  $*CHO$  adsorption is observed at the Cu site, rendering the transition from  $*CO$  to  $*CHO$  unfavorable. As the oxidation state of Cu increases, the C-C coupling step shifts toward  $*CHO$  dimerization, and the  $*CO$  to  $*CHO$  transition becomes more favorable. Remarkably, the optimal oxidation state for CC coupling was identified to be around +0.5. Importantly, the selectivity for  $C_{2+}$  products can be tailored through doping with transition metals, which have the capacity to alter the Cu oxidation state. The presence of these metal dopants can be discerned through the utilization of artificial intelligence clustering based on physical characteristics [206]. Notably, one promising avenue for enhancing the electrocatalytic performance of copper involves promoting its surface with alumina ( $AlO_x$ ) clusters. This strategy has led to the development of highly selective and stable catalysts capable of catalyzing the transformation of  $CO_2$  into ethylene and other multicarbon compounds. The catalyst, formed from Cu-aluminum (Cu-Al) layered double hydroxide nanosheets and promoted with  $AlO_x$ , has demonstrated remarkable performance in this regard, offering potential solutions for sustainable carbon utilization and emissions reduction [207]. Table 9 shows an overview of different materials designed by following Cu surface engineering strategy for e- $CO_2R$  to different valuable products.

**Table 9:** By examining the details of the materials used the table investigates how surface engineering strategies, for copper impact  $CO_2R$ . It offers an analysis of electrocatalyst materials designed specifically to convert  $CO_2$ . The main focus lies on studying their properties selectivity in product formation and overall efficiency under conditions.

N	Material	electrolyte	V vs RHE	≈ FE %									R.f.
				H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	
1	La <sub>2</sub> CuO <sub>4</sub> NBs			38	10	4	43	--	--	--	--	--	[2]
2	La <sub>2</sub> CuO <sub>4</sub> NRs	0.1 M KHCO <sub>3</sub>	-1.1	55	7	8	25	--	--	--	--	--	[1]
3	bulk La <sub>2</sub> CuO <sub>4</sub>			18	84	2	--	--	--	--	--	--	[1]
4	Bulk CuO			--	--	8	--	--	--	--	--	--	
5	CuO NS			--	--	12	4	--	--	--	--	--	
6	1 % SnO <sub>2</sub> -CuO NS	0.5 M KHCO <sub>3</sub>	-1.0	--	--	12	21	--	--	--	--	--	[2]
7	3 % SnO <sub>2</sub> -CuO NS			--	--	15	24	--	--	--	--	--	[20]
8	5 % SnO <sub>2</sub> -CuO NS			--	--	13	13	--	--	--	--	--	[1]
9	10 % SnO <sub>2</sub> -CuO NS			--	--	11	8	--	--	--	--	--	
10	Cavity Cu			11	9	8	23	4	--	--	6	--	[2]
11	Solid Cu	1 M KOH	-0.7	31	7	19	15	3	--	--	2	--	[2]
12	Sn			--	--	--	--	37	--	--	--	--	[2]
13	H-SnO	0.5 M KHCO <sub>3</sub>	-0.95	--	--	--	--	40	--	--	--	--	[3]
14	SnO			10	20	--	--	41	--	--	--	--	[1]



15	SnO <sub>2</sub>	--	--	--	--	41	--	--	--	--	View Article Online DOI: 10.1039/D4MA00321G		
16	Ag-as prepared	63	2	8	--	18	--	--	--	6	--		
17	Ag-5 mint O <sub>2</sub> plasma	0.1 M KHCO <sub>3</sub>	-1.1	75	1	2	--	13	--	--	16	--	[2
18	Pt-as prepared	83	1	2	--	10	--	--	--	3	--	08	
19	Pt-5 mint O <sub>2</sub> plasma	91	1	1	--	8	--	--	--	2	--	]	
20	Cu <sub>2</sub> O	--	--	--	45	--	--	--	--	17	--	[2	
21	Cu <sub>2</sub> O(CO)	0.1 M KHCO <sub>3</sub>	-1.0	--	--	--	55	--	--	--	13	--	04
22	Cu <sub>2</sub> O(H <sub>2</sub> )	--	--	--	38	--	--	--	--	17	--	]	
23	Cu After 1 Hour	--	1.6	--	0.25	--	--	--	--	--	--	--	
24	Cu <sub>2</sub> O After 1 Hour	0.1 M KHCO <sub>3</sub>	-1.0	--	8	--	1.5	--	--	--	--	--	]
25	NH <sub>2</sub> -Cu After 1 Hour	--	22	--	12	--	--	--	--	--	--	--	]
26	NH <sub>2</sub> -Cu After 12 Hour	--	15	--	14	--	--	--	--	--	--	--	]
27	4H Au@Cu	0.1 M KHCO <sub>3</sub>	-1.06	18	52	--	14	9	--	--	--	--	]
28	4H/fcc Au@Cu	22	23	3	43	7	--	--	--	--	--	--	]
29	Od-Cu	--	--	--	38	--	--	--	--	--	--	--	]
30	AP-Cu	0.1 M KHCO <sub>3</sub>	-1.05	--	--	--	32	--	--	--	--	--	]
31	Hd-Cu	--	--	--	50	--	--	--	--	--	--	--	]

## 6.7. Doping strategy

Doping plays a role, in developing e CO<sub>2</sub>R. It involves intentionally introducing foreign atoms, such as metals or non-metals into the catalysts structure to modify its electronic and chemical properties. This technique is extremely significant, in the field of electrocatalysis because it allows for adjustment of the catalysts ability to react with and select CO<sub>2</sub> conversion products.

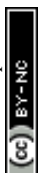
### 6.7.1. Metal doping

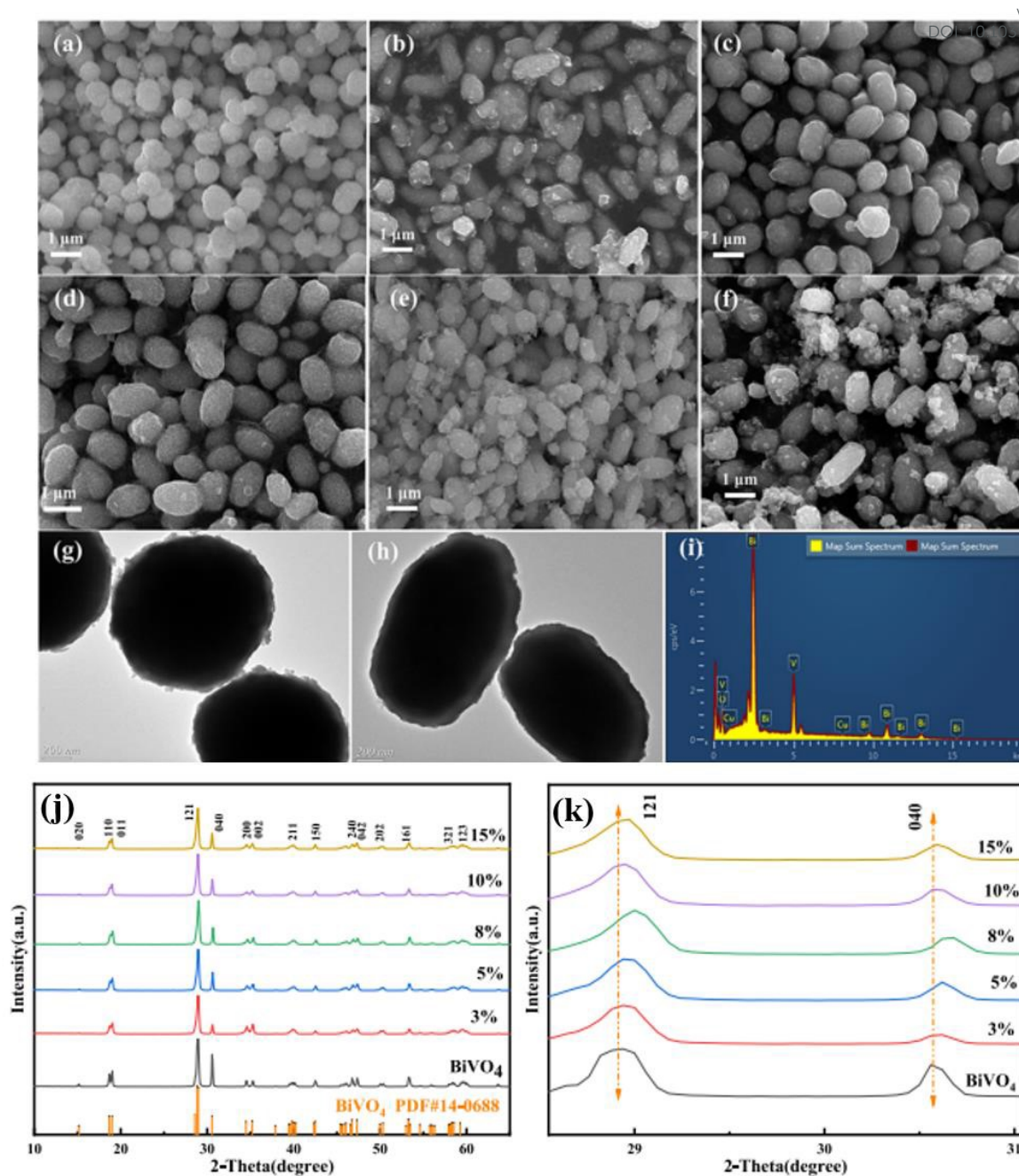
The strategy of incorporating metal into electrocatalysts for e CO<sub>2</sub>R is a method to enhance their performance. By introducing amounts of metal atoms into the catalyst structure we can modify its electronic properties, surface reactivity and how strongly it binds with CO<sub>2</sub> intermediates. Metal doping holds significance as it allows us to fine tune catalysts, for CO<sub>2</sub> conversion. Through selection of dopants researchers can adjust the catalysts' structure leading to stronger interactions with CO<sub>2</sub> molecules and intermediate species. This results in improved activity and selectivity effectively addressing the challenges associated with CO<sub>2</sub>R. There are methods available such as wet impregnation, chemical vapor deposition and atomic layer deposition that enable precise control over dopant concentrations when creating metal doped catalysts. This approach not contributes to the development of energy conversion technologies but also enhances our understanding of the fundamental catalytic mechanisms involved in CO<sub>2</sub>R reactions. Ultimately metal doping offers a pathway towards developing selective electrocatalysts that are essential, for a more sustainable and environmentally friendly future.



Xu et al. have investigated e-CO<sub>2</sub>R efficiency of Cu, Ni, and Mn doped CNTs. The overpotential values of Cu, Ni, and Mn doped CNT(8, 0) and CNT(6, 6) catalysts were found to be lower than those obtained with individual metal catalysts [210]. Additionally, the Ce-Cu nanoparticles (NPs) exhibited exceptional performance in e-CO<sub>2</sub>RR, particularly in the production of C<sub>2</sub>H<sub>4</sub> product, with Ce-Cu-2 NPs achieving an impressive 53% FE for C<sub>2</sub>H<sub>4</sub> at 150 mA cm<sup>-2</sup>. The addition of Ce, to Cu resulted in an increase in the number of sites for catalysis and a reduction in particle size. This played a role in enhancing the activity of Ce-Cu NPs. Experimental evidence, including XANES and XPS analyses indicated that the presence of Ce altered the state of Cu and caused the formation of OVs in regions. Furthermore in situ SERS experiments provided support to suggest that Ce doping helped stabilize CuO<sub>x</sub> species enabling adsorption of CO and subsequent interactions, between carbon atoms [211].

In order to explore how various compositions and structures of Cu-ZrO<sub>2</sub> catalysts affect the conversion of CO<sub>2</sub>, to CH<sub>3</sub>OH through hydrogenation a group of researchers led by Mao synthesized a range of catalysts. The catalytic performance of these catalysts was found to be influenced by factors, like OVs low valence copper species, the surfaces of ZrO<sub>2</sub> and the size of pores. Methanol selectivity was particularly impacted by the interface between low-valence Cu species and ZrO<sub>2</sub>, where OVs were abundant [212]. In another study, the research focused on the synthesis of Pd and Cu doped g-C<sub>3</sub>N<sub>4</sub> nanotubes with a porous structure. These nanotubes exhibited exceptional gas-phase CO oxidation activity and durability, alongside enhanced e-CO<sub>2</sub>R activity attributed to their high surface area [213]. In a different study, hydrothermal synthesis method was used to prepare a Cu-doped BiVO<sub>4</sub> catalyst for e-CO<sub>2</sub>R (Figure 20). This catalyst had excellent electrocatalytic performance, the highest FE<sub>HCOO</sub> of which was 87.15%, at -1.0 V versus RHE, and a maximum current density of -20.68 mA cm<sup>-2</sup> at -1.3 V versus RHE. The introduction of Cu was conducive to changing the electronic structure of BiVO<sub>4</sub> and produced more active adsorption sites. Also, in a photo-electrocatalytic system, a WO<sub>3</sub> nanotube array was made into a photoanode, which further improved the catalyst's performance. In the PEC system, formate yield was 3.3-fold higher at -0.9 V versus RHE than in the electrochemical system. Reflecting this fact was that there is a synergistic effect between photocatalysis and electrocatalysis [214].





**Figure 20:** The provided images (a-f) display SEM images of BiVO<sub>4</sub> samples doped with varying concentrations of copper (Cu), including pristine (a), 3% (b), 5% (c), 8% (d), 10% (e), and 15% (f) Cu-doped BiVO<sub>4</sub>. TEM images of undoped BiVO<sub>4</sub> (g) and BiVO<sub>4</sub> doped with 8% Cu (h). The sample being referred to is EDS of 8% Cu-doped BiVO<sub>4</sub> (i). The study also examines the XRD pattern of pristine BiVO<sub>4</sub> and various proportions of Cu-doped BiVO<sub>4</sub>. Reproduced with permission from Ref. [214] Copyright 2023, Elsevier.

A remarkable C<sub>2+</sub> FE of 76.4% was found for Cu-Al MONFs at a high current density of 600 mA cm<sup>-2</sup>, demonstrating their superior ability in the electrocatalytic reduction of e-CO<sub>2</sub>R to

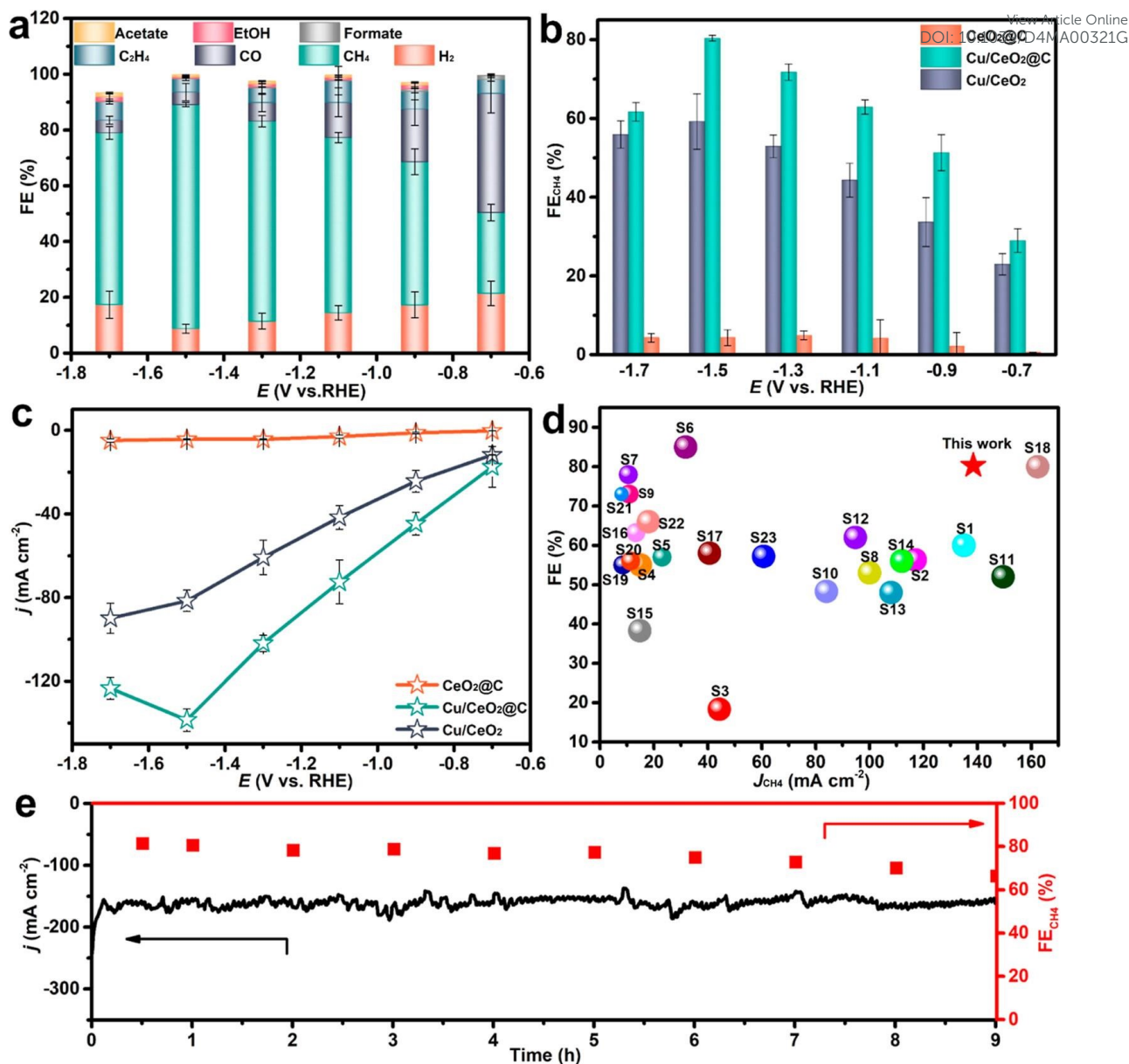




C<sub>2</sub>+ products. This marked a significant difference compared to CuO nanofibers, which exhibited weak C<sub>2</sub>+ products and excessive hydrogen evolution. The introduction of aluminum through doping modified the electronic structure of Cu, optimizing intermediate binding and CC coupling, while also creating a mesoporous structure during the etching process [215]. The study explored the in situ activation of Sn-doped Cu bimetallic electrocatalysts using pristine SnO<sub>2</sub>-decorated CuO nanoparticles. These catalysts demonstrated near-unity selectivity for CO<sub>2</sub> to CO conversion and maintained steady performance for up to 15 hours. Ex-situ electron microscopy, X-ray spectroscopy, and diffraction experiments shed light on the native shape and structure of these electrocatalysts. The in situ activated Sn-doped Cu electrocatalysts significantly enhanced the electrochemical conversion of CO<sub>2</sub> to CO, achieving a record Faradaic efficiency of 98% for CuO-0.4% Sn at a 0.75 V applied potential versus RHE. In situ Raman spectroscopy and XRD measurements revealed catalyst activation and adsorbed species, both dependent on time and potential. The findings indicated that clean surface CuO was rapidly reduced within seconds, paving the way for the development of high-performance, low-cost electrocatalysts by doping Cu-based electrocatalysts with post-transition metals [216]. Another study introduced Cu-doped CeO<sub>2</sub> nanocrystals coated with carbon, synthesized through a one-step pyrolysis of MOFs (Figure 21). These nanocrystals exhibited significant CH<sub>4</sub> partial current density of 138.6 mA cm<sup>-2</sup>, coupled with the highest  $FE_{CH_4}$  of 80.3%. The outstanding activity and selectivity of these nanocrystals were attributed to the synergistic effect of carbon encapsulation and the Cu/CeO<sub>2</sub> active component [217].

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**Figure 21:** The performance of  $e\text{-CO}_2\text{RR}$  was evaluated for various samples in the flow cell. The FEs of all the products for the  $\text{Cu}/\text{CeO}_2@\text{C}$  catalyst were measured at different applied potentials (a-b). The comparison of  $\text{CH}_4$  selectivity and  $\text{CH}_4$  partial current density among various samples (c). The  $\text{CH}_4$  selectivity and partial current density of  $\text{Cu}/\text{CeO}_2@\text{C}$  were compared to those of previously reported electrocatalysts (d). A long-term stability test was conducted on  $\text{Cu}/\text{CeO}_2@\text{C}$  at a potential of  $-1.5$  V for a duration of 9 hours (e). Reproduced with permission from Ref. [217] Copyright 2023, American Chemical Society.

Kim *et al.* demonstrated that the production rate of CO in a CoCu SAA with trace doping levels of Co atoms in Cu could be doubled compared to bare Cu. The material also displayed a high  $j_{\text{C}_2\text{H}_4}$  of  $282 \text{ mA cm}^{-2}$  at  $1.01$  V vs RHE in a neutral electrolyte. This alloy improved the



coverage of \*CO intermediates necessary for the synthesis of multicarbon products and accelerated the conversion of CO<sub>2</sub> to CO. The selectivity of CoCu SAA was enhanced toward ethylene over ethanol due to its active sites, which promoted the deoxygenation of \*HOCCH, resulting in a yield of 15.6% ethylene [218]. A high-performance Vo-CuO(Sn) catalyst containing OV<sub>s</sub> for e-CO<sub>2</sub>RR-to-CO conversion was produced using one-pot synthesis. The electrode's FE<sub>CO</sub> was greater than 95% across a broad range of operating potentials, and its partial current density for CO was 35.22 mA cm<sup>-2</sup>. The catalyst's high activity stability was further demonstrated by its ability to achieve an optimal 99.9 % FE at a low potential [219]. Through in situ structural rebuilding of a CuS-Bi<sub>2</sub>S<sub>3</sub> heterojunction precursor, a CDB electrocatalyst with an ampere-level current density and remarkable durability for e-CO<sub>2</sub>RR to formate was created. The catalyst's high conversion rate can be attributed to the electron-rich surface, a critical point both for its stability, and it can effectively smooth the kinetic barrier in the reaction [220].

In another investigation, researchers explored the Cu/Sn ratio for e-CO<sub>2</sub>RR to CO. In undertaking experiments to use Sn-decorated Cu electrodes, they found that the catalyst is believed to be a Cu-SnO overlayer. These studies showed that for particles shaped electrodes, the CO partial current density becomes saturated at high overpotentials and then decreases. However, this phenomenon was not seen in dendritic shaped electrodes. Dendrite morphology increased the concentration of CO<sub>2</sub> at the electrode surface, thus maintaining relatively constant FE<sub>CO</sub> over a wide potential range [221]. Another study explored electrochemically produced C<sub>2</sub>H<sub>6</sub> from CO<sub>2</sub> using a Cu<sub>2</sub>O-derived Cu working electrode and PdCl<sub>2</sub> in a 0.1 M KHCO<sub>3</sub> catholyte. The FE of up to 30.1% at a potential of 1.0 V was achieved. The process involved the initial reduction of CO<sub>2</sub> at Cu sites, followed by hydrogenation using PdCl<sub>x</sub> to produce C<sub>2</sub>H<sub>6</sub>. This approach required the presence of both copper and PdCl<sub>x</sub> sites for effective reduction, and the conversion efficiency of other palladium-based particles was found to be comparatively lower [222]. In another investigation, the study had revealed extremely porous Fe-CNPs through a process of amorphous SiO<sub>2</sub> coating, carbonizing, and acid leaching. The presence of these nanoparticles had greatly aided the e-CO<sub>2</sub>RR to CO process, with their FE in a 1.0 M KHCO<sub>3</sub> electrolyte reaching 98.8%. The research had also shown that the selectivity for e-CO<sub>2</sub>R had changed with porosity. Additional investigations on ZIF-derived carbon catalysts with Ni- and Co-doping had indicated that mesopores and macropores might enhance CO selectivity [223].

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Furthermore, Li *et al.* had demonstrated that doping Cu with p-block metal atoms could enhance e-CO<sub>2</sub>R to C<sub>2+</sub> products at high current density by inducing p-d orbital hybridization. At a potential of -1.07 V vs RHE, the CuGa catalyst had achieved a remarkable C<sub>2+</sub> FE of 81.5% at a current density of 0.9 A cm<sup>-2</sup>. The catalyst had maintained its high C<sub>2+</sub> productivity at 1.1 A cm<sup>-2</sup> and a FE of 76.9%. P-d hybridization between Cu and Ga had increased C<sub>2+</sub> selectivity, strengthened binding to the \*CO intermediate, reduced the reaction energy barrier for CC coupling, and guaranteed an abundance of catalytic reactive sites [224]. In a different study, Ni-substituted CuO and CuO catalysts had been synthesized using solution combustion synthesis. The research had demonstrated the significance of ionic nickel substitution through electrochemical analyses of Cu<sub>0.9</sub>Ni<sub>0.1</sub>O and Cu<sub>0.95</sub>Ni<sub>0.05</sub>O, both of which had exhibited exceptional redox-active behavior and higher electrocatalytic performance compared to CuO. Ionic connection between Ni<sup>2+</sup> and Cu<sup>2+</sup> had been crucial, as evidenced by the enhanced electrocatalytic activities of Cu<sub>0.9</sub>Ni<sub>0.1</sub>O and Cu<sub>0.95</sub>Ni<sub>0.05</sub>O in comparison to Ni metal and NiO-supported CuO. Steady-state chronoamperometry at a fixed potential of 0.2 V vs RHE in the CO<sub>2</sub> saturated electrolyte had also revealed the high activity and stability of nickel-doped catalysts. On Cu<sub>0.9</sub>Ni<sub>0.1</sub>O, the FE% values of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> had been roughly 3 and 4 times higher than those on CuO, significantly increasing the hydrocarbon selectivity [225]. In another investigation, Al-PILC doped with Cu<sup>2+</sup> ions and mixed metal pillars had both increased basal spacing, indicating effective dispersion of aluminum and copper. This increased surface area and volume had facilitated the adsorption and reduction of CO<sub>2</sub>. It is noteworthy that the CO<sub>2</sub>R reaction activity has been found to increase with the proportion of copper in the composite electrode [226]. Information on a number of representative catalysts prepared through metal doping to convert CO<sub>2</sub> into organic fuel is given in Table 10.

**Table 10:** The potential, selectivity, and efficiency of the product are also listed in the table. This information provides clues as to how CO<sub>2</sub> might be turned to other fuels by adopting Metal doping strategy.

N	Material	electrolyte	V		≈ FE %								Ref.	
			vs RHE		H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH		C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>
1	Ce-Cu-3 NPs	1 M KOH	100 mA cm <sup>2</sup>		--	35	--	47	--	--	--	--	--	
2	Ce-Cu-2 NPs			--	38	--	47	--	--	--	--	--		
3	Ce-Cu-1 NPs			--	42	--	38	--	--	--	--	--	[211]	
4	Cu Nps			--	69	--	12	--	--	--	--	--		
5	Cu-doped BiVO <sub>4</sub>	0.5 mol/L NaHCO <sub>3</sub>	- 1.0		7	--	--	--	16	--	--	--	--	
6	Cu-doped BiVO <sub>4</sub> -3%			3	--	--	--	48	--	--	--	--		
7	Cu-doped BiVO <sub>4</sub> -5%			4	--	--	--	67	--	--	--	--	[214]	
8	Cu-doped BiVO <sub>4</sub> -8%			1	--	--	--	87	--	--	--	--		
9	Cu-doped BiVO <sub>4</sub> -10%			5	--	--	--	60	--	--	--	--		



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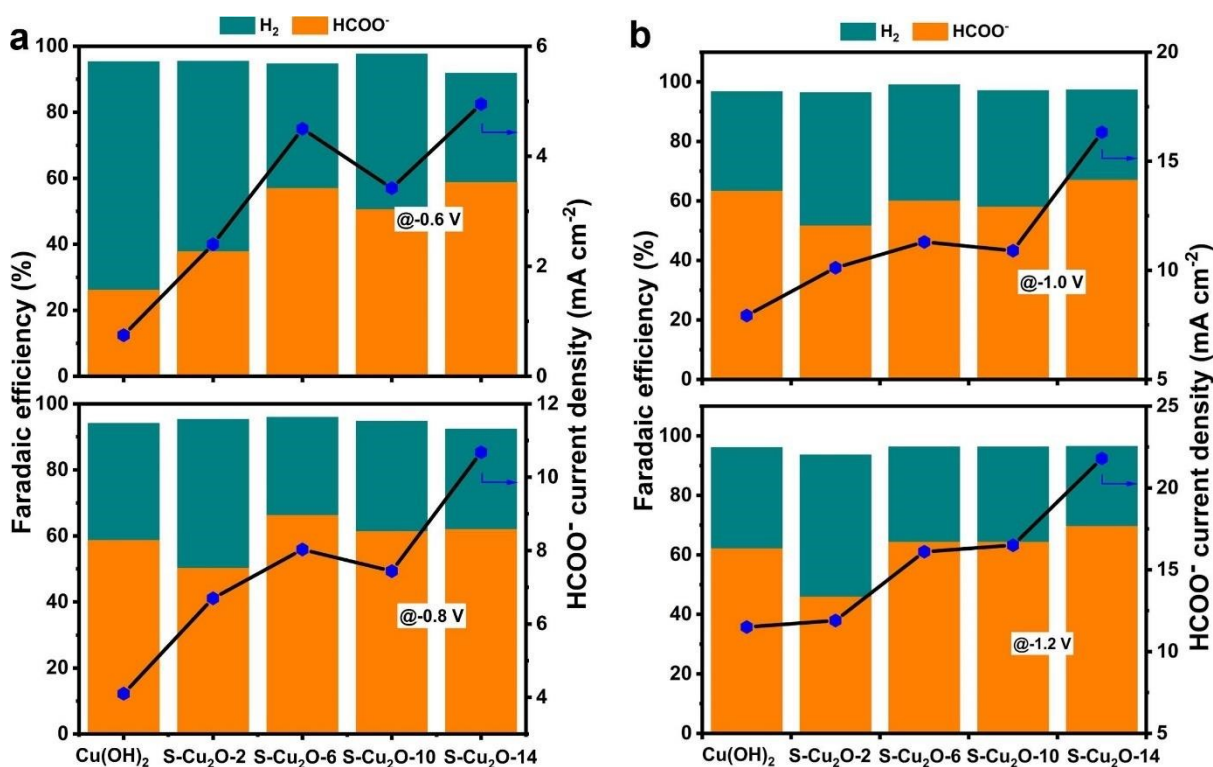
10	Cu-doped BiVO <sub>4</sub> -15%			16	--	--	--	45	--	--				
11	Cu <sub>3</sub> Al MONFs		100	12	51		18	9	--	--				
12	Cu ONFs	1 M KOH	mA cm <sup>2</sup>	30	13	1	19	15	--	--	13	2		[215 ]
13	Cu foil			57	19	--	9	13	--	--	--	--		
14	CuO			41	40	--	3	14	--	--	--	--		
15	CuO-0.4% Sn	0.1 M KHCO <sub>3</sub>	-0.75	3	98	--	--	--	--	--	--	--		[216 ]
16	CuO-0.6% Sn			17	77	--	--	--	--	--	--	--		
17	CuO-0.8% Sn			27	68	--	--	--	--	--	--	--		
18	CeO@C			--	--	5	--	--	--	--	--	--		
19	Cu/CeO@C	0.1 M KOH	-1.1	13	12	60	9	--	--	--	1	1		[217 ]
20	Cu/CeO			--	--	45	--	--	--	--	--	--		
21	Bare CuO			40	32		8	13	--	0.2	4	--		
22	0.2% Co-doped CuO		100	27	41	0.4	8	19	--	0.2	3	--		[218 ]
23	1.0% Co-doped CuO	1 M KHCO <sub>3</sub>	mA	27	32	--	9	26	--	0.2	3	--		
24	3.0% Co-doped CuO		cm <sup>2</sup>	30	26	0.3	5	35	--	0.1	2	--		
25	5.0% Co-doped CuO			50	6	0.3	7	27	--	0.5	5	--		
26	Vo-CuO(Sn)			9	91	--	--	--	--	--	--	--		[219 ]
27	Vo-CuO	0.1 M KHCO <sub>3</sub>	-1.03	15	75	--	2	8	--	--	--	--		
28	CuO			31	19	--	5	45	--	--	--	--		[220 ]
29	Cu-doped Bismuth	1 M KOH	-1.05	--	--	--	--	92	--	--	--	--		
30	Cu-Sn dendrite			18	75	--	2	4	--	--	2	--		
31	Cu-Sn particle			62	2	--	19	10	--	--	8	--		[221 ]
32	electropolished Cu	0.1 M KHCO <sub>3</sub>	-1.1	24	1	6	20	3	--	--	10	--		
33	Cu <sub>2</sub> O-derived Cu			85	1	1	10	1	--	--	8	--		
34	Cu <sub>2</sub> O-derived Cu with PdCl <sub>2</sub>			26	1	1	4	2	--	--	10	--		
35	Fe-CNPs-w/o				48	--	--	--	--	--	--	--		
36	Fe-CNPs			--	59	--	--	--	--	--	--	--		
37	Ni-CNPs			--	60	--	--	--	--	--	--	--		[223 ]
38	Ni-CNPs-w/o	1.0 M KHCO <sub>3</sub>	-0.88	--	45	--	--	--	--	--	--	--		
39	Co-CNPs			--	38	--	--	--	--	--	--	--		
40	Co-CNPs-w/o			--	15	--	--	--	--	--	--	--		
41	Cu	1 M KOH	1.1	38	10	--	29	2	--	--	19	--		
42	CuGa-II			20	2	--	46	2	--	--	22	--		[224 ]
43	Cu <sub>0.9</sub> Ni <sub>0.1</sub> O			25	2	29	13	--	--	--	--	--		
44	Cu <sub>0.95</sub> Ni <sub>0.05</sub> O	0.5 M NaHCO <sub>3</sub>	-0.2	28	3	19	8	--	--	--	--	--		[225 ]
45	CuO			35	3	9	5	--	--	--	--	--		

### 6.7.2. Non-metal doping

In terms of e-CO<sub>2</sub>R catalysts, incorporating metal elements is a crucial technique for raising their performance characteristics. Elements like nitrogen, sulfur or phosphorus are able to alter the behavior of the catalyst, making them essential in certain cases. CO<sub>2</sub>RR activity and selectivity depend on the right amount of non-metal doping. However, the method improves performance by making it easier to bind CO<sub>2</sub> molecules and their intermediates on catalyst surfaces, It also promotes more rapid electron transfer. This leads to better efficiency and

higher yields of methane or ethylene. Different techniques like chemical vapor deposition, ion exchange or solvothermal synthesis allow us to precisely control the distribution of metal dopants, within the catalysts structure. This strategy holds importance in advancing energy technologies by making electrochemical CO<sub>2</sub>R more efficient and sustainable while deepening our understanding of catalytic mechanisms at a molecular level.

In a study Yuan *et al.* explored novel materials for electrochemical reduction, they investigated Cu<sub>2</sub>S-X materials with varying starting morphologies (Figure 22). These materials were successfully transformed into S-Cu<sub>2</sub>O-X through electrochemical reduction. By strategically optimizing the electronic structure and increasing surface area via microstructure rebuilding, the efficiency of the catalyst in e-CO<sub>2</sub>R reduction and formate selectivity was significantly enhanced. Notably, the team demonstrated the ability of S-Cu<sub>2</sub>O-14 catalysts in formate synthesis, achieving an impressive 18% increase in current and a remarkable selectivity of 66.1% [227].



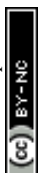
**Figure 22:** The  $FE_{HCOO^-}$  and partial current density were measured for  $Cu(OH)_2$ ,  $S-Cu_2O-2$ ,  $S-Cu_2O-6$ ,  $S-Cu_2O-10$ , and  $S-Cu_2O-14$  electrodes at various applied potentials ranging from  $-0.6$  V to  $-1.2$  V vs. RHE.com. Reproduced with permission from Ref. [227] Copyright 2023, Elsevier.

In a parallel manner, using a co-doping approach Dai *et al.* converted CO<sub>2</sub> to CH<sub>4</sub> using copper-based catalysts. The Cu-N<sub>2</sub>B<sub>2</sub> planar unit within their B-doped Cu-N<sub>x</sub> set-up was the main focus of concern. Incorporation of boron into the coordination layer facilitated methane synthesis by increasing the strength of binding towards both CO\* and CHO\* intermediates. This strategic



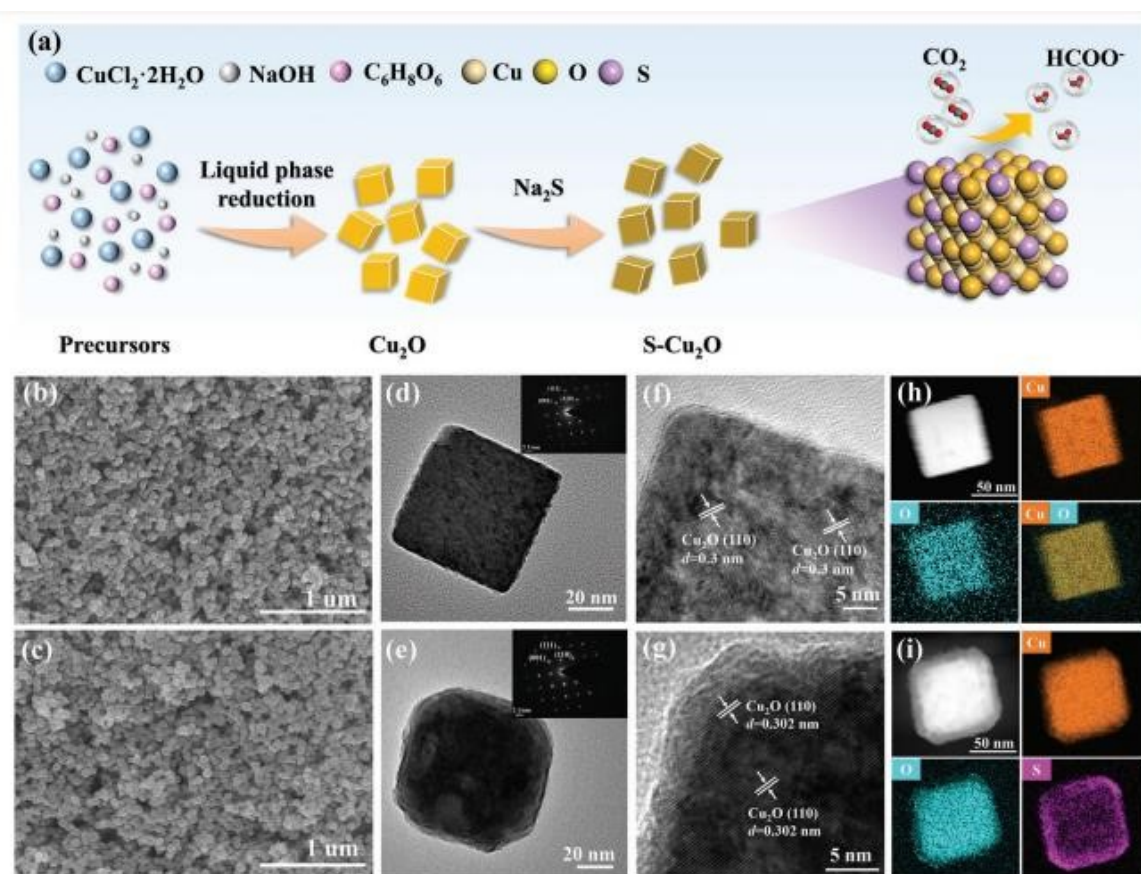
approach has been very successful, with the maximum FE for methane reaching as high as 73% and a peak methane partial current density of  $-462 \text{ mA cm}^{-2}$  at  $-1.94 \text{ V}$  vs. RHE. This demonstrates the excellent methane yield of the B-doped  $\text{Cu-N}_x$  material. The underlying reaction mechanism of the  $\text{Cu-N}_2\text{B}_2$  coordination complex was exactly analyzed, employing a comprehensive two-dimensional reaction phase diagram. This multifaceted investigation contributes valuable insights into the design and performance of copper-based catalysts for efficient and sustainable  $\text{CO}_2$  conversion processes [81]. Another research led to alternative breakthrough as scientists ingeniously dispersed Cu and Zn onto microporous N-doped carbon, resulting in a remarkable catalyst tailored for the e- $\text{CO}_2\text{R}$  to produce  $\text{CH}_4$ . The catalyst's performance metrics surpassed expectations, showcasing above-average efficiency, production rate, partial current density, and an exceptional 45-hour lifespan. The success was attributed to the unique combination of microporosity, excellent electrical conductivity, and the synergistic effect of Cu and Zn surface areas, which played pivotal roles in elevating its overall effectiveness [228]. Simultaneously, Zhang *et al.* delved into the electrocatalytic landscape, scrutinizing the potential of various SACs and DACs for  $\text{CO}_2\text{RR}$ . The results unveiled the secure attachment of Cu and Er atoms to the graphene framework, with ErNC emerging as the prime choice for facilitating the conversion of  $\text{CO}_2$  to CO. Among these options, CuErNC-I exhibited remarkable catalytic ability, favoring the production of CO molecules with minimal energy barriers [229]. In a parallel endeavor, scientists harnessed the power of a Cu electrocatalyst supported by Ni-Ni-C, facilitating the transformation of carbon dioxide into hydrocarbons. Through ammonia-driven deposition precipitation, they effectively deposited copper nanoparticles onto carbon black and nickel-nitrogen-doped carbon substrates. The results, presented at potentials of  $-1.0 \text{ V}$  vs RHE, unveiled the impressive activity of these particles in driving the synthesis of methane and ethylene. Particularly notable, Cu nanoparticles supported by Ni-N-AC demonstrated a reduced  $\text{C}_1/\text{C}_2$  product ratio, leading to a tenfold increase in CO generation and a twofold increase in partial ethylene current density [230].

In a separate manner of investigation, Patra *et al.* observed a phenomenon of high selectivity for  $\text{C}_{2+}$  hydrocarbons in boron-doped CuO, achieved alongside a simultaneous reduction in overpotential requirements. The operational spectra of ATR-SEIRAS unveiled distinct CO intermediate species present on BCuO, attributed to the active sites of  $\text{Cu}^+$  and  $\text{Cu}^0$ . This nuanced insight was linked to the availability of multiple CO adsorption sites and heightened CO binding energy within BCuO [231]. In a separate advancement, Yang *et al.* introduced an innovative approach to  $\text{CO}_2\text{R}$  through the utilization of copper selenide nanocatalysts. This introduction marked a novel path to methanol synthesis, boasting exceptional FE and current density at remarkably low overpotentials [232]. Another study offered a method to fabricate Br-doped CuO multilamellar mesoporous nanosheets on Cu foam for e- $\text{CO}_2\text{R}$ . These nanosheets showcased a prolonged retention time for carbonaceous intermediates and provided



numerous active sites for CO<sub>2</sub> adsorption. Through the incorporation of Br ions, the electronic structure of CuO was transformed, inducing the formation of OVs and thereby amplifying CO<sub>2</sub> adsorption capacity. With a admirable FE of 53.3%, the optimized Br<sub>1.95%</sub>-CuO emerged as a catalyst of choice for driving the e-CO<sub>2</sub>R to C<sub>2</sub>H<sub>5</sub>OH [233]. Saxena *et al.* demonstrated that CuCo<sub>2</sub>Se<sub>4</sub> was a highly selective catalyst for converting carbon dioxide into carbon-rich, high-value compounds. It generated acetic acid and ethanol at low potentials and formic acid in trace amounts at high potentials [234].

Another study highlighted a high-performance e-CO<sub>2</sub>RR electrocatalyst (ONCuO) sustaining good selectivity for the C<sub>2+</sub> product over time. Utilizing oxide-derived CuO and heteroatom doping, oxygen-assisted nitrogen doping on CuO resulted in defects such as OVs and grain boundaries. The selectivity for the C<sub>2+</sub> product was 77%, and ONCuO remained stable for 22 hours [235]. Ma *et al.* revealed that sulfur-modified Cu<sub>2</sub>O electrocatalysts could provide more targeted product dispersion (Figure 23). The selectivity of these electrocatalysts for formate was extremely sensitive to the orientation of the Cu<sub>2</sub>O crystal faces. The improved S<sub>3</sub>-Cu<sub>2</sub>O-70 electrocatalyst displayed a formate efficiency of 90% and an extended lifetime [236].



**Figure 23:** The synthesis and subsequent characterization of a particular structure. Schematic representation of the process for preparing electrocatalysts (a). The SEM images of S<sub>0</sub>-Cu<sub>2</sub>O-70 (b) and S<sub>3</sub>-Cu<sub>2</sub>O-70 (c) are shown. TEM images of S<sub>0</sub>-Cu<sub>2</sub>O-70 and S<sub>3</sub>-Cu<sub>2</sub>O-70, along with their





corresponding SAED patterns as insets, are presented. The HRTEM images of  $S_0$ -Cu<sub>2</sub>O-70 (f) and  $S_3$ -Cu<sub>2</sub>O-70 (g) are shown. The elemental mappings for  $S_0$ -Cu<sub>2</sub>O-70 (h) and  $S_3$ -Cu<sub>2</sub>O-70 (i) are also shown. Reproduced with permission from Ref. [236] Copyright 2023, Wiley.

The mechanism of the e-CO<sub>2</sub>RR for the formation of highly selective formic acid was studied using sulfur-modified Cu electrodes. It was discovered that most sulfur existed in unstable forms, with the stability of individual sulfur atoms dependent on their immediate surroundings and symmetry. The study observed that CO\* coverage was up to 3.9 times higher than on clean Cu surfaces due to the significant adsorption of CO\* by sulfur atoms [237]. The selective production of formate using a sulfide-derived copper (SD-Cu) catalyst was attributed to stronger CO intermediate binding from subsurface sulfur atoms [238]. Tabel 11 provides an overview for evaluating electrochemical performance of different electrocatalysts designed by following non-metal doping strategy for conversion of CO<sub>2</sub> to sustainable fuel.

**Table 11:** In essence the table offers an overview of non-metal doping specifically engineered for sustainable CO<sub>2</sub> conversion. It focuses on evaluating electrocatalysts designed to facilitate conversion of CO<sub>2</sub> as depicted in the accompanying table. The research dives into the behavior of these tailored electrocatalysts providing valuable insights for advancing energy conversion applications with sustainability.

N	Material	electrolyte	V		≈ FE %								Ref.	
			vs RHE	H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>		
1	Cu(OH) <sub>2</sub>			37	--	--	--	61	--	--	--	--	--	
2	S-Cu <sub>2</sub> O-2			54	--	--	--	43	--	--	--	--	--	
3	S-Cu <sub>2</sub> O-6	0.1 M KHCO <sub>3</sub>	-1.2	35	--	--	--	63	--	--	--	--	--	
4	S-Cu <sub>2</sub> O-10			35	--	--	--	63	--	--	--	--	--	
5	S-Cu <sub>2</sub> O-14			33	--	--	--	65	--	--	--	--	--	
6	Cu-SAs/NC			--	--	11	--	--	--	--	--	--	--	
7	Zn-SAs/NC	KHCO <sub>3</sub>	-1.2	--	--	12	--	--	--	--	--	--	--	
8	CuZn-SAs/NC			--	--	70	--	--	--	--	--	--	--	
9	Ni-N-AC			48	52	--	--	--	--	--	--	--	--	
10	Ni-N-EC			46	46	--	--	--	--	--	--	--	--	
11	Cu-VC	0.1 M KHCO <sub>3</sub>	-1.07	--	3	12	14	12	--	--	--	--	--	
12	Cu-EC			--	3	22	15	8	--	--	--	--	--	
13	Cu-Ni-N-AC			--	10	15	30	--	--	--	--	--	--	
14	CuO			20	31	2	23	15	--	--	3	1	--	
15	B-CuO	1 M KOH	-0.6	13	35	2	32	7	--	--	4	1	--	
16	Cu <sub>2</sub> O			78	5	--	--	11	--	6	--	--	--	
17	Cu <sub>2</sub> S			43	20	--	--	17	--	19	--	--	--	
18	Cu <sub>2</sub> Se	0.5 M H <sub>2</sub> SO <sub>4</sub>		33	12	--	--	31	--	23	--	--	--	[2
19	Cu <sub>1.63</sub> Se(1/3)	[Bmim]PF <sub>6</sub>	-2.1.		2	--	--	21	--	78	--	--	--	32
20	CuSe	CH <sub>3</sub> CN-H <sub>2</sub> O	Ag/Ag <sup>+</sup>	35	28	--	--	22	--	19	--	--	--	]
21	CuS			63	15	--	--	10	--	12	--	--	--	
22	CuO			42	23	--	--	22	--	5	--	--	--	



23	Cu			62	20	--	--	10	--	3					
24	CuO			62	32	--	--	--	--	--					
25	Br1.95%-CuO	0.1 M KHCO <sub>3</sub>	-1.2	--	18	8		37	--	--	31				
26	CuCo <sub>2</sub> Se <sub>4</sub>	0.3 M NaHCO <sub>3</sub>	-0.9	2	--	--	--	26	--	17	24	26			
27	CuO			26	6	--	43	5	--	--	10	--			
28	5-N-CuO			58	8	--	24	24	--	--	3	--			
29	15-N-CuO			45	8	--	35	35	--	--	6	--			
30	25-N-CuO	0.1 M KHCO <sub>3</sub>	-1.0	38	6	--	38	38	--	--	7	--			
31	5-ON-CuO			23	8	--	49	49	--	--	9	--			
32	15-ON-CuO			24	5	--	54	54	--	--	9	--			
33	25-ON-CuO			21	5	--	52	52	--	--	10	--			
34	c-Cu <sub>2</sub> O			20	21	--	25	20	--	--	--	--			
35	t-Cu <sub>2</sub> O			23	18	--	32	18	--	--	--	--			
36	o-Cu <sub>2</sub> O	0.1 M KHCO <sub>3</sub>	-1.1	33	16	--	19	22	--	--	--	--			
37	S <sub>3</sub> -c-Cu <sub>2</sub> O			23	1	--	1	77	--	--	--	--			
38	S <sub>3</sub> -t-Cu <sub>2</sub> O			24	3	--	--	74	--	--	--	--			
39	S <sub>3</sub> -o-Cu <sub>2</sub> O			24	1	--	--	73	--	--	--	--			
40	N-Cu			18	11	--	48	1	--	--	19	--			
41	P-Cu			80	1	3	4	1	--	--	5	--			
42	S-Cu	KOH	1100	43	3	2	28	2	--	--	21	--			
43	O-Cu		mA cm <sup>-2</sup>	43	2	28	15	1	--	--	9	--			
44	Cu			53	3	1	23	3	--	--	11	--			
45	Cu-Foil			38	11	--	--	14	--	--	--	--			
46	SD-Cu1	0.1M KHCO <sub>3</sub>	-0.9	38	45	--	--	--	--	--	--	--			
46	S-DCu <sub>2</sub>			39	37	--	--	--	--	--	--	--			

## 6.8. Facet engineering approach

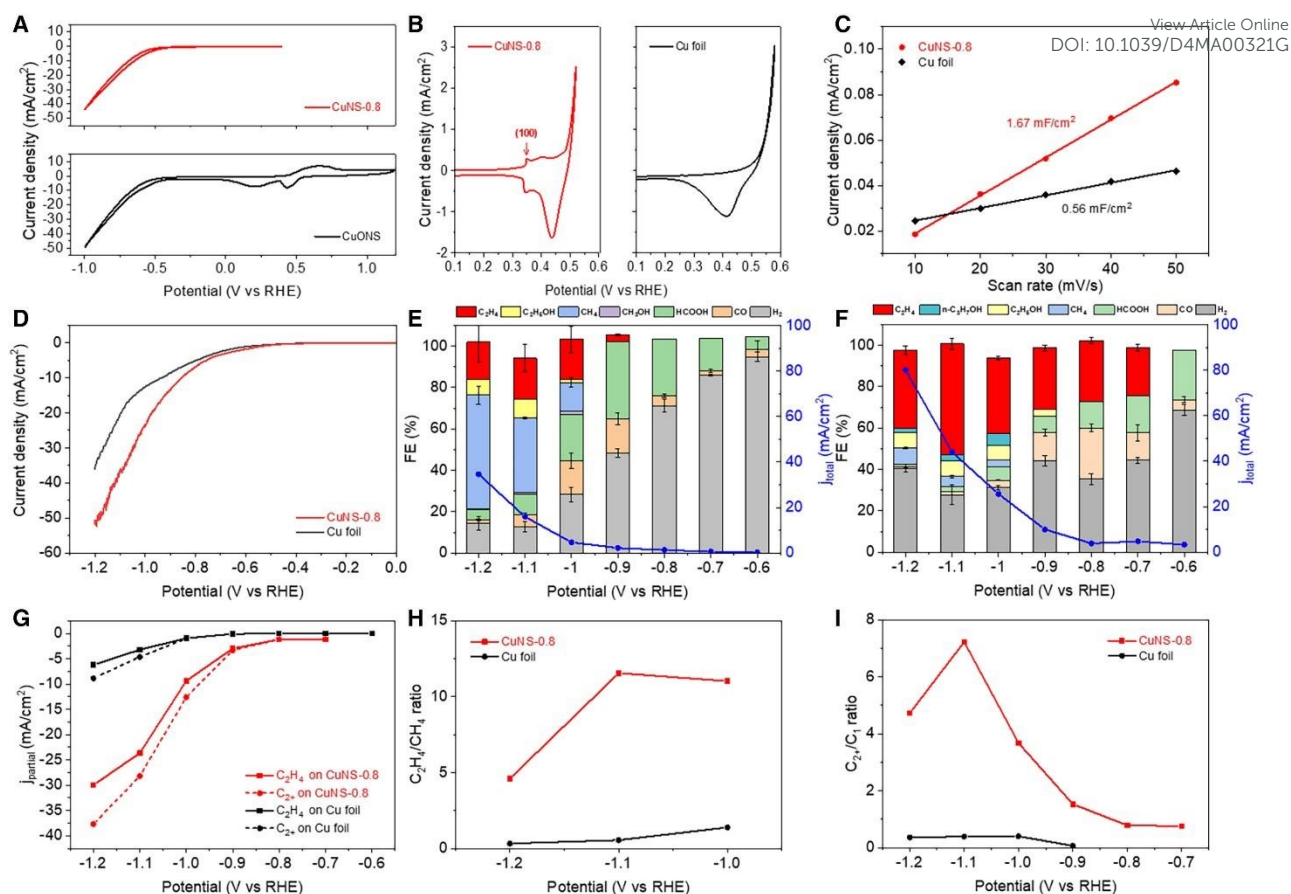
The facet engineering is particularly important in catalyst design for e-CO<sub>2</sub>R because it can control catalytic properties of designed materials. In this technique, faces of catalyst materials are responsible to the reactivity to desired reaction products. In the facet engineering approach, the basic idea is to pick crystalline faces for making catalysts that facilitate pathways while minimizing undesired side reactions. On a larger scale, this approach also optimizes the efficiency and cost-effectiveness of CO<sub>2</sub> capture and conversion systems. There are various methods available for incorporating the facet engineering strategy into CO<sub>2</sub>RR catalyst designs. A typical way is to synthesize catalyst materials on controlled growth so as to have specific crystal planes exposed, or by using templates to do it. Another approach would be to selectively etch facets already present in the catalysts, thereby bringing out the reactive site(s) of interest instead. Additionally surface modification techniques like depositing layers of metals or oxides, onto facets can be utilized to engineer the surface properties of the catalysts.



Researchers can tap into the power of facet engineering to fully utilize catalyst materials. This opens up opportunities, for developing selective catalysts for CO<sub>2</sub>RR, which play a vital role, in reducing greenhouse gas emissions and advancing sustainable energy conversion technologies.

Gao *et al.* have introduced a novel approach to immobilize ionic liquid on Cu, forming a collaborative "Cu-ionic liquid heterointerface" for e-CO<sub>2</sub>RR. The process involves dissolving Cu<sup>2+</sup> and AFIL in H<sub>2</sub>SO<sub>4</sub> electrolyte, directing their positive ions toward the GDL cathode, and embedding the deposited Cu. This embedding effect enhances Cu(100) production and incorporates more AFIL due to AFIL's capping influence. Consequently, Cu-IL/GDL exhibits smaller Cu particles with embedded AFIL, resulting in a lamellar particle structure. Operating under a total current density of 73.59 mA cm<sup>-2</sup> at 1.17 V vs RHE, this synergistic interaction between Cu and AFIL yields high selectivity for C<sub>2</sub> products, notably C<sub>2</sub>H<sub>4</sub> (40.67%). Especially, Cu-IL/GDL maintains relatively stable performance, with only a 3.8% decrease in current density observed after 5 hours of operation [240]. Yu *et al.* have developed copper nanosheet arrays on copper foils, which promote the formation of multi-carbon products, resulting in a remarkable multi-carbon to single-carbon ratio of 7.2 (Figure 24). Notably, potassium ions exhibit a fivefold higher adsorption density on the surfaces of copper nanosheets compared to pure copper foils [241].





**Figure 24:** Illustrates the electrochemical characteristics and efficacy of Cu foil and CuNS-0.8 (A). The CV curves of CuNS were obtained after reducing the CuONS at a potential of -0.8 V vs RHE (B). The OH- adsorption profiles of CuNS-0.8 and Cu foil are shown in the left and right panels, respectively (C). The plot shows the differences in charging current density between CuNS-0.8 and Cu foil as a function of scan rates (D). The LSV curves of CuNS-0.8 and Cu foil were obtained in a CO<sub>2</sub>-saturated 0.1 M KHCO<sub>3</sub> electrolyte using a scan rate of 10 mVs<sup>-1</sup> (E). This study examines the product distributions and current densities of Cu foil and CuNS-0.8 at various potentials. The error bars indicate the standard deviation of three measurements (F). The partial current densities of C<sub>2</sub>H<sub>4</sub> and C<sub>2+</sub> products were measured on CuNS-0.8 and Cu foil at various potentials (G). The study also investigates the variation in the C<sub>2</sub>H<sub>4</sub> to CH<sub>4</sub> ratio on CuNS-0.8 and Cu foil under different potentials (H). The study investigates the variation in the ratio of C<sub>2+</sub> products to C<sub>1</sub> products on CuNS-0.8 and Cu foil under different potentials (I). Reproduced with permission from Ref. [241] Copyright 2023, Elsevier.

Additionally, researchers have harnessed colloidal techniques to craft Cu-based nanocrystals with tailored dimensions, shapes, compositions, and interior structures. Importantly, their exceptional activity and selectivity for C<sub>2+</sub> during CO<sub>2</sub>R make them promising candidates for



electrocatalysis [242]. Shifting the focus to a different investigation, Mangione *et al.* investigates the geometry of copper electrodes in the context of e-CO<sub>2</sub>R, particularly over copper nanocubes. These cube-shaped copper catalysts, characterized by 100-degree terraces, 110-degree edges, and 111-degree corners, exhibit enhanced activity and selectivity in the production of ethylene. Nevertheless, the molecular mechanisms underlying this behavior have remained elusive. They also uncover a dual facet mechanism occurring at the interface of the 100 terraces and 110 edges, highlighting that the reactivity of shape-controlled nano-catalysts extends beyond facet selectivity observed in single crystals [243]. In a separate study examining the effectiveness of Cu(111) ML as a catalyst in the CO<sub>2</sub> hydrogenation process, it is revealed that the Cu(111) ML surface exhibits higher adsorption energies for intermediates compared to the bulk Cu(111) surface. This preference for the creation of the \*CO intermediate over the \*COH intermediate leads to selective hydrogenation to CH<sub>3</sub>OH. The study identifies two rate-limiting processes in CO<sub>2</sub> hydrogenation: the hydrogenation of CO<sub>2</sub> to COOH and the hydrogenation of CO to CHO. Notably, when compared to bulk Cu and Cu nanocrystal-based catalysts, the predicted working potential for selective CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH is lower on the Cu(111) ML surface [244].

In another study, Cu nano-catalysts were tested in a gas-fed flow cell, showcasing their facet-dependent selectivity. When compared to a standard H-cell setup, this configuration reduced hydrogen generation while increasing FE towards CO<sub>2</sub> reduction products. The interplay between the system and catalyst effects yielded cutting-edge product selectivity even at low applied voltage and high current densities. In 1M KOH, Cu cubes exhibited a mass activity of 700 mA mg<sup>-1</sup> and a selectivity of up to 57% for ethylene, while Cu octahedra achieved a selectivity of up to 51% for methane [245]. In a related effort, Kim *et al.* employed a modified CVD graphene growth technique to create a Cu catalyst featuring a high density of step-sites and a high-facet atomic arrangement. This catalyst stood out for its remarkable ethanol productivity, achieving a 40% FE at 0.9 V vs RHE. This represents one of the highest values reported for copper-catalyzed CO<sub>2</sub> conversion to ethanol. Furthermore, the fabrication process for this catalyst is simple and scalable [246].

In another investigation, the researchers explored the selectivity of Cu catalysts for CO<sub>2</sub>RR by employing Cu<sub>oh</sub> and Cu<sub>cub</sub> in a tandem arrangement with CO-producing Ag<sub>sph</sub>. Both Cu-Ag catalyst configurations exhibited greater selectivity and activity toward C<sub>2</sub>H<sub>5</sub>OH and C<sub>2</sub>H<sub>4</sub> compared to CH<sub>4</sub> and H<sub>2</sub>. Cu<sub>oh</sub>-Ag catalysts displayed higher selectivity for C<sub>2</sub>H<sub>5</sub>OH than Cu<sub>cub</sub>-Ag, with the C<sub>2</sub>H<sub>5</sub>OH to C<sub>2</sub>H<sub>4</sub> ratio reaching 2.4. DFT calculations and a simple model



revealed that active sites on the Cu<sub>cub</sub>-Ag catalyst preferred \*CH<sub>x</sub> and \*CO coupling, followed by subsequent reduction, while more extended facets continued to promote ethylene. Cu<sub>oh</sub>-Ag catalysts exhibited higher selectivity toward ethanol [247]. Furthermore, DFT simulations shed light on the facet-dependent nature of Cu electrode reactions, electrochemical potential, and product selectivity in CO<sub>2</sub>R. Cu(111) facilitates the synthesis of both methane and ethylene from a single CH<sub>2</sub> species by promoting the formation of a COH\* intermediate. In contrast, Cu(100) exhibits a preference for generating the CHO\* intermediate at lower potentials, leading to ethylene production through C-C coupling and the reduction of C<sub>2</sub> species. The competition between COH\* and CHO\* intermediates depend on the applied potential, impacting reaction rates and potential requirements, particularly involving the breaking of the C-OH bond. The partial reconstruction of the Cu(100) surface is proposed as a factor contributing to the observed differences between density functional theory predictions and electrokinetic studies [248].

In another research endeavor, Cu<sub>2</sub>O NPs with tunable morphology were synthesized for efficient electrocatalysis in the conversion of CO<sub>2</sub> to C<sub>2+</sub> products. Among various Cu<sub>2</sub>O catalyst forms, the o-Cu<sub>2</sub>O catalyst exhibited superior efficiency and current density for C<sub>2+</sub> generation during CO<sub>2</sub>RR. Impressively, it demonstrated stability during electrolysis at -1.1 V vs. RHE for 12 hours without destabilization. The abundance of active sites and the preservation of high-index faces in o-Cu<sub>2</sub>O led to increased C-C coupling during CO<sub>2</sub>RR [249]. Additionally, the synthesis of three distinct Ag-Cu JNS-100s was achieved through confined growth of Cu on one of six symmetrical faces of Ag NCs. Among these, the Ag<sub>65</sub>-Cu<sub>35</sub> JNS-100 demonstrated the highest  $FE_{C_2H_4}$  (54%) and  $FE_{C_{2+}}$  product (72%), showcasing its superior performance in CO<sub>2</sub>R towards C<sub>2+</sub> products. The observed shifts in C<sub>2</sub>H<sub>4</sub> production and the C<sub>2+</sub>/C<sub>1</sub> product ratio hold promise for improved CO<sub>2</sub>RR outcomes [250].

In a separate study, two nanoscale forms of copper molybdate (CuMoO<sub>4</sub> and Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub>) were synthesized, with their crystal structures significantly influencing their electrochemical properties. In a 0.1 M alkaline solution, Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> exhibited improved catalytic performance for both HER and OER, indicating its potential as a bifunctional water splitting catalyst in alkaline environments. The enhanced activity was found to be attributed by the presence of more active sites, potentially arising from OVs or the unique structure of Cu<sub>3</sub>Mo<sub>2</sub>O<sub>9</sub> crystals [251]. In another investigation, a new Cu<sub>2</sub>O NP film was produced using square-wave electrochemical redox cycling of high-purity Cu foils. This cathode achieved up to 98% FE for

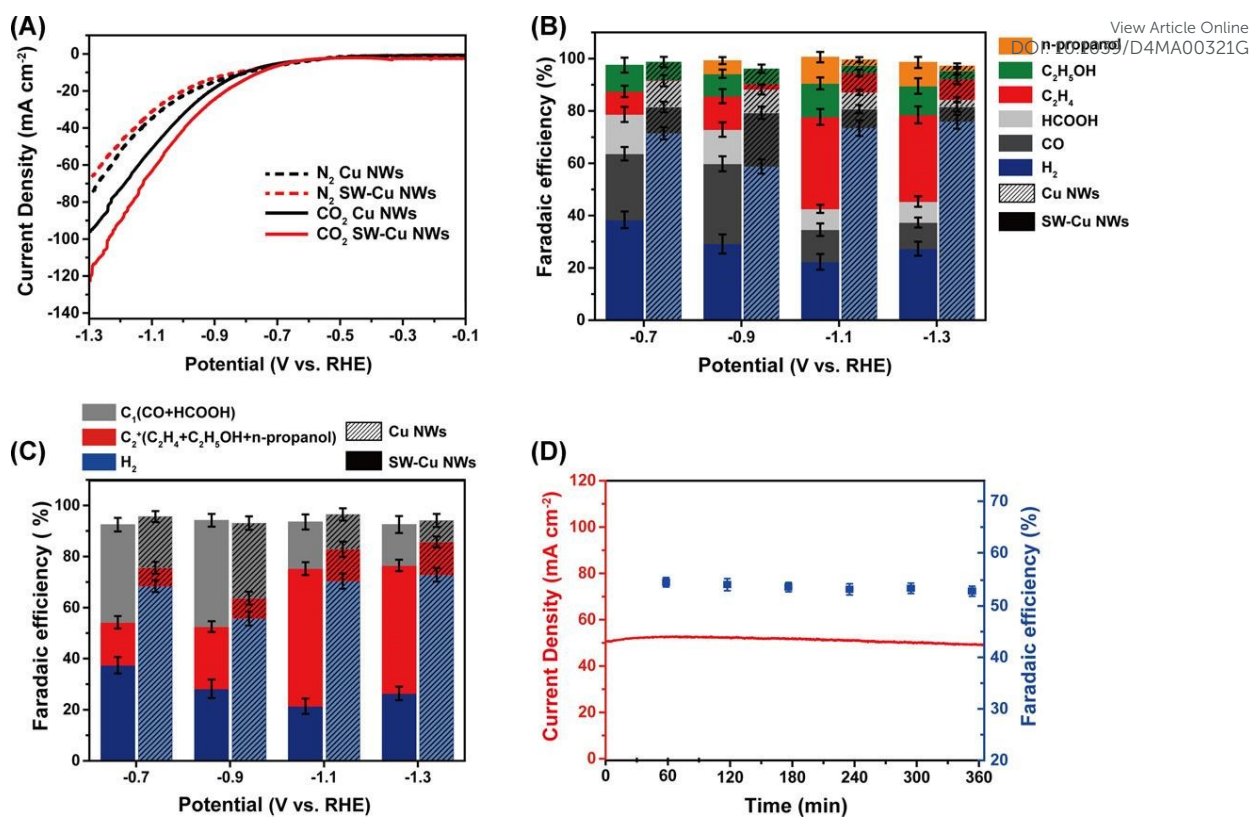


e-CO<sub>2</sub>R to practically pure formate under 45 atm of CO<sub>2</sub> in bicarbonate catholytes. A two-electrode high-pressure electrolysis cell, combined with a recently designed NiFe hydroxide-carbonate anode in KOH/borate anolyte, achieved a high energy conversion efficiency of up to 55.8% for continuous formate synthesis. Importantly, it was discovered that a Cu<sub>2</sub>O (111) oriented film was crucial for reducing CO<sub>2</sub> efficiently when producing formate [2].

Using density functional theory, Zheng *et al.* conducted an analysis of the e-CO<sub>2</sub>R on four distinct Pd<sub>3</sub>Au alloy bimetal catalyst surfaces. The findings demonstrated that the catalytic activity and selectivities were influenced by the catalysts' d-band populations, charge distributions, and morphologies. The Pd<sub>3</sub>Au (100) surface exhibited strong HER selectivity at low application potentials, while the Pd<sub>3</sub>Au (110) surface was more active in formic acid production. The (211) surface exhibited high selectivity for methanol synthesis during e-CO<sub>2</sub>RR [252]. In another study, a dynamic deposition-etch-bombardment approach was employed to regulate Cu(100) facets in e-CO<sub>2</sub>R, achieving a FE of 86.5% and a full-cell electricity conversion efficiency of 36.5% towards C<sub>2+</sub> products in a flow cell setup. The single-pass yield for C<sub>2+</sub> products from the electrode assembly system reached 13.2% at 12 A [253]. Additionally, in another investigation, the impact of high-index facets on e-CO<sub>2</sub>R was explored. Through SWP treatment, copper NWs catalysts with high selectivity for C<sub>2+</sub> products and excellent suppression of side reactions were synthesized (Figure 25). The FE of SW-Cu NWs at -1.1 V was found to be 57%, surpassing the FE of the original Cu NWs [254]. Table 12 offer a broad overview of different designed electrocatalysts for e-CO<sub>2</sub>RR following Facet engineering approach on Cu-based materials.

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**Figure 25:** LSV curves were obtained for Cu NWs and single-walled copper NWs (SW-Cu NWs) in  $N_2$  and  $CO_2$ -saturated aqueous 1 mol/L KCl electrolytes. The scanning rate used in this study was  $5 \text{ mVs}^{-1}$  (A). The FE of each product was measured on both Cu NWs and SW-Cu NWs electrodes at various applied potentials (B). The distribution of Cu NWs and SW-Cu NWs in terms of product distribution is examined. The gray  $C_1$  compound consists of CO and HCOOH, while the red  $C_{2+}$  compound is composed of  $C_2H_4$ ,  $C_2H_5OH$ , and n-propanol. The blue compound is  $H_2$  (C). The stability of SW-Cu NWs was tested at a potential of  $-1.1 \text{ V}$  vs. RHE (D). Reproduced with permission from Ref. [254] Copyright 2022, Wiley.

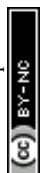
**Table 12:** This table digs deep into materials created through facet engineering: electrocatalyst. It focuses on their performance, describing how facet engineering can affect the distribution.

N	Material	electrolyte	V vs RHE	≈ FE %									
				$H_2$	CO	$CH_4$	$C_2H_4$	$HCOO^-$	$C_2H_5^+$	$CH_3OH$	$C_2H_5OH$	$C_2H_3O_2^-$	
1	GDL		--	90.5	--	--	2.5	--	--	--	--	--	--
2	IL/GDL		-1.18	82.9	--	--	2.6	--	--	--	--	--	--
3	Cu/GDL	KCl	-1.16	31.2	--	--	22.8	--	--	--	--	--	--
4	Cu-IL/GDL	$KHCO_3$	-1.17	15.7	--	--	40.6	--	--	--	--	--	--
5	Cu foil	0.1 M $KHCO_3$	-1.0	29	16	16	19	23	--	1	1	--	--





6	CuNS-0.8			32	2	3	37	7	--	--	9	--
7	A-CuNWs			7	1	3	56	--	--	--	--	--
8	H-CuNWs	0.5 M KHCO <sub>3</sub>	-1.02	12	4	3	50	--	--	--	--	--
9	Cu <sub>sph</sub>		-0.79	47	4	6	24	3	--	--	3	--
10	Cu <sub>cub</sub>		-0.75	12	10	3	60	2	--	--	3	--
11	Cu <sub>oh</sub>	0.1 M KHCO <sub>3</sub>										
11	Cu <sub>oh</sub>		-0.96	40	10	40	5	2	--	--	--	--
12	Cu film	0.1 M KHCO <sub>3</sub>		20	2	55	10	5	--	--	2	--
13	Wrinkled Cu			30	2	32	10	5	--	--	5	--
14	Cu film		-1.2	10	2	32	24	3	--	--	30	--
15	Wrinkled Cu	0.1 M KCl		15	2	32	23	8	--	--	30	--
16	Cu <sub>oh</sub>			39	3	15	10	8	--	--	7	--
17	Cu <sub>oh</sub> -Ag			32	50	--	2	2	--	--	--	--
18	Ag			38	52	--	--	--	--	--	--	--
19	Cu <sub>cu</sub>	0.1 M KHCO <sub>3</sub>	-1.1	22	3	13	32	13	--	--	5	--
20	Cu <sub>cu</sub> -Ag			20	55	1	8	--	--	--	--	--
21	Ag			38	52	--	--	--	--	--	--	--
22	o-Cu <sub>2</sub> O			25	7		34	13	--	--	15	--
23	d-Cu <sub>2</sub> O			27	5	3	19	29	--	--	9	--
24	c-Cu <sub>2</sub> O	1.0 M KCl	-1.1	28	8	2	15	32	--	--	9	--
25	Ag <sub>65</sub> -Cu <sub>35</sub> JNS-100			18	22	4	52	14	--	--	--	--
26	Ag <sub>50</sub> -Cu <sub>50</sub> JNS-100			16	23	1	54	16	--	--	--	--
27	Ag <sub>25</sub> -Cu <sub>75</sub> JNS-100	0.1 m KHCO <sub>3</sub>	-1.0	25	21	1	34	22	--	--	--	--
28	0.5h-SW-Cu <sub>2</sub> O/Cu @ 1 atm CO <sub>2</sub>			68.9	1	8.9	--	16.1	--	--	4.9	--
29	0.5h-SW-Cu <sub>2</sub> O/Cu @ 45 atm CO <sub>2</sub>	0.5 M KHCO <sub>3</sub>	-1.04	8.4	1	--	--	79.4	--	--	3.7	--
30	0.5h-SW-Cu <sub>2</sub> O/Cu @ 60 atm CO <sub>2</sub>			16	1	--	--	81.2	--	--	1	--
31	HRS-Cu	0.1 M KHCO <sub>3</sub>	-0.95	10	1	2	53	--	--	--	22	--
32	Cu NWs			78	2	--	8	1	--	--	2	--
33	SW-Cu NW	1 M KCl	-1.1	28	10	--	32	4	--	--	10	--



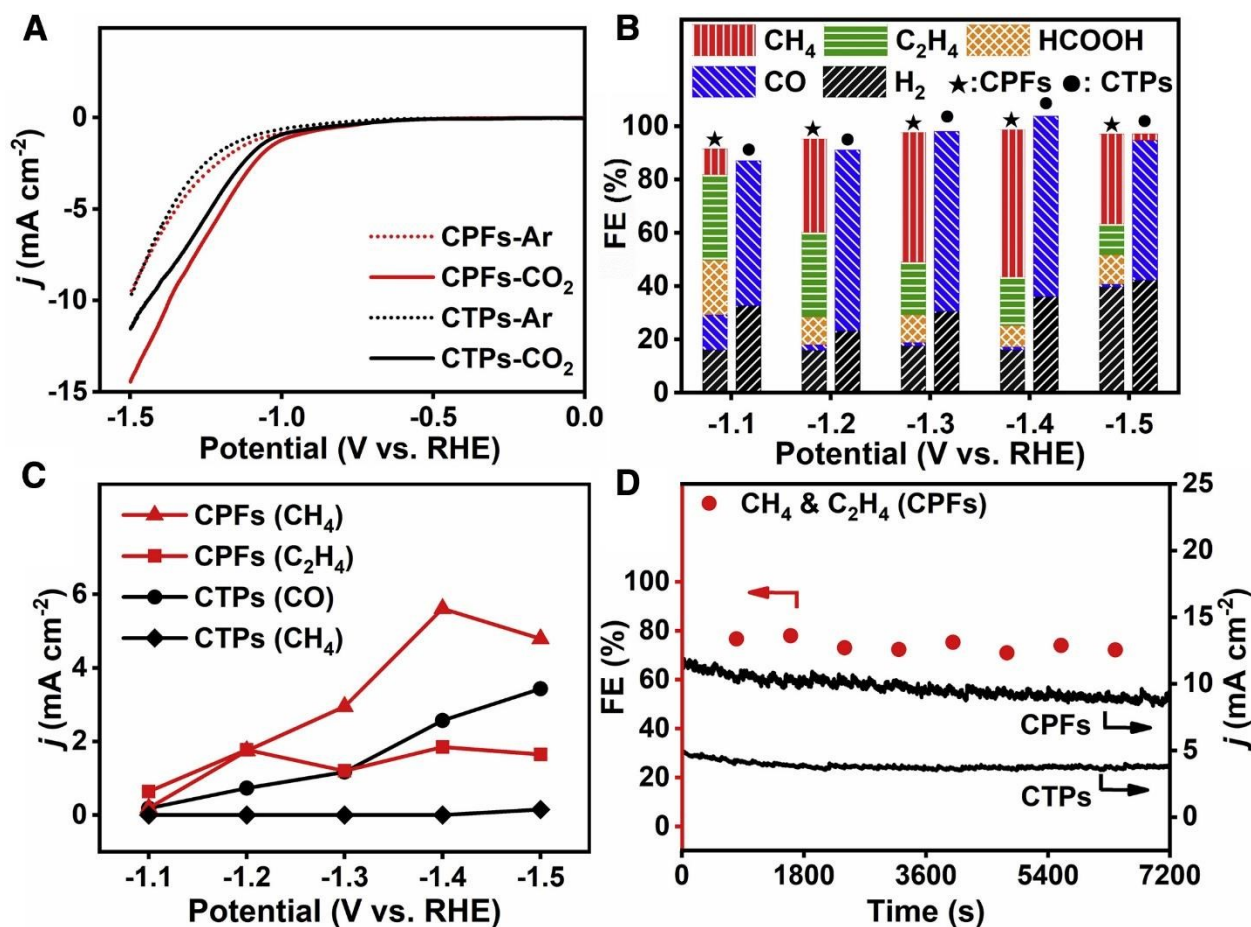
## 6.9. Coordination engineering approach

In the design of e-CO<sub>2</sub>RR catalysts, coordination engineering has taken on great importance as a means of achieving control over the behavior of the materials involved. This approach works through influencing the coordination environments surrounding metal atoms in catalyst structures. Coordination environment manipulation, however, can have a great effect on reaction rate and selectivity. Accordingly, the importance of coordination engineering lies in its potential to fine-tune the binding energies of CO<sub>2</sub> and reaction intermediates so as to steer the pathways of reactions. These coordination sites designed by scientists are able to be observed as selective for specific e-CO<sub>2</sub>R products. However, to implement the coordination engineering strategy for designing electrocatalysts, there are several methods that can be employed. One used approach involves designing coordination polymers where the coordination environment around metal centers might be set up via ligand choices and metal ions in the medium. Another technique involves modifying surfaces using techniques like layer deposition, which allows for controlled deposition of catalytically metal atoms onto support materials enabling the creation of well-defined sites, for coordination reactions. Furthermore, when two distinct metals are deliberately combined the creation of catalysts can result in improved performance by leveraging synergistic effects. By employing coordination engineering techniques, we can effectively optimize CO<sub>2</sub>R catalysts thereby promoting the advancement of sustainable carbon capture and utilization technologies and facilitating the transition, towards a low carbon future.

In a comprehensive exploration of e-CO<sub>2</sub>R, multiple Cu-doped ZIF-8 samples were synthesized. These Cu-doped ZIF-8 catalysts exhibited excellent selectivity for methane and carbon monoxide, with the highest  $FE_{CH_4}$  achieved by Cu30%ZIF-8 at -1.6 V vs. Ag/AgCl. Furthermore, it demonstrated a peak current density of -40 mA cm<sup>-2</sup> at -2.1 V vs. Ag/AgCl, indicating high catalytic efficiency [259]. Furthermore, copper (II) bis-triazine bipyridine complex supported on carbon black was designed by Garcia *et al.* for e-CO<sub>2</sub>R. The electrocatalytic performance of the catalyst was monitored using differential mass spectrometry. They exposed the simultaneous production of methanol, formic acid, formaldehyde, carbon monoxide, and methane, indicating that the catalyst lacked product selectivity. Optimal results, with a FE of around 22%, were achieved with both a 2.5% and a 5% composition of the Cu complex on carbon black, making them suitable for polymeric



electrolytic reactor fuel cell applications [260]. Furthermore, a separate investigation showcased the potential of porphyrin-based catalysts for CO<sub>2</sub> conversion. For this, a molecular Cu-porphyrin built porous framework demonstrated an excellent FE of 73.6%, indicating the promise of porphyrin-based catalysts in CO<sub>2</sub> conversion (Figure 26). Interestingly, this system produced only carbon monoxide as a hydrocarbon on the Cu-porphyrin support. Abundant copper-active sites efficiently absorbed CO<sub>2</sub>, and finite-element modeling highlighted the importance of isolating CO intermediates for hydrocarbon production [261].



**Figure 26:** e-CO<sub>2</sub>R performance of carbon-based transition metal catalysts (CTPs) and carbon-based precious metal-free catalysts (CPFs) was evaluated by LSV curves at a scan rate of 10 mV s<sup>-1</sup> in both Ar and CO<sub>2</sub>-saturated solution (A). The FEs of various products (B). The partial current densities of various products (C). The FE and current density of CPFs and CTPs were measured at a potential of 1.4 V versus RHE (D). Reproduced from Ref. [261] Open access article, Elsevier.

Furthermore, the research proposed the utilization of the generalized coordination number (GCN) as an activity descriptor for e-CO<sub>2</sub>RR on Cu surfaces. This approach established linear



scaling relations between CO<sub>2</sub>RR intermediates and GCN at various surface sites, including cavities, step edges, twists, and adatoms. The activity-GCN volcano plot was employed to calculate the theoretical overpotential limit on Cu surfaces, revealing that overpotentials exceeding 0.12 V could not be reduced by surface engineering alone. It was suggested that dimerized surfaces might minimize the overpotential for converting CO<sub>2</sub> to methane. Adatom surface engineering showed potential for reducing CO<sub>2</sub>RR overpotentials while inhibiting competitive HER [262]. In a complementary effort, Zhou *et al.* have proposed the optimization of cobalt-nitrogen functionalized materials for CO<sub>2</sub>R processes through coordination engineering. This approach involved constructing a volcano diagram to assess activity levels in relation to CO adsorption energies. The study revealed that the absence of bonding in Co-O bonds, in contrast to Co-C or Co-N bonds in cobalt-centered motifs, contributed to increased catalytic activity. Moreover, the variation in vacancy formation energy of the cobalt atom emerged as a predictive factor for catalytic activity [263].

Besides, another experiment showed that porous hollow copper microspheres (H-Cu MPs) were produced by combining the properties of EDTA-2Na to chelate ions and their natural ability to self-assemble. The adsorption of EDTA anions induced modifications in the geometrical structure and electronic distribution of H-Cu MPs, facilitating the selective production of ethene [264]. In a related development, the Cu<sub>2</sub>O@Cu-MOF system was created through in-situ etching, dissolving, and restructuring, resulting in a hybrid catalyst for the e-CO<sub>2</sub>R. The system exhibited an impressive overall FE of 79.4%, particularly excelling in forming hydrocarbon products, notably CH<sub>4</sub>. The remarkable FE ratio of 3.89 for CH<sub>4</sub> to C<sub>2</sub>H<sub>2</sub> underscores the excellent selectivity of this catalyst [265]. Moreover, the results of another investigation unveiled the potential of Cu catalysts with varying Sn molar ratios for CO<sub>2</sub>RR. Cu/Sn catalysts containing less than 1.5% Sn exhibited higher FE in CO production, while maintaining nearly identical FEs in hydrocarbon production. Notably, the Cu/Sn-1.5 sample achieved a substantial CH<sub>4</sub> partial current density of -27.5 mA cm<sup>-2</sup> at -1.25 V vs RHE [266]. Furthermore, the research demonstrated the remarkable e-CO<sub>2</sub>R to C<sub>2</sub>H<sub>4</sub> facilitated by a crystalline CuPc/C catalyst, which exhibited both high selectivity and reactivity. The crystallinity of CuPc was identified as a critical factor for efficient and selective C<sub>2</sub>H<sub>4</sub> synthesis [267].

In a related study, crystalline single-chain models (Cu-PzH, Cu-PzCl, Cu-PzBr, and CuPzI) were constructed to investigate product selectivity during e-CO<sub>2</sub> in a flow cell. Predictions indicated different selectivities for CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> due to variations in the lengths and dihedral



angles between bi-copper atoms, which were contingent on the coordination microenvironment. Cu-PzH, at 1.0 V and a high current density, exhibited the highest  $FE_{C_2H_4}$  (60%) among all materials, while Cu-PzI, under the same conditions, showed the highest  $FE_{CH_4}$  (52%). These selectivity differences were found to be due to the synergistic effects between surrounding catalytic active sites and the adsorption ability of the catalytically active center on critical reaction intermediates. [268]. Furthermore, excellent performance in selective  $CO_2R$  into  $C_2$  compounds has been demonstrated when using a metal-azolate frameworks with a tetranuclear copper(I) cluster as a catalyst for e- $CO_2R$ . The multinuclear copper cluster in CuBPZ, which may encourage C-C coupling to create  $C_2$  chemicals, is believed to be responsible for the observed performance [269]. In a complementary effort to enhance the selectivity of e- $CO_2R$  to  $CH_4$ , Zhang *et al.* developed a single crystal of a copper(II) complex containing hydroxy groups, known as 5,10,15,20-tetrakis(3,4-dihydroxyphenyl)porphyrin copper(II) (Cu-PorOH). Cu-PorOH was found to serve as a highly efficient heterogeneous electrocatalyst for catalyzing the e- $CO_2R$  to methane. The hydroxy groups within Cu-PorOH construct solid three-dimensional frameworks and stabilize intermediate species, resulting in a remarkable FE of 51.3% for  $CH_4$  and a substantial partial current density of  $23.2 \text{ mA cm}^{-2}$  at 1.5 V vs RHE in H-cell [270].

Additionally, the research highlights that ligand-protected Cu-hydride nanoclusters, such as  $Cu_{32}H_{20}L_{12}$ , exhibit exceptional selectivity for e- $CO_2R$  at modest overpotentials. When copper clusters contain negatively charged hydrides, HCOOH becomes the preferred reduction product due to its lower overpotential compared to CO. However, at low overpotentials, hydrogen evolution competes more favorably than the lattice hydride process. Electrochemical studies of the  $Cu_{32}H_{20}L_{12}$  cluster support these predictions, indicating that HCOOH is the dominant product at low overpotential, while hydrogen production becomes more prominent at higher overpotentials [271]. In a related effort to enhance the activity and stability of GDE for  $CO_2$  gas diffusion electrolysis, a hydrophobic molecular functionalization was incorporated into the Cu catalyst layer. This modification enabled strong-current electrolysis without flooding, due to the 1-octadecanethiol-modified Cu catalyst layer on the GDE. The modified GDE exhibited robust  $C_{2+}$  FEs of over 70.0% in the current density range of 100 to  $800 \text{ mA cm}^{-2}$ , with a peak  $FE_{C_{2+}}$  of 85.2% at  $800 \text{ mA cm}^{-2}$  [272]. Another study aimed at enhancing e- $CO_2R$  to acetic acid, Xiao *et al.* have developed helical porphyrinic MOF CuTCPP on the surface of  $Cu(OH)_2$  nanoarrays. Electrodeposition was employed to create the nanoarrays on Cu foil, followed by immersion in a TCPP solution to assemble the chiral



HCuTCPP@Cu(OH)<sub>2</sub> nanoarrays. The electrocatalytic results demonstrated a high FE<sub>Acetic acid</sub> of 26.1% at a potential of -1.6 V vs. Ag/Ag<sup>+</sup>, surpassing the performance of nHCuTCPP@Cu(OH)<sub>2</sub> (19.8%) [273].

In a related research effort, the feasibility of e-CO<sub>2</sub>R into valuable alcohols was investigated. The study employed an elongated and fluorinated porphyrin structure to single out three model bicentric copper complexes, elucidating the relationship between their structure, properties, and performance. It was found that complexes with strong intramolecular tension and coordination asymmetry exhibited more active Cu centers. The hybrid structure of a Cu cluster and a partly reduced O-containing hexaphyrin ligand enabled the production of up to 32.5% ethanol and 18.3% n-propanol from CO<sub>2</sub> [274].

In other research, a method was used to generate ultra-stable copper dendrites (Cu CF) with a high FE<sub>C<sub>2</sub></sub>. The Cu CF was found to have FE<sub>C<sub>2</sub></sub> of 90.6%. The partial current density of this value is 453.3 mAcm<sup>-2</sup>. In the experiment, stable operation at a large industrial current of 10A was proved. A 400-hour continuous electrolysis obtained in their synthesis worked at 800 mA. The formation of a coordination compound was credited with having solved the problem. It generates a Cu(II) carboxylate on the surface of Cu CF, ensuring the stability of the Cu<sup>+</sup> state and the material's hydrophobicity [275]. Furthermore, the electrocatalyst is critical to obtaining and managing product selectivity in e-CO<sub>2</sub>R. In their study, two types of 2D MOFs were investigated copper naphthalenedicarboxylate (Cu-UNDC) and copper benzenedicarboxylate (Cu-UBDC) to see how their ligand environment affected their selective properties and themselves. When ligand modifications were made, the MOF structure was altered, as well as the electrical environment around the copper center. This resulted in changes to product selectivity. The research team found that ligand modifications changed the structure of the MOF and thereby also its electrical environment around the center of the copper - which affected product selectivity. Under light exposure, Cu-UNDC had a  $[[FE]](C_2)$  of 24.3%, and Cu-UBDC 26.2% [276]. In addition, Han et al. combined the traditional HKUST-1 layout using the atomic layer infiltration (ALI) method to control the determining conditions at the Cu metal location. When Zn-O-Zn sites were added uniformly to HKUST-1, its FECO increased significantly from 20-30% to 70-80%. This change was made by reinforcing contact bonds and thus increasing the enthalpy of CO<sub>2</sub> adsorption, as evidenced by density functional theory simulations [277].



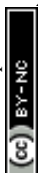
In another study related to the e-CO<sub>2</sub>R to high-energy-density C<sub>2+</sub> products, the creation of carbon-carbon bonds was explored, particularly the OC-COH coupling pathway over the CO dimerization pathway. Density functional theory simulations in this study demonstrated that the adsorption of \*CO coupled with their hydrogenation species, \*COH, took precedence over CO dimerization on low-coordinated copper sites, where the \*CO binds were enhanced. Remarkably, at 300 mA cm<sup>-2</sup>, the researchers achieved a FE<sub>C<sub>2</sub></sub> of 77.8% using a fragmented Cu catalyst with an abundance of low-coordinated sites [278]. In a separate study, Cu<sub>2</sub>SnS<sub>3</sub> nanoplates were synthesized and shown to be formate-selective over a wide potential and current range. When tested in a flow cell with a gas-diffusion electrode, the thiocyanate-capped Cu<sub>2</sub>SnS<sub>3</sub> nanoplates exhibited a maximum formate FE of 92% and partial current densities of up to 181 mA cm<sup>-2</sup>. The high formate selectivity was attributed to favorable adsorption of HCOO\* intermediates on cationic Sn sites, which were electrically regulated by thiocyanates coupled to neighboring Cu sites [279].

Furthermore, the research evaluates the performance of MOFs for the e-CO<sub>2</sub>RR, contrasting those based on square-pyramidal CuO<sub>5</sub> nodes with those based on square-planar CuO<sub>4</sub> nodes. With a FE of 56% and a current density of 11.4 mA cm<sup>-2</sup> at 1.4 V vs RHE, the MOF (Cu-DBC) built from CuO<sub>5</sub> nodes and catechol-derived ligands demonstrates excellent performance in the e-CO<sub>2</sub>R to CH<sub>4</sub>. On the other hand, Cu-HHTP and Cu-THQ are two additional MOFs that only produce CO as a reduced product. The study also shows that the CuO<sub>5</sub> active sites can effectively hydrogenate CO into CH<sub>4</sub> because the energy levels of metal d-orbitals in the square-pyramidal CuO<sub>5</sub> site are higher than those in the square-planar CuO<sub>4</sub> site, leading to the formation of CH<sub>4</sub> rather than CO [280]. Moreover, oxide-derived Cu (OD-Cu)-type catalysts was designed by Lu *et al.* with Improved C<sub>2+</sub> production may result from Cu sites that are undercoordinated. Undercoordinated Cu sites have not been investigated for their stability in alkaline e-CO<sub>2</sub>R environments. Different crystalline phases and Sr/Cu ratios in strontium copper oxide catalysts were prepared. The C<sub>2+</sub> FE of a SrCuO<sub>2</sub> tetragonal phase catalyst is 53%, demonstrating its remarkable selectivity for C<sub>2+</sub> products. SrCuO<sub>2</sub> catalysts can keep or recover oxidized Cu species after being subjected to reductive e-CO<sub>2</sub>R conditions, as shown by ex situ X-ray absorption spectroscopy [281]. The different electrocatalysts designed by following coordination engineering approach are summarize in accordance to their CO<sub>2</sub> conversion to different valuable products in table 13.



**Table 13:** In this overview the table discusses designed electrocatalysts for CO<sub>2</sub>R that utilize coordination engineering techniques. It investigates their performance. Evaluates how these techniques impact product selectivity and efficiency across various reaction conditions.

N	Material	electrolyte	V		≈ FE %								Ref.
			vs RHE	H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	
1	Cu <sub>30</sub> %ZIF-8			84	7	1	--	--	--	--	--	--	[259]
2	Cu <sub>20</sub> %ZIF-8	0.1 M KHCO <sub>3</sub>	-1.2	80	8	2	--	--	--	--	--	--	[259]
3	Cu <sub>10</sub> %ZIF-8			82	8	--	--	--	--	--	--	--	[259]
4	1 % Cu Complex			--	--	--	--	--	--	9	--	--	[259]
5	2.5 % Cu Complex			--	--	--	--	--	--	21	--	--	[259]
6	5 % Cu Complex	----	-1.2	--	--	--	--	--	--	13	--	--	[282]
7	10 % Cu Complex			--	--	--	--	--	--	20	--	--	[282]
8	20 % Cu Complex			--	--	--	--	--	--	19	--	--	[282]
9	CPFs	0.1		18	12		31	20	--	9	--	--	[283]
10	CTPs	KHCO <sub>3</sub>	-1.1	33	55	--	--	--	--	--	--	--	[283]
11	H-Cu MPs	0.1 M KHCO <sub>3</sub>	-0.91	22	4	17	50	4	--	--	--	--	[264]
12	Cu <sub>2</sub> O@Cu-MOF			--	--	62	17	--	--	--	--	--	[284]
13	Cu-MOF	0.1 M KHCO <sub>3</sub>	-	--	--	35	11	--	--	--	--	--	[284]
14	Cu <sub>2</sub> O			--	--	3	42	--	--	--	--	--	[284]
15	Cu			22	16	12	12	--	--	--	--	--	[284]
16	Cu/Sn-0.5		-1.25	9	31	13	3	--	--	--	--	--	[266]
17	CuSn-1.5			7	43	15	3	--	--	--	--	--	[266]
18	Crystalline CuPC			--	5	5	26	--	--	--	--	--	[285]
19	Non-Crystalline CuPC	KHCO <sub>3</sub>	-1.6	--	28	2	6	--	--	--	--	--	[285]
20	Crystalline CuPC (Restored)			--	5	5	35	--	--	--	--	--	[285]
21	I-Cu-PzH			10	23	9	48	--	--	--	--	--	[286]
22	II-Cu-PzCl	1 M KOH	-1.1	22	20	18	30	--	--	--	--	--	[286]
23	III-Cu-PzBr			20	18	20	30	--	--	--	--	--	[286]
24	IV-Cu-PzI			22	14	39	20	--	--	--	--	--	[286]
25	CuBPZ	0.1 M KHCO <sub>3</sub>	-1.1	20	28	2	--	2	--	--	45	--	[287]
26	Cu-PorOH	KHCO <sub>3</sub>	-1.2	--	8	7	8	--	--	--	--	--	[288]
27	H-GDE	1.0 M KOH	100	13	10	1	26	2	--	--	38	--	[289]
28	Cu(OH) <sub>2</sub>			--	--	--	--	19	--	--	--	--	[273]
29	nH-CuTCPP@Cu(OH) <sub>2</sub>	----	-1.4	--	--	--	--	14	--	--	--	--	[273]
30	H-CuTCPP@Cu(OH) <sub>2</sub>			--	--	--	--	6	--	--	--	--	[273]
31	Hex-2Cu-O			13	28	--	4	27	--	--	7	--	[274]
32	Hex-2Cu-2O	0.1 M KHCO <sub>3</sub>	-1.0	45	--	--	5	33	--	--	--	--	[274]
33	Oct-2Cu			60	38	--	--	--	--	--	--	--	[274]





## 6.10. Site engineering approach

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Site engineering can be used to design e-CO<sub>2</sub>R catalysts by precisely controlling the catalytic sites on the surface of a material. In this method, the sites such as metal atoms, defects are selectively used. By doing that, reactivity and selectivity of the catalyst in reducing CO<sub>2</sub> into different products can be optimized. Researchers can enhance the ability of these catalysts to facilitate desired chemical transformations while minimizing side reactions by designing and engineering these sites. Such a level of control is needed for shaping catalysts to produce CO<sub>2</sub>RR products and, therefore, makes site engineering a powerful tool in developing sustainable energy conversion and carbon capture technologies. Many methods can be used to put the site engineering tactics into practice for designing CO<sub>2</sub>RR catalysts. The favored approach is to deposit metal nanoparticles or single metal atoms onto a support material to gain control over the sites. On the catalyst surface, pointed out earlier, defect engineering can also be considered as a form of site engineering. This strategy involves developing catalysts within a molecular framework that show promise for a defined and specific active site. Researchers can improve the efficiency of catalysts by tuning the arrangement and properties of these sites. As a matter of fact, it facilitates the design of catalysts, which produce CO<sub>2</sub>RR products that are indispensable in an energy-efficient use of captured carbon dioxide and response global demands to address the problem of climate change.

To enhance CO<sub>2</sub>RR performance under a range of calcination conditions, MOF Cu(btc) was designed with tunable valence states of Cu(II), Cu(I), and Cu(0) sites. Catalysts for the reactions of air, hydrogen, and nitrogen were all created using variations of the Cu/C-T-gas system. C<sub>2</sub>H<sub>4</sub> was generated by Cu/C-T-air catalysts, which may have been due to the presence of both Cu(I) and Cu(II) and an abundance of V<sub>O</sub>. After 12 hours, the Cu/C-450-air demonstrated remarkable CO<sub>2</sub>RR characteristics, with a  $FE_{C_2H_4}$  of 34.8% at 1.1 V vs RHE. Smaller grain size and a thinner carbon layer may have led to greater exposure to active sites and faster electron transport in the Cu/C-T-H<sub>2</sub> system, leading to the production of C<sub>2</sub>H<sub>4</sub>, while in the Cu/C-T-N<sub>2</sub> system, CH<sub>4</sub> was generated [290].

In parallel work, Liu *et al.* have provided a framework for exploring intrinsic activity differences between e-ND-Fe(II) and c-ND-Fe(II) in the context of CO<sub>2</sub>-to-CO conversion. Atomic Fe catalysts with changeable porosity architecture were synthesized via the pyrolysis of N-rich bimetallic Fe/Zn 2D ZIF, shedding light on the impact of ND configurations on the CO<sub>2</sub>RR activity of Fe-N<sub>4</sub> active sites. Electrochemical studies revealed that the concentration



of e-ND-Fe(II) in A-Fe@NG-Li<sub>x</sub>K<sub>y</sub> catalysts was positively correlated with CO<sub>2</sub>RR activity. DFT calculations and in situ ATR-IR spectroscopy studies demonstrated higher electron density surrounding e-ND-Fe(II), which reduced CO bonding on metal sites, favoring CO<sub>2</sub>RR. The optimized sample A-Fe@NG-Li1K<sub>3</sub> showed excellent performance, with a maximum FE<sub>CO</sub> of 95% [291]. Furthermore, Zhu *et al.* have optimized electrosynthesis pathways for selective fuel production by studying aqueous e-CO<sub>2</sub>R on Cu. Electrocatalysts with voltage and facet-dependent CO<sub>2</sub>R selectivities were devised and produced from nine large-area single-crystal Cu foils with different surface orientations [292]. Furthermore, the 2Bn-Cu@UiO-67 catalyst, doped with N-heterocyclic carbene (NHC) was designed and achieves the e-CO<sub>2</sub>R to CH<sub>4</sub> at a current density of 420 mA cm<sup>-2</sup> with an outstanding FE of 81%. The catalyst maintains a FE<sub>CH<sub>4</sub></sub> of greater than 70%, and it achieves a record-breaking turnover frequency of 16.3 s<sup>-1</sup> [293].

Moreover, Cheng *et al.* investigated the active sites of OD-Cu catalysts for e-CO<sub>2</sub>R to multi-carbon compounds. Utilizing molecular dynamic simulation and density functional theory computations, it describes realistic models of the OD-Cu surface and explores more than 150 surface locations. Ethylene formation is observed at planar-square sites and convex-square sites, while alcohol formation is favored at step-square sites due to the geometric influence of stabilizing acetaldehyde intermediates and destabilizing Cu-O interactions [294]. Furthermore, lamellae of copper phyllosilicate are created in this research with CuO particles that are uniformly scattered and hence readily reducible to Cu<sup>+</sup> and Cu<sup>0</sup>. Synthesizing a series of CuO/CuSiO<sub>3</sub> with varying Cu loadings yields Cu<sup>+</sup>-Cu<sup>0</sup> sites. On 20% Cu/CuSiO<sub>3</sub>, the e-CO<sub>2</sub>R activity is greatly improved, with a FE<sub>C<sub>2</sub>H<sub>4</sub></sub> of 51.8% and FE<sub>C<sub>1</sub>+C<sub>2</sub></sub> of 82% being attained. Activation of CO<sub>2</sub>, adsorption of \*CO, and C-C coupling are all shown to involve Cu<sup>0</sup> and Cu<sup>+</sup>, as calculated by in situ ATR-IR and DFT [295].

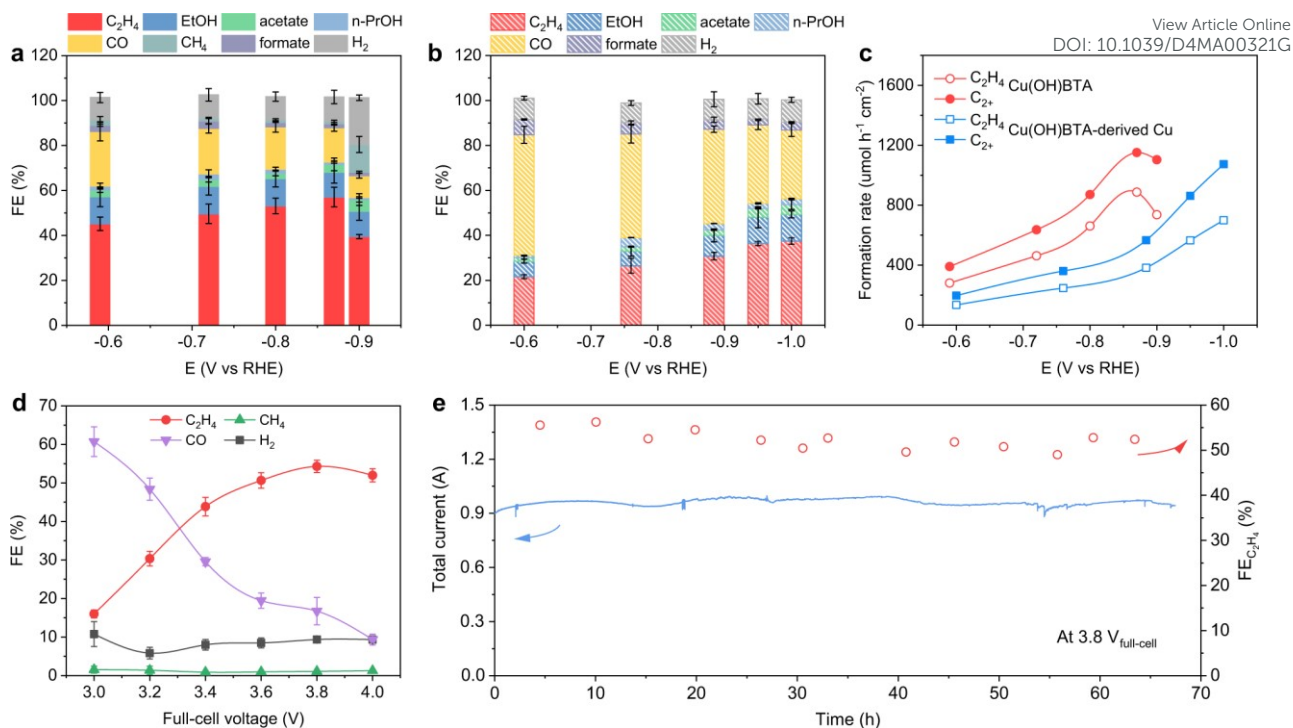
Furthermore, Guan *et al.* showed that a nitrogen-coordination technique can be used to evenly distribute single-atom Cu catalysts over nitrogen-doped carbon. Nitrogen in nitrogen-doped carbon frameworks with Cu-N<sub>x</sub> topologies promotes efficient dispersion and attachment of atomic Cu species. The pyrolysis temperature allows for fine-tuning of the doping concentrations and Cu-N<sub>x</sub> combinations. For C-C coupling to occur and C<sub>2</sub>H<sub>4</sub> to be produced, a very high concentration of Cu (4.9% mol) is required. The production of CH<sub>4</sub> as C<sub>1</sub> products is favored at low Cu concentrations due to the considerable distance between Cu-N<sub>x</sub> species [296]. Moreover, another research investigates physical vapor deposition as a viable method



for growing large-format Cu thin films intended for e-CO<sub>2</sub>R. These films epitaxially grow on Al<sub>2</sub>O<sub>3</sub>(0001), Si(100), and Si(111) substrates, each exhibiting a distinct out-of-plane orientation. X-ray pole figures reveal that Cu can be oriented in both low and high Miller index directions depending on the single-crystal substrate's orientation. In-situ structural investigations identify three distinct Cu surface structures. Electrochemical tests demonstrate that thin-film orientations with more undercoordinated sites exhibit higher activity and selectivity for C-C coupling. Cu(751), characterized by fewer nearest neighbors on the Cu(S)-[n(110) (100)] surface, achieved the highest oxygenate/hydrocarbon ratio at 0.89 V vs RHE [297].

Additionally, the creation of a conductive di-nuclear cuprous complex with a short CuCu contact, formed by combining 1H-[1,10]phenanthroline-2-one with Cu(I) ions, resulted in Cuophen. This complex demonstrated robust activity for the e-CO<sub>2</sub>R to C<sub>2</sub>H<sub>4</sub>, achieving a FE of 55.11% and a current density of 580 mA cm<sup>-2</sup>. Notably, a \*CO species bridged two copper ions, forming a stable intermediate transition state and facilitating C-C interaction due to the reduced CuCu distance [298]. In addition to this, the development of a novel single-site copper coordination polymer known as Cu(OH)BTA has made the e-CO<sub>2</sub>R using renewable electricity (Figure 27). This polymer demonstrates a C<sub>2</sub>H<sub>4</sub> selectivity 1.5 times higher than its metallic analogue and maintains a stable structure during the reaction. The presence of adjacent Cu in the polymer allows for the formation of a \*OCCHO intermediate after CO hydrogenation, acting as a dual site. These polymers enable full-device CO<sub>2</sub> electrolysis to run for 67 hours at an applicable current within a membrane electrode assembly [299].





**Figure 27:** The study investigated the FEs of various products at different applied potentials using Cu(OH)BTA (a) and Cu(OH)BTA-derived Cu (b) in a 1 M KOH electrolyte. The formation rates of C<sub>2+</sub> products and C<sub>2</sub>H<sub>4</sub> under various applied potentials using Cu(OH)BTA and Cu(OH)BTA-derived Cu in a 1 M KOH electrolyte. The measured the FEs of various gas products within the voltage range of 3.0-4.0 V using a membrane-electrode assembly (MEA) device. The electrosynthesis of C<sub>2</sub>H<sub>4</sub> was performed in a MEA with a geometric electrode area of 4 cm<sup>2</sup>. The catalyst maintains its overall current and ethylene FE for a duration of 67 hours. The error bars for the uncertainty in FE represent one standard deviation, which is calculated using three independent runs. Reproduced from Ref. [299] Open access article, Nature.

Moreover, a technique has been established to achieve the site-selective generation of AgPd nanodendrites on Au nanoparticles by using H<sub>2</sub>PdCl<sub>4</sub> to galvanically replace the Ag layers on Au@Ag nanoprisms and a coreduction process involving silver and palladium ions. The selectivity of AgPd nanodendrite deposition on Au nanoprisms is determined by the concentration of H<sub>2</sub>PdCl<sub>4</sub>. These nanoprisms exhibit a strong electrochemical activity for CO<sub>2</sub>R, particularly at the most favorable reduction potential for CO<sub>2</sub> at 0.18 V vs RHE [300]. Furthermore, a novel technique has been developed to create atomically scattered Fe-N<sub>5</sub> sites on defect-rich porous carbon nanofibers through electrospinning and annealing. The Fe-N<sub>5</sub>/DPCF electrocatalyst exhibits exceptional e-CO<sub>2</sub>RR, with a substantial j<sub>CO</sub> of 9.4 mA cm<sup>-2</sup>, high FE<sub>CO</sub> (>90%), and sustained stability even after 25 hours of electrolysis. This catalyst



operates reliably for an extended period and provides a high power density of  $1.3 \text{ mW cm}^{-2}$  [301]. Additionally, Varandili *et al.* have introduced Cu/CeO<sub>2-x</sub> heterodimers (HDs) to illustrate the synergistic effects at metal/metal oxide interfaces that enhance selectivity in the e-CO<sub>2</sub>RR. The Cu/CeO<sub>2-x</sub> HDs achieve up to 80% selectivity against CO<sub>2</sub>RR and 54% FE for methane at -1.2 V vs RHE, which is five times higher than in the case of physically mixed Cu and CeO<sub>2-x</sub> nanocrystals. In-situ and in-operando X-ray absorption spectroscopies reveal the partial conversion of Ce<sup>4+</sup> to Ce<sup>3+</sup> in the HDs during CO<sub>2</sub>RR [302]. Furthermore, to construct catalysts with high selectivity towards C<sub>2</sub> products in e-CO<sub>2</sub>R, a Cu foil kinetic model featuring numerous nanocavities and a larger reaction rate constant *k* is presented by Han *et al.* This model promotes the production of C<sub>2</sub>H<sub>4</sub> by increasing the concentration of adsorbed CO and decreasing the C-C coupling barrier for CO intermediates. The C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> ratio on commercial Cu foil treated with cyclic voltammetry is 4.11, aligning with this concept and representing an 18-fold increase compared to untreated Cu foil [303].

Further, Cu-based MOF as a catalyst was used by Zhu *et al.* with FE of 92%/88%, and the partial current density was 9.8/18.3 mA cm<sup>-2</sup> at a potential of 1.2/-1.3 V, making it the most active system for producing methane. The trigonal pyramidal Cu(I)N<sub>3</sub> produced on site acts as the electrochemical active site, stabilizing critical intermediates and suppressing HER [304]. Furthermore, three Cu-MOFs with varying copper(II) site distributions were reported. The FE of Cu<sub>1</sub> was four times higher than that of *FE*<sub>H<sub>2</sub></sub>, while the FE of Cu<sub>2</sub> was twice as high [305]. The different electrocatalysts and their e-CO<sub>2</sub>R products developed by site engineering approach are tabulated in table 14.

**Table 14:** The table provides an overview of electrocatalyst materials developed using site engineering strategies for CO<sub>2</sub>R. It thoroughly analyzes their characteristics with a particular emphasis, on understanding how site engineering influences the resulting products.

N	Material	electrolyte	V		≈ FE %								Ref.
			vs RHE	H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	
1	Cu/C-550-air			--	--	--	27	--	--	--	--	--	
2	Cu/C-450-air			--	--	--	35	--	--	--	--	--	
3	Cu/C-350-air			--	--	--	26	--	--	--	--	--	
4	Cu/C-550-N <sub>2</sub>			--	--	20	6	--	--	--	--	--	
5	Cu/C-450-N <sub>2</sub>	0.1 M KHCO <sub>3</sub>	-1.1	--	--	35	11	--	--	--	--	--	[306]
6	Cu/C-350-N <sub>2</sub>			--	--	12	25	--	--	--	--	--	]
7	Cu/C-550-H <sub>2</sub>			--	--	--	28	--	--	--	--	--	
8	Cu/C-450-H <sub>2</sub>			--	--	--	33	--	--	--	--	--	
9	Cu/C-350-H <sub>2</sub>			--	--	--	16	--	--	--	--	--	



10	Cu <sub>2</sub> S/CM	0.1 M KHCO <sub>3</sub>	-1.1	50	--	--	--	--	--	--	--	[307]
11	A-Fe@NG-Li1K <sub>3</sub>	0.5 M KHCO <sub>3</sub>	-0.75		22	--	--	--	--	--	--	[291]
12	Fe/Mn-N-C			33	65	--	--	--	--	--	--	
13	Fe-N-C	0.1 M KHCO <sub>3</sub>	-1.0	75	30	--	--	--	--	--	--	[308]
14	Mn-N-C			85	12	--	--	--	--	--	--	
15	N-C			68	10	--	--	--	--	--	--	
16	20% Cu/CuSiO <sub>3</sub>	0.1 M KHCO <sub>3</sub>	-1.1	16	14	4	53	--	--	--	8	[309]
17	Cu-N-C-800			--	--	3	9	--	--	--	--	[296]
18	Cu-N-C-900	0.1 M KHCO <sub>3</sub>	-1.0	--	--	7	1	--	--	--	--	
19	Cuophen	0.1 M KHCO <sub>3</sub>	-1.0	69	2	6	10	--	--	--	--	[310]
20	Cu(OH)BTA			35	10	1	42	2	--	--	8	[311]
21	Cu(OH)BTAdescribed Cu	0.1 M KHCO <sub>3</sub>	-0.9	10	43	--	30	5	--	--	2	
22	DPCF			--	82	--	--	--	--	--	--	
23	Fe-N <sub>x</sub> -PCF	0.5 m KHCO <sub>3</sub>	-0.7	--	50	--	--	--	--	--	--	[312]
24	Fe-N <sub>5</sub> -DPCF			--	63	--	--	--	--	--	--	
25	Cu (15 nm)/CeO <sub>2</sub> HDs			40	1	9	25	15	--	--	1	
26	Cu (24 nm)/CeO <sub>2</sub> HDs			25	16	12	31	4	--	--	--	[302]
27	Cu (36 nm)/CeO <sub>2</sub> HDs	0.1 M KHCO <sub>3</sub>	-1.1	20	5	40	18	1	--	--	--	
28	Cu (54 nm)/CeO <sub>2</sub> HDs			35	14	23	8	13	--	--	--	
29	Fe-N-C			65	43	--	--	--	--	--	--	
30	Ni-N-C			10	80	--	--	--	--	--	--	
31	Mn-N-C	---	-0.7	72	30	--	--	--	--	--	--	[313]
32	Co-N-C			92	10	--	--	--	--	--	--	
33	Cu-N-C			62	28	--	--	--	--	--	--	

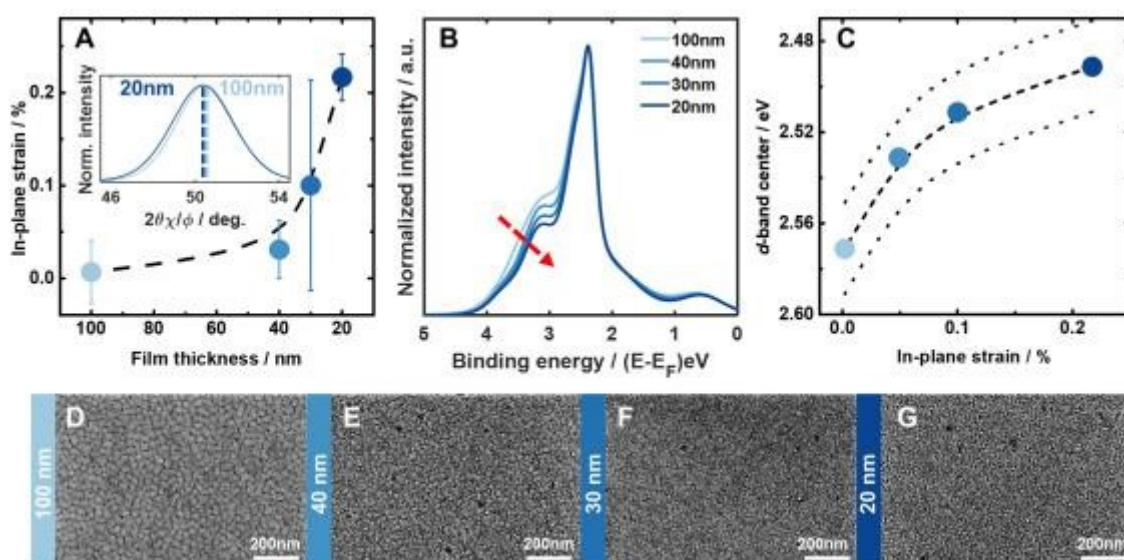
## 6.11. Strain engineering approach

The approach of strain engineering has become a strategy, in designing catalysts for e-CO<sub>2</sub>R. Its significance lies in the ability to finely adjust the properties of materials, especially copper and other metal catalysts to enhance CO<sub>2</sub>RR performance. By incorporating controlled strains into the crystal structure of catalyst materials researchers can manipulate the arrangement of atoms on the surface. This has an effect on the selectivity and activity of the catalyst allowing for the production of carbon-based products like ethylene or ethanol while minimizing unwanted byproducts. The goal of strain engineering is to improve the efficiency of CO<sub>2</sub>R by developing new catalyst formulations. Thus, it holds promise as a sustainable path toward energy solutions based on chemistry and also possible new carbon capture technologies. There is a way to practice strain engineering on CO<sub>2</sub>RR catalyst design. One common technique is nano-structuring through methods such as electrodeposition and chemical vapor deposition, these create nanomaterials with specific shapes and sizes. Another effective method is surface doping or alloying which involves introducing atoms or molecules onto the catalyst surface to



induce strain and alter its properties. Furthermore, subjecting the catalyst material to stress or pressure can induce strain, which has demonstrated potential in improving the performance of CO<sub>2</sub>RR.

Kim *et al.* have shown that CO<sub>2</sub> distribution on model-strained Cu(001) surfaces can be controlled using strain engineering (Figure 28). The kinetics of CO<sub>2</sub>R to single-carbon products are influenced by tensile strain, which moves the center of the d-band closer to the fermi level as the film thickness lowers. While C<sub>2+</sub> product activity remains stable, CO<sub>2</sub>R reduction kinetics slow down, leading to fewer single-carbon products. Increases in adsorption energy and surface coverage of CO and H are suggested by the greater d-band center, which improves selectivity for C<sub>2+</sub> products relative to CO and CH<sub>4</sub>. Hydrogen adsorption becomes more attractive as tensile strain rises, surpassing the faradic current for CO<sub>2</sub>R [314].



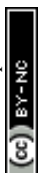
**Figure 28:** The study examines the structural properties of epitaxial Cu(001) on single-crystal Si(001). The in-plane strain at the surface was measured as a function of film thickness using grazing-incidence XRD. The inset illustrates the decrease in the angle of the Bragg peak as the film thickness decreases. The obtained He-I ultraviolet photoelectron spectroscopic valence band spectra. The d-band center from the ultraviolet photoelectron spectroscopy is examined as a function of in-plane strain. The 99% confidence interval is represented by dotted lines. SEM images of Cu(001) films with varying thicknesses were obtained. The thicknesses of the films are as follows: (D) 100 nm, (E) 40 nm, (F) 30 nm, and (G) 20 nm. Reproduced with permission from Ref. [314] Copyright 2021, American Chemical Society.



Additionally, Kang *et al.* have demonstrated the effectiveness of self-supported PS-Cu catalysts with tensile strain and a porous microstructure. These catalysts outperform Pt foil at high current densities and exhibit superior pH-universal catalytic activity for the HER compared to Cu NPs and Cu foam. Importantly, PS-Cu displays resistance to corrosion and remains stable over time [315]. Moreover, an analysis of the impact of water solvation and uniaxial lattice strain on CO<sub>2</sub>RR across Cu(211) and Cu(100) surfaces has been conducted by Du and An. The results reveal that tensile strain enhances the binding strength of COOH and CHO, while diminishing the binding strength of CO and COH. This phenomenon arises due to the distinct strain effects induced at the surface site by their respective binding arrangements. Notably, the study highlights the variability between implicit solvation corrections and explicit water solvation, which is crucial for accurately estimating the solvation effect on CO<sub>2</sub>RR [316].

Analyzing the pure ligand effect on Cu and the combined influence of ligand and strain effects on Cu, Maark *et al.* have investigated two types of bimetallic hetero-surfaces: Cu<sub>i</sub>/M<sub>j</sub>/Cu<sub>k</sub> sandwiched surfaces and Cu/M<sub>j</sub> overlayers. To mitigate the ligand impact independently, several strategies were employed, including moving the M layer deeper into the Cu lattice, placing two MLs of M directly below the top Cu layer, and combining these two strategies in the sandwiched surfaces. By doubling the number of Cu MLs in the overlayers, the ligand impact was effectively reduced. The research findings indicate that the ligand effect strengthens the binding energies of all adsorbates in Cu<sub>1</sub>/M<sub>1</sub>/Cu<sub>4</sub> and Cu<sub>1</sub>/M<sub>5</sub>, leading to an increase in overpotential for Rh and a slight decrease for Ni [317]. Furthermore, another study delves into the investigation of adsorption energies for critical intermediates in CO<sub>2</sub>R processes over core-shell type heterostructure catalysts. It explores the impacts of strain and ligand effects on these adsorption energies. Notably, the research observes that the adsorption of \*CO and \*COH is less sensitive to strain compared to the adsorption of \*COOH and \*CHO on the Cu(111) surface, revealing that the adsorption energy variations are dependent on the specific adsorbate. The findings highlight certain catalyst models among Cu-M hetero-layered slab structures that exhibit promise for reducing overpotential during e-CO<sub>2</sub>R due to the interplay of strain and ligand effects. Additionally, the research emphasizes that strain-insensitive adsorbates like \*CO and \*COH tend to benefit more from the ligand effect [318].

In a separate study, an initial metastable Au overlayer was synthesized using a two-step solution approach. The success of this approach is attributed to the significant interface strain within the AuCu<sub>3</sub>@Au core-shell structure, which provided support for the overlayer. The





metastable Au exhibited increased FE and enhanced specific activity for CO<sub>2</sub>R to CO. This increase in reaction rate can be attributed to the downshift of the energy barrier for the production of the intermediate COOH\* due to the upshift in the d-band center [319]. Another line of research focuses on the e-CO<sub>2</sub>RR facilitated by heteroatom-doped Cu-based catalysts, known for their high activity and selectivity. However, the complexity of Cu-based materials often makes it challenging to pinpoint the specific factors responsible for performance improvements. This study highlights that lattice strain adjustment in Cu-based catalysts can be used to control the activity and selectivity of e-CO<sub>2</sub>RR. Specifically, tensile-strained Sn/Cu alloy catalysts, by suppressing the dimerization process and promoting the formation of HCOOH and H<sub>2</sub>, enhance CO production due to the predominant adsorption of CO and lower adsorption free energies of COOH [320]. Furthermore, in a separate study, a synthetic method is presented to maintain tensile strain in a copper/ceria heterostructure, thereby increasing selectivity for CO<sub>2</sub>R. This approach employs metal/metal oxides. The research demonstrates that carbonaceous intermediates are better adsorbed due to the tensile strain in the copper domain, and it facilitates \*CO dimerization by creating an inadequate electron environment around interfacial Cu sites. Consequently, this method leads to a maximum FE of 76.4% and increases the efficiency of converting half-cell power to 49.1% [321].

In a separate investigation, Feng *et al.* explores the influence of atomic dopants on the activity of copper-based electrocatalysts during CO<sub>2</sub>R processes. Notably, doping Cu<sub>2</sub>O with atomic Gd is found to significantly enhance the catalyst's performance. To achieve this, Gd<sub>1</sub>/CuO<sub>x</sub> catalysts were developed, taking advantage of the unique electrical structure and large ion radii of Gd. Gd doping induces tensile strain during the reaction, stabilizing the Cu<sup>+</sup> species and resulting in superior catalytic performance. These catalysts achieved a partial current density of 444.3 mA cm<sup>-2</sup> at 0.8 V against a hydrogen electrode, with a remarkable FE of 81.4% for C<sub>2+</sub> products [322]. In another study, bimetallic alloy structures with engineered strain play a crucial role. A remarkable FE of 96.6% for CO<sub>2</sub>-to-CO conversion was achieved by strategically managing lattice stresses in bimetal MNi alloys using a strain relaxation technique. Molecular dynamics simulations were employed to reveal that the relaxation of strained PdNi alloys can be controlled by increasing the synthesis temperature. DFT simulations further demonstrated that strain relaxation, by maximizing the energies of intermediate production, enhances CO<sub>2</sub>RR activity and selectivity [323]. Furthermore, a novel class of Pd/Cu core/shell icosahedra with a tensile-strained Cu shell has enabled the efficient production of syngas with controllable compositions via the CO<sub>2</sub>RR. By adjusting the Pd/Cu composition, the molar ratio



of H<sub>2</sub>/CO in syngas can be tuned from 1/1 to 2/1 and 3/1 [324]. Table 15 showed effect of strain on different electrocatalysts synthesized by strain engineering approach upon CO<sub>2</sub> conversion products.

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**Table 15:** The table provided delves into the utilization of strain engineered materials as a solution, for CO<sub>2</sub>R. It thoroughly investigates designed electrocatalyst materials and examines how the strain induced changes in these materials affect their catalytic performance under different reaction conditions.

N	Material	electrolyte	V		≈ FE %								Ref.
			vs RHE	H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	
1	FCC Au	0.1 M KHCO <sub>3</sub>	-1.0	--	60	--	--	--	--	--	--	--	319
2	o-AuCu <sub>3</sub> @fct Au			--	88	--	--	--	--	--	--	--	]
3	Cu <sub>2</sub> O/CeO <sub>2</sub> -0.18	KOH	-0.75	12	16	2	38	2	--	--	15	--	321
4	Pd ico/C	0.1 M KHCO <sub>3</sub>	-1.0	78	17	--	--	--	--	--	--	--	]
5	Pd <sub>2.2</sub> Cu ico/C			48	37	--	--	--	--	--	--	--	]
6	Pd <sub>6.1</sub> Cu ico/C			51	17	--	--	--	--	--	--	--	]
7	Pd <sub>4.3</sub> Cu ico/C			63	21	--	--	--	--	--	--	--	]
8	CuOx	2 M KOH	-1.0	25	9	--	40	2	--	--	20	--	322
9	6.5 % GD1/CuO <sub>x</sub>			18	8	1	40	1	--	--	30	--	]
10	s-PdNi/CNFs-1000	0.1 M KHCO <sub>3</sub>	-1.18	--	52	--	--	--	--	--	--	--	]
11	s-PdNi/CNFs-800			--	64	--	--	--	--	--	--	--	]
12	PdNi/C			--	83	--	--	--	--	--	--	--	]
13	s-AuNi/CNFs	1 M KOH	-1.0	--	90	--	--	--	--	--	--	--	]
14	s-AgNi/CNFs			--	68	--	--	--	--	--	--	--	]
15	CuO			26	19	--	28	22	--	--	5	--	320
16	Sn-CuO-7.5			13	75	--	--	15	--	--	--	]	

## 6.12. Precursor derived approach

In the development of catalysts for e-CO<sub>2</sub>R, the approach that relies on precursor materials is becoming increasingly important. It makes possible the composition and structure of catalysts to be controlled. That involves the creation of catalyst materials by synthesizing them from selected precursor compounds, from which these compounds can change once they have been prepared. The main benefit of this method is that it enables the creation of designated catalysts, with chemical compositions, atomic structures and surface properties displayed in an orderly array. And by selecting precursor compounds, and optimizing synthesis conditions, researchers are free to tailor the properties of catalysts to achieve high selectivity and activity in converting CO<sub>2</sub> for valuable products such as hydrocarbons or alcohols. There are also scalability and affordability benefits to the precursor-based approach, which therefore promises an



encouraging possibility for solving the problems associated with carbon capture and utilization.

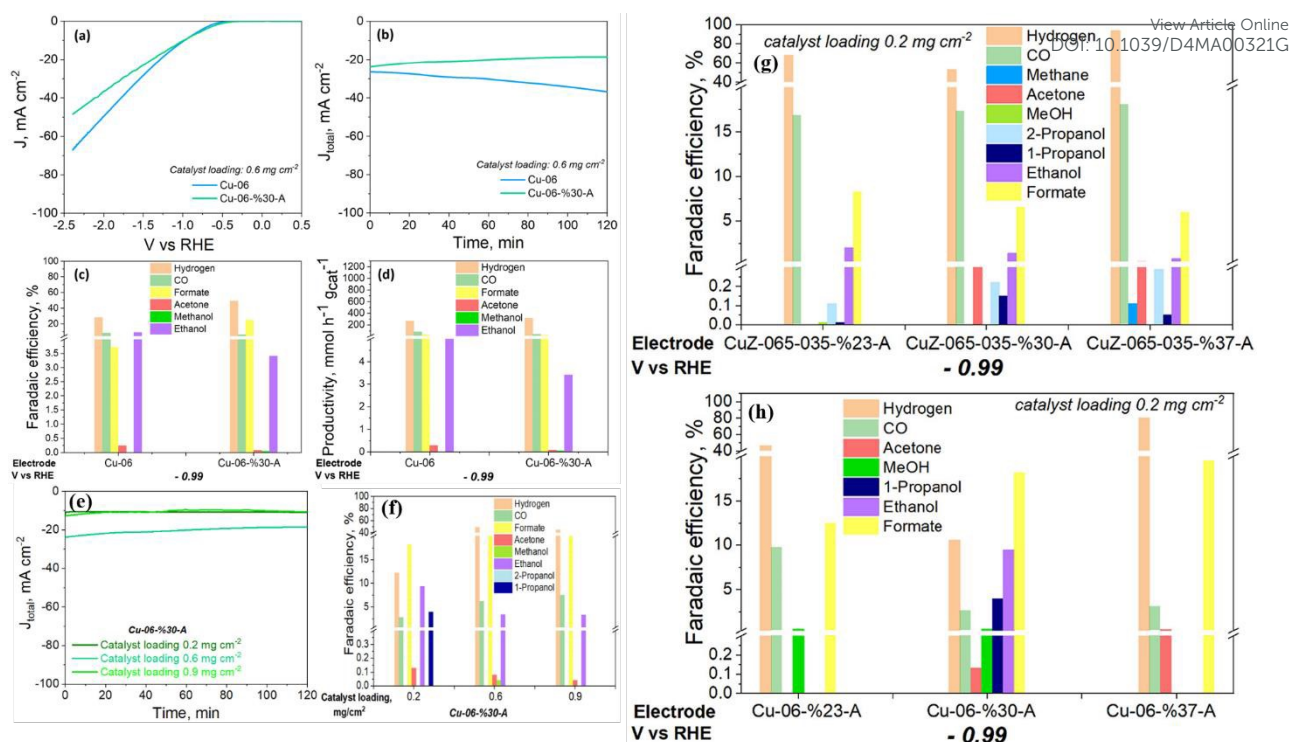
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The precursor-based approach also has a number of techniques for designing CO<sub>2</sub> reduction catalysts. In one method, inorganic precursor materials are decomposed to carbon-based catalysts having defined structures and active sites by controlled heating at a temperature or by pyrolysis. Another process is called sol-gel, in which precursor compounds are mixed in a solution and then, by controlled drying and controlled thermal processing, transformed into catalytic materials. Chemical vapor deposition (CVD) is a method that allows the placement of catalysts derived from precursors onto substrates. This enables integration of these catalysts, into setups promoting their usefulness in achieving a sustainable and low carbon future. Researchers can effectively utilize the potential of the precursor derived approach, by selecting precursor compounds and optimizing synthesis parameters resulting in the development of highly efficient and selective CO<sub>2</sub>RR catalysts.

In a specific study, Using ultrasonic irradiation, Guzmán *et al.* have developed novel catalysts for e-CO<sub>2</sub>R, achieving increased selectivity towards H<sub>2</sub> and C<sub>1</sub> products (CO and formate) in aqueous media (Figure 29). These catalysts harnessed the synergistic interaction between ZnO and CuO metal oxides, resulting in over a 1.4-fold increase in syngas productivity for the ultrasound-prepared CuZ catalysts. Furthermore, adjusting ultrasonic amplitudes increased the BET surface area by 100%, leading to a more than 14% improvement in FE towards alcohols in the RDE system at a catalyst loading of 0.2 mg cm<sup>-2</sup>. They have also discussed the electroactivity performance concerning precursor concentration, duration of ultrasound-assisted precipitation, and calcination temperature of the synthesized powders, allowing fine-tuning of the physical and chemical properties of the nanoparticles. To optimize the synthesis of \*CO intermediates and facilitate their dimerization into multi-carbon products, mesoporous materials with a mean pore size of approximately 20 were engineered to create ideal conditions [325].





**Figure 29:** The LSV responses, evolution time of total current density for the  $e\text{-CO}_2\text{R}$ , FE, and productivities of gas and liquid products were measured for Cu-06 and Cu-06-%30-A ( $0.6 \text{ mg cm}^{-2}$ ) in a  $1 \text{ M KHCO}_3$  aqueous electrolyte at a potential of  $-0.99 \text{ V vs RHE}$ . The chronoamperometry responses (e) and FEs were measured for a Cu-06-%30-A catalyst with varying catalyst loading. The tests were conducted in a  $1 \text{ M KHCO}_3$  aqueous electrolyte at a potential of  $-0.99 \text{ V vs RHE}$  (f). The FE of the US-prepared CuZ-06-035 (g) and US-prepared Cu-06 (h) catalysts, with a loading of  $0.2 \text{ mg cm}^{-2}$ , were evaluated in a  $1 \text{ M KHCO}_3$  aqueous electrolyte at a potential of  $-0.99 \text{ V vs RHE}$ . Reproduced with permission from Ref. [325] Copyright 2023, Elsevier.

In the quest for phase-pure, solid  $\text{Cu}_3\text{P}$  NPs, Downes *et al.* have developed a molecular precursor method. This approach involves using a mixture of hydrocarbons and amines as a solvent for the high-temperature decomposition of  $[\text{Cu}(\text{H})(\text{PPh}_3)]_6$  to produce  $\text{Cu}_3\text{P}$  NPs. The electrocatalytic efficiency of  $\text{Cu}_3\text{P}$  NPs for  $\text{CO}_2\text{R}$  in  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  aqueous solutions was thoroughly examined.  $\text{Cu}_3\text{P}$  NPs demonstrated exceptional dispersibility, allowing them to be easily deposited onto carbon paper electrodes. However, it was observed that  $\text{Cu}_3\text{P}$  NPs exhibited instability under electrocatalytic conditions. Further investigation revealed that increasing the phosphorus content improved electrochemical stability, while decreasing the



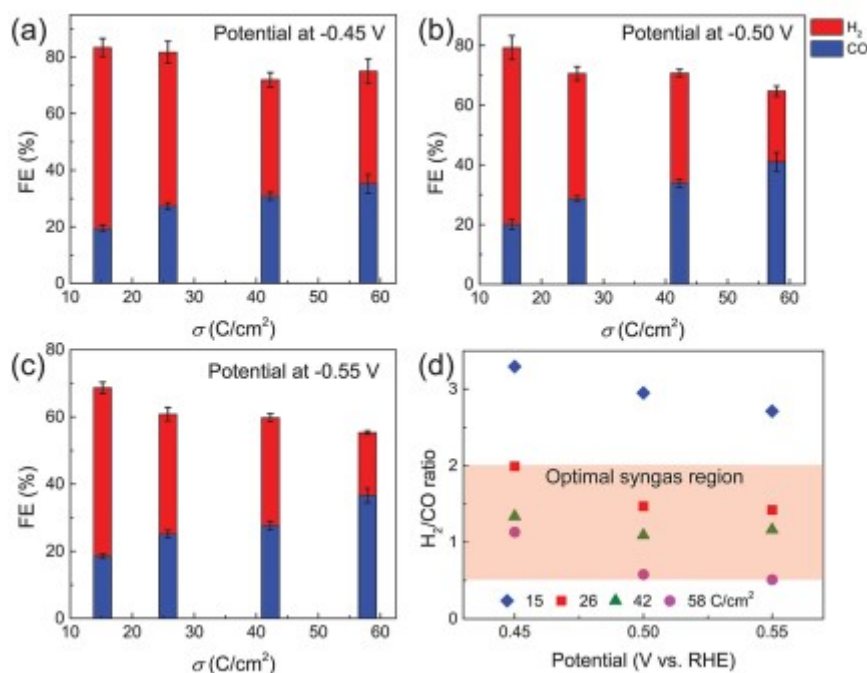
Cu<sub>3</sub>P content enhanced stability [326]. In another study, nanocomposites of ZIF-L (zeolitic imidazolate framework with large cavities) and GO (graphene oxide) were developed, showcasing excellent electrical conductivity, a substantial active surface area, and robust electrocatalytic performance. Particularly, the Cu GNC-VL (Cu zeolitic imidazolate framework-derived nitrogen-doped porous carbon) exhibited a remarkably high current density of 10.4 mA cm<sup>-2</sup> at -0.87 V vs. RHE and an impressive FE for ethanol production of 70.52% [327].

In a related study, Dou *et al.* have developed a method for creating CuS nanosheet arrays on brass mesh through a single-step chemical bath deposition process. When subjected to e-CO<sub>2</sub>R at the CuS/BM electrode, increased production of HCOO<sup>-</sup> was observed. This electrochemical process induced reconstruction, resulting in a nanowire network with multiple active centers. The reconstituted Cu(111)/CuS(102) structure was identified as a key contributor to the electrode's strong selectivity towards HCOO<sup>-</sup> generation. Moreover, the presence of sulfur (S) beneath the Cu<sup>0</sup> layer led to reduced binding energies of HCOO\* and \*COOH compared to the Cu(111) plane, facilitating the production of HCOOH or HCOO<sup>-</sup> [328]. In another innovative approach, synthetic control over Cu NPs and Ag NPs has been achieved through a newly developed seeded-growth colloidal method, resulting in the production of AgCu nanodimers (NDs) with varying Cu domain sizes. This method also applies to other dimer systems like Cu–Ru, Cu–Rh, and Cu–Ir, where two metals are traditionally unmixable in the bulk phase. To examine the compositional and structural sensitivity of e-CO<sub>2</sub>R in this bimetallic system, model catalysts were made from Ag/Cu nanocrystals. In particular, the Ag<sub>1</sub>Cu<sub>1.1</sub> NDs displayed a 3.4-fold increase in FE for C<sub>2</sub>H<sub>4</sub> and a 2.0-fold improvement in the combined e-CO<sub>2</sub>RR activity over Cu NPs of comparable size and shape [126].

In another research, Chen *et al.* controlled the aspect ratio and composition of alloyed nanorods made of Cu through a co-reduction synthesis process using seeds. They demonstrated different catalytic activities for p-nitrophenol reduction by the Cu<sub>3</sub>Au nanorods tuning across the visible to infrared spectrum [329]. Zheng *et al.* have made significant progress in synthesizing e-CO<sub>2</sub>RR catalyst materials and created highly efficient Au-Cu knot structures, referred to as NSs in this study. NSs of all types were formed by Cu growth on the concave surface of a Au seed. The final products are obtained by using o-phenylenediamine (OPDA) as capping agents and Cu(acac)<sub>2</sub>, a precursor. A growth mode and high exposure to Au are typical of the anisotropic nature of the products. The Au-Cu NSs exhibited remarkable selectivity for C<sub>2+</sub> product generation, with an optimum FE<sub>2+</sub> of 67% and a C<sub>2+</sub> partial current density of 0.29 A



$\text{cm}^{-2}$  at 0.75 V vs RHE [330]. In a separate study, Wang *et al.* have developed effective catalysts for e- $\text{CO}_2\text{R}$  by generating dense OD-Cu NPs using a three-step process (Figure 30). This process involved the thermal oxidation of  $\text{CuO}_x$  on a Cu mesh, followed by reduction through annealing, and finally the conversion to OD-Cu by applying a cathodic potential to the partially reduced  $\text{CuO}_x$ . These OD-Cu NPs maintained their shape and exhibited the capability to produce various types of syngas at high rates with modest overpotentials [331].



**Figure 30:** The FEs of  $\text{H}_2$  and  $\text{CO}$  production on OD-Cu NPs were measured at different applied potentials: (a) -0.45 V, (b) -0.50 V, and (c) -0.55 V. The controllable composition of syngas varies depending on both the applied potentials. Reproduced with permission from Ref. [331] Copyright 2020, American Chemical Society.

Additionally, Wang *et al.* have grown scalable arrays of metallic 2D  $\text{Cu}_2\text{Te}$  nanosheets on copper foils. During the growth process, chemical etching and vapor deposition, exposure to potential active sites at edges of these nanosheets, facilitated  $\text{CO}_2\text{R}$  to  $\text{CH}_4$  at lower overpotentials [332]. Moreover, Han *et al.* have employed the atomic layer infiltration method using the HKUST-1 template. By uniformly adding Zn-O-Zn sites throughout HKUST-1, the FE for CO increased from 20-30% to 70-80%. Computational density-functional-theory studies revealed that this modification lowered the activation energy barrier for the reaction and accelerated CO production by increasing the enthalpy of  $\text{CO}_2$  adsorption [277]. Furthermore, a potential electrocatalyst for  $\text{CO}_2\text{R}$  has been introduced by Sirisomboonchai *et al.* This



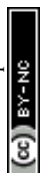
electrocatalyst, consist of In and Zn deposited over Cu foam, exhibited improved CO<sub>2</sub>R to CO with a remarkable FE of 93.7% and a 100-hour operational lifetime [333]. In a related study, the impact of various sulfur precursors on the structure-property-activity relationships of copper-based catalysts for e-CO<sub>2</sub> conversion was investigated by Gao *et al.* The CuS-TU catalyst, synthesized using thiourea as the sulfur precursor, exhibited a distinctive flower-like structure and the highest sulfur vacancy concentration. This unique structure facilitated interfacial mass transfer during CO<sub>2</sub>R. The abundance of sulfur vacancies on the catalyst's surface played a crucial role in increasing CO generation through the \*COOH route by enhancing the adsorption of COOH intermediates. Subsequently, the CuS-TU catalyst achieved a CO selectivity of 72.67% at -0.51 V vs RHE [334]. Table 16 showed different materials designed by precures derived approach for e-CO<sub>2</sub>R.

**Table 16:** This resourceful table provides an examination of electrocatalyst materials employed in CO<sub>2</sub> conversion processes. It simplifies exploration and comprehension within this domain by scrutinizing the electrochemical properties of catalysts, particularly how different precursor derived approach influence product distribution.

N	Material	electrolyte	V		≈ FE %								Ref.
			vs RHE	H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	
1	CuZ-065-035			52	22	--	--	5	--	--	10	--	[325]
2	CuZ-065-035-%30-A	1 M KHCO <sub>3</sub>	-0.99	80	22	--	--	2	--	--	2	--	[ ]
3	Cu GNC-VL			40	--	--	--	5	--	13	42	--	[327]
4	Cu ZIFL@GO	0.5 M KHCO <sub>3</sub>	-1.07	60	5	--	--	9	--	14	12	--	[ ]
5	CuS/BM	0.5 M KHCO <sub>3</sub>	-1.0	60	--	--	--	48	--	--	--	--	[328]
6	Ag NPs			92	10	--	--	--	--	--	--	--	[ ]
7	Cu NPs	0.1 M KHCO <sub>3</sub>	-1.4	34	1	32	8	1	--	--	--	--	[126]
8	Ag <sub>1</sub> -Cu <sub>1,1</sub> -NDs			50	2	30	12	2	--	--	--	--	[ ]
9	Au-Cu Janus			-0.75	--	--	--	37	--	--	20	--	[330]
10	Au@Cu Core-Shell	3 M KOH	-0.95	--	--	--	20	--	--	--	10	--	[ ]
11	Cu NPs			-0.81	--	--	--	37	--	--	17	--	[ ]
12	OD-Cu NA	0.1 M KHCO <sub>3</sub>	-0.55	60	19	--	--	--	--	--	--	--	[331]

### 6.13. Polymer modification approach

The utilization of polymer modification is an approach, in the development of e-CO<sub>2</sub>R catalysts. It plays a role in enhancing the selectivity, activity and stability of these catalysts. When researchers incorporate polymers into the structure or surface of the catalyst, they achieve some advantages. Polymers serve as stabilizers too, preventing the aggregation or dissolution of species during the CO<sub>2</sub>RR process. This makes the catalyst more durable.

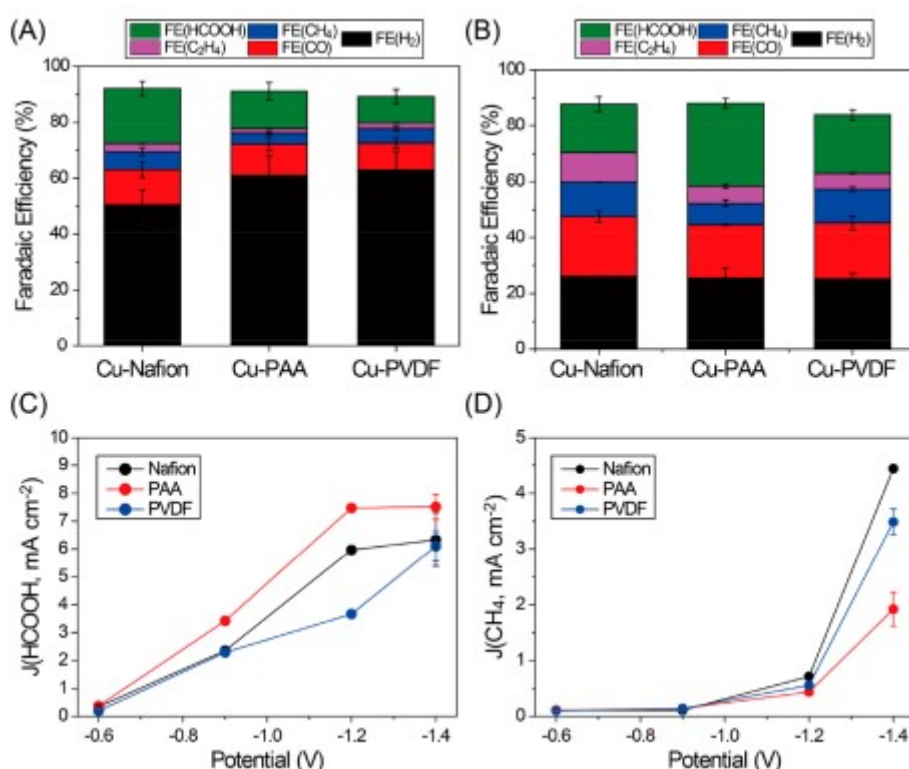


Polymers also are effective as templates for controlling the nanostructure and catalyst material morphology, influencing its performance. Furthermore, the modification of polymers promotes the formation of active sites essential for efficient conversion of CO<sub>2</sub> into more valuable products like hydrocarbons or alcohols. The reason this is important is that making CO<sub>2</sub>RR catalysts better and more efficient by means of such engineering will foster sustainable carbon capture and utilization technologies. Polymer-modified catalysts with catalytic metal cores can be synthesized by multiple methods for designing CO<sub>2</sub>RR catalysts. One of these is electrochemical deposition, in which polymer films grow onto a catalyst surface allowing precise control of thickness and composition is achievable. And another, polymers can be incorporated into the catalyst matrix when synthesized to produce the material combining characteristics of metals together with the stabilizing and templating effects caused by polymers. Additionally, researchers may go with a couple of possible synthesis techniques, such as chemical or physical adsorption, to introduce polymer modifiers on the catalyst surface. Poly(ionic liquid) (PIL) NPs with multilamellar chain stacking were prepared by free radical homopolymerization. By manipulating the carbon used in the polymerization process, PIL NPs of various sizes and shell thicknesses could be synthesized. Molecular dynamics simulations corroborated the mechanism of PIL NV formation, emphasizing the role of the polymerization degree of PIL chains in determining assembly behavior. These well-defined PIL NVs with hollow interiors allowed for high loading amounts of ultra-small Cu NPs for e-CO<sub>2</sub>R. The strong electronic interactions between PIL units and Cu atoms on the surface of Cu NPs resulted in a high FE toward C<sub>1</sub> products, primarily CH<sub>4</sub> [335]. In another study, the impact of a poly(4-vinylpyridine) P4VP layer on the e-CO<sub>2</sub>RR on both poly Cu and Au electrodes was investigated by Ye *et al.* The research revealed that a P4VP layer inhibits the HER and enhances CO<sub>2</sub>RR, particularly the production of HCOOH. In in-situ ATR-SEIRAS tests, fewer CO adsorption bands were observed on P4VP-modified Cu electrodes, while higher ICO<sub>2</sub>/IHCO<sub>3</sub> ratios were detected on P4VP-modified Au electrodes. These observations suggest that the mass transfer of H<sub>2</sub>O and HCO<sub>3</sub> from the bulk to active sites is impeded by the P4VP modification. Importantly, the hydrophilicity of the electrode surface is altered by the presence of P4VP, leading to increased HCOOH production at low overpotentials [336]. Furthermore, polymer coatings, which can modify local pH levels, hydrophilicity/hydrophobicity, and reactant concentrations. Jun *et al.* have demonstrated that polymer coatings can enhance the catalytic selectivity of Cu-based catalysts in CO<sub>2</sub>RR while also improving electrocatalytic stability [337].





Additionally, the impact of three different ionomers on Cu-catalyzed CO<sub>2</sub>RR under high-current conditions were investigated. In this investigation, it was observed that the anionic ionomer Nafion had a negligible effect on CO<sub>2</sub>RR, likely due to the negatively charged nature of the electrode/catalyst interface. However, the cationic ionomers XA-9 and PTP had significant effects on the selectivity of CO<sub>2</sub>RR with Cu catalysts. Specifically, PTP led to increased HER and formate synthesis, likely due to decreased mass transport. In contrast, XA-9 favored the production of CO at the expense of C<sub>2+</sub> products [338]. Moreover, another study highlights the influence of different polymeric binders used during electrode fabrication on the selectivity of CO<sub>2</sub>RR on Cu electrodes (Figure 31). The research findings demonstrate that the choice of binder material can significantly modify the selectivity of CO<sub>2</sub>RR products. Specifically, it was observed that Cu electrodes with polyvinylidene fluoride as the binder favored the production of CH<sub>4</sub>, while Cu electrodes with polyacrylic acid as the binder exhibited greater selectivity for HCOOH generation [339].

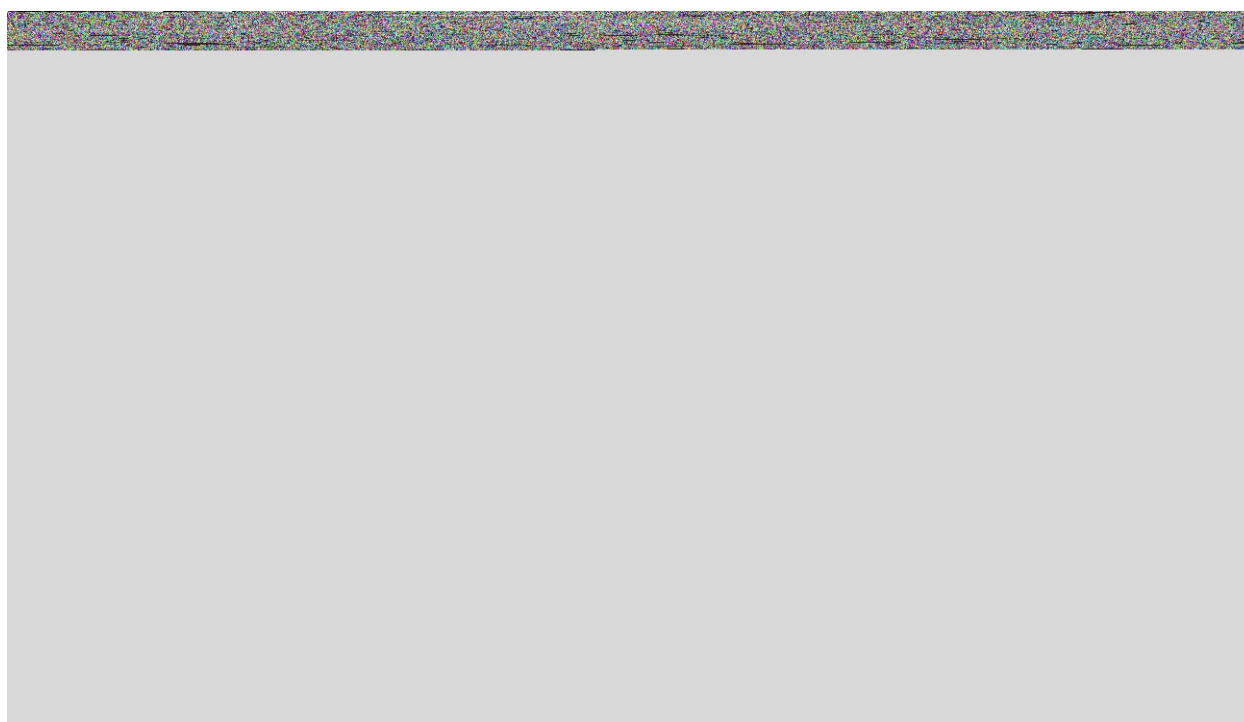


**Figure 31:** The CO<sub>2</sub>RR performance of various Cu/C catalysts with different binders was evaluated. The FE of HCOOH, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and H<sub>2</sub> were evaluated at two different potentials: -0.6 V and -1.4 V. The partial current density profiles of HCOOH and CH<sub>4</sub> are presented. Reproduced from Ref. [339] Open access article, American Chemical Society.



Liang *et al.* have developed a novel single-site copper coordination polymer known as Cu(OH)BTA. Notably, this polymer exhibits a 1.5 times higher selectivity for producing C<sub>2</sub>H<sub>4</sub> compared to its metallic counterpart (Figure 32). An interesting feature of this catalyst is that it maintains its structural integrity throughout the reaction. This advantageous characteristic allows for the formation of an energetically favorable \*OCCHO intermediate during CO hydrogenation, facilitated by suitably-distanced dual sites provided by adjacent copper atoms in the polymer. The study also demonstrates the practical applicability of these polymers by running full-device CO<sub>2</sub> electrolysis for 67 hours at an appropriate current in a membrane electrode assembly [311].

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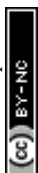


**Figure 32:** *The study investigated the FEs of various products at different applied potentials using Cu(OH)BTA (a) and Cu(OH)BTA-derived Cu (b) in a 1 M KOH electrolyte. The study also investigates the formation rates of C<sub>2+</sub> products and C<sub>2</sub>H<sub>4</sub> under varying applied potentials using Cu(OH)BTA and Cu(OH)BTA-derived Cu in a 1 M KOH electrolyte. The study also measured the FEs of various gas products within the voltage range of 3.0-4.0 V using a membrane-electrode assembly device. The electrosynthesis of C<sub>2</sub>H<sub>4</sub> was conducted in a membrane-electrode assembly with a geometric electrode area of 4 cm<sup>2</sup>. The catalyst maintains its overall current and ethylene FE for a duration of 67 hours. The error bars for the uncertainty of the FE analysis represent one standard deviation, which is calculated based on three independent samples. Reproduced from Ref. [311] Open access article, Nature.*



Additionally, Wang *et al.* have explored a unique approach to enhancing the selectivity of heterogeneous Cu catalysts for CO<sub>2</sub>RR employing random copolymers as surface modifiers. Among these copolymers, a tricomponent variant demonstrated superior performance in maximizing the FE for ethylene and C<sub>2+</sub> products during CO<sub>2</sub>RR. Surface characterization conducted under CO<sub>2</sub>RR conditions highlighted the copolymer's resilience, attributed to the presence of a phenylpyridinium component. Advanced techniques, including AFM, SEM, and XPS, were utilized to counter the presence of nanostructuring and electrical effects. Molecular dynamics simulations illustrated that the optimal polymer modifier led to localized increases in CO<sub>2</sub> content. Moreover, compared to block copolymers, random copolymers exhibited greater porosity, facilitating improved access and mass transport of reactants [340]. Furthermore, Wei *et al.* demonstrated that coating Cu surfaces with a PANI thin film can significantly alter the catalytic activity and selectivity for CO<sub>2</sub>RR. The NH group on PANI interacts with CO<sub>2</sub> molecules, enriching the presence of CO<sub>2</sub> and inhibiting the HER on Cu surfaces. Consequently, the CO<sub>2</sub>RR current density at the Cu/PANI interface experiences a substantial increase. This transformation leads to a shift from 15% C<sub>2+</sub> hydrocarbon production on pure Cu to over 60% on Cu-PANI, making C<sub>2+</sub> hydrocarbons the dominant products [341].

On another front, researchers have synthesized and evaluated two stable Cu(I)-based coordination polymer electrocatalysts, NNU-32 and NNU-33(H), designed for e-CO<sub>2</sub>RR within a flow-cell electrolyzer. These electrocatalysts exhibit exceptional selectivity for converting CO<sub>2</sub> into CH<sub>4</sub>, achieving a FE of 82% at -0.9 V vs RHE. The outstanding selectivity is attributed to the presence of cuprophilic interactions within the catalysts. Furthermore, a dynamic in-situ crystal structure transformation from NNU-33(S) to NNU-33(H) enhances cuprophilic interactions and CO<sub>2</sub> adsorption. This structural change, involving the substitution of hydroxyl radicals for sulfate radicals, significantly contributes to the superior performance of these electrocatalysts. It's worth noting that cuprophilic contacts play a pivotal role in CH<sub>4</sub> production, and the selectivity for CH<sub>4</sub> varies with the number and proximity of interacting cuprophiles [342]. Furthermore, Li *et al.* have found that by stabilizing a metal-bound CO intermediate, Nafion-modified electrodes can significantly enhance the production of CH<sub>4</sub>. To precisely regulate the transfer of protons to the metal-CO intermediate, Cu electrodes were constructed using a polymer blend of Nafion and polyvinylidene fluoride. This precise control mechanism leads to increased rates of production for C<sub>2+</sub> products such as ethylene, ethanol, and 1-propanol. Importantly, under these controlled conditions, hydrogen evolution does not occur, as almost all carbon-containing products can be extracted from Cu electrodes equipped



with a 15 m Nafion overlayer [343]. Furthermore, the e-CO<sub>2</sub>R to high-energy-density C<sub>2</sub> products necessitate carbon-carbon interactions. In this context, Zhang *et al.* have explored the use of capping agents and electrochemical treatment to fabricate polycrystalline Cu catalysts. These catalysts exhibit a 34% FE for the production of C<sub>2</sub>H<sub>4</sub> at -1.5 V vs RHE. Importantly, a critical \*COOH intermediate was observed on the Cu surfaces, as confirmed by quasi-in situ total reflection FTIR analysis [344]. Different polymers were used for modification of e-CO<sub>2</sub>R performance of different materials, which is summarized in table 17.

**Table 17:** The table comprehensively summarizes electrocatalyst materials explicitly designed for reducing CO<sub>2</sub> emissions with a focus on polymer modification techniques. It explores the performance of polymers. Investigates how modifications impact both selectivity and efficiency, in producing desired products.

N	Material	electrolyte	V		≈ FE %								Ref.
			vs RHE	H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	
1	NWs/Cu	0.1 M KHCO <sub>3</sub>	-1.0	27	34	7	14	--	--	--	--	--	[335]
2	Pristine CuNPs			30	15	3	22	--	--	--	--	--	[ ]
3	Poly Cu	0.1 M KHCO <sub>3</sub>	-0.9	57	12	4	2	27	--	--	--	--	[336]
4	P4VP-modified Cu			95	5	3	2	32	--	--	--	--	[ ]
5	Cu-P1	1 M KOH	-0.97	1	5	--	73	1	--	--	1	--	[337]
6	Cu-P4			30	3	2	35	15	--	--	1	--	[ ]
7	Cu	0.5 M KHCO <sub>3</sub>	-0.86	--	6	--	7	15	--	--	3	--	[ ]
8	Cu/Nafion			--	5	--	7	6	--	--	1	--	[338]
9	Cu/XA-9	0.1 M KHCO <sub>3</sub>	-1.4	--	12	--	8	20	--	--	2	--	[ ]
10	Cu/PTP			--	2	--	--	10	--	--	--	--	--
11	Cu-Nafion	0.1 M KHCO <sub>3</sub>	-1.4	28	20	12	10	18	--	--	--	--	[339]
12	Cu-PAA			28	18	6	4	34	--	--	--	--	--
13	Cu-PVDF	0.1 M KHCO <sub>3</sub>	-0.6	28	20	12	4	18	--	--	--	--	[ ]
14	Cu(OH)BTA			10	23	2	45	2	--	--	13	--	[311]
15	Cu(OH)BTAdescribed Cu	10	55	--	20	7	--	--	8	--	[ ]		
16	Cu	0.1 M KHCO <sub>3</sub>	-1.04	39.7	0.5	25.6	22.3	1.8	--	--	5.9	--	[ ]
17	Cu-1			94.6	--	1.5	--	0.7	--	--	--	--	--
18	Cu-2	69.3	1	14.1	5.3	6.6	--	--	--	--	--	[ ]	
19	Cu-3	37.8	2.8	14	21.5	11.1	--	--	--	3.4	--	[ ]	
20	Cu-4	34.1	0.4	33.1	19	3.8	--	--	--	3.9	--	[ ]	
21	Cu-5	33.6	0.5	28.1	25.4	1.1	--	--	--	6	--	[ ]	
22	Cu-6	32.5	1.1	22.3	30.4	1	--	--	--	9.3	--	[340]	
23	Cu-7	16.5	1.2	4.7	49.5	2.2	--	--	--	16	--	[ ]	
24	Cu-8	11.9	0.7	1.9	55.6	1.9	--	--	--	17.4	--	[ ]	
25	Cu-9	19.2	0.4	2.8	53.8	0.9	--	--	--	15.5	--	[ ]	
26	Cu-10	35	1	11.5	36.8	1.8	--	--	--	9.5	--	[ ]	
27	Cu-11	36.2	2.3	8.7	31.7	9	--	--	--	4.3	--	[ ]	
28	Cu-12	44.8	0.5	25	20.4	1.4	--	--	--	5.2	--	[ ]	
29	Cu-13	21.9	0.6	5.7	59.8	1.3	--	--	--	11.8	--	[ ]	
30	Cu-block-8	30.5	0.6	14.1	34.5	2.4	--	--	--	11	--	[ ]	
31	Cu	0.1 M KHCO <sub>3</sub>	-1.1	45	3	5	5	27	--	--	10	--	[ ]

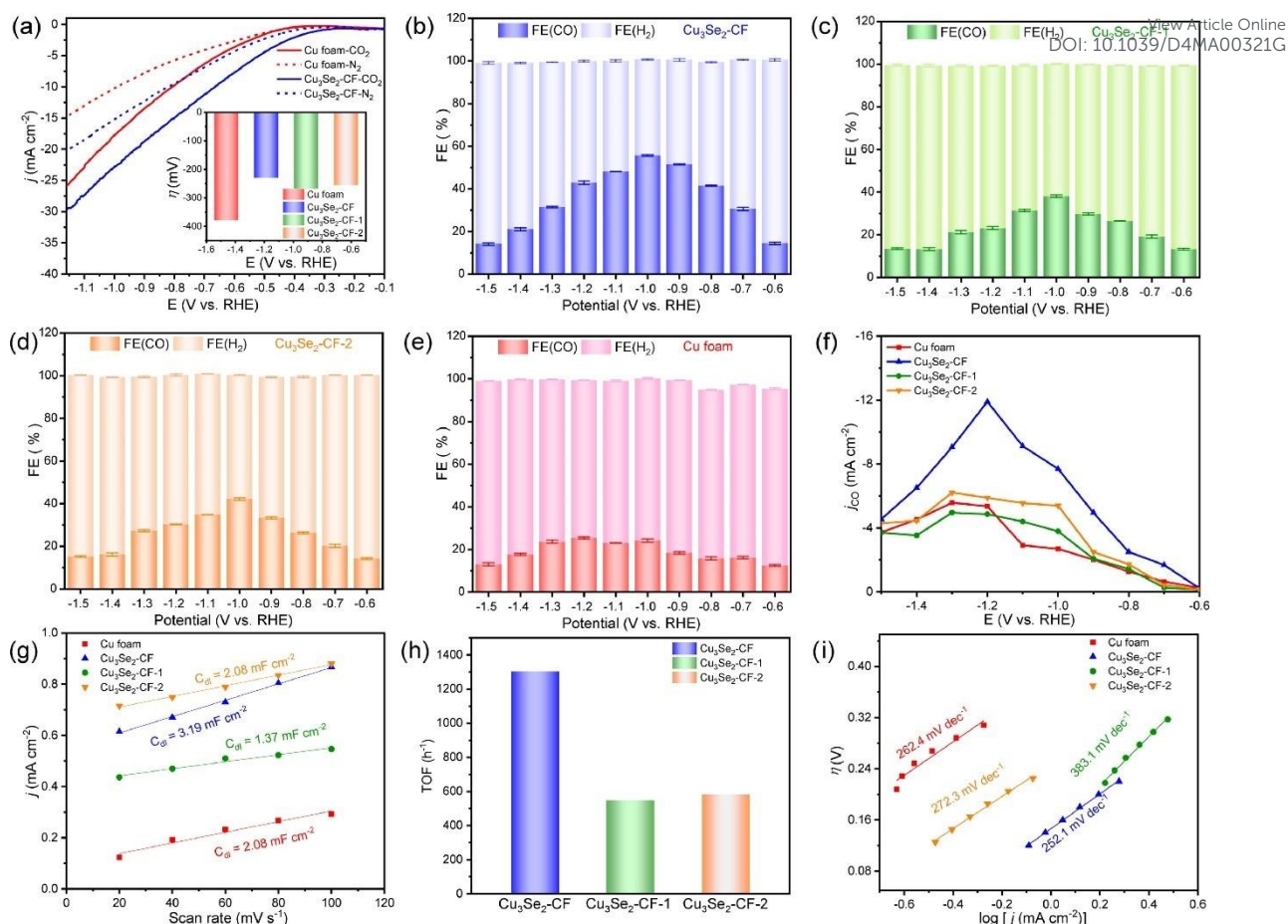


32	Cu-PANI			17	2	11	30	10	--	--	--	--	View Article Online DOI: 10.1039/D4MA00321G	[341 ]
33	NNU-33(H)	1 M KOH	-1.0	13	12	63	13	--	--	--	--	--		[342 ]

### 6.14. Support engineering approach

Support engineering plays a role, in the design of e-CO<sub>2</sub>R catalysts as it focuses on selecting and modifying support materials to improve catalytic performance. This approach enables researchers to optimize the sites of the catalyst by providing a conductive platform for reactions. By choosing support materials and manipulating their properties scientists can enhance the efficiency, durability and economic viability of CO<sub>2</sub>RR catalysts for sustainable carbon capture and utilization technologies. In the strategy of support engineering for CO<sub>2</sub>RR catalyst design there are methods that can be employed. One common approach is depositing nanoparticles or single atoms onto support materials like graphene, carbon nanotubes or metal oxides such as TiO<sub>2</sub> and ZnO. Another method involves modifying support materials through surface functionalization or doping to influence the binding energies of CO<sub>2</sub> and reaction intermediates thereby customizing the selectivity of the catalyst. Additionally creating materials by combining components, with suitable supports offers a versatile solution that combines advantages from both components. In the quest for effective e-CO<sub>2</sub>R to value-added syngas, a technique has been devised utilizing anion-regulated self-supported Cu<sub>3</sub>Se<sub>2</sub> nanosheet-assembled fibers (Figure 33). These fibers exhibit an excellent TOF of 1303 h<sup>-1</sup> over a wide potential window and accommodate a broad range of H<sub>2</sub>-to-CO ratios from 0.8 to 6.0. Remarkably, it can sustain bulk electrolysis for 10 hours, owing to its high current density and minimal attenuation [345].





**Figure 33:** The CO<sub>2</sub>R of Cu foam and Cu<sub>3</sub>Se<sub>2</sub>-CF nanocatalysts. LSV traces were obtained in CO<sub>2</sub>-saturated or N<sub>2</sub>-saturated electrolyte using a scan rate of 5 mV s<sup>-1</sup> (a). An inset in (a) shows the onset potential. The total FE was determined for gaseous products only, specifically H<sub>2</sub> and CO (b-e). The *j*<sub>CO</sub> was measured at different applied potentials (f). The double-layer capacitance was measured (g). TOFs were calculated (h). Tafel slopes were determined for Cu foam, Cu<sub>3</sub>Se<sub>2</sub>-CF, Cu<sub>3</sub>Se<sub>2</sub>-CF-1, and Cu<sub>3</sub>Se<sub>2</sub>-CF-2 (i). The data was collected under standard ambient temperature and pressure conditions, using a CO<sub>2</sub> stream with a flow rate of 20 sccm. Error bars represent the standard deviation of a minimum of three independent measurements. Reproduced with permission from Ref. [345] Copyright 2023, Elsevier.

Furthermore, the oxide-derived composite materials supported on N-doped graphene was designed by Dongare *et al.* it was found that by adjusting the Cu to Zn ratio during the coprecipitation process, one can customize the electrocatalyst's composition to meet specific requirements. Notably, an electrode containing 20 wt% Zn in conjunction with copper exhibits the highest selectivity for ethanol production (FE = 34.25%), while the CuO/NGN electrode demonstrates lower selectivity for ethanol and other C<sub>2</sub> compounds [346]. Furthermore,



pyrolyzing mixed precursors of  $\text{Cu}(\text{NO}_3)_2$  and polyvinyl pyrrolidone produces Cu/NC composite electrocatalysts for catalyzing  $\text{CO}_2$  reduction. Among these, Cu-20/NC stands out due to its substantial Cu nanoparticle size and extensive coverage of the carbon support surface, resulting in highly competitive HER activity. Conversely, Cu-5/NC, with its nanoparticle morphology, favors poor C-C coupling activity and  $\text{CH}_4$  formation. Meanwhile, Cu-10/NC exhibits remarkable selectivity for CO and hydrocarbons, leading to an impressive 37%  $FE_{\text{C}_2\text{H}_4}$  at -1.2 V and enhanced e- $\text{CO}_2\text{R}$  to  $\text{C}_2\text{H}_4$  conversion activity, selectivity, and durability [347]. Moreover, Gu *et al.* underscores the incorporation of Cu onto PCC supports yields intriguing e- $\text{CO}_2\text{R}$  outcomes, particularly with improved selectivity for  $\text{C}_2$  products like ethanol and ethylene. Among Cu<sub>5</sub>-PCC, Cu<sub>10</sub>-PCC, and Cu<sub>20</sub>-PCC, Cu<sub>15</sub>-PCC outperforms in various applied potentials, offering a more cost-effective approach to e- $\text{CO}_2\text{R}$  by leveraging affordable and abundant minerals as the foundation for suitable electrocatalysts [348].

In another study, Lim *et al.* have developed  $\text{CuS}_x$  catalyst for e- $\text{CO}_2\text{R}$  dipping Cu foil into an industrial  $\text{CO}_2$ -purged electrolyte containing  $\text{H}_2\text{S}$  gas. Increasing the  $\text{H}_2\text{S}$  concentration significantly improved the maximum  $FE_{\text{HCOOH}}$  from 22.7% to 71.8%, attributed to the reaction between Cu foil and sulfur species. Notably, these catalysts demonstrated excellent performance in both pure  $\text{CO}_2$ -purged electrolytes and industrial  $\text{CO}_2$ -purged electrolytes, maintaining stability for 12 hours [349]. Furthermore, Kim *et al.* have explored the e- $\text{CO}_2\text{R}$  on copper through pulsed electrolysis. The cathode's potential was cyclically shifted between -0.8 V vs RHE and -1.15 V versus RHE over durations ranging from 5 seconds to 25 seconds. Notably, static electrolysis at -1.15 V vs RHE resulted in a decreased  $FE_{\text{HER}}$  while simultaneously increasing the FE for the  $\text{CO}_2\text{RR}$ . However, when pulsed electrolysis was employed, the  $FE_{\text{HER}}$  decreased, whereas the FE for  $\text{CO}_2\text{RR}$  increased. The optimal duration for pulsed electrolysis was found to be 10 s at each potential, achieving the lowest FE for the HER and the highest FE for the  $\text{CO}_2\text{RR}$ . Additionally, pulsed electrolysis introduced changes in the ratio of oxygenated to hydrocarbon products and significantly boosted the FE for  $\text{C}_2+$  products [350].

Moreover, by enhancing the geometric partial current density of hydrocarbons through surface modification of copper foam with poly(acrylamide), the faradaic output of ethylene can be doubled. While poly(allylamine) completely impedes  $\text{CO}_2\text{R}$ , poly(acrylic acid) exerts only a transient impact. Through mechanisms such as CO activation for dimerization, stabilization of CO dimers via hydrogen bond interactions, and facilitation of CO adsorption in proximity to



the polymer, poly(acrylamide) adheres to copper through oxygen on carbonyl groups, thereby increasing the efficiency of ethylene formation. Achieving high CO<sub>2</sub> mass transfer rates, utilizing modified poly(acrylamide), and employing porous copper catalysts all contribute to improved ethylene production [351]. In another study, the e-CO<sub>2</sub>R was demonstrated using Bi-doped SnO nanosheets on a Cu foam substrate. Remarkably, the Bi-SnO/Cu foam electrode achieved the highest FE (93%) and HCOOH selectivity (99%), with exceptional long-term stability over 30 hours of operation. The Bi doping played a pivotal role in stabilizing divalent tin on the electrocatalyst, making its reduction to metallic tin more challenging. Additionally, the presence of Cu foam influenced the catalysis by promoting electron transfer, thereby maintaining tin in a positively oxidized state favorable for the adsorption of \*OOCH intermediates [352].

In a separate investigation, various synthetic approaches were employed to produce Cu nanoparticles with sizes ranging from 10 to 30 nm, supported by VC, KB, and SWNTs. Importantly, these carbon-supported Cu nanocatalysts demonstrated higher selectivity for C<sub>2</sub>H<sub>4</sub> production compared to electrodeposited Cu. The onset potentials for C<sub>2</sub>H<sub>4</sub> generation exhibited significant shifts for well-dispersed 40 wt% Cu/VC and 20 wt% Cu/SWNT catalysts in comparison to electrodeposited Cu [353]. In another work, a porous Cu-NC composite catalyst for e-CO<sub>2</sub>R was synthesized using a scalable glucose blowing process. The catalyst exhibited remarkable efficiency (69% at 590 mV) in converting CO<sub>2</sub> to C<sub>1</sub> products, underscoring its strong catalytic activity [354]. Furthermore, the one-step pyrolysis synthesis of Cu Ps/BCF from butterfly wing carbon fibers and copper salt results in a material with unusual geometric features, including low-coordinated active spots at stepped surfaces. Increased conductivity from nitrogen dopants allows CO<sub>2</sub> to be reduced to C<sub>2</sub>H<sub>4</sub> at a low applied voltage while maintaining excellent selectivity and long lifetime [355].

Additionally, Kordus *et al.* have analyzed the activity and selectivity of ZnO-supported Cu nanoparticles in methanol synthesis, revealing that the shape of the pre-catalyst (cubic vs. spherical) played a significant role. Cubic Cu particles exhibited higher activity for methanol synthesis but significantly reduced selectivity compared to spherical particles, underscoring the substantial changes in morphology and content of shaped pre-catalysts under reaction conditions [356]. Also, another research has demonstrated that Cu<sub>1.8</sub>Se nanowires on Cu foam serve as effective electrocatalysts for the selective CO<sub>2</sub>R to higher-value C<sub>2</sub> products, such as C<sub>2</sub>H<sub>4</sub> and EtOH, with promising applications in the chemical and fuel industries. These

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nanowires exhibit impressive FE of 55% and 24% at -1.1 V and maintain exceptional stability over extended periods. The presence of significant concentrations of CO<sub>2</sub> and Se species were likely responsible for the observed high selectivity toward the C<sub>2</sub>/C<sub>1</sub> product [357].

In a related study, a series of Cu catalysts with adjustable particle sizes were constructed within a Zn, N-doped carbon matrix generated from ZIF-8. Crystal diameters ranging from 8.9 to 27.3 nm were observed in the enclosed Cu metal catalysts. Notably, catalysts with a grain size of 15.7 nm exhibited the highest FE<sub>CO</sub> (approximately 80%), directly correlating with their performance in the CO<sub>2</sub>RR [358]. In a separate investigation, Lou *et al.* have conducted experiments in an H-type reaction cell and a continuous-flow membrane electrode assembly (MEA) reactor to evaluate the performance of CuBi bimetallic catalysts in selectively reducing CO<sub>2</sub> to formate. The study revealed that co-electrodeposition potentials of 0.6 V yielded the best performance, with the catalyst achieving a remarkable FE<sub>formate</sub> (98.3%) at a current density of 56.6 mA cm<sup>-2</sup> in the continuous-flow MEA reactor, outperforming the H-type reaction cell. Additionally, the study identified the optimal elemental ratio of Cu to Bi at 0.6 V to maximize the catalyst's activity [359].

In another breakthrough, a novel fast-reduction approach was employed to create a Cu-decorated porous Bi/Bi<sub>2</sub>O<sub>3</sub> nanofoam, denoted as P-Cu-BiNF. The nanoparticles forming the 3D porous network architecture of P-Cu-BiNF are consistently sized at 15-20 nm. The inclusion of Cu into P-Cu-BiNF enhances CO<sub>2</sub>R performance by controlling the morphology and local electronic state of Bi/Bi<sub>2</sub>O<sub>3</sub>. Remarkably, P-Cu-BiNF exhibits a CO<sub>2</sub>-to-formate FE exceeding 90% across a wide potential range of 0.78 to 1.08 V, providing a high formate partial current density of 62.7 mA cm<sup>-2</sup> at 1.18 V while maintaining exceptional stability over time [360]. Additionally, another research has investigated nanosized Cu<sub>2</sub>O three different carbon-based substrates, namely BG (positively charged), NG (negatively charged), and rGO (weakly negatively charged), for e-CO<sub>2</sub>R with promising results. The use of these substrates led to an increase in the FE of C<sub>2</sub> products, with the FE<sub>C<sub>2</sub></sub>/FE<sub>C<sub>1</sub></sub> ratio ranging from 0.2 to 7.1, where rGO/Cu > BG/Cu > pure Cu > NG/Cu. Notably, under CO<sub>2</sub>R conditions, the negatively charged NG stabilized Cu<sup>+</sup> species, thereby improving CO\* adsorption and enhancing C-C coupling for C<sub>2</sub> products. Consequently, at high current densities, the FE<sub>C<sub>2</sub>+</sub> was significantly increased to around 68% [361]. Moreover, It is proposed that introducing different functional groups to Cu based electrocatalysts (N-, G-, COOH, NH<sub>2</sub>, and OH) can modify their selectivity and, in turn, their ability to adsorb crucial intermediates. Catalysts containing N and OH functional



groups exhibit selectivities for C<sub>1</sub> products close to 90% during e-CO<sub>2</sub>R catalysis [362].

Conclusively, support engineering approach is considered as an efficient approach for designing e-CO<sub>2</sub>R catalysts. The overview of different materials designed by following this approach is given in table 18.

**Table 18:** This table explores how support engineering approaches influence electrocatalyst materials within the context of CO<sub>2</sub>R. The table showcases a range of electrocatalyst materials that have been specifically created for CO<sub>2</sub>R. Through examining the behavior product selectivity and efficiency of these materials valuable insights are gained

N	Material	electrolyte	V vs RHE	≈ FE %									Ref.	
				H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>		
1	Cu foam			76	24	--	--	--	--	--	--	--		
2	Cu <sub>3</sub> Se <sub>2</sub> -CF	0.1 M KHCO <sub>3</sub>	-1.1	52	48	--	--	--	--	--	--	--	[345]	
3	Cu <sub>3</sub> Se <sub>2</sub> -CF-1			33	67	--	--	--	--	--	--	--	[ ]	
4	Cu <sub>3</sub> Se <sub>2</sub> -CF-2			65	35	--	--	--	--	--	--	--	--	[ ]
5	CuO-NGN			--	--	--	--	--	--	--	3	--	--	[ ]
6	CuZn <sub>10</sub> -NGN	0.1 M KHCO <sub>3</sub>	-1.0	--	--	--	--	--	--	--	7	--	[346]	
7	CuZn <sub>20</sub> -NGN			--	--	--	--	--	--	--	13	--	[ ]	
8	CuZn <sub>30</sub> -NGN			--	--	--	--	--	--	--	3	--	[ ]	
9	CuZn <sub>40</sub> -NGN			--	--	--	--	--	--	--	3	--	[ ]	
10	Cu-0/NC			65	3	--	14	--	--	--	--	--	--	[ ]
11	Cu-5/NC	0.1 M KHCO <sub>3</sub>	-1.0	22	23	5	19	--	--	--	--	--	[347]	
12	Cu-10/NC			16	18	3	8	--	--	--	--	--	--	[ ]
13	Cu-15/NC			38	20	1	7	--	--	--	--	--	--	[ ]
14	Cu-20/NC			62	6	1	3	--	--	--	--	--	--	[ ]
15	Pure Cu samples			25	7	1	17	--	--	--	--	--	--	[ ]
16	Cu5-PCC	0.1 M KHCO <sub>3</sub>	-1.0		18		2	27	--	--	6	--	[ ]	
17	Cu10-PCC			10		5	23	--	--	6	--	[348]		
18	Cu15-PCC			22	2	12	26	--	--	16	--	[ ]		
19	Cu20-PCC			15		8	20	--	--	5	--	[ ]		
20	CuS <sub>x</sub>			0.1 M KHCO <sub>3</sub>	-1.0	--	32	--	--	15	--	--	--	[363]
21	Cu foam			15	1	4	13	--	--	--	--	--	[ ]	
22	Cu-P-Acrylamide	0.1 M NaHCO <sub>3</sub>	-0.96	15	2	2	27	--	--	--	--	--	[351]	
23	Cu-P-Acrylic Acid			16	1	3	17	--	--	--	--	--	[ ]	
24	Cu-P-Allylamine			30	--	0.5	--	--	--	--	--	--	--	[ ]
25	Bi-SnO/Cu Foam			10	2	--	--	87	--	--	--	--	[ ]	
26	SnO/Cu Foam	0.1 M KHCO <sub>3</sub>	-1.6	17	3	--	--	77	--	--	--	--	[352]	
27	Cu Foam			Ag/AgCl	58	4	--	--	15	--	--	--	--	[ ]
28	Electrodeposited Cu			38	37	1	2	--	--	--	--	--	[ ]	
29	20 wt% Cu/VC			50	10	1	2	--	--	--	--	--	[ ]	
30	40 wt% Cu/VC	0.1 M KHCO <sub>3</sub>	-1.6	30	20	1	11	--	--	--	--	--	[364]	
31	20 wt% Cu/SWNT			40	18	1	17	--	--	--	--	--	--	[ ]
32	50 wt% Cu/KB			41	17	5	10	--	--	--	--	--	--	[ ]
33	Cu-NC 1:1			--	10	--	--	43	--	--	--	--	[ ]	
34	Cu-NC 2:1	0.1 M KHCO <sub>3</sub>	-1.0	--	13	--	--	35	--	--	--	--	[365]	
35	Cu-NC 1:2			--	13	--	--	42	--	--	--	--	--	[ ]



36	NC			--	12	--	--	--	--	--	--	--	View Article Online DOI: 10.1039/D4MA00321G	
37	Cu@Vul			52	28	8	3	--	--	--	--	--		[366]
38	Cu@KB	0.5 M KHCO <sub>3</sub>	-1.0	43	49	2	5	--	--	--	--	--		]
39	Cu@MGS			42	48	5	1	--	--	--	--	--		
40	Cu Ps/BCF	0.1 M KHCO <sub>3</sub>	-1.0	35	2	1	54	8	--	--	--	--		[355]
41	Cu <sub>1.8</sub> Se	0.1 M KHCO <sub>3</sub>	-1.0	--	2	--	30	3	--	--	20	--		[367]
42	ZNC			80	20	--	--	--	--	--	--	--		
43	Cu@ZNC-1			55	42	--	--	--	--	--	--	--		[358]
44	Cu@ZNC-2	0.1 M KHCO <sub>3</sub>	-0.7	38	65	--	--	--	--	--	--	--		]
45	Cu@ZNC-3			23	80	--	--	--	--	--	--	--		
46	Cu@ZNC-4			43	60	--	--	--	--	--	--	--		
47	CuBi	0.5 M KHCO <sub>3</sub>	-1.07	--	--	--	--	98.3	--	--	--	--		[359]
48	Bulk BI			--	--	--	--	91	--	--	--	--		]
49	P-Bi	0.5 M KHCO <sub>3</sub>	-1.0	--	--	--	--	85	--	--	--	--		[368]
50	P-Cu-BiNF			--	--	--	--	90	--	--	--	--		]

## 6.15. Defects engineering approach

Defect engineering plays a role, in designing e-CO<sub>2</sub>R catalysts as it greatly influences their reactivity, selectivity and overall performance. Defects like vacancies, dislocations and grain boundaries serve as sites for reactions affecting the binding energies of reactants and intermediates. The significance of this approach lies in its ability to customize the surface chemistry of catalyst materials promoting reaction pathways and desired products while minimizing side reactions. By introducing and controlling defects researchers can enhance the efficiency of CO<sub>2</sub> conversion into chemicals and fuels contributing to sustainable energy conversion and carbon capture technologies. To incorporate engineering into CO<sub>2</sub>RR catalyst design several methods can be employed. One approach involves synthesizing nanostructured materials with defects like metal nanoparticles with lattice imperfections. Another method includes treating catalysts after synthesis through annealing in atmospheres to induce formation. Surface modification techniques such as chemical functionalization or atomic layer deposition can also be utilized to introduce controlled defects onto the catalyst surface. Furthermore, combining strain engineering with defect engineering can lead to effects, in improving CO<sub>2</sub>RR performance.

In a related investigation, the study focused on faulty graphene-supported Cu<sub>4</sub>S<sub>2</sub> clusters and isolated Cu<sub>4</sub>X<sub>n</sub> clusters for e-CO<sub>2</sub>R to C<sub>1</sub> products. DFT simulations reveal that among the C<sub>1</sub> products on Cu<sub>4</sub>X<sub>2</sub> clusters, CH<sub>3</sub>OH exhibits the most favorable limiting potential, spanning from Cu<sub>4</sub>S<sub>2</sub> to Cu<sub>4</sub>Se. When it comes to selectivity and catalytic activity (-0.48 V), the Cu<sub>4</sub>S<sub>2</sub>



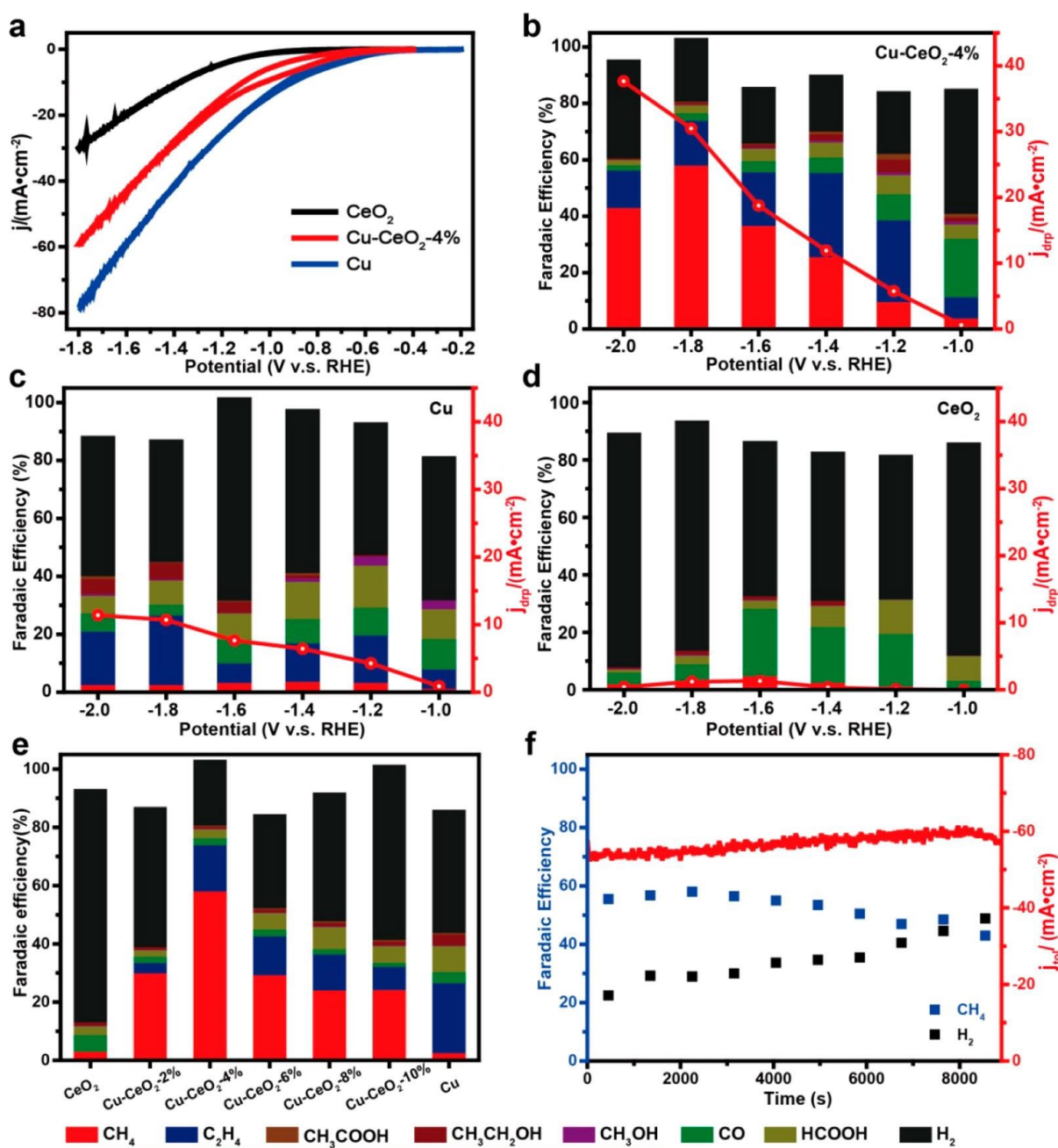
cluster stands out in the CO<sub>2</sub> conversion process. The introduction of defect-engineered graphene raises a robust interaction between the cluster and substrate, leading to enhanced catalytic performance. Crucially, the Cu<sub>4</sub>S<sub>2</sub>/SV catalyst excels in suppressing competing reactions such as HER, CO, and HCOOH generation, thereby exhibiting superior activity in producing CH<sub>3</sub>OH at low potential [369]. In a related study, Zhang *et al.* investigated e-CO<sub>2</sub>R, with a specific focus on the use of nano-defective Cu nanosheets as catalysts, aiming to enhance the production of ethylene efficiently. Remarkably, the results demonstrate that at a current density of approximately 60 mA cm<sup>-2</sup>, the ethylene FE can be significantly increased to an impressive 83.2% when employing these nano-defective Cu nanosheets as catalysts. The key role played by these nano-defects involves providing highly concentrated atomic defects that enrich reaction intermediates while limiting OH<sup>-</sup> availability. This dual effect facilitates C-C coupling reactions and ultimately enhances ethylene production [24].

Simultaneously, another study has successfully synthesized and dispersed CeO<sub>2</sub> nanotubes with diameters ranging from 100 to 300 nm and 30 to 50 nm. Importantly, these nanotubes maintain their morphology even after being loaded with Cu and Ni. The interaction between these metals leads to enhanced dispersion and reducibility within the bimetallic Cu-Ni system, effectively reducing the activation barrier for CO adsorption and promoting hydrogenation to CH<sub>3</sub>OH. Notably, robust Cu-Ni alloy-CeO<sub>2</sub> interactions further increase the reducibility of surface CeO<sub>2</sub>, facilitating the transition from Ce<sup>4+</sup> to Ce<sup>3+</sup> [370]. In another significant development, Zhou *et al.* have conducted hydrothermal synthesis to create catalysts based on MoS<sub>2</sub> with varying levels of Cu doping. The incorporation of metallic Cu into the catalyst resulted in improved crystallinity, layer thickness, and an increased number of sulfur vacancies. Notably, the 5% Cu-MoS<sub>2</sub> catalyst exhibited CH<sub>3</sub>OH production that was 2.27 times higher than that of the pure catalyst, indicating its superior efficiency in converting CO<sub>2</sub> to methanol [371]. Furthermore, La<sub>2</sub>CuO<sub>4</sub> perovskite catalyst was also designed for e-CO<sub>2</sub>R, leading to the generation of CH<sub>4</sub>. At -1.4 V vs. RHE, this catalyst achieved a partial current density of 117 mA cm<sup>-2</sup> for CH<sub>4</sub> production, with a high FE of 56.3%. Interestingly, during cathodic CO<sub>2</sub> methanation, the perovskite structure evolves simultaneously with the formation of a Cu/La<sub>2</sub>CuO<sub>4</sub> heterostructure [372].

Additionally, Deng *et al.* have explored the e-CO<sub>2</sub>R to formate using a sulfur-doped copper catalyst. Sulfur dopants were found to play a crucial role in enhancing the AC-CuS<sub>x</sub> catalyst's ability to selectively produce formate. The presence of sulfur on the copper surface altered the adsorption strengths of adsorbed HCOO\*, resulting in increased formate synthesis and reduced

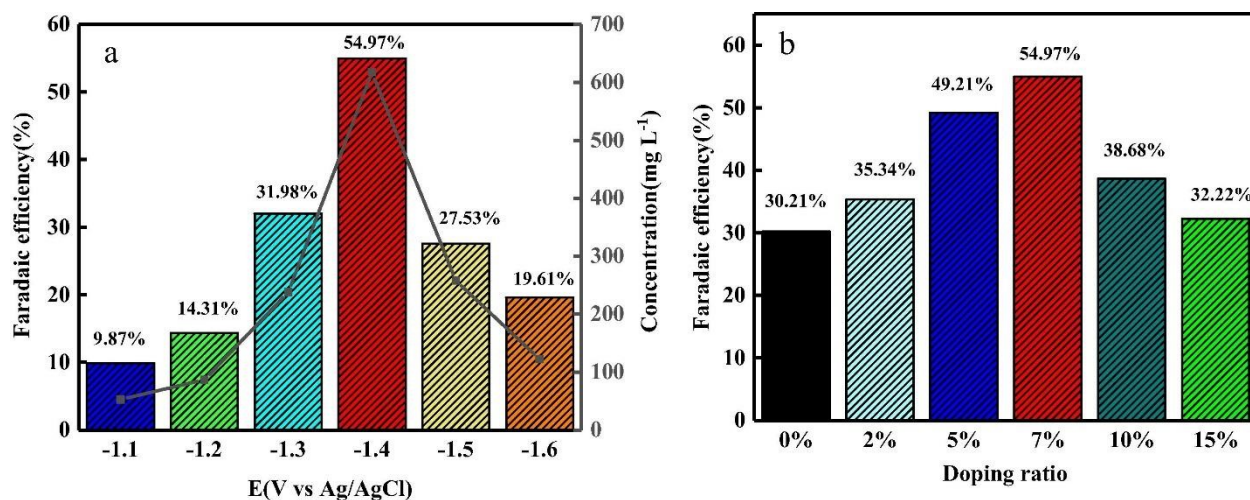


\*COOH generation, which is an intermediate in the pathway to CO production. [373] In another significant development, Wang *et al.* have successfully created a Cu-doped CeO<sub>2</sub> electrocatalyst for the selective CO<sub>2</sub>R to CH<sub>4</sub>. The strong interaction between CeO<sub>2</sub> and Cu results in the formation of single-atomic-distributed Cu species, which in turn enriches numerous OV in close proximity to one another (Figure 34). This atomic dispersion of electrocatalytic Cu sites, coupled with the surrounding OV and the cooperative effect from the CeO<sub>2</sub> framework, accounts for the exceptional efficiency of this catalytic site in converting CO<sub>2</sub> molecules into CH<sub>4</sub> [374].



**Figure 34:** Performances of e-CO<sub>2</sub>R. CV curves for Cu-CeO<sub>2</sub>, CeO<sub>2</sub>, and Cu (a). FE (bars, left y-axis) and  $j_{\text{arp}}$  (red curves, right y-axis) of Cu-CeO<sub>2</sub>-4% (b), pure Cu (c), and undoped CeO<sub>2</sub> (d) at different overpotentials. The first five goods in the legends at the bottom, which were marked with a red line, were the deep reduction products. A comparison of the FE of samples with different amounts of Cu doping (e). On the left side of the y-axis, the squares show how stable FE<sub>CH<sub>4</sub></sub> (blue) and FE<sub>H<sub>2</sub></sub> (black) (f). Total current density ( $j_{\text{total}}$ ) of Cu-CeO<sub>2</sub>-4% at 1.8 V is shown by the red arcs on the right side of the y-axis. Reproduced with permission from Ref. [374] Copyright 2018, American Chemical Society.

In the quest for more efficient catalysts for CO<sub>2</sub>R, Yang *et al.* have explored the synthesis of a (Cu, N) co-doped SnO<sub>2</sub> material through hydrothermal synthesis and calcination (Figure 35). This doping strategy significantly improved the catalyst's activity, selectivity, and long-term stability. Notably, the catalyst achieved its highest catalytic activity, reaching 54.97%, when co-doped with 7% Cu and N. Furthermore, this doping strategy reduced the material's band gap from 1.058 eV (pure SnO<sub>2</sub>) to 0.518 eV (7% doped SnO<sub>x</sub>), enhancing its ability to absorb visible light [375].



**Figure 35:** The FE of CO<sub>2</sub> reduction to formate was investigated using a carbon paper electrode loaded with 7%-(Cu, N)-SnO<sub>x</sub> at various potentials (a). The Faradaic efficiency of CO<sub>2</sub>R to formate was studied using different electrodes with varying amounts of (Cu, N) doping at a potential of -1.4 V, with an electrolysis time of 1 hour. Reproduced with permission from Ref. [375] Copyright 2020, Elsevier.

Zhang *et al.* have developed copper nanowires with a high density of flaws for e-CO<sub>2</sub>R to C<sub>2</sub>H<sub>4</sub>. These nanowires exhibit a broad potential window for C<sub>2</sub>H<sub>4</sub> synthesis and a high selectivity for



$\text{CO}_2$  products [376]. In a related study, Wu *et al.* have inserted point defects and planar defects into the Cu substrate. These defects are then used to successfully construct a highly diluted SnCu polycrystal. The electrical effect is optimized through the combined use of Sn doping and grain boundaries, which prevent  $\text{H}_2$  evolution and encourage  $\text{CO}_2$  hydrogenation [377]. In another research endeavor, density functional theory calculations were employed to examine  $\text{CO}_2\text{R}$  over three defective facets in  $\text{Cu}_2\text{O}$ . OVs were found to significantly reduce the activation barrier for C-O bond breakage, from 3.2 to approximately 1 eV. Furthermore, when  $\text{Cu}_2\text{O}$  is combined with plasmonic metals, the remaining barrier is further reduced or even eliminated under plasmon-excited states [378]. Furthermore, Wang *et al.* reveals a method for producing binder-free, OVs-rich Cu/ $\text{CuO}_x$  in-plane heterostructured nanosheet arrays (Cu/ $\text{CuO}_x$ /CF) using Cu foam as a support. The nanosheet morphology plays a crucial role during electrocatalysis by promoting efficient mass and charge transfer through the exposure of active sites. The electronic structure of these active sites is modified through the synergistic effects of in-plane heterojunctions and OVs, influencing adsorption characteristics and preventing the formation of byproducts [379].

Moreover, Zhang *et al.* have developed a CuPc/DG composite for the e- $\text{CO}_2\text{R}$  into formic acid. The presence of defective graphene in the composite plays a significant role in altering the electronic structure of Cu active centers through  $\pi$ -stacking interactions. The composite exhibits a partial current density of  $5.28 \text{ mA cm}^{-2}$  for  $\text{HCOOH}$  production, a remarkable FE of 44.6% at 0.78 V vs RHE for  $\text{CO}_2\text{RR}$  to  $\text{HCOOH}$ , and exceptional stability, maintaining its performance for at least 20 hours of continuous reaction [380]. Furthermore, in the pursuit of methane generation at single-atomic Cu active sites, Patra *et al.* have successfully developed a Cu/ceria catalyst with excellent selectivity. It was found that high selectivity during  $\text{CO}_2\text{RR}$  is regulated by the calcination temperature due to the increased concentration of OVs on the catalyst surface. Additionally, it was observed that a higher alkaline pH creates more active sites for hydrogen evolution, supporting the hypothesis that pH plays a crucial role in regulating surface termination [381]. In a related study, the importance of the Zr-O-Cu interface for  $\text{CO}_2\text{R}$  was highlighted. This study utilized Cu nanoparticles for  $\text{CO}_2\text{R}$  reduction on a UiO-66 MOF with missing-linker defects. The research revealed that the presence and quantity of linker defects significantly influence the kinetics, efficiency, and side-product production in  $\text{CO}_2\text{R}$ . An optimal range of five to seven missing linkers per unit cell was identified, striking a balance between steric effects and binding at the Zr node [382]. The crystalline or morphological defects engineering strategies has been adopted as described earlier and a number of designed



electrocatalysts are summarized in table 19. Defect engineering can focus on both crystalline and morphological aspects. The strategies have been stated before. Table 19 contains several designed electrocatalysts.

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**Table 19:** The key target is now to study how defects engineering can modify the properties of catalysts to a high precision. The table analyses the properties sanely, foregrounding what role defects play in addressing sustainable energy challenges.

N	Material	electrolyte	V		≈ FE %								Ref.
			vs RHE	H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	
1	n-CuNS	0.1 M KHCO <sub>3</sub>	-1.0	27	--	--	73	--	--	--	--	--	[24]
2	OD-Cu	0.1 M KHCO <sub>3</sub>	-0.9 5 V	37.4	1.17	1.3	30.5	6.4	--	--	12.5	--	[383]
3	La <sub>2</sub> CuO <sub>4</sub>	0.1 M KHCO <sub>3</sub>	-1.4	--	--	50	--	--	--	--	--	--	[372]
4	Cu bare		-2.54 mAc <sup>m</sup>	70.1	--	7.1	4.4	--	--	--	--	--	
5	AC-CuS <sub>x</sub>	0.1 M KHCO <sub>3</sub>	-7.4 9 mAc <sup>m</sup>	88.4	--	1.6	1.6	0.2	--	--	--	--	[373]
6	DS-CuS <sub>x</sub>		-10. 45	90.9	--	0.4	2.5	--	--	--	--	--	
7	0%-(Cu, N)-SnO <sub>x</sub>			--	--	--	--	30.21	--	--	--	--	
8	2%-(Cu, N)-SnO <sub>x</sub>			--	--	--	--	35.34	--	--	--	--	
9	5%-(Cu, N)-SnO <sub>x</sub>	0.1 M KHCO <sub>3</sub>	-1.4	--	--	--	--	49.21	--	--	--	--	[375]
10	7%-(Cu, N)-SnO <sub>x</sub>		vs Ag/AgCl	--	--	--	--	54.97	--	--	--	--	
11	10%-(Cu, N)-SnO <sub>x</sub>			--	--	--	--	38.68	--	--	--	--	
12	15%-(Cu, N)-SnO <sub>x</sub>			--	--	--	--	32.22	--	--	--	--	
13	10h-CuNWs			--	--	--	55	--	--	--	--	--	
14	15h-CuNWs			--	--	--	58	--	--	--	--	--	[376]
15	20h-CuNWs	1 M KOH	-1.0	--	--	--	38	--	--	--	--	--	
16	25h-CuNWs			--	--	--	47	--	--	--	--	--	
17	Cu			78	23	--	--	--	--	--	--	--	
18	SnCu	2.5 M KOH	-0.9	63	37		5	--	--	--	--	--	[377]
19	pc-SnCu			20	30	11	45	--	--	--	--	--	
20	0%-Cu/CeO <sub>2</sub>			85	2	--	--	--	--	--	--	--	
21	0.5%-Cu/CeO <sub>2</sub>			48	4	32	3	--	--	--	--	--	
22	1%-Cu/CeO <sub>2</sub>	1 M KOH	-0.89	43	2	42	2	--	--	--	--	--	[381]
23	1.6%-Cu/CeO <sub>2</sub>			50	5	25	4	--	--	--	--	--	
24	2.3%-Cu/CeO <sub>2</sub>			65	3	8	10	--	--	--	--	--	

## 6.16. Metal Organic Frameworks (MOF) Derived Approach

MOF based method to design e-CO<sub>2</sub>R catalysts is important because researchers can use it to design more environmentally friendly products. What's interesting about MOFs is they provide a platform that can be easily adjusted to meet the demands of catalyst development. There are



lots of MOFs which consist of metal ions bound to ligands, differing in qualitative properties from each other because of their unique structures. By choosing appropriate metal ions and ligands researchers can prepare MOFs that are able to be used as catalytic materials. The method which is advocated here has control over the composition, structure and surface properties of the catalyst. Many ways can be used for us to apply the MOF derived approach in the design of CO<sub>2</sub>RR catalysts. One method widely used is that MOFs are thermo chemically decomposed by calcination in a controlled atmosphere, hence forming carbon-related materials which have definite structure and active site. In situations MOFs can serve as templates, for depositing metal nanoparticles or individual atoms. This enables the development of catalysts that exhibit improved properties. The approach derived from MOFs offers a foundation for designing CO<sub>2</sub>RR catalysts. By leveraging the characteristics of these materials, we can tackle the urgent issues related to carbon capture and conversion while fostering a sustainable and environmentally friendly future, with reduced carbon emissions.

Zhao *et al.* offers a strategy by using a Cu-based MOF (HKUST-1) and created oxide-derived Cu/carbon (OD Cu/C) catalysts. At -0.1 to -0.7 V vs RHE, the resultant materials exhibited a total FE of 45.2%-71.2%, demonstrating highly selective CO<sub>2</sub>R to alcohol molecules. Ethanol and methanol yields were optimized to 3.7-13.4 mg L<sup>-1</sup>h<sup>-1</sup> and 5.1-12.4 mg L<sup>-1</sup>h<sup>-1</sup>, respectively. Near -0.1 V, or 190 mV overpotential, C<sub>2</sub>H<sub>5</sub>OH production began to occur [384]. In another work, Cu<sub>3</sub>(BTC)<sub>2</sub> (Cu-MOF) is incorporated into carbon paper-based GDEs as a CO<sub>2</sub> capture agent. This incorporation results in higher FEs of CH<sub>4</sub> on GDEs with Cu-MOF weight ratios, greatly improving the conversion efficiency and product selectivity of CO<sub>2</sub> electroreduction [385]. In a related field, Ma *et al.* designed CTF-B constrained Cu catalysts with an impressive maximum FE of 81.3% for CO<sub>2</sub>R. Their investigations revealed the dynamic development of Cu-ACs, active sites for CO<sub>2</sub>RR, in response to potential, as demonstrated through in vivo XAFS investigations [386]. In a complementary study, Kim *et al.* successfully controlled the shape of Cu-MOFs into nanoparticles with diameters of 80 nm using a seed-mediated solvothermal polyol method. During more than 10 hours of e-CO<sub>2</sub>RR under neutral conditions, the MOF-based copper catalysts exhibited maximum selectivity towards ethylene and C<sub>2+</sub> products. By employing a GDE technique, they maintained high FE and generated a high partial geometric current density toward C<sub>2+</sub> products in alkaline circumstances [387].

In a related investigation, a thin film of organic additives like N-toylpyridinium can effectively restrict H<sup>+</sup> mass passage to the electrode without impeding CO<sub>2</sub> transit. This strategic



modification leads to improved production of  $C_{2+}$  products and a reduction in the competitive HER. Modified copper electrodes enhance selective  $CO_2R$  to  $C_{2+}$  products, even in very acidic electrolytes and at low alkali cation concentrations and operating current densities [388]. In a separate investigation, another study explores the effectiveness of electrolysis at a constant potential in six different electrolytes ( $KHCO_3/H_2O$ , TBAB/DMF,  $KBr/CH_3OH$ ,  $CH_3COOK/CH_3OH$ , TBAB/ $CH_3OH$ , and TBAP/ $CH_3OH$ ) for the  $CO_2R$ . Notably,  $KHCO_3/H_2O$  and TBAB/ $CH_3OH$  showed a lower onset potential. Across all electrolytes, the primary product generated was HCOOH, although with varying maximum formic acid concentrations. Interestingly, when using a 0.1 M TBAB/DMF electrolyte, the synthesized MOF material exhibited a high efficiency of 58% in forming both HCOOH and  $CH_3COOH$  products [389]. Furthermore, through a novel approach of carbonizing Cu-btc at steady temperatures, a new catalyst ( $Cu_2O/Cu@NC-800$ ) was developed. Carbonizing the catalyst at 800 °C significantly increased its activity and selectivity toward formate production. The formation of low-index facets and the uniform distribution of metallic nanoparticles within N-doped carbon frameworks played a key role in enhancing the catalyst's activity. The increased nitrogen content in the  $Cu_2O$  lattice lowered the binding energy of  $*OCHO$ , facilitating easier formate synthesis via the  $*OCHO$  pathway [390].

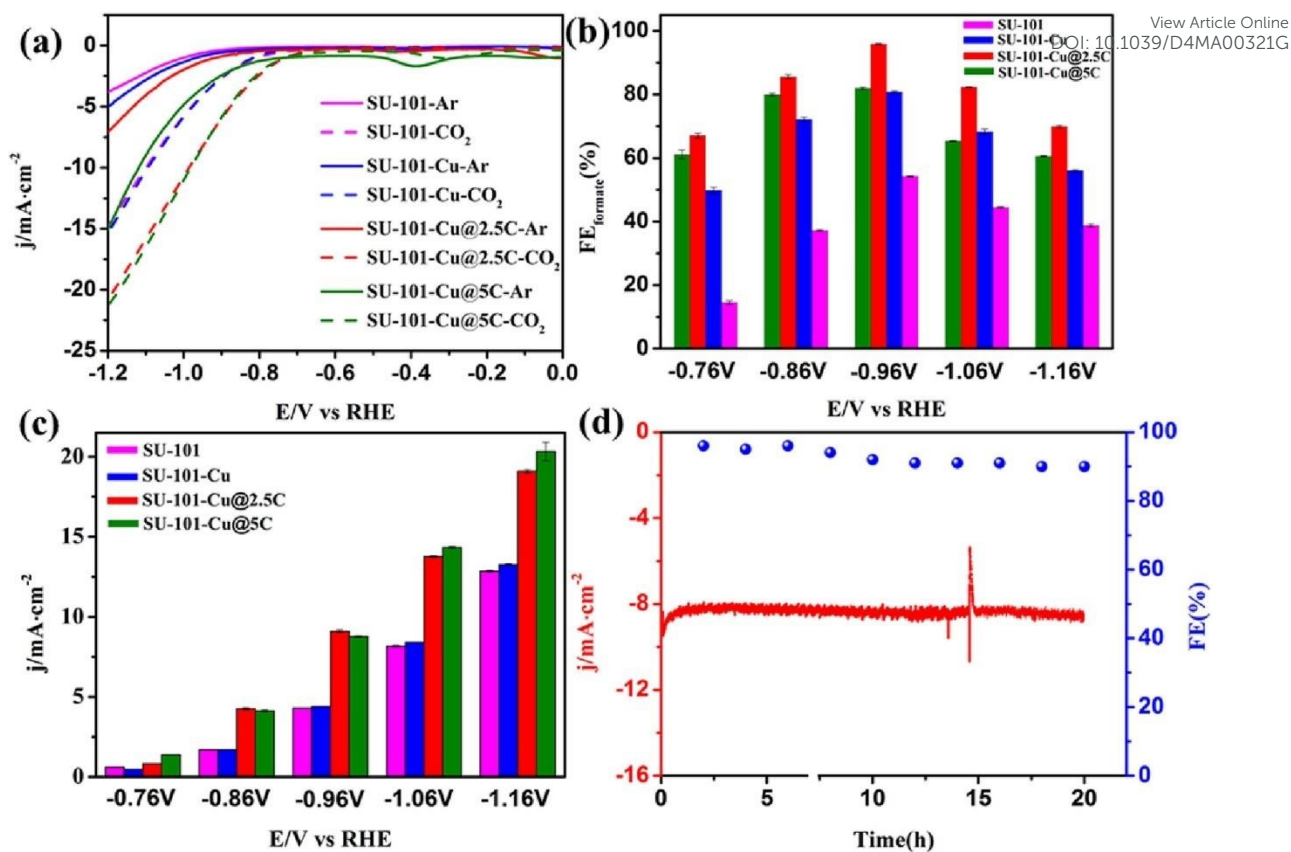
In a related context, another research focused on regulating the structural evolution of porous materials during e- $CO_2RR$  to develop new electrocatalysts. To promote the coupling of C radical intermediates for the creation of  $C_{2+}$  products, TCNQ was introduced as a second electron acceptor to expedite the reduction of Cu(II) sites to Cu(I) species. The resulting TCNQ@CuMOP-p/CP catalyst exhibited a high selectivity of 68% for  $C_{2+}$  products at a total current density of 268 mA  $cm^{-2}$  and 2.27 V vs. RHE, making it competitive with the best Cu(II)-MOF-derived catalysts for  $CO_2RR$  [391]. Furthermore, Cheng *et al.* revealed that the e- $CO_2RR$  performance of Cu catalysts derived from MOFs is greatly influenced by the amount and types of nitrogen present in the carbon shell. The remarkable selectivity for the production of ethylene and ethanol can be attributed to the high pyrrolic-N and Cu-N doping in the carbon support, which provides numerous  $CO_2$  adsorption sites and facilitates carbon-carbon coupling processes. However, an abundance of graphitic-N and oxidized-N atoms can lead to severe competition from the HER. Therefore, enhancing the synergy between Cu and the nitrogen-doped carbon support requires modifications to the N structure [392].



In related research, the synthesis of a single-atom copper catalyst based on MOFs via plasma activation was described by Wei *et al.* The plasma bombardment increases low-coordinated copper sites and creates OV<sub>s</sub>, while also forming a hierarchically porous structure that effectively adsorbs reactant molecules. This unique combination of features greatly enhances e-CO<sub>2</sub>R activity, resulting in a maximum FE of 75.3%. Products with carbon content achieve a total FE of 96.5 % [393]. Furthermore, the research reveals that homemade e-CO<sub>2</sub>R reactors can be constructed using CuIn-MOF series catalysts coated on carbon paper. These catalysts have low over-potentials, large current densities, and selective activity toward CO and formic acid. The stability can be enhanced by adjusting the relative molar ratio of Cu/In, which results in a current density between 20.1 and 88.4 mA cm<sup>-2</sup>. Cu<sub>1</sub>In<sub>1</sub>-MOF-SO<sub>4</sub> exhibits the highest e-CO<sub>2</sub>R activity, while Cu<sub>1</sub>In<sub>3</sub>-MOF-NO<sub>3</sub> and Cu<sub>1</sub>In<sub>3</sub>-MOF-SO<sub>4</sub> have the highest FE<sub>CO</sub> and FE<sub>HCOO<sup>-</sup></sub> values [394]. In another study, MOF-derived In-Cu bimetallic oxides were used in a 0.5 M KHCO<sub>3</sub> aqueous solution for the e-CO<sub>2</sub>R to CO. With a total current density of 11.2 mA cm<sup>-2</sup> and a FE of 92.1%, InCuO-0.92 was found to be a very effective and stable catalyst. The improved performance was traced back to the synergistic impact between In and Cu oxides, the increased electrochemical surface area, the greater CO<sub>2</sub> adsorption, the lower charge transfer resistance, and the porous mass diffusion structure [395]. Furthermore, through in-situ modification of MWCNTs, a novel BiCu bimetallic organic framework composite catalyst, SU-101-Cu@2.5C, was effectively developed and synthesized (Figure 36). The catalyst's efficiency in converting e-CO<sub>2</sub>R to formate was investigated. The combination of BMOFs and MWCNTs created a synergistic effect that facilitated electron transport, ultimately enabling efficient e-CO<sub>2</sub>R to formate [396].

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**Figure 36:** The electrocatalytic performance of SU-101, SU-101-Cu, and SU-101-Cu@xC was evaluated through LSV measurements in CO<sub>2</sub> and Ar atmospheres (a). The measurements included different applied potentials, FE<sub>formate</sub> (b), and current density (c). The SU-101-Cu@2.5C was tested for long-term durability at a voltage of -0.96 V vs RHE for a duration of 20 hours (d). Reproduced with permission from Ref. [396] Copyright 2023, Elsevier.

Additionally, Cu-MOF808 was pyrolyzed to produce Cu@ZrO<sub>2</sub> with a hollow structure. This transformation allowed for the control of the porosity structure and metal-support interaction through varying pyrolysis temperatures. Notably, the numerous Cu-ZrO<sub>2</sub> interfaces created during proper calcination were instrumental in facilitating the hydrogenation of CO<sub>2</sub> to methanol. CO<sub>2</sub> primarily found absorption and activation sites at the fundamental locations of Cu-ZrO<sub>2</sub> interfaces, underscoring the significance of the Cu<sup>+</sup>/Cu<sup>0</sup> ratio. Among these catalysts, CM-300 at 220 °C demonstrated the most remarkable efficacy for converting CO<sub>2</sub> into methanol, boasting a 5% conversion rate and an 85% selectivity for methanol [397]. Furthermore, electrocatalytic stability and performance in hydrocarbon synthesis can be substantially enhanced by post-synthetic alterations of copper-based MOFs. This improvement involves converting free COOH/-OH groups into amide/amine groups. The modified MOFs



exhibit high electrocatalytic performance (total FE = 81%, with  $FE_{C_1} = 62\%$  and  $FE_{C_2} = 19\%$ ) and remarkable stability [398].

Moreover, Liu *et al.* have developed Cu-N coordinated MOFs for selective  $C_2H_4$  production, and in situ electrochemical reconstruction was employed to construct highly active Cu/Cu<sub>2</sub>O nanoclusters. The FE for  $C_2H_4$  production, measured by partial current density at 1.03 V vs RHE in the CO<sub>2</sub>RR, reached  $70.2 \pm 1.7\%$  [399]. In addition, Parambath *et al.* have utilized a Cu-based MOF, namely HKUST-1. Remarkably, these materials exhibited high selectivity in CO<sub>2</sub>R to alcohol molecules, with total FE ranging from 45.2% to 71.2% at potentials between -0.1 and -0.7 V vs RHE. Ethanol and methanol yields were optimized to 3.7-13.4 mg L<sup>-1</sup> h<sup>-1</sup> and 5.1-12.4 mg L<sup>-1</sup> h<sup>-1</sup>, respectively. The overpotential for CO<sub>2</sub> reduction, as indicated by the onset potential for C<sub>2</sub>H<sub>5</sub>OH production, was modest and close to -0.1 V [400]. Table 20 showcased different MOF designed for e-CO<sub>2</sub>R to yield valuable products.

**Table 20:** The table presents an overview of electrocatalyst materials that have been developed using strategies derived from MOF for CO<sub>2</sub>R. This overview focuses on comprehensively examining the characteristics of MOF and its influence on the resulting products.

N	Material	electrolyte	V vs RHE	≈ FE %									Ref.	
				H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	HCOO <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>		
1	OD Cu/C-1000	0.1 M KHCO <sub>3</sub>	-0.7	--	--	--	--	9	--	15	33	--	[384]	
2	Cu/C1000			--	--	--	--	16	--	4	12	--	[385]	
3	Cu-MOF-10 %	0.5 M NaHCO <sub>3</sub>	-1.8	47	--	11	16	--	--	--	--	--	[401]	
4	NNU-50	--	-1.1	--	--	66	--	--	--	--	--	--	[402]	
5	Cu <sub>6</sub> MePz			--	--	22	--	--	--	--	--	--	--	[403]
6	n-MDC-225	1.0 M KOH	-1.01	45.9	7.3	9.8	29.6	5.8	--	--	5.2	--	[404]	
7	n-MDC-250			13.4	2.3	1.9	63.1	3.2	--	--	12.5	1.2	[405]	
8	n-MDC-300			22.2	5.0	0.5	52.6	9.6	--	--	2.0	7.7	[406]	
9	m-MDC-250			36.0	10.4	3.3	34.7	11.7	--	--	5.6	--	[407]	
10	m-MDC-265			27.7	2.7	1.4	48.3	5.9	--	--	11.6	0.1	[408]	
11	m-MDC-300			27.8	7.7	0.7	25.1	24.6	--	--	7.9	6.0	[409]	
12	Cu	H <sub>3</sub> PO <sub>4</sub> /KH <sub>3</sub> PO <sub>4</sub> , [K <sup>+</sup> ] = 0.1 M	-1.2	95	0.14	--	--	1	--	--	--	--	[410]	
13	Cu / 10 mM tolyl-pyr		9	-1.4	23.7	0.7	1.9	24.3	3.4	--	--	23.8	--	[411]
14	Cu <sub>2</sub> O/Cu@NC-700	0.1 M KHCO <sub>3</sub>	-0.88	--	--	--	--	28	--	--	--	--	[412]	
15	Cu <sub>2</sub> O/Cu@NC-800			--	--	--	--	42	--	--	--	--	--	[413]
16	Cu <sub>2</sub> O/Cu@NC-900			Ag/AgCl	--	--	--	--	20	--	--	--	--	--



17	TCNQ@CuMOP-p/CP		--	18	1	15	10	--	--	6	--	
18	HKUST-1-p/CP		--	20		10	5	--	--	7	--	[404
19	TCNQ@HKUST-1-p/CP	1.0 M KOH	-1.07	--	25	15	8	--	--	6	--	]
20	CuMOP-p/CP		--	18	1	12	8	--	--	5	--	
21	PA-CuDBC-1		15	15	60	10	--	--	--	--	--	
22	CuDBC	0.5 M KHCO <sub>3</sub>	-1.0	43	42	--	1	--	--	--	--	[405
23	PA-CuDBC-2		30	30	30	10	--	--	--	--	--	]
24	CuIn-MOF-SO4		--	50	--	--	--	--	--	--	--	
25	CuIn-MOF-NO <sub>3</sub> (Cu/ In molar ratio ¼ 1:3)	0.5 M KHCO <sub>3</sub>	1.06	--	38	--	--	--	--	--	--	[406
26	In <sub>2</sub> O <sub>2</sub>		--	10	--	--	--	--	--	--	--	]
27	InCuO-0.15		--	30	--	--	--	--	--	--	--	
28	InCuO-0.37	0.5 M KHCO <sub>3</sub>	-1.0	--	50	--	--	--	--	--	--	[407
29	InCuO-0.55		--	70	--	--	--	--	--	--	--	]
30	InCuO-0.72		--	83	--	--	--	--	--	--	--	
31	InCuO-0.92		--	91	--	--	--	--	--	--	--	
32	SU-101-Cu@5C		28	2	--	--	65	--	--	--	--	
33	SU-101-Cu@2.5C	0.5 M KHCO <sub>3</sub>	-1.06	5	2	--	--	82	--	--	--	[396
34	SU-101-Cu		15	10	--	--	70	--	--	--	--	]
35	SU-101		43	7	--	--	45	--	--	--	--	

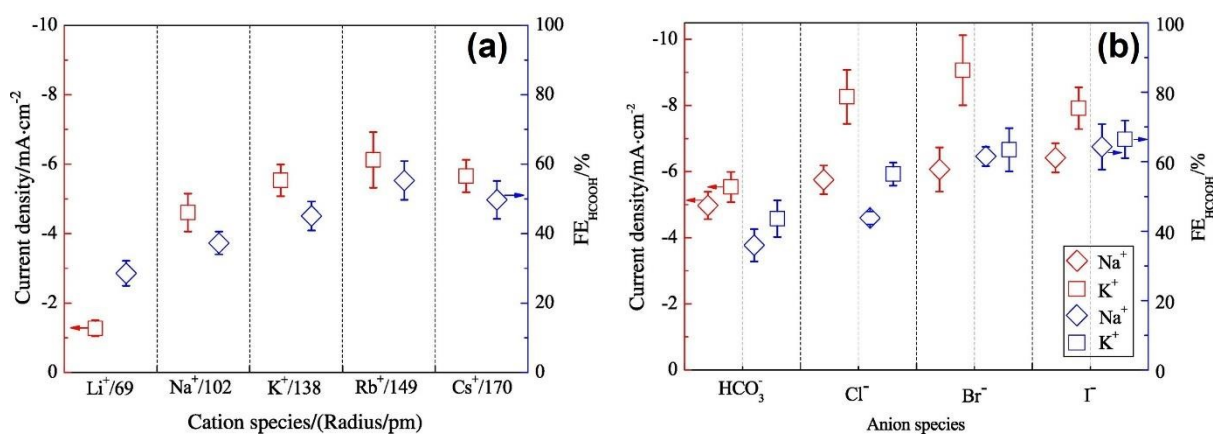
## 6.17 Alkaline Metal Cations and Halide Anions on Cu Electrocatalysts

The modification of Cu electrocatalysts through the adsorption of alkaline metal cations and halide anions has shown significant impact on the e-CO<sub>2</sub>RR. This section explores the mechanisms and outcomes of such modifications. Alkaline metal cations, such as Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup>, play a crucial role in CO<sub>2</sub>RR. These cations interact with the electric double layer at the catalyst surface, affecting the local electric field and the binding strength of reaction intermediates. The size and hydration energy of these cations influence their specific adsorption properties, which in turn modify the catalytic activity and selectivity [408]. Smaller cations like Li<sup>+</sup> have higher charge densities and stronger hydration energies, leading to different adsorption behaviors compared to larger cations like Cs<sup>+</sup> [409]. These differences impact the stabilization of key intermediates such as CO<sub>2</sub>•<sup>-</sup> and \*CO. Adsorbed cations can alter the local electric field at the catalyst surface, influencing the electron transfer kinetics. For example, larger cations may create a more diffuse electric field, which could enhance the formation of multi-carbon products by stabilizing the required intermediates [410].

Halide ions on copper surfaces play a crucial role in e-CO<sub>2</sub>RR by weakening the C-O bonds of CO<sub>2</sub>, lowering hydrogenation potential barriers. Understanding halide modified copper electrocatalysts (Cu-X) can help design efficient Cu-X electrocatalysts for e-CO<sub>2</sub>RR. Factors influencing catalytic performance include morphology, oxidation state, and electrolyte pH/composition [411]. Halide anions, including Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>, adsorb on the Cu surface and



modify the catalytic properties through electronic and geometric effects. Yuan et al. have presented a method to immobilize Cu-based catalysts during the e-CO<sub>2</sub>RR, revealing the fundamental mechanism of specific adsorption of halide ions. The method involves pre-reduction in aqueous KX electrolytes and e-CO<sub>2</sub>RR using non-buffered K<sub>2</sub>SO<sub>4</sub>. In situ spectroscopy shows that specific adsorption enhances the adsorption of \*CO intermediates, achieving a high selectivity of 84.5% for C<sub>2+</sub> products [412]. Zhang and co have investigated the impact of alkali metal cations and anions on the current density and product selectivity of e-CO<sub>2</sub>RR into HCOOH on a SnO<sub>2</sub>/carbon paper electrode. Results showed that cations promote current density and faradaic efficiencies, while anions decrease current density and FEs for HCOOH formation [413]. The current density and FE<sub>HCOOH</sub> were found to be in the order of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, and Rb<sup>+</sup>. The cation species' effect is attributed to the change in surface charge density influenced by the radius of hydrated cations and the pH values determined by the small number of bare cations. The anions' promotion of current density was found to be in the order of NaHCO<sub>3</sub> < NaCl < NaBr < NaI and KHCO<sub>3</sub> < KCl ≈ KI < KBr, and the effect on FE<sub>HCOOH</sub> was in the order of HCO<sub>3</sub><sup>-</sup> < Cl<sup>-</sup> < Br<sup>-</sup> < I<sup>-</sup>. The influence of anions on ER<sub>CO<sub>2</sub></sub> to HCOOH is mainly due to changes in CO<sub>2</sub>, H<sup>+</sup>, and OH<sup>-</sup> transport, as well as anions' adsorption (Figure 37).



**Figure 37:** Current density and  $FE_{\text{HCOOH}}$  as functions of electrolyte type and the cation size, measured using an SnO<sub>2</sub>/C electrode at  $-1.4$  V in (a)  $0.1 \text{ molL}^{-1}$  MHCO<sub>3</sub> ( $M = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$ ) and NaX and KX ( $X = \text{HCO}_3^-, \text{Cl}^-, \text{Br}^-$  and  $\text{I}^-$ ), respectively. Reproduced with permission from Ref. [413] Copyright 2020, Elsevier.



## 7. Summary

In the process of developing technology to fight climate change, e-CO<sub>2</sub>R copper-based catalysts can be rationally designed, offering hope for the future of this method. Among engineering strategies, the single crystal and atom approach is a standout technique. This innovative technique involves dispersing individual copper atoms onto a support material resulting in efficiency and selectivity for CO<sub>2</sub>R. By distributing metal atoms scientists can minimize the use of scarce metals while maximizing catalytic activity. Control over sites and this approach are appropriate to address challenges, and offer opportunities for efficiency and selectivity.

Another important strategy in designing copper-based catalysts is oxidation state engineering. In designing copper-based catalysts, another important possibility is oxidation state manipulation. The structure of the catalyst allows for optimization of e-CO<sub>2</sub>R, through tailoring. Balance between activity and selectivity is achieved by this approach. Utilizing alloys is also a robust strategy for designing copper-based catalysts. Copper and metals are strategically combined here. With customized properties, these alloys have been adapted. Compound alloys further take this concept by introducing elements into the alloys that not only increase its strength but make it more accurate. In catalyst design, these strategies allow for fine tuning of activity and selectivity.

The methods of composite engineering involve the addition of copper-based catalysts to other functional materials in order to increase their stability and activity. Typically, these composites are made up of copper nanoparticles incorporated in a supportive matrix that gives them improved performance. Another way is to add other metals to the structure of copper-based catalysts, to produce changes in their properties and catalytic behavior. This approach may result in high activities and selectivity but sustainability as well as cost are among its drawbacks. On the hand nonmetal doping offers an approach to modify the properties of Cu catalysts by introducing nonmetal elements into their structure. This allows researchers to tailor their properties and reactivity for optimized CO<sub>2</sub>R efficiency and selectivity. Surface anchoring focuses on attaching metal nanoparticles to support materials preventing agglomeration and enhancing stability.

Molecular surface functionalization involves modifying the surface of the catalyst with molecules to enhance CO<sub>2</sub> adsorption and reactivity. This strategy improves activity and selectivity by customizing the surface properties of the catalyst. Interfacial engineering aims at optimizing interactions between the catalyst and reactants thereby improving CO<sub>2</sub> reduction





efficiency. Additionally controlling the chemical species, on the surface of Cu, through speciation influences its behavior. Facet engineering focuses on manipulating the crystal surfaces of Cu based catalysts to optimize the adsorption and conversion of CO<sub>2</sub>. The coordination engineering approach involves adjusting the arrangement of Cu atoms, in the catalyst, which affects their reactivity. The site engineering approach aims to control the sites on the catalysts surface to optimize CO<sub>2</sub> adsorption and conversion. Strain engineering employs chemical methods to introduce strain into the catalyst structure, which impacts its properties and catalytic activity. The catalyst pre oxidation approach involves controlled oxidation to enhance its performance.

The precursor deriving methods use precursor materials to fabricate Cu-based catalysts with the properties desired. As an alternative, polymer modification procedures introduce polymers into the catalyst structure and increase stability and reactivity. By taking an engineering perspective, assisting in optimizing the support material of the catalyst for better performance. Defect engineering methods involve carefully forming defects within catalysts as sites for the adsorption and reduction of CO<sub>2</sub>. By reducing costs, increasing both activity and selectivity, this process also turns Cu to a primary catalyst material.

## 8. Conclusions

To sum up, by producing copper-based catalysts for e-CO<sub>2</sub>R, one can hit three birds with one stone by fighting global warming, alleviating energy tension and facilitating sustainable technologies. Various engineering techniques, from doping of atoms to changing defects, have been studied to improve these catalysts' performance. The single atom approach controls sites effectively and attains outstanding efficiency and selectivity in CO<sub>2</sub> reduction. Therefore, this approach will prove an asset in future catalyst modification. Moreover, strategies involving oxidation state manipulation, alloy combinations, and composite designs offer flexibility in catalyst development, providing customized properties that match specific needs. Doped with both metal and non-metal additives, as well as surface functionalization techniques, these are ways to modify catalysts for greater reactivity. Interfacial, facet, coordination, site, strain, and speciation engineering approaches allow fine-tuning of catalyst behavior. Catalyst preoxidation, precursor-derived, polymer modification, support engineering, and defect engineering help to further improve the optimization of catalysts. Cost effectiveness plays a vital part in making CO<sub>2</sub> utilization a commercial reality. While the costs of such techniques may be raised by approaches like doping with elements, defect engineering with low-cost Cu as the main material offers an economically viable option. For practical applications, stability

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is essential, and much attention is paid to these problems. Combined with defect engineering, single-atom methods have shown excellent stability, while metal doping with noble metals also helps protect against corrosion and agglomeration. Long-term catalyst reliability can also be achieved through proper defect engineering, strict control of sites for activities, and strain engineering.

Based on the comprehensive analysis presented in this review, it is evident that no single approach stands out as the universally best strategy for designing Cu-based electrocatalysts for e-CO<sub>2</sub>R. However, the combination of several engineering strategies appears to be the most promising pathway. Specifically, integrating doping techniques with surface and defects engineering can synergistically enhance the catalytic performance by improving both the activity and selectivity of the catalysts. This multi-faceted approach leverages the strengths of each individual strategy, offering a balanced solution that addresses the various challenges associated with CO<sub>2</sub>R. Moreover, the incorporation of advanced in-situ spectroscopic and computational studies provides critical insights into the reaction mechanisms and intermediate species, guiding the rational design of these hybrid catalysts. This combination not only allows for real-time monitoring and optimization of catalytic processes but also facilitates the prediction and screening of potential modifications at an atomic level. Therefore, a holistic strategy that combines experimental advancements with theoretical insights is recommended as the best approach for the development of high-performance Cu-based electrocatalysts for CO<sub>2</sub> electroreduction.

## 9. Future Outlook

Cu-based e-CO<sub>2</sub>R catalysts project a bright future for further innovation and development. There are several main directions and problems we would like to discuss. In addition, given advances in materials science, future catalysts may be designed to carry out various reactions simultaneously, as applications progress in this area. The realizability of Cu-based catalysts is necessary for real-world usage. Researchers must work out high-capacity synthesis methods and steps. Under industrial conditions, maintaining long-term durability and reliability of Cu-based catalysts is all-important. Taking steps to lessen catalyst deterioration ought to be a target of future research. The integration of catalysts into CO<sub>2</sub> capture and utilization systems will facilitate the realization of efficient CO<sub>2</sub>R processes. Integrating e-CO<sub>2</sub>R with solar and wind power, among other renewable sources, can make the technology more ecological and manageable. We need to tailor Cu-based catalysts so that they can selectively make ethylene or ethanol or other multi-carbon products in order to satisfy various industrial demands. To



ensure these techniques overall sustainability, rigorous assessments of the environmental and energy impacts of Cu-based CO<sub>2</sub> reduction technology are necessary. Regulations and policies should be introduced as Cu-based catalysts and CO<sub>2</sub> utilization technologies mature to support their deployment and promote environmentally sound practices. To accelerate the use of Cu-based catalysts and development of new candidates, in cooperation with researchers, industry participants, and governments from around the world, a collaborative approach will be required.

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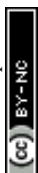


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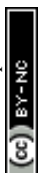
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