Understanding the Mechanism of Electrochemical Reduction of CO₂ Using Cu/Cu-Based Electrodes: A Review

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ABSTRACT: Interestingly, copper has been identified as an ideal metal catalyst for an industrial scale electrochemical reduction of CO₂ to various value-added chemicals relative to other metal catalysts reported so far. This is due to the fact that copper and copper based materialshave the potential to convert CO₂ to oxygenates such as ethanol, methanol, formates etc. and hydrocarbons such as ethane, methane etc. Mechanistic details on how these products are formed on the catalyst-electrolyte interphase during the reduction process have remained relatively uncovered. This review, therefore, seeks to uncover the mechanism of electrochemical reduction of CO₂ on Cu/Cu based electrodes, factors that affect catalytic activity and selectivity for these electrodes as reported in various literatures. This paper is, therefore, organized as follows: section 1 covers the introduction; an overview of some basic concepts in electrochemical CO₂ reduction (ECR) was discussed in section 2, experimental studies were discussed in section 3, and, finally, we have conclusion.

KEYWORDS: Copper electrode, Catalyst, mechanism, CO₂ reduction, Selectivity

GRAPHICAL ABSTRACT:
1. Introduction
Since the industrial revolution of the 19th century, the global trend in technological advancement has always been on the increase, and so is the exploitation of fossil fuels (i.e., coal, petroleum and natural gas) as the main source of energy in order to sustain our economies and societies. These fossil fuels as non-renewable energy sources get depleted on an increasing basis which gives rise to a series of problems [1–3]. On the one hand, the aforementioned advancement, coupled with rapid population growth has resulted to increased energy demand, while fossil fuels as non-renewable resources have very limited reserves, which is gradually leading towards an aggravated energy crisis. Due to the huge consumption of fossil fuels, carbon dioxide (CO\textsubscript{2}) as one of the by-product of the combustion of fossil fuels has been constantly emitted and kept accumulated in the atmosphere year by year. Various studies have shown that, the concentration of atmospheric CO\textsubscript{2} as of 22\textsuperscript{th} July, 2017 is as high as 406.38 parts per million (ppm), which far exceeds the threshold safety value of 350 ppm for atmospheric CO\textsubscript{2} [4]. This increased in CO\textsubscript{2} levels has been associated with undesirable climatic effects such as global warming, desertification, rising sea levels, and more erratic weather patterns. Therefore, alleviating the effects caused by the heavy CO\textsubscript{2} emission has become a pressing issue to the modern society [5,6]. Different strategies have been adopted for the reduction of CO\textsubscript{2} emission and mitigating climatic change which include; the use of clean renewable energy sources such as solar, wind and tide in place of fossil fuels, and direct capture and sequestration of CO\textsubscript{2} for a long time isolation from the atmosphere (“carbon capture and Storage” CCS) [7–10]. The captured CO\textsubscript{2} emissions can also be considered as a valuable resource because CO\textsubscript{2} can be catalytically converted into industrially relevant chemicals and fuels. This is an extremely attractive approach since it can reduce the carbon footprint associated with fossil-fuel-powered processes, thus allowing the sustainable use of current fossil-fuel resources, and generate revenue to offset the costs associated with other CO\textsubscript{2} capture, storage, and transport efforts. Several methods have been proposed for the conversion of CO\textsubscript{2} to value added chemicals; however, thermochemical, photochemical, and electrochemical CO\textsubscript{2} conversion are all promising catalytic approaches [11]. Electrochemical CO\textsubscript{2}-conversion technologies are appealing
because they operate with high reaction rates and good efficiencies under ambient conditions, use environmentally benign aqueous electrolytes, easily couple with carbon-free electricity sources (e.g., wind, solar, hydroelectricity, etc.) and the reaction rate can be controlled easily by tuning the external bias (i.e., overpotential) [12]. Another benefit of electrochemical CO\textsubscript{2} conversion is that several voltage-dependent products are accessible, including formic acid, carbon monoxide, methane, and ethylene etc. [13,14]. Although the electrochemical reduction of CO\textsubscript{2} to value-added products has promised the high overpotential of this reaction, low selectivity and production rate, however, activity of the currently known catalysts still hampers this process from becoming close to commercialization. This is backed by the fact that typical current densities have been in the order of milliamps per square centimeter (mA/cm\textsuperscript{2}) of electrode and catalyst surface whereas industrial water electrolyzers operates at the magnitude of 2A/cm\textsuperscript{2} [15,16]. Current researches in this field are aimed at obtaining an ideal catalyst, capable of electrochemical conversion of CO\textsubscript{2} at an industrial scale with improved efficiency, low overpotential and high selectivity towards a particular product. In this way, CO\textsubscript{2} electrochemical reduction to liquid fuels and other value-added chemical feed stocks could become a sustainable way to store chemical energy in liquid forms.

Studies have shown that several metallic elements such as Cu, Au, In, Sn, Pb, Zn, Ag, Pd, Bi and Carbon based materials are catalytically active for the electrochemical CO\textsubscript{2} reduction in aqueous electrolytes [17–27]. However, several factors have been identified to affect the yield and type of products obtained during electrochemical reduction of CO\textsubscript{2}. These factors include; the type, nature and morphology of the metal electrode used as the catalyst, the type of electrolyte used, the medium in which the reaction was conducted, the applied potential and reaction conditions such as temperature and pressure. These aforementioned metals with catalytic activity for the reduction of CO\textsubscript{2} are grouped into three classes based on the major products obtained during their electrochemical reaction. Elements such as Sn, Hg, Pb, and In, etc., are classed as group 1 metals because they generate formate or formic acid as their main products [21]. Au, Ag, Zn, and Pd are typical representatives of the group 2 metals whose predominant reaction product is CO [15,16], whereas Cu is a representative of the group 3 family and
greater attention is given to Cu/Cu-based materials because it is the only catalyst known to electrochemically convert CO$_2$ to hydrocarbons and/or oxygenates such as ethanol at considerably high Faradaic efficiency (FE) [28]. Intensive research efforts, both experimental and theoretical, have focused on improving the overpotential and selectivity of Cu-based catalysts for the electrochemical reduction of CO$_2$ to specific products. Among the range of value-added chemicals into which CO$_2$ can be reduced to, ethanol and hydrocarbons receive more attention because of their economic importance and application as alternative sources of fuels (biofuels) other than fossils, they can also serve as feed stocks for various chemical industries.

Several quality reviews have been published which discussed the catalytic conversion of CO$_2$ to value-added chemicals on various metal catalysts. However, few among such reviews were dedicated to Cu and Cu-based materials. This review, therefore, seeks to dig deep into the world of Cu/Cu-related catalysts in order to understand the mechanism of electrochemical reduction of CO$_2$ taking into account, the effects of electrolytes, morphology of the catalysts, nature of the crystallites, effects of functional groups, surface modification, grain boundary, effects of cocatalysts, Cu overlayers, effects of product selectivity and many more.

The table presented in this review has been constructed using data from various sources. We have made as much effort as possible to present the data in a way that is useful to the reader, allowing one to compare results from different research groups, based on published results from various sources to generate all the relevant data. The quality of the published data, however, varied quite a bit and we had to make judicious choices in selecting relevant and reliable data.

1. An Overview of Some Basic Concepts in Electrochemical CO$_2$ Reduction (ECR)

Before delving deep into the world of electrochemical reduction of CO$_2$ to value-added chemicals on Cu and Cu-based materials, one needs to understand the fundamentals of this unique chemical process. Below is a brief overview of some important concepts used in the study of ECR:

### 2.1 Chemical/Thermodynamic Stability of CO$_2$
Carbon dioxide (CO$_2$) is a linear and non-polar molecule, fully oxidized and extremely stable molecule. Inducing a chemical conversion from this stable state requires efficient and robust electrocatalysts to promote this kinetically sluggish reduction process. Therefore, a real-world catalysts often require large overpotentials (as can be seen where a single-electron reduction of CO$_2$ to form CO$_2^-$ require as high as -1.9V vs RHE reduction potential; this high value is due to the rearrangement of the molecule from a linear to a bent structure.), to promote the reaction at satisfactory rates and product selectivity. The energy needed for CO$_2$ conversion should arise from sustainable low-carbon sources (e.g. solar, wind, tidal energy etc.) in order to have an impact on atmospheric CO$_2$ concentration. The major challenge therefore, is to fabricate an electrocatalyst that can achieve high conversion efficiency, high product selectivity at low overpotential barrier.

2.2 Reaction Mechanism of ECR

The mechanism for electrochemical CO$_2$ reduction has been studied for many years, with the typical aim of the research being directed towards understanding why different metals give different products. Researchers across the world have proposed and continue to propose novel reaction pathways for ECR based on their understanding of CO$_2$ reduction on metallic electrodes.

Electrochemical reduction of CO$_2$ is a multi-step reaction process generally involving two, four, six, or eight-electron reaction pathways [29], which often take place at the electrode-electrolyte interface, where the electrode is a solid electrocatalyst while the electrolyte is usually an aqueous solution saturated with CO$_2$. Typically, this catalytic process involves three major steps:

i. Chemical adsorption of CO$_2$ on an electrocatalyst

ii. Electron transfer and/or proton migration to cleave C–O bonds and/or form C–H bonds

iii. Configuration rearrangement of products to desorb them from the electrocatalyst surface and diffuse into the electrolyte [30]. The electrocatalyst employed and the electrode potential applied has a great influence on the final reduction products. In general, the reaction products are a mixture of carbon compounds with different oxidation states, and they often include carbon monoxide (CO), formate (HCOO$^-$) or formic acid (HCOOH), methane (CH$_4$), ethylene (C$_2$H$_4$), ethanol (C$_2$H$_5$OH), methanol (CH$_3$OH), etc [31,32]. Since ECR is a surface phenomenon, there is no
generalized reaction pathways towards the products obtained. In fact, the mechanism of the reaction must depend on the type, nature and morphology of the catalyst, the catalyst’s relative selectivity towards a particular intermediate (i.e. the relative ease with which a catalyst adsorbs and desorbs an intermediate), the number of electrons transferred and the energy barrier required for this electron transfer (standard reduction potential) as demonstrated by the sets of equations in the Table 1.

Table 1. List of Several ECR reaction products, the CO$_2^-$ intermediate, and the H$_2$ evolution reaction with their reaction mechanisms and standard reduction potentials (E$^\circ$) [33]

<table>
<thead>
<tr>
<th>Products</th>
<th>Reaction</th>
<th>E$^\circ$(V vs. RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>CO$_2$ + 2e$^-$ + 2H$^+$ → CO + H$_2$O</td>
<td>-0.11</td>
</tr>
<tr>
<td>HCOOH</td>
<td>CO$_2$+2e$^-$ +2H$^+$ → HCOOH</td>
<td>-0.25</td>
</tr>
<tr>
<td>HCOH</td>
<td>CO$_2$+4e$^-$+4H$^+$→ HCOH+H$_2$O</td>
<td>-0.07</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>CO$_2$+4e$^-$+4H$^+$→CH$_3$OH+2H$_2$O</td>
<td>0.02</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>CO$_2$+8e$^-$+8H$^+$→CH$_4$+2H$_2$O</td>
<td>0.17</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>CO$_2$+12e$^-$+12H$^+$→C$_2$H$_4$+4H$_2$O</td>
<td>0.06</td>
</tr>
<tr>
<td>CO$_2^-$</td>
<td>CO$_2$+e$^-$ → CO$_2^-$</td>
<td>-1.5</td>
</tr>
<tr>
<td>H$_2$</td>
<td>2H$^+$ +2e$^-$ → H$_2$</td>
<td>0.0</td>
</tr>
</tbody>
</table>

As stated earlier, the electrochemical CO$_2$ reduction reaction (CO$_2$RR) occurs in three steps. The first step involves one-electron transfer to CO$_2$ to form a key intermediate CO$_2^-$, which is the rate limiting step in the reaction, largely due to the structural rearrangement from a linear molecule to a bent radical. This requires an enormous amount of energy usually, an overpotential of -1.9V vs. RHE is needed in order to promote this kinetically sluggish reduction process at a satisfactory rate. After the first step, the obtained CO$_2^-$ which is very reactive undergoes several proton-coupled multiple-electron-transfer reactions, which are thermodynamically more favourable and takes place almost instantaneously.

2.3 Some important parameters used in the study of CO$_2$RR

i. CO$_2$ Reduction Efficiency

There are two distinct types of efficiencies, Faradaic efficiency (FE) and Energy efficiency. Faradaic efficiency is quite simple to calculate and understand: it is the
percentage of electrons that end up in the desired product. In other words, it is defined as the percentage of electrons consumed for the formation of a given product and can simply be expressed as:

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

Where, \( \alpha \) is the number of electrons transferred, \( n \) is the number of moles of the target product, \( F \) is the Faradaic constant and \( Q \) is the quantity of charge consumed or passed.

On the other hand, the Energy Efficiency is the amount of energy in the products divided by the amount of electrical energy put into the system which is the overall energy utilization of the system and can be expressed as:

\[ E_{\text{energetic}} = \frac{E_{\text{eq}}}{\frac{E_{\text{eq}}}{n} \times E_{\text{faradaic}}} \]

Where, \( E_{\text{eq}} \) is the equilibrium potential and \( n \) is the overpotential.

ii. **Overpotential**

This is the difference between the applied potential (onset potential) versus the reference electrode under which the desired product is yielded at a detectable amount, and the standard reduction potential \( (E^\circ) \) which is given as \( \eta = (E_{\text{applied}} - E^\circ) \).

iii. **Current Density**

Current density for \( CO_2 \) reduction is the ratio of the magnitude of current to the geometric surface area of the working electrode. Partial current density for specific products can be obtained by multiplying the corresponding FE by the overall current density.

2. **Experimental Studies**

As stated earlier, Cu is the only metal catalyst that shows catalytic activity towards electrochemical reduction of \( CO_2 \) to a variety of hydrocarbons and alcohols. This unique ability therefore makes Cu and Cu-related catalysts to be seen as ideal materials to be used for commercial and/or industrial \( CO_2 \) conversion to value-added chemicals in order to solve energy and environmental problems arising from excessive atmospheric accumulation of \( CO_2 \) gas. Researchers around the globe have dedicated their time, energy and resources, exploring novel materials and structures as well as the dynamics of this catalytic process on the metal surfaces. Even though this area of research is still growing and the current progress recorded is still far from
commercialization, the useful contributions of these researchers and their findings are making headway for the future, and some of these findings shall be discussed in this section taking into consideration, the mechanisms of their electrochemical reduction and the factors that affects the selectivity, improved overpotential and faradaic efficiency of the products obtained.

3. Cu/Cu-based catalysts for CO$_2$RR
Loiudice et al fabricated Cu Nanocrystals (NCs) used for CO$_2$RR [34]. Their study reveals a structure/property relationship between the fabricated Cu Nanocrystals and their catalytic activity (Fig. 1). The selectivity over hydrogen evolution reaction (HER), and activity of the NCs towards C$_2$ products predominantly C$_2$H$_4$, depends on the morphology as well as the size of the nanocrystals. Within the same morphology, smaller NCs exhibited higher activity; however, overall, the cube-shaped NCs where more intrinsically active than the spheres. The Cube-shaped NCs (24 nm, 44 nm, and 63 nm sized NCs) shows a non-monotonic size-dependent selectivity in which the 44 nm cube-shaped NC exhibited the best catalytic performance with 80% efficiency towards selectivity of CO$_2$RR over HER and FE of 41% for C$_2$H$_4$ as shown in Table 2. This recorded selectivity was attributed to the presence of active sites on the surface of the Nanocrystals (plane, edge and corner). The X-ray Diffraction pattern (XRD) reveals that the (100) plane facets predominate on the surface as shown in the model used in Figure 1. As the size of the Nanocubes increases, the relative number of atoms on the edges and the corners decreases while the number on the planes increases. This therefore results into a surface configuration closer to one single crystal with all the surface atoms lying in the (100) plane. The studies concluded that, since uncoordinated sites in nanocrystals such as corners, steps, kinks, etc. favours HER selectivity, the trends of the Cu nanocubes towards coordinated (100) plane sites are responsible for the improved CO$_2$RR selectivity. This active site/size trend suggests that the unique reactivity of the 44 nm Cu NC cubes derives from an optimal balance between plane and edge sites, while the edges are responsible as ethylene-selective active sites in the Cu NC cubes.

Song and co-workers [35] reported the catalytic activity of Cu Nanocrystals on a highly textured N-doped Carbon nanospikes (Cu/CNS) with selectivity of 84% and the FE of 63% at -1.2V vs RHE for ethanol production (Table 2). Here, Cu/CNS
exhibited unusual behaviour because it favours ethanol formation rather than methane and ethylene; this is because ethanol requires C-C coupling between surface-adsorbed intermediates at some points during the reduction reaction. This high selectivity for C$_2$ product suggests that C-C coupling was preferred to desorption of the C$_1$ intermediate.

![Diagram](image)

**Fig. 1.** On the left axis: Density of adsorption sites in Cu NC cubes reported versus the edge length (d). On the right axis: trend of $N_{\text{edge}}/N_{100}$ and $N_{100}/N_{\text{edge}}$ versus d, where $N_{\text{edge}}$ is the number of atoms at the edge and $N_{100}$ is the number of atoms on the (100) plane [34].

This preference was suggested to be as a result of the nanostructured nature of the surface which improves the stability of the adsorbed C$_1$ intermediate keeping it long enough until a second intermediate is available for C$_2$ coupling. The coupling reported could be between two surface bound intermediates or between surface bound intermediate and a nearby C$_1$ intermediate in solution. Furthermore, the ethanol production dominates the competitive reduction of the coupled C$_2$ to ethylene or methane. This unique behavior was reported to be as a result of electron-withdrawing effects in the graphene π-conjugated system, which in turn, polarizes...
the carbon atoms adjacent to nitrogen positively. This polarization was suggested to provide an active site adjacent to the copper for the C₂ intermediates to adsorb, which may inhibit complete electroreduction. Density Functional Theory (DFT) calculations performed by the group also suggested that the strongly curled morphology of the CNS aids in the adsorption of C₂ intermediates. CNS reported in their study was puckered curled, indicating local corrugation on the surface. Such local deformation and curvature naturally embedded into the CNS could help in strengthening the bond between C₂ and CNS.

Moreover, Song and co-workers [35] also studied the interaction between C₂ intermediates (OCCO) and the Cu surface; they found out that there is a strong covalent bond when the molecule approaches the Cu surface oriented with one end closer to the surface. This covalent bond is comparatively stronger than the OCCO/NCS bond which ensures that desorption of C₂ intermediates are prevented, the group therefore proposed that, the C₂-intermediates is covalently bound on reactive copper surface for complete reduction to -CH₃, while the oxygen atom on the other end of the C₂-intermediates is adsorbed on less reactive CNS hence forming -CH₂OH, and protected from competitive reduction, thereby providing a pathway towards selective reduction to ethanol.

Zhiyuan et al [36] reported highly selective reduction products on Ag@Cu Bimetallic catalyst. The group fabricated an Ag@Cu core-shell system whose nanoparticles were controlled by tuning the heating reaction time in a simple polyol reduction method (0-20 mins) and the following were obtained Ag@Cu-5, Ag@Cu-7, Ag@Cu-10, Ag@Cu-15, Ag@Cu-20, Ag@Cu-25 respectively (i.e. Ag@Cu-reaction time). The peak activity was recorded at Ag@Cu-7 for CO generation whose FE was 82% and decreases dramatically to 20% for Ag@Cu-10, while Ag@Cu-20 gave a peak FE of 28.6% for C₂H₄ (Table 2), as this clearly demonstrates that Ag@Cu-7 (Ag-dominant) and Ag@Cu-20 (Cu-dominant) bimetallic materials achieved better activities for CO₂RR than other counterparts. The authors pointed out that there exist a composition and structure dependent activity and selectivity in the series of the as-prepared Ag@Cu bimetallic catalysts, and that geometric effects rather than electronic effects was the key factor in determining the
selectivity. The peak activity at Ag@Cu-7 towards CO as suggested, resulted from functional Ag (modified) with more oxygen affinitive Cu via oxygen-metal interaction which helped to stabilize *COOH intermediate, a key point to lower the energy requirement for CO$_2$RR and gain higher FE towards CO. Furthermore, the small amount of Cu for Ag@Cu-7 cannot offer the possibility to stabilize of *CO intermediate to protonate successively to hydrocarbons. Conversion to ethylene came as a result of the increase in Cu content at Ag@Cu-10 and above. It was concluded that, synergistic reactions rather than pure dilution effects between Ag and Cu for these AgCu bimetallic electrocatalysts mainly derived from the mixing pattern of the components played an important role in producing the higher CO or hydrocarbons.

Ma and co-workers [37] reported Cu-Pd bimetallic catalysts with different mixing patterns used for the electrochemical reduction of CO$_2$. Their study examines a range of bimetallic Cu-Pd catalysts with ordered, disordered, and phase-separated atomic arrangements (Cu$_{at}$:Pd$_{at}$=1:1), as well as two additional disordered arrangements (Cu$_3$Pd and CuPd$_3$ with Cu$_{at}$:Pd$_{at}$ =3:1 and 1:3). The result reveals high selectivity for C$_1$ products(mainly CH$_4$) in the ordered structure while the phase-separated and the Cu$_3$Pd exhibited high selectivity for C$_2$ products (Table 2) where the following cases were observed; CO is an important precursor for C$_2$ chemicals production and the phase-separated CuPd catalyst converts adsorbed CO to C$_2$ chemicals more easily than the ordered CuPd catalyst, with latter converting adsorbed CO more easily to CH$_4$ than the phase-separated catalyst. The high selectivity of the phase-separated CuPd structure for C$_2$ products was as a result of dimerization of adjacentely adsorbed CO to COCOH intermediates due to interacting neighbouring features of Cu atoms with favourable molecular distances between them and small steric hindrance (Fig. 2).

Similarly, the preference for CH$_4$ on the ordered-CuPd (Fig. 2) structure was due to presence of Cu-Pd intermetallic structures which adsorbed CO on a Cu and further converted it to CHO intermediate whose oxygen atom is partially adsorbed to Pd atom which stabilizes the adsorption of CHO intermediate and favours the production of CH$_4$. The study also reveals that, as the concentration of Cu increases from Pd, CuPd$_3$, CuPd, to Cu$_3$Pd and Cu, the FEs for C$_2$ products also increased which further supported the idea that the dimerization of adsorbed CO to form C$_2$ chemicals may be preferred on the sites
with neighboring Cu atoms. The group therefore concluded that the selectivity of the Cu-Pd bimetallic catalyst can be determined by geometric effects. This implies that the selectivity of different products can be tuned by altering the geometric arrangements of the catalyst.

![Image](image.png)

**Fig. 2.** Schematic illustration of prepared CuPd Nanoalloys with different structures [37]

Lum et al [38] reported that trace levels of copper in carbon shown significant electrochemical CO$_2$ reduction activity. The study investigated the catalytic activities of pure graphite (PG), graphene oxide (GO), and carbon nanotubes (CNT) dispersed on glassy carbon (GC) for the electrochemical CO$_2$ reduction reaction in aqueous solution (Table 2). It was observed that carbon support materials exhibited significant electrocatalytic behaviours attributable to the presence of impurities in them. However, the presence of Cu as impurity in GO configuration revealed a significant yield of methane. Interestingly, it was revealed that the catalytic activity of the GO-supported material dropped significantly when nearly all the impurities were washed away in ultrapure nitric acid. On re-introduction of Cu, the catalytic behavior surfaced which increases with increase in the amount of Cu deposited. On comparison between Cu electrodeposited on GO/GC, PG/GC and GC systems, it was revealed that the activity per mass of Cu is ~ 4-5 times higher for GO/GC or PG/GC than GC, attributable to preferential deposition of Cu-NPs at defects present on the graphene
layers of GO and PG with latter having the highest activity for methane production (Table 2). The group therefore suggested that, a highly active catalyst for methane formation via the CO$_2$RR can be created for the future by the introduction of defects into graphene layers, onto which Cu can then be electrodeposited.

Hahn and co-workers [39] studied the surface structure of Cu thin films catalysts in order to probe the relationship between active sites and catalytic activity for the electroreduction of CO$_2$ to fuels and some value added chemicals. In their study, they reported a vapor deposition of Cu thin films on large-format single-crystal substrates ($\text{Al}_2\text{O}_3$(0001), Si(100), and Si(111)), and confirm epitaxial growth in the (100), (111), and (751) orientations respectively (Fig. 3). Results of electrochemical CO$_2$ reduction reveals that the three orientations all make $>2e^-$ reduction products in the tested potential range between −0.89 and −1.10 vs. RHE. However, Cu(100) and Cu(751) are both active and selective for C-C coupling reaction than Cu(111) and Cu(751) is the most selective for the $>2e^-$ oxygenate formation at low overpotential. The group pointed out that the difference in selectivity could be due to due to a lower kinetic barrier for CO dimerization on Cu(100) compared with Cu(111). This therefore suggest that there is a strong correlation between C–C coupling selectivity and the coordination number of the surface, which was favoured by the less coordinated Cu(100) and Cu(751) than the more coordinated Cu(111) (Fig. 3).

On the other hand, analysis of oxygenate vs. hydrocarbon selectivity was conducted on the three orientations and they came to a conclusion that at −0.89 V vs. RHE, Cu(751) has the highest oxygenate/hydrocarbon ratio, and the group put forward a suggestion that this improvement in oxygenate selectivity is related to the fewer number of nearest neighbors on the Cu($S$)–[n(110) × (100)] (in-situ surface structure of Cu(751) where ‘n’ varies from 2 to 7) surface, or the top most layer of the Cu(751) film, because barriers for hydride transfer are predicted to be lower than those for proton- coupled electron transfer at lower overpotentials.
Zhang et al [40] investigated CO$_2$ electroreduction on Cu overlayers on tetrahexahedral Pd nanocrystals (THH Pd NCs) with (310) high-index facets. The study revealed catalytic activity/selectivity towards alcohols (ethanol and methanol). Cu$_{1}$ML/THH Pd NCs exhibited high activity and selectivity for CO$_2$electroreduction to ethanol with ~20% FE at -0.46 V vs. RHE. The selectivity of the alcohol was readily tuned by varying the coverage of Cu on THH Pd NCs in which methanol was obtained at Cu$_{0.8}$ML/THH Pd NCs with FE of 19.5% (Table 2). According to the group, the results demonstrated that the electroreduction of CO$_2$ is a surface-structure-sensitive reaction and the (310) high-index facets facilitate the formation of ethanol.

Mixed iron-copper (Fe-Cu) oxide catalyst was reported by Yang et al [41] for the electrochemical reduction of CO$_2$ to acetate with FE of 80% and 76% using Ar-purged, phosphate-buffer and NaHCO$_3$
electrolytes respectively (Table 2). The catalyst reported here is a mixed phase material consisting CuFeO$_2$ and CuO. The study reveals that competing production of formate over the mixed structure existed which was favoured by the increase in concentration of Cu relative to Fe. Here, the selectivity of the catalyst towards either acetate which is the primary product or formate is a function of the iron-copper atomic ratio represented as Fe:Cu. At a ratio of 1:3, the catalyst favours the production of acetate but as the concentration of Cu increases relative to Fe from 1:3 through 0:5, and 0:1, the products obtained was predominantly formate. This result therefore suggested that varying the Fe:Cu atomic fractions, the selectivity of the catalyst can be tuned from primarily acetate to primarily formate. Furthermore, the morphology of the as-prepared catalysts is also a function of their composition which was reported that the grain size decreases slightly as a function of increasing Fe:Cu ratio.

Copper nanofoams with hierarchical porosity was investigated for the electrochemical reduction of CO$_2$ [42]. This study reveals an improved product distribution and faradaic efficiency which far exceed the one obtained from smooth electropolished Cu-electrodes (Table 2). This result was attributed to high surface roughness, hierarchical porosity, and confinement of reactive species.

Oxide-derived Cu$_x$Zn catalysts was reported by Ren et al [43], used for the electrochemical reduction of CO$_2$. Where Cu$_x$Zn = Cu$_{10}$Zn, Cu$_6$Zn, and Cu$_2$Zn. Cu and its oxides are used to demonstrate that the selectivity of CO$_2$ reduction to ethanol could be improved by introducing a co-catalyst to generate an in-situ source of mobile CO reactant, achievable by doping the Cu-based oxides with varying amounts of Zn dopants. This observation was also accountable for tuning the selectivity for the production of ethanol over ethylene by a factor of ~12.5. Peak production of ethanol was recorded on Cu$_4$Zn at $-1.05$V vs RHE, with a faradaic efficiency of 29.1% and a partial current density of $-8.2$ mA/cm$^2$ (Table 2).
The formation of ethanol and ethylene on Cu₄Zn surfaces could be as a result of synergistic interaction between Cu and Zn which promotes the formation of ethanol. The group therefore postulated that, gaseous CO formed from the Zn sites may have further reacted to give ethanol. This postulation was strengthened by the observation that the potential where the FE of ethanol had peaked shifted to a more negative value on Cu₄Zn, and Cu₂Zn in comparison to Cu catalyst. This is because the CO needed for enhanced ethanol formation could only be generated in greater quantities on the Zn sites at more cathodic potentials. They also proposed in the mechanism of reaction that, for ethanol to be produced on a roughened surface (Fig. 4) such as Cu₄Zn, CO is needed for insertion into the bond between into the bond between Cu and *CH₂ to form *COCH₂,
whose further reduction yields acetaldehyde and finally ethanol.

Similarly, selective electrochemical CO₂ reduction to ethylene and ethanol on copper (I) oxide catalysts was investigated by Ren and co-workers [44]. They reported that the Faradaic yield for both ethylene and ethanol can be systematically tuned by changing the thickness of the deposited overlayers. Peak selectivity was observed for the film thickness of 1.7–3.6 μm at −0.99 V vs RHE, with faradic efficiencies (FE) of 34–39% for ethylene and 9–16% for ethanol (Table 2). This selectivity was optimized according to material analysis, with the 1.7–3.6-μm-thick films, which consisted of 0.5–1-μm-sized Cu polyhedron particles. They also proposed that during the CO₂ reduction, stepped surfaces with edges and terraces are likely to be formed as copper (I) oxide reduce to metallic Cu. Therefore, the optimum combination of these features must be necessary to dissociate CO₂ and to optimize the chemisorption energies of the CH₂O intermediate. Edges with under-coordinated Cu atoms plays a vital role in promoting the build-up of a large coverage of CH₂O reactive intermediates, to facilitate their dimerization. The study was concluded that variation of the local pH at the surface of the catalyst was also a factor that boosted the catalysts’ selectivity; however, higher selectivity was attributed to step and edge morphological features of the catalysts.

Recently, Reller and co-workers [45] reported nano dendritic Cu catalysts which were selective for the electrochemical reduction of CO₂ towards ethylene at high current density. The result reveals a 57% FE for ethylene and a current density of 170 mAcm⁻² (Table 2). The dendritic structure consists of mainly Cu and Cu₂O. The in-situ deposition of Cu in acidic pH environment forms the catalytic layers which enables the selective formation of ethylene. It was also revealed that, the catalytic performance of the material does not depend on the supported material [45]. Furthermore, structural changes of the active sites were observed during the electrolysis such as sintering and/or dissolution/re-deposition and oxidation of the Cu, results to structural degradation and coarsening of the initially formed active species. This leads to the lost of the much required high index facets with low coordinated sites responsible for the formation of ethylene, thereby, creating new catalytic centers having lower hydrogen overpotential which favours the formation of hydrogen.

Recently, Cu/SnO₂ core/shell structure was reported by Li et al [46], used
for the electrochemical reduction of CO$_2$ to CO. During the reduction, thin layer of SnO$_2$ was coated on Cu-nanoparticles. It was observed that, the reduction was Sn-thickness dependent. About 1.8 nm thick shell shown Sn-like activity to generate formate while the thinner 0.8 nm shell is selective to the formation of CO with the conversion Faradaic efficiency reaching 93% at -0.7V vs. RHE (Table 2). Their study proposed that the formation of CO by the 0.8 nm thick SnO$_2$ shell could be as a result of alloying with trace of Cu which causes a morphological change such that, the SnO$_2$ lattice become uniaxially compressed and also, the tinted contamination of SnO$_2$ with Cu, favours the formation of CO over formate. Therefore, synergistic effects between Cu and SnO$_2$ in the core/shell Cu/SnO$_2$ structure as explained above, accounts for the preference and could be used to tune the selectivity of electrochemical CO$_2$ reduction towards CO products. Higher yield and faradaic efficiency (38%) for CH$_3$OH was observed at Cu (I) active sites as compared to air-oxidized and anodized Cu electrodes (Table 2). This suggested that, Cu (I) active sites might have played a vital role in the catalyst’s selectivity to CH$_3$OH. The results also, revealed that at the required potentials for CO$_2$ reduction, copper oxides are reduced to metallic Cu and the products yields are dynamic. Furthermore, it was revealed that the Cu (I) active specie might be responsible for improving the stability of the intermediates, and enhance the selectivity towards CH$_3$OH by enabling hydrogenation of oxygen atoms from H$_3$CO adsorbates.

Ke and co-workers reported a CuO-derived porous copper nano-ribbons array [48], used to electrochemically convert CO$_2$ to C$_2$ products. At applied potential of $-0.701$V vs RHE, the C-C coupling reaction is favoured whose total faradaic efficiency towards the formation of C$_2$H$_4$, C$_2$H$_6$ and C$_2$H$_5$OH reached up to $\sim40\%$ (Table 2), while suppressing the formation of C$_1$ products. The authors therefore established the preference for C$_2$ products over C$_1$ products can be attributed the presence of surface defects and large number of grain boundaries on the CuO-derived copper
nanoporous ribbon arrays. The roughened porous channels of these electrodes allowed for facile diffusion of electrolyte and provided large number of active step sites for CO₂ reduction.

Similarly, electrochemical CO₂ reduction on Cu₂O-derived copper nanoparticles was studied by Kas et al [49], by controlling its activity towards hydrocarbon production. In this report, selectivity of the CO₂ electroreduction was found to depend largely on Cu₂O film thickness, rather than on the initial crystal orientation. This was due to the fact that the Cu₂O reduction itself seems to be highly favoured relative to the CO₂ reduction or water splitting. Therefore, the catalytic behavior was predominantly due to the layer thickness associated with local pH changes, thus impacting the hydrocarbon selectivities. The group therefore suggests that optimum number density of nanoparticles with the combination of the right electrolyte (pH) can open up routes for highly selective ethylene formation via electrochemical CO₂.

Hossain and co-workers performed the electrochemical reduction of CO₂ using copper/reduced graphene oxide nanocomposite catalysts (Cu-rGO) [50]. The study reveals a catalyst which could effectively reduce CO₂ to CO, HCOOH and CH₄ with a faradaic efficiency of 76.6% at -0.4V vs RHE and excellent stability (Table 2). Uniformly distributed small Cu nanoparticles on the rGO and the synergistic coupling effect of the formed nanocomposite were responsible for the superior electrocatalytic activity and stability of the Cu-rGO nanocomposite achieved. The electron transfer between the rGO and Cu nanoparticles might have increased localized electron concentrations, resulting in significant enhancement of the catalytic activities of the nanocomposite for the electrochemical reduction of CO₂.

In a research work conducted by Hoang et al [51], nanoporous copper films were fabricated by additive-controlled electrodeposition (i.e. 3,5-diamino-1,2,4-triazole (DAT) as an inhibitor), used in CO₂ reduction catalysis. By varying different synthesis parameters such as pH and deposition current density, the morphologies of the thin films are tuned into dots, wire and amorphous structures. The wired structure exhibited the best catalytic activity with high faradaic efficiency for C₂H₄ product as reported in Table 2. The Cu films were reported to produce active sites i.e. small and stable pores which allow for gas permeability thereby, making the resulting structures tunable depending on the deposition
conditions. On the same vein, the preference of the Cu-DAT wire structure for C₂ over C₁ products was reported to be as a result of the presence of steps and edges with low coordinated Cu atoms which promotes the adsorption of C₁ products and its subsequent dimerization to C₂ products.

The underlying causes for the selectivity of CO₂ electroreduction toward ethylene on Cu₂O-derived Cu catalysts were studied by Handoko et al. [52]. They reported that there exist, an inverse relationship between the crystallite sizes of the Cu₂O-derived Cu particles and the selectivity of the CO₂ reduction towards C₂H₄. Interestingly, decrease in the particle’s crystallite size from 41 to 18 nm, results in an increased Faradaic efficiency (FE) of C₂H₄ formation increased from 10 to 43%. It was also revealed that samples with smaller particle crystallite sizes were found to possess more diverse adsorption sites for CO intermediate, which is important for C–C coupling of C₁ adsorbates. The group therefore asserted that, this result could offer a better platform to fully explore Cu₂O-derived Cu as ideal catalysts for producing chemical feed-stocks and fuels from CO₂ reduction.

Plasma activated Cu nanocube catalysts with tunable Cu (100) facet morphology, defect and oxygen contents was recently studied by Gao and a group of co-workers [53]. Their findings reveals a high catalytic activity and selectivity for ethylene and ethanol (Table 2). This high catalytic performance was ascribed to the presence of defects, surface and sub-surface oxygen species, including oxygen ions associated with Cu⁺ species, achievable by tuning the catalysts’ morphology and defect density, ion content, and surface roughness via plasma induced pre-treatment. This group therefore concluded that, the presence of oxygen species in surface and sub-surface regions of the nanocube catalysts is key for achieving high activity and hydrocarbon/alcohol selectivity, even more important than the presence of Cu(100) facets.

Oxide-derived mesoporous foam catalyst fabricated via template-assisted electrodeposition process by Dutta et al [54], was reported to selectively reduce CO₂ to C₂H₄ and C₂H₆ with a combined faradaic efficiency of 55% for the C₂ product as shown on Table 2. This high selectivity was attributed to due to the availability of the surface sites (i.e. surface pore diameter) for C–C coupling reaction and the temporal trapping of gaseous CO and C₂H₄ intermediates inside the mesoporous
catalyst material during CO₂ electroreduction. As reported, the key point to the creation of a high abundance of surface active sites for C-C coupling for the catalyst activation was the in operando reduction of a Cu₂O phase.

In another work reported by Chung et al [55], a series of hierarchical Cu electrodes were used to catalytically convert CO₂ to formic acid and a negligible amount of CO. The peak activity was recorded for the member of the series Cu-h 5 electrode, in which it demonstrated an FE of 28% as shown in Table 2. This peak activity was due to increased (111) facet in the electrocatalyst which energetically favoured HCOOH production. This is because the majority of the surface lattice, the (111) facet, leads to the formation of F-intermediate, and as a result, CO₂ is mostly reduced to HCOOH. Another well-known intermediate is C-intermediate, which bind to the (100) facet, is presumably reduced to HCOOH. This is because enhanced electron transfer amplified by surface modification assisted the reduction to end up with HCOOH and hinders CO formation.

The electrochemical reduction of CO₂ to C₂H₄ and subsequent hydrogenation to C₂H₆ was observed for a Cu₂O-derived Cu/PdCl₂ catalyst by Chen et al [56], a significant FE for ethane was observed (Table 2). Detailed mechanistic studies revealed that, CO₂ was first reduced to C₂H₄ at the Cu sites and then underwent hydrogenation with the help of the adsorbed PdCl₃ to generate C₂H₆. Interestingly, both sites were responsible for the reduction to C₂H₄ and subsequently to C₂H₆, but it was inferred from the study that, PdCl₂ dopants alongside a working electrode could offer a new methodology to expand on the type of products that could be obtained from a CO₂ building blocks.

The product yield and the relationships between surface chemistry and reaction behavior for surface oxidized copper electrodes were investigated by Keerthiga et al [57]. Even though there was no clear explanation for the enhanced production of ethane as the major product during electrochemical reduction of CO₂ at the surface of the electrodes, it was hypothesized that Cu (I) species played a vital role in the selectivity of the catalyst, further investigation was recommended by the group in order to understand the mechanistic details of the reaction.

However, Cu nanoclusters on single crystal (1010) ZnO electrodes were studied by Andrews and co-workers [58]. By comparing the catalytic activity/selectivity of Cu electrodes and Cu nanocluster-ZnO electrodes at a potential of -1.4V vs
Ag/AgCl, it was observed that there was improved selectivity for methanol and ethanol recorded for Cu/ZnO electrode. FT-IR analysis on the products obtained revealed a characteristic absorption behavior for formats and methoxy adsorbates. The mechanism for the formation of ethanol was not clear, however, the methoxy adsorbates were closely associated to alcohol since other products were obtained experimentally. Several possible mechanisms that could lead to enhanced alcohol selectivity were proposed, including reactions at Cu-Zn interfaces or charge effects arising from ZnO substrates. The ZnO may strengthen the Cu-C bond via σ-donor interactions and π back-bonding which allows for improving hydrogenation of the carbon atom, increased methoxy generation and selectivity to alcohols. However, the Cu-ZnO electrodes demonstrated a stable surface for continuous CO2 reduction and significantly increases in alcohol yields, independent of the aforementioned pathway.

Lv et al [59] reported a Tin-based film on copper plate, used for the electrocatalytic reduction of carbon dioxide to formate. This shows a catalytic performance with a faradaic efficiency of 74.1% (Table 2). This catalytic activity was influenced and enhanced by exposing the Sn/Cu electrode to air. The as-prepared Sn/Cu electrode exposed for 24 hours showed a better catalytic performance for CO2 reduction which was explained to be as result of the Sn film surface that became gradually oxidized and form an oxide layer which can inhibit the competing HER.

Tang et al [60] reported a structurally precisioned copper-hydride nanoclusters (Cu32H20L12 where L is a dithiophosphate ligand). The major product obtained by the electrochemical synthesis on the nanocluster was HCOO– with over 80% selectivity, with other minor products such as CO and H2 at low potentials. DFT investigation also explained that both the Cu and the hydride ligand surfaces (Fig. 5) played a vital role in pushing the reduction towards CO2 reduction over HER at low potentials which leads to the formation of HCOOH. The HCOOH formation follows a two steps lattice-hydride reduction; CO2 reacts directly with the capping hydride to form HCOO* which then reacts with another interstitial hydride to form HCOOH, and then the hydride vacancies are readily regenerated by the electrochemical proton reduction.
In addition, Kim et al [61], have shown that by ordering the atomic transformation of AuCu nanoparticles, one could activate them as selective electrocatalyst for CO$_2$ reduction. Unlike the disordered alloy nanoparticles which showed preference for HER, the ordered AuCu nanoparticles selectively reduced CO$_2$ to CO at an FE of 80%. A structural investigation thus revealed that this enhanced catalytic activity for the ordered AuCu nanoparticles was due to the formation of a compressively strained three-atoms-thick gold overlayer that form over the inter-metallic core following the ordering transformation. This therefore suggests that surface enrichment of gold at the atomic level may be the origin of the enhanced catalytic behavior.

4. Concluding remarks
In this review, we have discussed the mechanistic behavior of CO$_2$ electrochemical reduction on various copper/copper based catalytic materials. More works should focus on utilization of porous materials and the study of the CO$_2$ adsorption and activation on the heterogeneous catalysts surfaces, these are very crucial for the successive reduction steps and the suppression of the competing HER. Structural and morphological controlled of electrocatalysts should be studied extensively theoretically and experimentally. Details of how certain morphological features, and other factors
that determines the selectivity of the reaction to target products were also discussed and summarized in Table 2) with the hope that this would spark up an improved interest to explore copper and copper-based materials in order to solve the world’s energy and environmental challenges. However, understanding the mechanistic aspect of CO$_2$ adsorption modes and effects of some operational parameter such as pH, surface functional groups, cocatalysts, and external bias needed detail attention. The mechanism of CO$_2$ reduction needs requires more deep investigation in the future studies. The findings of the reaction barriers and rate-determining steps in CO$_2$ electroreduction is important for the further improvement of the conversion efficiency.

**Acknowledgements**

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## Table 2. State-of-the-art progress of Cu/Cu-based electrodes

<table>
<thead>
<tr>
<th>S/N</th>
<th>Name of Catalyst/Chemical formula (Cathode)</th>
<th>Morphology</th>
<th>Electrolyte/pH/physical state of the electrolyte</th>
<th>Overpotential</th>
<th>Current density</th>
<th>Various Products obtained</th>
<th>Faradaic efficiency</th>
<th>Anode</th>
<th>Cathode</th>
<th>Synthesis method</th>
<th>Reaction conditions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Copper(Cu) Nanocrystals</td>
<td>Cu NC spheres (7.5 nm and 27 nm), Cu NC cubes (24nm, 44nm and 63 nm). Within the same morphology, smaller NCs exhibited higher activity; however, overall, the cube-shaped NCs where more intrinsically active than the spheres</td>
<td>CO$_2$-saturated 0.1M KHCO$_3$ was used as the electrolyte in aqueous medium; pH of the solution not specified</td>
<td>Not specified</td>
<td>Not specified</td>
<td>C$_2$H$_4$ and CH$_4$</td>
<td>The selectivity of Cu NCs cubes towards CO$_2$RR selectivity are; 24 nm = 43% 44 nm = 80% 63 nm = 63%. FE for C$_2$H$_4$ was 41%</td>
<td>Platinum foil was used as the counter electrode and Ag/AgCl electrode</td>
<td>Cu NC Cubes/spheres spin-coated on glassy carbon</td>
<td>For the synthesis of Cu-nanocubes (24, 44 and 63 nm); Varying concentration of CuBr and TOPO were dissolved into oleylamine in a three-necked flask by vigorous magnetic stirring at 80°C for 15mins. The resulting solution was heated upto 210-260°C and refluxed at this temperature for about 1-2.5h. For the synthesis of Cu spheres, 35 ml oleylamine and 3 mmol of CuBr were mixed in a three-necked flask by strong magnetic stirring at 80 °C for 15 mins, 6 mmol TOPO was injected into the mixture. After an additional stirring at 80 °C for 5 mins the mixed solution was heated upto 260 °C quickly and kept at this temperature for 3h before cooling to room temperature. The Cubes were precipitated out by centrifugation.</td>
<td>Reaction was performed at room temperature</td>
<td>[34]</td>
</tr>
<tr>
<td>2</td>
<td>Copper Nanoparticle/N-Doped Graphene (Cu/CNS)</td>
<td>Graphene in the form of Carbon NanoSpikes (CNS) is electronucleated with Cu Nanoparticles. These well-dispersed Cu particles ranged from about 30nm to 100nm with average size of</td>
<td>CO$_2$-saturated 0.1M KHCO$_3$ electrolyte in aqueous medium. pH not specified</td>
<td>-1.2V vs RHE</td>
<td>Not specified but the maximum current density achieved at -1.0 vs RHE</td>
<td>C$_2$H$_5$OH, CH$_4$, and CO</td>
<td>C$_3$H$_7$OH = 63%, CH$_4$ = 6.8% CO = 5.2%</td>
<td>Glassy Carbon electrode</td>
<td>Cu/CNS</td>
<td>Not specified in the article</td>
<td>Reactions operated at room temperature and in water</td>
<td>[35]</td>
</tr>
</tbody>
</table>
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| 3 | Ag@Cu Bimetallic Nanoparticles | Core-shell structured Bimetallic Nanoparticles prepared at different reaction time; Ag@Cu-5, Ag@Cu-7, Ag@Cu-10, Ag@Cu-15, Ag@Cu-20 and Ag@Cu-25 | Cu and CO \_2 saturated 0.1M KHCO \_3 solution in aqueous medium. pH of the solution ≈ 6.8 | -1.06V vs RHE | Not specified | CO and C \_2H \_4 | Ag@Cu-7 gave the highest FE for CO=82% and decreased dramatically to 20% for Ag@Cu-10. Ag@Cu-20 gave a peak FE for C\_2H\_4=28.6\% | Pt gauge and Saturated Calomel electrodes (SCE) served as counter and reference electrodes respectively | L-type glassy carbon electrode with a diameter of 5mm on which 20μL ink-formulation of the electrocatalyst was dropped | The catalyst was synthesized by means of one-step polyol method to fabricate the epitaxial growth of noble metal to core-shell structure by adjusting the temperature control method and reaction time | Reactions was carried out at room temperature | [36] |

| 4 | Bimetallic Cu-Pd catalyst with different mixing pattern | Bimetallic Cu-Pd catalyst with ordered, disordered and phase-separated atomic arrangement with different atomic ratios (1:3 to 3:1). | 1M KOH electrolyte whose physical state was not specified was used. pH was not specified. | Over potentials not specified. At Cathode Potentials more positive than -0.3 vs RHE favours CO while potentials more negative than -0.3 vs RHE favours C2 products | The Phase separated sample achieves highest total current density of 370mAcm \^\text{-2} | CO, CH\_4, C\_2H\_4 and C\_2H\_3OH | Ordered CuPd=[(\textgreater 80\%) FE for C1 products]; Phase-separated CuPd and CuPd=[(\textgreater 60\%) FE for C2 Products] | Not specified | Each of the Bimetallic Cu-Pd catalyst was deposited onto a gas diffusion layer to form a gas diffusion Electrode (GDE) | The reader are advised to read Ma et al 2017 [37] | The reaction was performed in potentiostatic mode under Ambient conditions | [37] |

<p>| 5 | Trace level of Cu impurities in Carbon support materials | Cu Nanoparticles electrochemically deposited on Pure Graphite (PG), Graphene Oxide (GO), and Carbon Nanotubes (CNT) all supported by Glassy Carbon (GC) and GC itself. | 0.1M NaHCO _3 solution saturated with CO_2 for 1h pH was 6.8. To prepare Cu Spiked electrolytes, appropriate amount of Cu(ii) sulfate hydrate was added to make 0.1M | Overpotentia l was not specified but the reaction was carried out at an applied potential of 1.3V vs RHE for 2h | For Cu(2)GO/ GC, the Current Density is \textasciitilde 4.6 mAcm ^\text{-2} | H_2, CO, CH_4, and HCOOH | For both Cu(1)GO/GC and Cu(1)PG/GC, the FE for methane is about \textasciitilde 40%. The highest selectivity for methane is observed on Platinum foil was used as the counter electrode while Ag/AgCl electrode was used as reference electrode. | Cu Nanoparticles drop-cast and spin-coated onto a glassy carbon | Cu Nanoparticles were synthesized by the thermal decomposition of Cu acetylacetonate (Cu(acac)_2) in oleflamine | Ambient pressure CO_2 electrolysis was carried out in a customary made gas-tight electrobiochem ic cell made of polycarbonate and fitted with | [38] |</p>
<table>
<thead>
<tr>
<th>NaHCO₃ solutions</th>
<th>Cu(2)PG/GC= 38.8% FE and Cu(2)GO/GC = 43.6% FE</th>
<th>C₃H₈, C₅H₁₀ and various organics such as carbonyls and alcohols</th>
<th>Cu thin-films on large format Al₂O₃(0001), Si(100) and Si(111) substrates in a three-source Physical Vapour Deposition (PVD).</th>
<th>Buna-NO-rings</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 Cu Thin Films</td>
<td>Vapour Deposition of Cu Thin-film on large single crystal substrates resulting in epitaxial growth in the (100), (111) and (751) out-of-plane orientations on Al₂O₃(0001), Si(100) and Si(111) substrates respectively, i.e. Cu(100), Cu(111) and Cu(751)</td>
<td>Pt counter electrode and a miniature leakless Ag/AgCl (3.4 M KCl) reference electrode</td>
<td>Thin-films of Cu were synthesized on large format (27mm x 42mm) Al₂O₃(0001), Si(100) and Si(111) substrates</td>
<td>The experiment was performed using Chronoamperometry at a single potential for 1h</td>
</tr>
<tr>
<td>7 Cu Overlayers on Tetrahexahedral Pd Nanocrystals (Cu/THH Pd NCs)</td>
<td>Cu Overlayers on tetrahexahedral Pd nanocrystals with (310) high-index facets</td>
<td>Cu(111)-faceted Pd NCs exhibits selectivity to C₂H₅OH at FE♂=20% while Cu(100)/(111)-faceted Pd NCs=6.1%. CH₃OH was obtained on Cu₃OH/THH Pd NCs with FE of 19.5%.</td>
<td>The THH Pd NCs were prepared by a programmed square wave potential (SWP) method on a glassy carbon electrode in 0.2 mM PdCl₂ + 0.1 M HClO₄ solution. The (111)-faceted Pd NCs were prepared by constant potential electrodeposition at 0.20 V for 500 s. Cu overlayers were prepared by underpotential deposition (UPD) of Cu on the Pd NCs in 1 mM CuSO₄ + 0.5 M H₂SO₄</td>
<td>The reaction was carried out under ambient conditions</td>
</tr>
<tr>
<td>8 Fe-Cu Oxide Catalyst</td>
<td>The selective catalyst is a mixed phase material consisting of CuFeO₂ and CuO. Fe:Cu atomic ratio was varied from 1.3 to 0.1</td>
<td>Acetate was 80% (H₂PO₄) and 76% for (NaHCO₃)</td>
<td>The reaction was catalysed by electrodeposition on FTO glass substrate using dimethyl sulfoxide (DMSO) plating solution containing 1 mM Cu(NO₃)₂, 1 mM Fe(CIO₃)₃, and 0.1 M KClO₄ electrolyte. The as-deposited catalysts</td>
<td>The reaction was carried out at −0.4 V bias vs. Ag/AgCl under constant white light illumination.</td>
</tr>
</tbody>
</table>
was annealed at 650 °C for 3.5 hours in the air.

<p>| 9 | Cu Nanofoams | Cu Nanofoams with hierarchical porosity | 0.1M KHCO$_3$, pH 6.8 | The onset potential was −1.0V vs Ag/AgCl | &gt;0.5 A/cm$^2$ | HCOOH, H$_2$, and CO$_2$ | FE for HCOOH was 37% at −1.5V | Copper sulfate | Al-substrate coated with copper foam | Three-dimensional foams of copper were electrodeposited onto mechanically polished copper substrates. This procedure is simple to perform and results in an electrode with hierarchical porosity. | The reaction was performed under ambient pressure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | Oxide-Derived Cu$_x$Zn Catalysts | Oxide-derived Cu$<em>x$Zn catalysts with different quantities of Zn dopants (Cu$</em>{10}$Zn, Cu$_4$Zn, and Cu$_2$Zn). The as-deposited Cu oxides were in the form of smooth polyhedron particles of sizes 100 nm to 1 μm, while the Zn oxide films were interconnected platelets with lengths of hundreds of nanometers. The Cu$_x$Zn oxide catalysts showed spherical particles that were hundreds of nanometers in sizes. | An aqueous 0.1 M KHCO$_3$ electrolyte, pH is not specified. | The applied potential was between −0.65 and −1.15 V vs RHE | −8.2 mA/cm$^2$ | C$_2$H$_5$OH and C$_2$H$_6$ | FE for ethanol production was 29.1% at −1.05 V vs RHE, Ag/AgCl electrode (saturated KCl, Pine) and Pt wire were used respectively as the reference and counter electrodes. | Oxide-Derived Cu$_x$Zn | The oxide films Cu$_x$Zn, Cu$_4$Ag, and Cu$_2$Ni were galvanostatically deposited onto polished Cu disks. Zinc oxide films were prepared similarly, except that they were deposited onto Zn disks. The electrodepositions were performed using a potentiostat with applied currents of −0.92 mA/cm$^2$ for 600 s. The electrolytes were kept at 60 °C and stirred at 300 rpm during the deposition process. | The reaction was performed under ambient pressure in aqueous 0.1 M KHCO$_3$ electrolyte, using 60mins chronoamperometry at potentials between −0.65 and −1.15 V. The cathodic and anodic compartments of the cell were separated by an anion exchange membrane. Both compartments were infused with a continuous flow of CO$_2$ at 20 cm$^3$/min. | [42] | [43] |</p>
<table>
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<tr>
<th>11</th>
<th>Copper(I) Oxide Catalysts</th>
<th>Oxide films of Cu of varying thickness</th>
<th>An aqueous 0.1 M KHCO$_3$ and 0.1 M K$_2$HPO$_4$ buffer was used as electrolyte was used. The latter was purified by pre-electrolysis under N$_2$ gas for 20h.</th>
<th>An overpotential of $-0.99$ V vs RHE was recorded. Applied potential was between $-0.59$ and $-1.19$ V vs RHE.</th>
<th>Not specified</th>
<th>C$_2$H$_5$OH and C$_2$H$_4$</th>
<th>$34\text{--}39%$ for C$_2$H$_4$ and $9\text{--}16%$ for C$_2$H$_5$OH.</th>
<th>Copper(I) Oxide</th>
<th>Flat Cu discs, served as substrates for all the catalysts. They were first polished to a mirror-like finish using SiC paper and diamond slurries. Cu$_2$O layers were then galvanostatically deposited onto these Cu discs from a copper lactate solution. Cu$_2$O films of different thicknesses were obtained by varying the deposition time between 1 and 60 min. Seven Cu$_2$O films with varying thicknesses were prepared. Electropolished Cu surfaces were prepared by electropolishing the copper discs at $+260$ mA/cm$^2$ for 60 s in 85% phosphoric acid, followed by rinsing with ultrapure water.</th>
<th>[44]</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>Nanodendritic Cu catalyst</td>
<td>In situ deposited copper nanodendrites</td>
<td>0.1 M KBr was used as catholyte (100 mL) and 1 M KHCO$_3$ as anolyte (100 mL). $p^0$ was not specified.</td>
<td>The optimized working potential of the cathode was located in a voltage range experiments between ($-1.5$ and $-1.55$ V) versus Ag/AgCl.</td>
<td>$170$ mA cm$^{-2}$.</td>
<td>C$_2$H$_4$</td>
<td>$57%$</td>
<td>A solid IrO$_x$ coated Ti electrode was used as counter electrode.</td>
<td>Cu nanodendrites</td>
<td>Cu nanodendrites were obtained during an in situ electro deposition in acidic medium ($pH = 2.5$) under high over potential ($&lt;2$ V vs Ag/AgCl). The CO$_2$ reduction was carried out under constant current ($170$ mA cm$^{-2}$) to maintain stable electrolysis conditions. The electrolyte flow was controlled by an eight channel</td>
</tr>
<tr>
<td>13</td>
<td>Cu/SnO₂ Core/Shell Structure</td>
<td>A thin layer of SnO₂ coated over Cu nanoparticles, with a Cu/SnO₂-core/shell nanoparticle structure.</td>
<td>CO₂ saturated 0.5 M KHCO₃ was used as the electrolyte. The pH of the electrolyte was not mentioned.</td>
<td>The onset potential of CO₂ reduction to CO is at -0.5 V, while the highest FE was achieved at a potential of -0.7 V vs RHE.</td>
<td>4.6 mA/cm²</td>
<td>CO₂, H₂, and formate.</td>
<td>FE for Co was recorded as 93%. When the SnO₂ shell becomes thicker (1.8 nm), the core/shell NPs function as a SnO₂ NP catalyst and formate is the major product (85% FE at -0.9 V).</td>
<td>The counter/reference electrodes were not mentioned in the main text. Monodisperse core/shell Cu/SnO₂ NPs were synthesized via a seed-mediated method via the decomposition of tin acetylacetonate (Sn(acac)₂) in the presence of 7 nm Cu NPs at 250°C for 1 h. In this synthesis, the SnO₂ shell thickness was controlled by the amount of Sn(acac)₂ added.</td>
<td>The reaction was performed at ambient conditions of pressure and temperature.</td>
<td>[46]</td>
</tr>
<tr>
<td>14</td>
<td>Copper Oxide catalyst</td>
<td>Electrodeposited cuprous oxide thin film</td>
<td>An aqueous 0.5M KHCO₃ saturated with ultrapure CO₂ was used as electrolyte. pH of 7.6</td>
<td>The reaction was conducted at potentials ranging from -1.0 to -1.9 V (SCE). Current density was not recorded in the main text.</td>
<td>CH₃OH, H₂, and trace amounts of CO.</td>
<td>38% for CH₃OH</td>
<td>Ag/AgCl electrode saturated with NaCl was selected as the reference electrode along with a Pt wire as the counter electrode. Cuprous oxide thin films, electrodeposited on stainless steel substrates was used as the cathode.</td>
<td>Electrodes for CO₂ reduction were fabricated via oxidization of Cu foils or thin film electrodeposition. Airoxidized electrodes were prepared by first cleaning the foil in 0.1 M HCl for 20 s followed by oxidation in an air furnace at 403 K for 17 h. Anodized electrodes were created by electrochemically oxidizing Cu foil in 0.5 M KHCO₃ at a constant potential of 1.25 V (SCE) for 3 min. Cuprous oxide thin films were electrodeposited on stainless steel substrates at -0.555 V (SCE) and 333 K for 30 min in a lactate</td>
<td>CO₂ reduction experiments were performed in a typical three electrode cell (30 mL volume). During the reaction, CO₂ was bubbled into the electrolyte for 30mins at 298K.</td>
<td>[47]</td>
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solution including 0.4 M CuSO4 and 3 M lactic acid at pH 9.0 with Cu foil as the anode.

CuO-derived Copper catalysts

CuO-derived porous copper nanoribbon arrays

CO2 gas bubbled in aqueous 0.1M KHCO3 solution via gas dispenser was used as the electrolyte. pH was not mentioned.

The overpotential recorded was ~0.816 V vs. RHE

Current density was not recorded in the main text

The products obtained are C2H4, C2H6 and C2H5OH

The total FE for the C2 compounds is ~40%

A Pt foil and Ag/AgCl were used as the counter and reference electrode, respectively.

CuO-derived Copper

CuO-derived porous Cu NRAs electrode was prepared by the electrochemical reduction of CuO NRAs. NaOH, NaCl, Na2S2O8, and CuSO4 were dissolved into 100 mL deionized water. Cu foil with a geometric surface area of 4 cm2 was immersed in the as-prepared solution at 86°C for 8 min, during which Cu was oxidized to CuO. The foil was then taken out of the solution, rinsed with deionized water, and dried in air. A thin layer of Cu2O was grown in a basic solution, which included NaOH, NaCl, and CuSO4, at temperature of 60°C for 10 s. The CuO NRA electrode was reduced under ~0.18 V vs. RHE for 30 min to obtain Cu electrodes consisting of nanoporous ribbon array structure.

The reaction was conducted under ambient pressure and temperature. The potentiostatic electrolysis of CO2 was carried out in a conventional three-electrode cell by using a potentiostat.
| 16 | Cu$_2$O-derived copper nanoparticles | Cuprous oxide films with [100], [110] and [111] orientation and variable thickness were electrodeposited by reduction of copper(II) lactate on commercially available copper plates from Cu$^{2+}$ containing solutions prepared using 0.4 M CuSO$_4$ and 3 or 4 M lactic acid at 60 or 70$^\circ$C. The electrodeposition was conducted in a standard three-electrode cell where platinum mesh and Ag/AgCl in 3 M NaCl served as counter and reference electrodes, respectively. | 85 ml of 0.1 M KHCO$_3$ was used as electrolyte at pH 6.8, as obtained after saturation with CO$_2$. CO$_2$ was continuously purged at a rate of 20 ml min$^{-1}$ for 30 minutes before each experiment, to attain saturation of the electrolyte. Then the flow rate was decreased to 5 ml min$^{-1}$. The electrochemical reduction at a cathodic potential of -1.1 V vs RHE favours triangular pyramid orientation in the (110) direction where the (100) and (010) facets are exposed. Increasing the current density to 2 mA cm$^{-2}$ at pH 12 favours the growth in (100) directions with three-faced pyramids, where the sides of the pyramids expose (111) facets. | 0.8 mA cm$^{-2}$ at pH 12 favours triangular pyramid orientation in the (110) direction where the (100) and (010) facets are exposed. Increasing the current density to 2 mA cm$^{-2}$ at pH 12 favours the growth in (110) directions with three-faced pyramids, where the sides of the pyramids expose (111) facets. | Not specified | Pt mesh was used as a counter electrode and Ag/AgCl was used as reference electrode. |
| 17 | Copper NPs and reduced graphene oxide nanocomposite catalyst (Cu-rGO) | Unique nanocomposite consisting of Cu nanoparticles (NPs) and reduced graphene oxide (rGO) supported on a Cu substrate. The nanocomposite was optimized in terms of the composition of Cu | The electrolyte used was CO$_2$ saturated 0.1M NaHCO$_3$ solution whose pH was 6.65. | Not specified | CO, HCOOH and CH$_4$. | 76.6% | Ar-saturated 0.1 M NaHCO$_3$, and Ar-saturated 0.1 M Na$_2$SO$_4$ whereas, Nanocomposite consisting of Cu nanoparticles (NPs) and reduced graphene oxide (rGO) supported on Cu substrate; the Cu-rGO nanocomposite was formed directly on a Cu substrate using a facile electrochemical reduction method. A mixture of GO and Cu$_{2}^{+}$ precursors was cast on an etched Cu substrate; and the reaction was conducted at three potentials (−0.4, −0.5, and −0.6 V) for six hours of electrolysis. A gas-tight | The Cu-rGO nanocomposite was formed directly on a Cu substrate using a facile electrochemical reduction method. A mixture of GO and Cu$_{2}^{+}$ precursors was cast on an etched Cu substrate; and the reaction was conducted at three potentials (−0.4, −0.5, and −0.6 V) for six hours of electrolysis. A gas-tight |
NPs and rGO as well as the overall amount. a Cu substrate was used as the cathode simultaneous formation of Cu-rGO nanocomposite was achieved via cyclic voltammetry (CV), which was carried out in 0.1 M Na2SO4 in the potential range from 0.62 to −0.58 V vs. RHE for five cycles. The composition and thickness of the formed Cu-rGO nanocomposite were also optimized two-compartment electrochemical cell was used for the product formation and analysis. A cationic exchange membrane was utilized as a separator in the cell. Each compartment contained 35.0 ml of the electrolyte

<p>| 18 | Nanoporous copper films catalysts | Nano Porous Copper Films by Additive-Controlled Electrodeposition. The morphologies of the Cu films are varied to exhibit wire, dot, or amorphous structures. | the electrolyte used was CO2 saturated KHCO3 aqueous solution. pH was not specified | The cathodic potentials recorded are −0.5 V vs. RHE for C2H4 and −0.5 V vs. RHE for C2H5OH | Not s | C2H4 and C2H5OH | The FE recorded are 40% for C2H4 and 20% for C2H5OH | Pt mesh counter electrode and an Ag/AgCl reference electrode were used. The Ag/AgCl reference electrode was calibrated before each experiment with a normal hydrogen electrode (NHE) in 1M HClO4. | Nanoporous copper films catalysts | Nanoporous Cu film from plating baths containing 3,5-diamino-1,2,4-triazole (DAT) as an inhibitor was synthesized using electrodeposition method with high surface area and tunable morphology. | Cyclic voltammetry (CV), chronoamperometry (CA), and chronopotentiometry (CP) evaluating CO2 reduction performed at room temperature. [51] |</p>
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<td>19</td>
<td><strong>Cu₂O-Derived Copper Catalysts</strong></td>
<td>Cu films of different thicknesses and morphologies. Aqueous 0.1 M KHCO₃ was used as the electrolyte. pH of 6.8. Electrochemistry and quantification of the products was measured at the potential of -0.98V vs RHE. Cu₂H₄, ethanol, and n-propanol. FE are 42.6% (jC₂H₄ = -13.3 mA cm⁻²), 11.8% (jC₂H₅OH = -3.7 mA cm⁻²), and 5.4% (jC₃H₇OH = -1.7 mA cm⁻²), were recorded respectively. Ag/AgCl and Pt wire are used as the reference and counter electrodes respectively. Cu₂O-Derived Copper Catalysts. Cu₂O films were grown hydrothermally onto mechanically polished Cu discs suspended on a custom-made Teflon holder in a Teflon-lined stainless steel autoclave at 145 °C for 90 min. A precursor solution consisting of 0.25 M of Cu(NO₃)₂·3H₂O and 0−1.75 M NH₃ dissolved in a solvent was used. The solvent consisted of a 23:13:2 volumetric ratio of ethanol, ultrapure water, formic and acid. The thickness of the films was expected to increase with the concentration of the NH₃. The as-prepared Cu₂O films were then washed with copious amounts of water, dried overnight at 60 °C and prerduced to Cu₀ in a separate 0.1 M KHCO₃ electrolyte for 300 s, before being used as catalysts for CO₂ reduction. We termed these as Cu₂O-derived Cu. Electrochemical measurements were performed using a Gamry 600 galvanostat/potentiostat using a three-electrode configuration. The electrodes were housed in a custom-made, gastight, two compartment Teflon cell.</td>
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<td>20</td>
<td><strong>Plasma-Activated Copper Nanocube Catalysts</strong></td>
<td>Cu nanocube catalysts with tunable Cu(100) facet. CO₂-saturated 0.1 M KHCO₃ solution (pH 6.8) was used as the electrolyte in aqueous medium. The applied potential recorded was −1.0 V vs RHE for 1 h. Not specified. Maximum FE for C₂ and C₃ is ~73%. Pt gauze and leak-free Ag/AgCl were used as counter and reference electrodes respectively. Commercial Cu foils were first cleaned with acetone and ultra-pure water in an ultrasonic bath, and then electropolished in phosphoric acid at 3 V vs titanium foil for 5 min. Cu nanocubes were prepared by electrochemically. Electrochemical measurements were carried out in a gas-tight H-cell separated by a Nafion 115 membrane.</td>
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anodizing the electropolished Cu foils in 0.1 M KCl with five triangular potential scans ranging from 0.4 V to 2.0 V vs RHE at a rate of 500 mV s\(^{-1}\). During each cycle, the potential was held at the positive and negative limits for 10 and 5 seconds, respectively. The Cu nanocube samples were then rinsed with a large amount of ultra-pure water to remove the electrolyte. Plasma pre-treatments were then performed in a plasma etcher at a gas pressure of 400 mTorr of O\(_2\), H\(_2\) or Ar and power of 20 W for different periods of time.

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| 21 | Oxide-derived Cu foam catalysts | Mesoporous Cu foams | CO\(_2\) saturated 0.5M NaHCO\(_3\) in aqueous medium, pH not mentioned | Highest at -0.4 to -1.0 V vs RHE. | H\(_2\), CO, HCOO\(^-\), CH\(_3\)COH, C\(_2\)H\(_4\), and C\(_2\)H\(_6\). | C\(_2\) efficiencies reaching FEC\(_2\) = 55\%. The total FE of all the major products lies between 89% and 96%. | A leakless Ag/AgCl electrode was used as the reference electrode and a bright Pt-foil (15mm x 5mm) was used as the counter electrode. | Cu foam catalysts. | Mesoporous Cu foam catalysts were electrodeposited on Cu blanket wafer coupons by a through mask plating process leaving a well-defined area covered with the Cu foam behind. | The electrolysis was carried out in a custom-built, air-tight glass cell (H-type). |

| 22 | Hierarchical Cu pillar electrode catalyst | Highly perpendicular Cu pillar Structures | The electrolyte used was CO\(_2\)-bubbled 0.1M KHCO\(_3\) aqueous solution (pH 6.6-6.7). | The electrochemical conversion of CO\(_2\) at various constant | Not specified | formic acid, HCOOH. | The Cu-0.5 h electrode performed well with a 28% FE to formic acid. | The standard calomel electrode (SCE) and Pt gauze were used. | Hierarchical Cu pillar structures were used as the working electrode. | Cu pillar electrodes (Cu-2.5 h, Cu-5 h) were fabricated by using an electrodeposition method i.e. Highly perpendicular Cu nanopillar structure was prepared by cathodic electrolyses were performed on a fuel-cell-like two-compartment electrochemical | [54]
<p>| 23 | <strong>Nanostructured Cu₂O-Derived Cu Catalyst</strong>&lt;br&gt;<strong>/Palladium(II) Chloride</strong> | <strong>Cu₂O nanoparticles</strong>&lt;br&gt;deposited on polished Cu disc electrode. The surface of an electropolished Cu electrode was smooth and featureless. | The electrolyte used was aqueous 0.1 M KHCO₃ + 100 mg PtCl₂, pH 6.8. | The conversion was performed at ~1.0 V vs RHE. | Not specified | C₂ products i.e. C₂H₄, C₂H₆ and ethanol. | FE of 3.4% was recorded for C₂H₄, and FE of 30.1% for C₂H₆. | The working electrode was Cu₂O nanoparticles deposited on polished Cu disc electrode. Cu₂O was electrochemically deposited onto a polished Cu electrode using a two-electrode cell with a platinum counter electrode. Deposition was performed at 60 °C, with a fixed current of −0.7 mA for 1200 s. The electrochemical reduction of CO₂ was performed in a Gas tight Teflon electrochemical cell. | [56] |
| 24 | <strong>Surface Oxidized Copper Catalyst</strong> | <strong>Pure Cu metal sheet</strong>&lt;br&gt;4cm², modified by surface oxidation. | The electrolyte used was CO₂ saturated 0.5 M dm⁻³ KCl. | The conversion was performed within the range of −0.9 to −2 V vs Ag/AgCl | Not specified | Methane and ethane | Not specified | The working electrode was Surface Oxidized Copper Electrodes The metal electrodes used in the present study are pure Cu sheet of 4 cm² where electrical connection is established through the same strip. The Cu strips were polished with fine emery paper and electrolytically treated in 1 mol dm⁻³ phosphoric acid and sulphuric acid, cleaned with acetone to remove grease, washed subsequently with water and used as working electrode. The same Cu | The electrochemical measurements were conducted with an EC epsilon potentiostat. The experiments were performed in a laboratory-made H-cell. | [57] |</p>
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<td>25</td>
<td>Cu Nanoclusters</td>
<td>Cu nanoclusters on single crystal (1010) ZnO electrodes. Electrochemical experiments were carried out in aqueous 0.1 M KHC\textsubscript{2}O\textsubscript{4} electrolytes saturated with CO\textsubscript{2}. The reduction experiments was conducted at −1.4 V versus Ag/AgCl. Not specified</td>
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<td>26</td>
<td>Tin Based Film on Copper Plate.</td>
<td>Sn/Cu electrode with the geometric surface area of 1 cm\textsuperscript{2}. The electrolyte used was 40 mL of 0.1 mol L\textsuperscript{−}\textsuperscript{1} KHC\textsubscript{2}O\textsubscript{4} aqueous solution, saturated with CO\textsubscript{2}; pH not specified in the text. The electrolysis was carried out at a potential of −1.8 V vs. Ag/AgCl. 5.08 mA cm\textsuperscript{−2}. Formate 74.1% at −1.8 V. Pt plate and an Ag/AgCl electrode (sat. KCl) were used as counter and reference electrodes respectively. The working electrode was Sn based film on Cu electrode (i.e. prepared Sn/Cu electrode with the geometric surface area of 1 cm\textsuperscript{2}). Sn based film with a thickness of 169 nm was electrodeposited on copper plate from a choline chloride/ethylene glycol based electrolyte containing SnCl\textsubscript{2}. The electrochemical deposition was performed on the Cu substrate in nonaqueous solution containing 0.1 mol L\textsuperscript{−}\textsuperscript{1} NaCl. Electrolysis was carried out potentiostatically using a LAND CT2001C cell performance testing instrument</td>
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<td>27</td>
<td>Copper-Hydride Nanoclusters</td>
<td>Structurally precise ligand protected Cu-hydride nanoclusters, such as Cu\textsubscript{32}H\textsubscript{32}L\textsubscript{12} (L is a dithiophosphate ligand). i.e. composite Cu32/C/GDL electrode. The electrolytes used were 60 mL of 0.1 M KHC\textsubscript{2}O\textsubscript{4} and 0.4 M KCl solution saturated with CO\textsubscript{2}; pH of 6.8. The onset potentials for the conversion of CO\textsubscript{2} to HCOOH and CO are -0.32 V and -0.81 V vs. SHE, respectively. The over potential recorded are (0.3 V, 0.4 V) and (0.5 V, Not specified</td>
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<td>28</td>
<td>AuCu Nanoparticles</td>
<td>Atomic Ordering Transformations of AuCu Nanoparticles. E.g. d-AuCu and o-AuCu NPs.</td>
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REFERENCES

18. W. Zhu, R. Michalsky, Ö. Metin, H. Lv, S. Guo, C.J. Wright, X. Sun,


