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A Review on Electrochemical Synthesized Copper-based Catalysts for Electrochemical Reduction of CO_2 to C_{2+} Products

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ABSTRACT: In recent decades, catalytic reduction of CO_2 is a hot topic in the research field of electrocatalysis. Copper is the only metal catalyst capable of producing multiple carbon (C_{2+}) products in electrocatalytic CO_2 reduction (ECR), however, there are still many challenges such as low selectivity, serious hydrogen evolution (HER) and poor stability. So far, various synthesis methods have been developed for Cu-based catalysts. Compared with ordinary chemical synthesis, electrochemical method has the advantages of simple process, controllable conditions, good safety and eco-friendly. In this review, the recent progress in synthesizing different types of Cu-based catalysts by means of the electrochemical method are comprehensively reviewed. The engineering strategies and the effects of the key preparation conditions on the catalytic performance of CO_2 electroreduction for C_{2+} products are discussed in details. Besides, copper-based catalysts synthesized by electrochemical methods combined with the ordinary methods (wet chemical methods, plasma activated methods and other methods) were also outlined. Finally, the development potential of electrochemical synthesis for Cu-based catalysts are recommended, which provides a direction for the future development of Cu-based catalysts with low cost and high ECR performance.

Keywords: Electrochemical synthesis; Copper-based catalyst; Electroreduction of CO_2; C_{2+} products

Contents:

1.Introduction

With the development of the world's economy and society, the growing demand for energy becomes a hot topic and an urgent problem to be solved. Although great progress have been made in the development and utilization of green renewable energy such as solar energy, wind energy and water energy, fossil energy is still the main raw material for social energy supply, accounting for more than 80%.[1] A large amount of CO_2 emitted from fossil energy combustion is trapped in the atmosphere, which leads to the imbalance of global carbon cycle, resulting in serious global climate change and environmental problems such as greenhouse effect and sea level rise.[2,3] Thus, in recent years, how to convert CO_2 into high value-added carbonaceous compounds has attracted extensive attention in the aspects of reducing atmospheric CO_2 concentration and alleviating social energy problems. Researchers have developed a series of methods to effectively convert CO_2 into useful carbon based compounds, such as chemical conversion,[4,5] biotransformation,[6,7] photocatalysis,[8,9,10] electrocatalysis,[11,12] etc. Among them, with the aid of the electric energy and appropriate catalysts, the electrocatalytic reduction of CO_2 (ECR) could convert CO_2 to other carbon products at ambient temperature and pressure. This kind of CO_2 reduction technology driven by renewable energy has good environmental compatibility and adaptability, so it has become a research hotspot in the field of CO_2 conversion.

In essence, the electrocatalytic reduction of CO_2 in aqueous solution is to convert CO_2 into carbon containing products such as carbon monoxide (CO), methane (CH_4), formic acid (HCOOH), methanol (CH_3OH), ethylene (C_2H_4), ethanol (C_2H_3OH) by electron and proton transfer. The chemical equations for each product and the corresponding standard electrode potential[13] (V vs. SHE) are shown in Table 1.

Table 1. Standard electrode potentials of CO_2 in aqueous solutions (V vs. SHE) at 1.0 atm and 25 ºC, calculated according to the standard Gibbs energies of the reactants in reactions.[13] Copyright 2014, The Royal Society of Chemistry.

Half electrochemical thermodynamic reactions	V vs. SHE	
$CO_2(g) + 2H^+ + 2e^- = HCOOH(l)$	-0.250	①
$CO_2(g) + 2H_2O(l) + 2e\text{-} = HCOO^-(aq) + OH^-$	-1.078	②
$CO_2(g) + 2H^+ + 2e^- = CO(g) + H_2O(l)$	-0.106	③
$CO_2(g) + 2H_2O(l) + 2e^- = CO(g) + 2OH^-$	-0.934	④
$CO_2(g) + 6H^+ + 6e^- = CH_3OH(l) + H_2O(l)$	0.016	⑤
$CO_2(g) + 5H_2O(l) + 6e^- = CH_3OH(l) + 6OH^-$	-0.812	⑥
$CO_2(g) + 8H^+ + 8e^- = CH_4(g) + 2H_2O(l)$	0.169	⑦
$CO_2(g) + 6H_2O(l) + 8e^- = CH_4(g) + 8OH^-$	-0.659	⑧
$2CO_2(g) + 12H^+ + 12e^- = CH_2CH_2(g) + 4H_2O(l)$	0.064	⑨
$2CO_2(g) + 8H_2O(l) + 12e^- = CH_2CH_2(g) + 12OH^-$	-0.764	⑩
$2CO_2(g) + 12H^+ + 12e^- = CH_3CH_2OH(l) + 3H_2O(l)$	0.084	⑪
$2CO_2(g) + 9H_2O(l) + 12e^- = CH_3CH_2OH(l) + 12OH\text{-}$	-0.744	⑫

The above equations are carried out in a standard atmospheric pressure and 25 ℃ aqueous solution, which only reflects the trend of the reaction without considering the kinetic mechanism of these reactions. In fact, as the applied voltage is satisfied, the reaction priority and reaction rate will change greatly according to electrolyte environment. Moreover, the type of catalyst also has serious effect on the reduction products. Different metal catalysts have disparate adsorption strength for the intermediate products of CO_2 reduction (as indicated by the volcano plot for carbon dioxide reduction on metals (**Figure 1**)),[14] thus contributes to the obviously different product distribution. In general, metal catalysts can be divided into the following four categories. (1) Pb,[15] In,[16] Sn[17][18] and Bi,[19,20] have weak bind energies to ECR intermediates, in which the C-M (metal) bond always breaks and a large amount of formic acid is produced after the simple two electron reaction of Formula ①. At the same time, this kind of catalyst, acting as an electron source in the reaction, also combines with H* weakly so that hydrogen evolution reaction is weak; (2) Au,[21] Ag,[22] Zn,[23] Pd[24][25] and Ga,[26] believed to bind to intermediates stronger than(1), are still kinds of weakly bound metals, and have a slightly stronger adsorption capacity for *H. Therefore, there are not enough protons in the reaction so that most of the reduction products are CO by formula ③; (3) Cu[27,28,29,30] is the only special metal which can produce C_{2+} compounds by multi electron reaction, which has moderate binding energy for intermediate products that could provide sufficient dimerization reaction time and also suppresses the hydrogen evolution reaction.; (4) The C-M bond of Ni, Fe, Pt and Ti is too strong, which results in serious hydrogen evolution reaction. Besides the metal catalysts, the two-dimensional transition metal carbide/nitride (MXene),[31,32,33] homogeneous catalyst such as transition-metal complexes with organic ligands[34] and copper-based multinary sulfides (CMSs)[35] were also been widely reported and reviewed in the electrocatalytic reduction of CO_2.

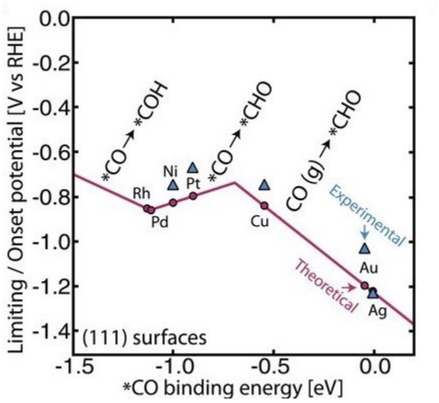

Figure 1 Volcano plot for carbon dioxide reduction on metals.[14] Copyright 2017,

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Cu-based catalyst has unique properties among metal catalysts and has been considered as an ideal material for electrocatalytic reduction of CO_2 to polycarbonate. Meanwhile, the practical application of Cu-based catalysts in the ECR still faces problems such as low current density, poor selectivity and poor stability. Therefore, developing efficient Cu-based catalysts to achieve the high current density, high C_{2+} selectivity and high stability have become the research hotspots in the area of electrocatalytic reduction of CO_2. Many rational design routes have been adopted for enhancing the performance of Cu-based catalysts in ECR, including the structural design (such as two-dimensional,[36] cubic,[37] dendritic,[38] grain boundaries[39]), size design,[40] composition design (bimetallic sites,[40] metalloid dopants)[42,43] and surface modification.[44] The operando characterization techniques (operando XAS, time-resolved electron microscopy, in situ electrochemical vibrational spectroscopy) have been applied to study Cu catalysts in situ.[45,46,47] In recent years, kinds of methods such as wet chemical method, solvothermal method, sol-gel method,[37] thermal treatment method,[48] plasma activation[49] and electrochemical method[50] were proposed to develop novel Cu-based catalysts. Compared with other methods, electrochemical synthesis mainly has the following advantages: 1. The parameters during electrochemical synthesis can be easily and precisely controlled, including the reaction electrode, current density, applied voltage, electrolyte composition and concentrations; 2. The preparation process is under mild conditions (at room temperature and pressure) with short reaction time. 3. The catalyst layer with good adhesive to on the electrode surface could be in situ formed under electrochemical synthesis, which is more suitable for preparing the electrocatalysts and avoids the dispersion and coating process. Therefore, the electrochemical synthesis has attracted more and more attention of the researchers in the field of Cu-based catalyst for ECR.

In this review, based on the unique advantages of Cu-based catalysts in the electrocatalytic reduction of CO_2 to C_{2+} and of electrochemical method in synthesizing electrocatalysts, the electrochemical synthesis methods of different types of Cu-based catalysts (such as monometallic Cu catalysts, oxide derived Cu catalysts and metal modified Cu-based catalyst) are systematically reviewed (as shown in **Figure 2**). The morphology structure, crystal phase, electronic states and catalytic performance of electrochemical synthesized Cu-based catalysts for electrochemical reduction of CO_2 to C_{2+} products are discussed in details. Besides, copper-based catalysts synthesized by electrochemical methods combined with the ordinary methods (wet chemical methods, plasma activated methods and other methods) were also outlined in this review. Finally, the development potential and cultivation space of electrochemical synthesized Cu-based electrocatalysts for ECR are prospected.

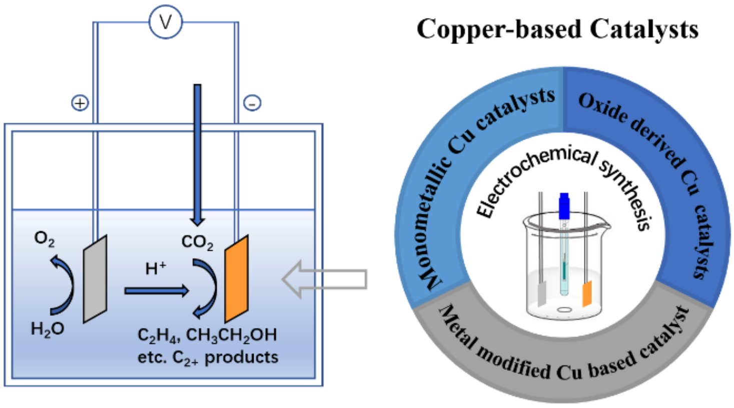

Figure 2 An overview of different types of Cu-based catalysts synthesized by electrochemical method for electrochemical reduction of CO_2 to C_{2+} products.

3. Electrochemical synthesized Cu-based catalysts for ECR to C_{2+} products

From the point of reaction kinetics, the dimerization reaction of intermediate (*CO) needs to overcome a high potential barrier. However, before the dimerization reaction, *CO tends to desorb and release C_1 product or the excessive adsorbed *H leads to the hydrogen evolution reaction. Hori et al. carried out a series of studies[51,52,53] and found that CO_2 can be reduced to ethylene and other C_2 products on copper catalysts, which broke new ground for metal catalysts to obtain C_{2+} products in ECR.[51] Since then, researchers have devoted to developing new Cu-based catalysts with lower over potential, larger current density, and higher selectivity, so as to convert CO_2 into ethylene, ethanol, ethane and other C_2 products, even C_3 and C_4 products. By precisely controlling the structure and morphology of the catalysts, great progress has been made for enhancing the faradic efficiency of C_{2+} products in ECR. In particular, electrochemical synthesis has been widely used in the preparation of electrocatalysts. Considering the unique advantages of electrochemical synthesis and its performance in

ECR reaction, the electrochemical synthesis methods of different types of Cu-based catalysts (such as monometallic Cu catalysts, oxide derived Cu catalysts and metal modified Cu-based catalyst) are mainly summarized in this section. The structure properties and catalytic performance of electrochemical synthesized Cu-based catalysts for electrochemical reduction of CO_2 to C_{2+} products are highlighted in details.

2.1 Monometallic Cu catalysts

Electrodeposition is the most common method to prepare metallic catalyst by electrochemical method. Using a three-electrode device, copper ions in the electrolyte can be electrodeposited on the cathode substrate by applying voltage or current. In electrochemical environment, the electrode surface can be reconstructed by adjusting the electrochemical conditions or changing the composition of the electrolyte.

The morphology of electrodeposits is sensitive to the cathodic potential applied and the electrolyte concentration.[54,55] T.Pardal et al. performed a series experiments to study the electrodeposition of copper for the electrochemical conversion of CO_2 to C_2 hydrocarbons. By varying the applied electrodeposition potential from -0.55 to -1.15 V vs. SCE for the same value of charge density, the morphologies of different electrodes were developed with dendritic, honeycomb and 3D foam structures. Specifically, as shown in **Figure 3** a, the increase in deposition potential leads to an enhancement of the copper dendrites (sample Ⅱ and Ⅲ) and a decrease of dendrite's length and number (sample Ⅳ and Ⅴ). For the electrolyte, the increased concentration of H_2SO_4 aggravated the hydrogen evolution reaction and promote the attachment of the hydrogen bubbles, resulting in copper particles agglomerating around the bubbles to form honeycomb surface as shown in **Figure 3** b (sample Ⅵ and Ⅶ). In addition, increasing the $CuSO_4$ concentration raises the comparative reduction of copper ions to HER and consequently the pore size and wall thickness increase (sample Ⅷ). The honeycomb and 3D foam structure formed by this simple method of dynamic hydrogen bubble template allow rapid transport of gas and liquid, and its high surface area is desirable for CO_2 electrochemical reaction, which contributes to the C-C coupling reaction and results in a selective production of C_2 hydrocarbons mixture instead of methane (**Figure 3** c).

Adding additives into the electrolyte are also applied to tailor the morphology of the electrodeposits. In the presence of additives, the three-dimensional structure with high specific surface area can be obtained with strong copper binding additives, while the arrangement of copper atoms could be regulated by the weaker binding additives. Andrew A. Gewirth et al. found that adding DAT (3,5-diamino-1,2,4-triazole), DTAB (Dodecyl trimethylammonium) or benzyl bromide as corrosion inhibitors in copper plating bath could delay the deposition rate of copper and promotes the formation of copper catalyst with high specific surface area.[56] The N atom in DAT coordinates with copper and reduce the nucleation sites of copper during deposition, which inhibits the growth of the copper deposits and give rise to steps and edges with low-coordinated Cu atoms. In addition, the copper electrode surfaces with different nanostructures such as nanodot, nanowire or amorphous morphology were obtained by controlling the pH value of the electrolyte and the deposition current density (**Figure 3** d-f). Among them, the copper electrode with nanowire structure is the most active in reducing CO_2 to C_{2+}

with the FE increased to more than 60% at -0.5 V vs RHE, and a mass activity for CO_2 reduction at -0.7 V vs RHE of ~700 A/g. Different from adding DAT to control the deposition kinetics of copper ions, polyvinylpyrrolidone (PVP) is a kind of inert polymer.[49] Jinlong Gong et al.[39] used PVP as the additive in the electrolyte to prepare grain-boundary-rich copper catalyst. Although PVP adsorbed on the copper surface is unstable and easy to desorbed quickly, it has a great impact on the arrangement of copper atoms on the electrode surface, leading to the reduced grain size of copper catalysts with rich grain boundaries (**Figure 3** g). DFT calculation in **Figure 3** h shows that this microstructure with rich grain boundaries can enhance and stabilize the adsorption of *CO. The binding strength of * CO at the convex site (GB1) and concave site (GB2) at the edge of grain boundary (GBs) in **Figure 3** i are stronger than that at other step sites (t1~t7). Moreover, GBs site also changes the coordination of the surrounding atoms and slightly increases the binding energy of * CO at t1, t2 and t7, which is conducive to the further dimerization of * CO, thus improving the selectivity of C_2 products.

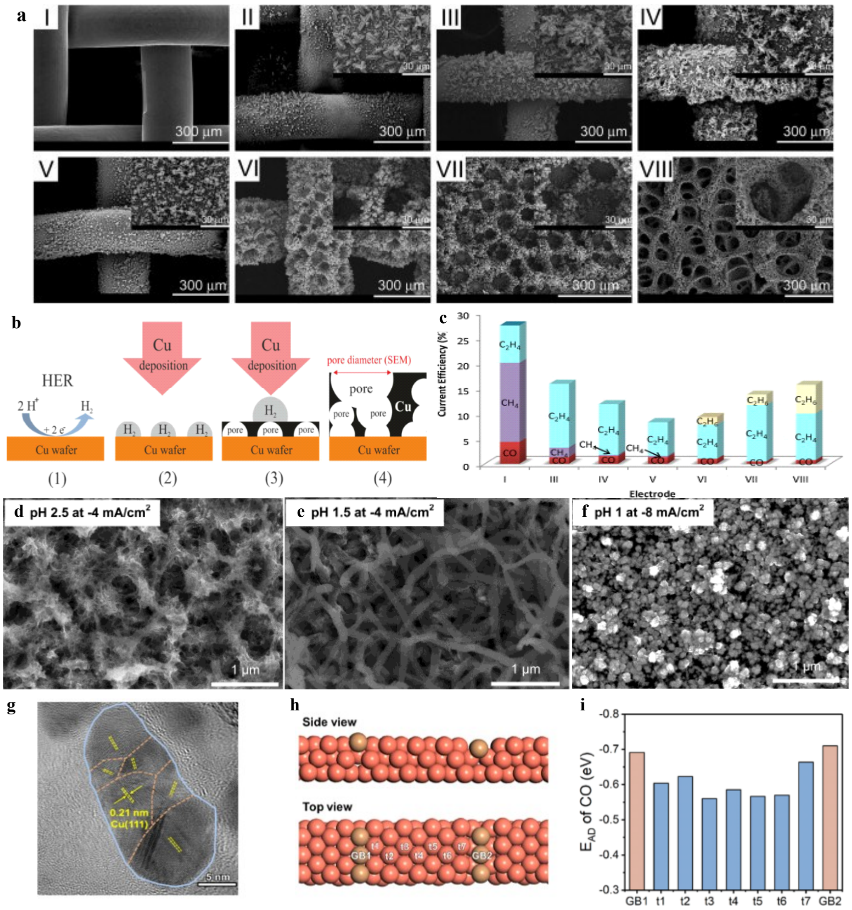

Figure 3. (a) SEM images of the electropolished copper electrode and the copper electrodes prepared by electrodeposition under different conditions on copper mesh and copper foil.[55] Copyright 2013, Elsevier. (b) Schematic representation of the key aspects of the template assisted Cu electrodeposition.[57] Copyright 2016, American Chemical Society. (c) Current efficiency of gaseous carbon products in the electroreduction of CO_2 at −1.9 V vs Ag/AgCl for different electrodes (see Figure 3 a), after 1 h 15 min of reaction.[55] Copyright 2013, Elsevier. The SEM images of Copper films deposited in CuSO4 and DAT solutions with different pH and current density: (d) amorphous, (e) wire and (f) dot electrode surfaces were obtained.[56] Copyright 2017, American Chemical Society. (g) image of rich grain boundary copper films (GB-Cu) deposited by PVP and $Cu(NO_3)_2$ solutions(GB-Cu).[39] Copyright 2020, American Chemical Society. (h) Different binding sites on the schemed atomic structure of GB-Cu.[39] Copyright 2020, American Chemical Society. (i) *CO binding energies in different sites of the schemed structure of GB-Cu.[39] Copyright 2020, American Chemical Society.

In summary, the applied cathodic voltage and the additives in the electrolyte are the key factors for the metallic Cu electrodeposits on the electrode, which adjust the morphology and structure from the kinetic deposit process that related to the exposed active sites and roughness of the catalyst surface. Via controlling these parameters of the electrodeposition process, the 3D morphology with high surface area, the exposure of low-coordinated Cu and the rich grain boundaries are favorable for the fast mass transfer and the dimerization of *CO, and the higher selectivity of C_2 production.

2.2 Oxide derived Cu (OD-Cu) catalysts

A most promising approach to boosting both efficiency and selectivity for electrochemical reduction of CO_2 is using oxide derived Cu (OD-Cu) electrodes. OD-Cu catalysts usually have rich grain boundaries, multiple low coordination sites and a certain amount of oxygen species, which are considered to be favorable factors for improving catalytic activity and selectivity for C_{2+} products. More importantly, the surface Cu^+ is believed to play an essential role. Specifically, CO adsorbs on the Cu^+ site more stable than on the metallic Cu^0 region. Further CO dimerization between CO bonding Cu^0 and a neighboring CO banding Cu^+ has a modest barrier to form the OCCO surface species. It is a favorable dimerization process on the OD-Cu catalysts that improves both kinetics and thermodynamics of C_2 products.[58] A variety of researches have been reported on the electrochemical synthesis of OD-Cu and its application in ECR reaction.[59,60,61,62,63,64]

In general, dense Cu_2O films can be obtained directly by electrodeposition in alkaline electrolyte with lactic acid added. Cu^{2+} ion in alkaline solution forms complex

$[CuL_2(OH)]^{3-}$ with lactate ion (L^{2-}) to prevent precipitation. The complex is reduced to Cu_2O on the surface of cathode. The specific reaction process is as follows：

Anode：$Cu^{2+} + OH^- + 2L^{2-} \rightarrow [CuL_2(OH)]^{3-}$

Cathode：$2[CuL_2(OH)]^{3-} + 2e^- \rightarrow H_2O + 4L^{2-} + Cu_2O(s)$

Based on the above reaction process, Jonas Baltrusaitis et al.[59] prepared various OD-Cu electrodes preferentially oriented in either (100), (110) and (111) directions by adjusting the electrodeposition conditions (**Figure 4** a-c). The results indicate there is not much difference in the performance of the samples with different orientations, however, it is certain that the OD-Cu film promotes the formation of C_2 with much higher selectivity (**Figure 4** d), attributed to their optimized density of steps and edges. Boon Siang Yeo's group[62] further studied OD-Cu film with various thicknesses from 0.2μm to 8.8 μm by varying the deposition time. The highest C_2 selectivities were optimized with the 1.7-3.6 μm thick films. Although Cu_2O films were reduced to Cu during CO_2 reduction, the stepped surfaces with edges and terraces promote to dissociate CO_2 and optimize the chemisorption energies of intermediates. Based on the thin film electrode obtained by electrodeposition, Jaeyoung Lee et al.[65] prepared chloride-induced bi-phasic Cu_2O-Cu catalyst formed by the application of a cathodic potential in the Cl-containing CO_2 electrolytic system. The chemo affinity between chloride Cl^- and Cu facilitates the formation of a uniquely shaped phase. The lattice fringe spacings of the (111) and (200) facet directions of Cu_2O, as well as the Cu (111) facet direction were shown in HRTEM (**Figure 4** e). Cu_2OCl nanoparticles appeared to be transformed into a crystallographic cuboctahedral shape, which enhanced Cu_2O stability and dramatically increased C_3 faradic efficiency to more than 10%.

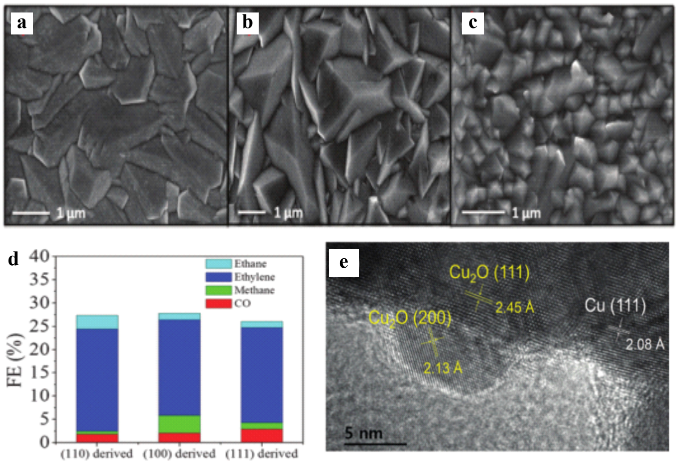

Figure 4. SEM images of as deposited Cu_2O films with predominant (a) (110), (b) (111) and (c) (100) orientations.[59] Copyright 2014, Royal Society of Chemistry. (d) FE of gaseous products from CO_2 reduction at -1.1 V vs. RHE for (a) (b) (c).[59] Copyright 2014, Royal Society of Chemistry. (e) HRTEM images mapping results for the in situ transformed bi-phasic Cu_2O and Cu electrode (Cu_2OCl) by applied cathodic potential for 10 min in 0.1m KCl having different crystal orientation.[65] Copyright 2015, John Wiley and Sons.

Electrochemical anodization is another common idea for preparing OD-Cu electrode by electrochemical method. Alexis T. Bell's group[64] compared three kinds of OD-Cu respectively prepared by electrochemical anodization, annealing and chemical oxidation. As shown in **Figure 5** a and b, the annealed Cu_2O electrode had higher selectivity for C_1 products such as CO and formate, while the catalyst prepared by electrochemical method showed better C_2H_4 selectivity on account of the rich oxygen species and mixed copper valence state (Cu^{2+} and Cu^{+}). Yun Jeong Hwang et al prepared anodic oxidized $Cu(OH)_2$ nanowires (AN-Cu) by applying constant current anodic oxidation of copper foil.[59] XPS spectra and LMM auger peak scanning (**Figure**

5 c and d) showed that the surface of the catalyst was rich in Cu^{2+}, while Cu^{2+} was obviously reduced to low valence species such as Cu^{+} and Cu^{0} after ECR reaction. The mixed valence copper may be closely related to the intermediates of ethylene production. Besides, the initial reduction condition affected the compositions, surface structure and catalytic activity of the catalysts. For AN-Cu with rapid pre-reduction at high potential (HPR Cu), there was still a small amount of $Cu(OH)_2$ after the reaction, which was conductive to the selective and stable ethylene production activity for more than 40 hours (**Figure 5** e). On the other hand, for AN-Cu with slow pre-reduction at low potential (LPR Cu), $Cu(OH)_2$ almost disappeared after pre-reduction although more obvious Cu_2O species were observed, which leads to the fact that LPR Cu became more favorable to methane production after few hours. The results provided a powerful support for the conclusion that mixed valence copper was beneficial to ethylene formation. Tayhas R. Palmore et al.[66] anodized the copper foil in an electrolyte containing halogen ions to obtain a halide electrode, and subsequent oxide formation in a $KHCO_3$ electrolyte by the following reaction formula:

$$2CuX(s) + OH^{-} \leftrightarrow Cu_2O(s) + 2X^{-} + H^{+}$$

The preparation diagram is shown in the **Figure** 5 f. Via anodic halogenation of Cu followed by surface reconstruction and electroreduction, a surface with high density of defect sites were created, and these sites stabilized species such as Cu^{+} and subsurface oxygen, which were known to promote C_{2+} production during the ECR. Among them, iodized electrode has the best performance with FE_{C2+} of 72.6% due to the high affinity of I^{-} to form CuI.

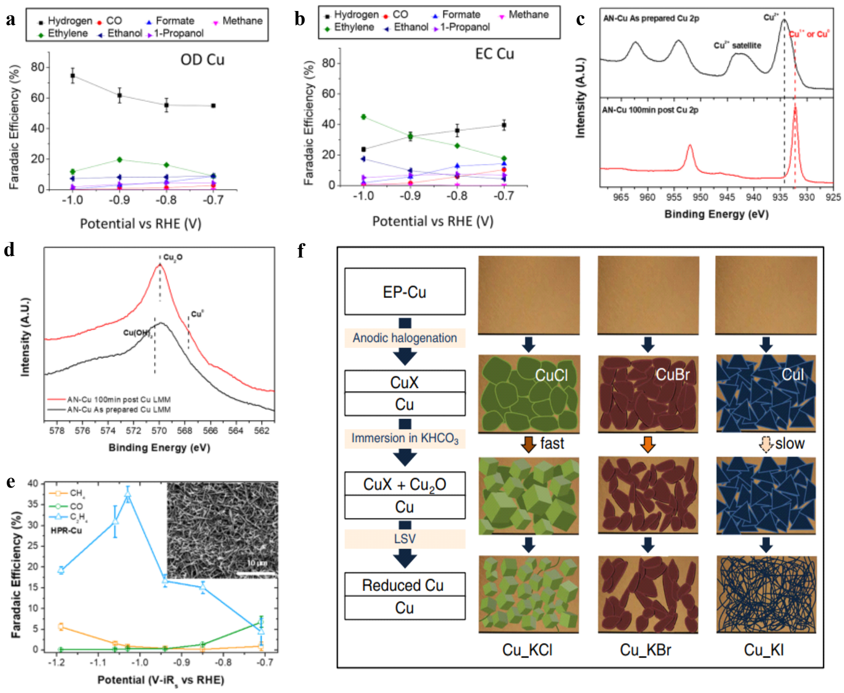

Figure 5. Faradaic efficiencies of major CO_2RR products from -0.7 V to -1.0 V vs RHE in 0.1 M $KHCO_3$ for: (a) oxide-derived nanocrystalline copper and (b) electrochemically cycled anodic oxidized copper.[64] Copyright 2017, American Chemical Society. (c) Cu 2p XPS spectra and (d) Cu LMM Auger spectra of the AN-Cu catalyst measured as-prepared and after 100 min of CO_2RR.[59] Copyright 2017, American Chemical Society (e) CO_2RR product selectivity of HPR-Cu catalyst on various applied potentials and its SEM image (inset).[60] Copyright 2017, American Chemical Society. (f)Schematics showing morphology of Cu catalysts. The method used to prepare Cu catalysts for electrochemical CO_2RR: anodic halogenation in KX solutions where X = halogen, oxide formation in basic $KHCO_3$, and electroreduction in neutral $KHCO_3$ by LSV. EP-Cu corresponds to electropolished Cu foils, LSV corresponds to linear sweep voltammetry.[66] Copyright 2020, Springer Nature.

Pulse voltage or current was recently found to be an effective means to prepare OD-Cu catalyst with controlled crystal facet and morphology. The specific crystal facets on surface can be exposed by continuous redox process and it is believed that the crystal facet and edge of Cu (100) are beneficial to the production of ethylene.[67,68,69] Haotian Wang et al.[70] creatively proposed a metal ion cycling method, which controlled the surface morphology and crystal surface exposure by adjusting the number of electrochemical cycles **(Figure 6** a). Compared with the traditional electrochemical deposition method, the multiple stripping/deposition cycles in $Cu(NO_3)_2$ solution gradually stabilized a layer of Cu_2O nanocubes on the surface of Cu foil. Under the ECR experiment condition, OD-Cu with regular cubic structure that selectively exposed the Cu (100) crystal face was formed, which improved the FE of C_{2+} products to 60% and inhibits the FE of H_2 below 20%. On the other hand, under pulse potential, the halogen ions also play an important role in tailoring the morphology and structure of the synthesized OD-Cu catalyst. B.S.yeo's group[71] used 0.1M KCl solution as electrolyte, and applied triangular potential on polished copper foil to coarsen Cu surface and form CuCl film. Then cathodic potential was applied in CO_2 saturated $KHCO_3$ solution for in-situ reduction. Since CuCl is easy to spontaneously transform into cubic Cu_2O in solution with $pH < 4$,[72] copper surface with regular nano cubic structure is reconstructed under reduction potential as shown in **Figure 6** b, and the reconstructed copper particles selectively exposed Cu (100) crystal face with the size of 30-50nm (**Figure 6** c-f). In ECR experiments, this special surface structure promoted the higher utilization of active sites on copper and contributes to more and stronger *CO adsorption, leading to the higher selectivity to C_2H_4 and higher stability to a certain extent. The results also confirmed that although the halogen ions in the catalyst were stripped during the pre-reduction process, they played an important role in shaping the special surface structure. Compared with the cubic polycrystalline copper with pulse potential applied by halogen-free electrolyte, the production of C_2H_4 was enhanced and the output of CH_4 was inhibited.[73] Alexis T. Bell et al.[74] also carried out in-depth research about the influence of halogen ions (F^-, Cl^-, Br^-, I^-) on the structural reconstruction of copper electrodes. The solubilities of CuX species decrease in the order CuF_2> CuCl> CuBr> CuI, which influence the degree of restructuring and the thickness of the Cu_2O layer formed (**Figure 6** g-j). As CuF_2 is the most soluble halide salt of Cu, the CuOx films it forms are the most porous and with the largest surface area, which introduce a large number of defects and grain boundaries and are highly selective active sites for C_2 product formation. For CuCl, CuBr, and CuI, the CuOx layer takes on a cubic morphology and the density of the CuO_x cubes on the surface follows the order Cl > Br > I. The exposure of a higher number of Cu(100) facets contributes to the increased C_2 selectivity. Therefore, the selectivity towards C_2 products of CuX derived OD-Cu catalysts follow the order of CuF_2> CuCl> CuBr> CuI, which are all higher than the flat polycrystalline copper surface. Besides using halide solution as electrolyte, Beatriz Roldan Cuenya et al.[75] recently studied the influence of the presence of carbonate in electrolyte on the morphology and ECR performance of copper electrode prepared by pulse potential circulation method. As shown in **Figure 6** k, different from the cube structure formed by adding halogen ions, in the presence of carbonate, the copper electrode surface forms a small pore structure of about 430 nm, which can achieve 71% faraday efficiency for C_{2+} product and better hydrogen suppression effect. However, in the stability test, the low coordination atoms on the surface were rapidly transformed into nanoparticles, so the structure and activity could not be well maintained in the time scale, which resulted a decreased current density in the stability test.

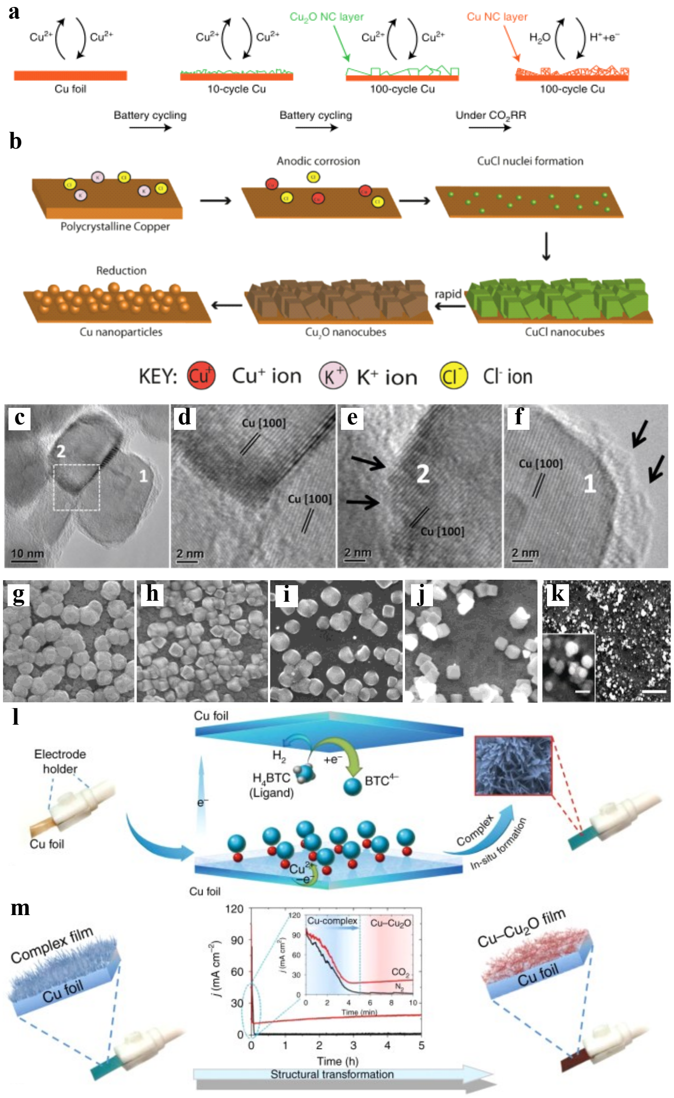

Figure 6. (a) Schematic of the Cu^{2+} ion cycling method for Cu_2O and Cu nanocubes (NCs) on Cu foils.[70] Copyright 2018, Springer Nature. (b) Plausible copper nanoparticle growth mechanism.[74] Copyright 2016, John Wiley and Sons. (c) HRTEM micrographs of Cu meso crystals after 4200s of ECR.[72] Copyright 2015, The Royal Society of Chemistry. (d-f) Local enlarged images of (c) (The dark arrows indicate some of the steps and edges present on Cu meso crystals.).[72] Copyright 2015, The Royal Society of Chemistry. SEM images of polycrystalline Cu cycled in (g) 4 mM KF, (h) 4

mM KCl, (i) 4 mM KBr, (j) 4 mM KI and (k) 0.1M K_2CO_3 electrolyte (The scale bars in the main images and insets are 1 mm and 200 nm).[74,75] Copyright 2016, John Wiley and Sons. Copyright 2019, John Wiley and Sons. (l) Schematic illustration of the process to prepare Cu-Complex film on Cu substrate using H_4BTC.[61] Copyright 2019, Springer Nature. (m) Schematic illustration of in situ electroreduction the process to obtain Cu-Cu_2O/Cu electrode, and reduction current density in 0.1M KCl solution saturated with CO_2 and N_2 at applied potential of -0.4V vs RHE.[61] Copyright 2019, Springer Nature.

Besides the cathodic electrodeposition of Cu_2O and the anodic oxidized $Cu(OH)_2$ or CuX, in situ electrodeposition of Cu-complex was reported to be an novel method to synthesize OD-Cu catalysts. The ordered porous structure with a large surface area and the excellent ability to adsorb CO_2 make metal-organic frameworks (MOFs) as a promising candidate for ECR. Buxing Han' group[61] fabricated 3D dendritic Cu-Cu_2O/Cu electrode via two steps, including in situ electrodeposition of Cu-complex (Cu-BTC) film on Cu substrate and in situ electroreduction of Cu^{II} in Cu-complex film (**Figure 6** l and m). The in situ electrochemical synthesized Cu-Cu_2O/Cu electrode shows low resistance between the catalyst and substrate of the electrode, as well as the charge transfer resistance between the electrolyte and electrode. The 3D dendritic structure provided the longer residue time of the reaction species and more opportunity for the C-C coupling. Therefore, as the applied potential was as low as -0.4 V vs. RHE, the FE of the 3D dendritic Cu-Cu_2O/Cu electrode for C_2 products reached 80% and the current density of 11.5 mA cm^{-2} in ECR.

In summary, the electrochemical methods show promising potential in preparing OD-Cu electrode by different ways, including electrodeposition, electro oxidation or surface reconstruction of Cu-complex. The texture and surface structure properties such as the thickness and crystal facet of Cu_2O layer, the electronic states and the surface oxygen content of OD-Cu could be remarkably regulated by the deposition time, the pulse voltage, the addition of halogen ions and the electroreduction potential, respectively. It is necessary to further explore the relationship between the preparation conditions and the properties of the electrochemical synthesized OD-Cu catalyst, which provides new strategies and opportunities for controlling the selectivity and durability of OD-Cu catalysts for ECR to value-added chemicals.

2.3 Metal modified Cu-based catalyst

Alloying or doping with heteroatoms are the common modification methods used for tuning the catalyst. The addition of foreign atoms not only changes the geometric structure of the parent material, but also regulates the electronic structure and generate synergistic effect between the foreign and parent atoms. Bimetallic sites were expected to regulate the adsorption strength of intermediates, reduce the over potential of the catalyst and promote the reaction path to obtain specific products. As for metal modified Cu-based catalysts, the alloying system such as Cu-Pd,[76] Cu-Au,[77] Cu-Sn[78,79] and other bimetallic systems[80,81,82] have been extensively investigated. Introducing Au into copper catalyst was identified to enhance the selectivity of CO,[83,84] while the addition of In could shift the product selectivity of copper catalyst to formic acid.[85,86,87] The above Cu-based catalysts with C_1 products are not detailly discussed here.

Jaeyoung Lee et al.[88] prepared Ag-incorporated Cu_2O by electrodeposition method and adjusted the elemental arrangement of the catalyst by varying the electrolyte solution. Phase-separated Ag-Cu_2O_{PS} with well-defined Ag/Cu biphasic boundaries (**Figure 7** a-b) was obtained in an NH_3-based electrolyte solution, and a KCN solution was used instead of NH_3 for phase-blended Ag-Cu_2O_{PB} with good dispersion of Ag and Cu (**Figure** 7 c-d). The incorporation of Ag into Cu_2O lead to the suppression of hydrogen (H_2) evolution. The Faradaic efficiency for C_2H_5OH on Ag-Cu_2O_{PB} was much higher than that of Ag-Cu_2O_{PS} and was 3 times higher than that of the Cu_2O without Ag dopant. This work emphasized the importance of Ag-Cu biphasic boundaries that could be adjusted by the doping pattern for the production of C_2H_5OH, in which CO generated on Ag was encouraged to mobile as a residual intermediate on a Cu site. Andrew A. Gewirth et al.[41] prepared nanoporous Cu-Ag alloys by electrodeposition with DAT as inhibitor. The additive DAT in the electrolyte lead to nanowire morphology of the Cu-Ag alloy (**Figure** 7 e). Compared with monometallic copper nanowire catalyst, Cu-Ag alloy catalyst showed larger active area and higher reduction current density. Although there was no significant change in the amount of hydrogen generated, the faradic efficiency of C_{2+} product was improved, which reaches nearly 60 and 25%, respectively for C_2H_4 and C_2H_5OH. The small amount of Ag (6%) that incorporated in the alloy stabilized the Cu_2O overlayer and the Ag active sites provided optimal availability of the CO intermediate for the dimerization of C_{2+}. Furthermore, Cu-Sn alloy catalyst was also obtained by DAT inhibitor assisted electrodeposition.[89] Different from Cu-Ag alloys, Cu-Sn alloy film showed a more compact structure and presents a unique spherical particle rather than a nanowire shape, due to the higher nucleation density (**Figure** 7 f). In situ surface enhanced Raman spectroscopy (SERS) showed that Sn can replace Cu_2O on Cu surface and form more active Cu adsorption sites. With the increased adsorption density of *CO on the electrode surface that facilitates C-C coupling reactions, CuSn-DAT has an enhanced FE for CO and C_2H_4 production compared with Cu-DAT and CuAg-DAT.

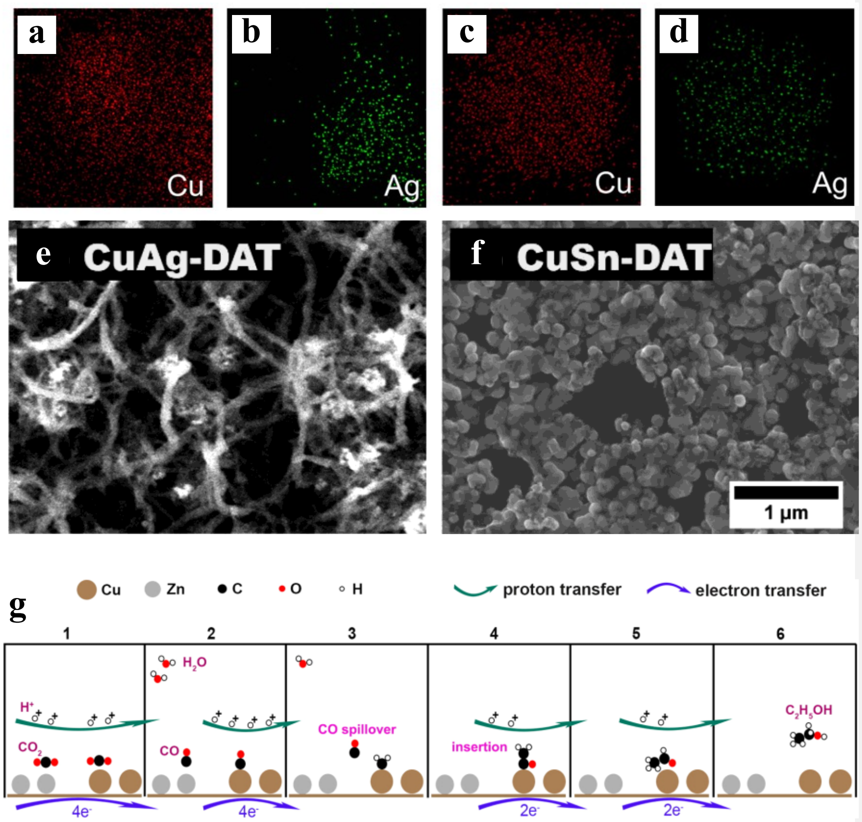

Figure 7. EDX mapping analysis of (a,b) Ag-Cu_2O_{PS} and (c,d) Ag-Cu_2O_{PB} identifying (a,c) Cu and (b,d) Ag.[88] Copyright 2017, American Chemical Society. SEM images obtained from (e) CuAg-DAT, and (f) CuSn-DAT samples electrodeposited on a GDL.[89] Copyright 2020, American Chemical Society. (g) Proposed mechanism for the electroreduction of CO_2 to ethanol on Cu_xZn catalysts.[90] Copyright 2016 American Chemical Society.

Zn was identified to be an effective dopant for Cu-based catalyst to enhance the efficiency and selectivity of ECR toward ethanol.[91,92] Boon Siang Yeo et al.[90] prepared a series of Cu-Zn alloy catalysts by electrodeposition with different amounts of Zn. In the ECR experiments, the ratio of the Faradaic efficiencies between ethanol and ethylene were tuned by a factor of up to ~12.5. Cu_4Zn showed maximized ethanol formation with the Faradaic efficiency and current density of 29.1% and -8.2 mA cm^{-2} at -1.05 V vs RHE. Based on the experiments, they proposed a mechanism of CO_2 reduction to ethanol over Cu-Zn Catalyst (**Figure** 7 g): Firstly, proton electron pairs are obtained respectively on the surface of copper and zinc to form *CO, and the *CO on copper is further reduced to $*CH_2$, while the *CO on the surface of Zn is desorbed and migrated near $*CH_2$ to form $*COCH_2$. Then the proton electron pair reduce $*COCH_2$ to CH_3CHO (acetaldehyde), and finally reduced to CH_3CH_2OH (ethanol). Moreover, the oxides (Cu_2O and ZnO) were rapidly reduced as proved by Raman spectroscopy and no vibration band of *CO was found before the oxides were reduced, which confirmed that the metallic copper and zinc rather the oxides were the key active site of the reaction.

The synergistic effect of Pd and Cu in ECR was also reported recently. Palladium is a good active hydrogen carrier in electrochemical reaction. By forming a co-active site with copper, palladium can promote the hydrogenation of C = C bond and the coupling of C-C, which is an effective way to improve the selectivity and efficiency of alkane.[93] On the basis of this idea, Andrew A. Gewirth et al. [94] designed Cu_2O-derived $Cu/PdCl_2$ catalyst with $PdCl_2$ electrodeposited on cuprous oxide film. The catalyst shows a cubic structure with the size of 100 nm, and $PdCl_2$ nanoparticles were uniformly loaded on the surface of the catalyst (**Figure 8** a). Compared with Pd^0 islands, $PdCl_x$ islands more favorably adsorbed C_2H_4 and tended to be reduced to Pd^0 as C_2H_4

is hydrogenated to ethane. Besides, this work also proved that the hydrogenation of C_2H_4 intermediate, rather than the dimerization of two adsorbed $*CH_3$, was the key reaction path to form C_2H_6 in ECR (**Figure 8** a). Peter Broekmann's group[94] implemented electro co-deposition of Cu and Pd in acidic electrolyte based on dynamic hydrogen bubble template method, which could not only prepare uniform Pd rich alloy electrode, but also kept porous structure. *CO and *H forms preferentially on the Pd-rich PdCu domains and the stabilization of the chemisorbed *CO on the catalyst surface and the efficient *H-transfer for the hydrogenation of the C-C coupled intermediates further direct the ECR towards multicarbon alcohol formation, which led the selectivity of the C_3 alcohol over the C_2 alcohol by a factor of two to 13.7%.

In addition, rare earth metal hydroxides acting as cocatalysts could adjust the intermediates that adsorbed on the surface of copper, so as to enhance the selectivity for alcohols in ECR. According to the calculation of quantum mechanics,[96,97] the protons and hydroxyls of the ECR products partly originates from the direct hydrolysis of water. Also, isotope tracking technique indicated that 60-70% of the ethanol contained O that originates from the solvent water rather than CO. The cooperative hydrolysis of *C-CH and H_2O produces *CH-CH(OH) intermediates, and then obtained ethanol. Therefore, the key factor to improve the ethanol selectivity of ECR reaction is to promote hydrolysis by adjusting the active sites. Modifying Cu with metallic oxides or hydroxides were found to effectively promote the hydrolysis process and simultaneously inhibit hydrogen production from HER.[98] For example, **Figure 8** b show that water dissociation is more favorable on the oxide/hydroxide-doped-Cu surface (by 0.48 eV and 0.39 eV for Ce and Mn oxide, respectively) in comparison with that on the pure Cu. Edward H. Sargent et al.[99] used electrodeposition method to cover a layer of cerium hydroxide on the Cu/PTFE electrode to construct the $Ce(OH)_x$/Cu/PTFE catalyst, which showed a homogeneous distribution of Cu and Ce throughout a single fiber (**Figure 8** c). The branching of ethylene vs. ethanol depends on *HCCOH. If *HCCOH first remove OH and form *CCH, then further hydrogenate to generate ethylene. Conversely, *HCOOH directly hydrogenated into *HCCHOH to produce ethanol. For $Ce(OH)_x$/Cu/PTFE catalyst, the cerium hydroxide enhance the coverage of H_{ad} that attacks the *HCCOH forming *HCCHOH, which consequently raises the ethanol selectivity in ECR.

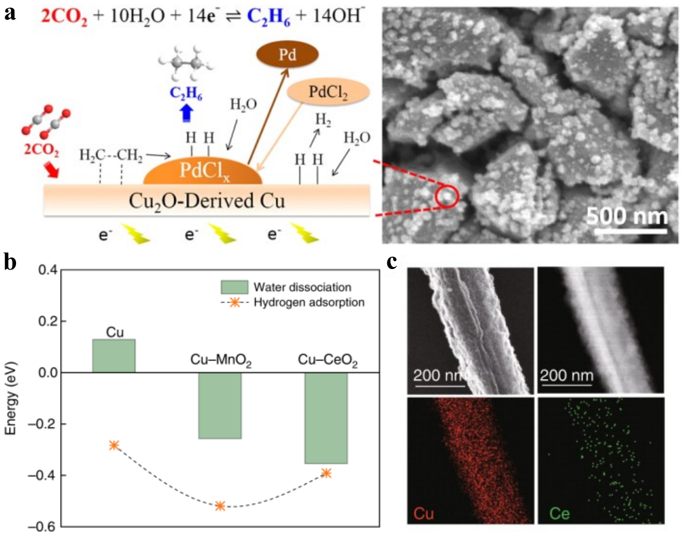

Figure 8. (a) The right area is SEM images of Cu_2O electrode after CO_2 reduction with $PdCl_2$ added to the electrolyte and the left area is schematic illustration of the electrochemical reduction of CO_2 to C_2H_6 via an adsorbed C_2H_4 intermediate on Cu_2O electrode with $PdCl_x$ islands.[93] Copyright 2015, American Chemical Society. (b) Calculated water dissociation reaction energies and hydrogen adsorption energies on

various surfaces.[99] Copyright 2020, Springer Nature. (c) STEM image and corresponding EDX mapping for Cu and Ce on Ce(OH)x/Cu/PTFE.[99] Copyright 2020, Springer Nature.

In summary, the co-electrodeposition of Cu_2O or Cu with adding M^{n+} ions in the electrolyte is widely used in synthesizing the bimetallic Cu-M catalysts. The co-active site with copper in Cu-M catalyst could be regulated via varying the heteroatoms and the preparation conditions (such as deposition potential, the concentration of M^{n+} and the addition of additives and halogen elements). The adsorption energies of the intermediates were greatly influenced by the dispersion and electronic states of the active sites in Cu-M catalyst, in which Cu-M (M= Ag, Zn, Sn, Pd and Cerium hydroxide) catalysts were proved to be active for the production of C_{2+} in ECR.

3. Other methods combined with electrochemical synthesis for Cu-based catalysts in ECR with C_{2+} products

Table 2 summarized the representative works in recent years related to Cu-based catalysts in ECR with C_{2+} products. The performance of each catalyst in ECR was introduced, including the highest C_2 product and Faraday efficiency, as well as maximum stability verified by experiments. The design strategy and conclusive remarks are also summarized. As shown in Table 2, Cu-catalyst synthesized by electrochemical method show quite outstanding performance in ECR, both with the rather high efficiency and stability. However, due to the specific electrode potential of different elements, the single electrochemical method is suitable for preparing the catalyst with simple component, which limits the application in synthesizing multiple-composite samples with complex structure. As listed in Table 2, the combination utilization of electrochemical methods and the ordinary preparation methods (such as wet chemical methods, thermal and plasma treatment) become a popular strategy for developing Cu-based catalysts with high C_{2+} efficiency, which contributes to break through the limitations of electrochemical method and broadens its application in preparing Cu-based catalysts for C_{2+} products.

Table 2. Kinds of representative Cu-based catalysts used to produce C_{2+} products in ECR in recent years

Catalyst	Preparation method	Main C_2 product, FE	Environment (vs.RHE)	Stability	Conclusive remarks	Ref.
Cu(B)	Precipitation	C_2H_4, 52.5%	At-1.1V, in 0.1M KCl	40h	Adjust Fermi level, reduce coupling energy	[100]
Cu NDs	Precipitation	C_2H_4, 22.3%	At-1.2V, in 0.1M $KHCO_3$	7h	High ECSA, efficient electron/mass transfer	[50]
Multi-hollow Cu2O	Precipitation	C_2H_4, 38.0±1.4%	At-0.61V, in 2M KOH	3h	Increase and stabilize CO adsorption	[101]
Cu_2S-Cu-V	Solvothermal	C_2H_6O, 24.7±2%	At-0.62V, in 1M KOH	16h	Stabilize CO adsorption and suppress C2H4 path	[102]
44nm Cu nanocube	Wet chemical	C_2H_4, 41.0%	At-1.1V, in 0.1M $KHCO_3$	1h	Balance between plane and edge sites for reaction	[37]
Cu NW-NH_2	Wet chemical	C_2H_6, 24.0%	At-1.9V, in 0.1M $KHCO_3$	20h	Reduce energy barrier for CHO*	[44]
4H Cu	Wet chemical	C_2H_4, 44.9%	At-1.1V, in 0.1M $KHCO_3$	9h	Lower Gibbs energy of COOH	[103]
Cu-on-Cu_3N	Wet chemical	C_2H_4, 39.0±2%	At-0.65V, in 0.1M $KHCO_3$	15h	Protection of active species	[104]
ERD Cu	Wet chemical, electrochemical	C_2H_4, 36.0%	At-1.0V, in 0.1M $KHCO_3$	1h	Sharper structures improve current densities and local pH	[105]
Reconstructed Cu	Wet chemical, electrochemical	C_2H_4, 56.0%	At-1.4V, in 0.1M $KHCO_3$	-	Increase surface active sites	[106]
F-Cu	Solvothermal, electrochemical	C_2H_4, 65.2%	At-0.89V, in 0.75M KOH	40h	Accelerate H_2O dissociation and electron transfer	[107]
Cu_2O thin films	Solvothermal, electrochemical	C_2H_4, 31.0%	At-0.98V, in 0.1M $KHCO_3$	70min	Efficient CO adsorption with small nanoparticle	[108]
HPR-LDH	Precipitation, electrochemical	C_2H_4, 36.3%	At-1.1V, in 0.1M $KHCO_3$	20h	High ECSA, efficient charge transfer	[109]
CuO_x-Vo	Thermal treatment, electrochemical	C_2H_4, 63.0%	At-1.4V, in 0.1M $KHCO_3$	13h	Facilitate the adsorption of *CO, *COH intermediates	[38]
3D porous CuO	Thermal treatment, electrochemical	C_2H_4, 35.8%	At-1.3V, in 0.1M $KHCO_3$	2h	Rapid gas transport	[109]
Cu np120	Thermal treatment, electrochemical	C_2H_4, 35.0%	At-1.3V, in 0.1M $KHCO_3$	8h	High ECSA, expose low-coordinated steps and edges	[111]
Plasma-activated Cu	Plasma treatment, electrochemical	C_2H_4, ~45%	At-1.0V, in 0.1M $KHCO_3$	5h	Regeneration of active species	[112]
30 /70 Cu Mesopore	Sputtering, electrochemical	C_2H_6, 46.0%	At-1.3V, in 0.1M $KHCO_3$	4h	Prolongation of reaction time	[113]
Cu_3N-D Cu NWs	CVD, electrochemical	C_2H_4, 66.0%	At-1.0V, in 0.1M $KHCO_3$	28h	Abundant grain boundaries	[114]
CSNP	Electrospray	C_2H_4, 48.7%	At-1.0V, in 0.1M $KHCO_3$	20h	Suppress H_2 evolution	[115]
Cu mesocrystal	Electrochemical	C_2H_4, 27.2%	At-0.99V, in 0.1M $KHCO_3$	6h	Increase and stabilize CO adsorption	[72]
100-cycle Cu	Electrochemical	C_2H_4, 32.0%	At-0.96V, in 0.25M $KHCO_3$	2h	Expose Cu (100)	[70]
Cu_CO_3	Electrochemical	C_2H_4, ~47%	At-0.95V, in 0.1M $KHCO_3$	22h	High ECSA, low-coordinated sites	[75]
CuDAT-wire	Electrochemical	C_2H_4, ~40%	At-0.5V, in 1M $KHCO_3$	8h	low-coordinated steps and edges	[56]
GB-Cu	Electrochemical	C_2H_4, ~38%	At-1.2V, in 1M KOH	3h	Increase and stabilize CO adsorption	[39]
Porous OD-Cu	Electrochemical	C_2H_6, 37.0%	At-0.7V, in 0.5M $NaHCO_3$	1h	Trap gaseous intermediates	[57]
Cu4Zn	Electrochemical	C_2H_6O, 29.1%	At-1.05V, in 0.1M $KHCO_3$	10h	Increase the population of free CO	[90]
HPR-Cu	Electrochemical	C_2H_4, 38.1%	At-1.08V, in 0.1M $KHCO_3$	40h	Abundant oxygen state of the Cu	[60]
Prism-shaped Cu	Electrochemical	C_2H_4, 27.8%	At-1.1V, in 0.1M $KHCO_3$	12h	Modification of the local pH	[116]
Ag-Cu_2O_{PB}	Electrochemical	C_2H_6O, 34.1%	At-1.2V, in 0.1M $KHCO_3$	3h	Ag-Cu biphasic boundaries effect	[88]
CuAg-wire	Electrochemical	C_2H_4, ~60%	At-0.7V, in 1M KOH	-	Inhibit reduction of active species	[41]
Cu-$PdCl_x$	Electrochemical	C_2H_6, 30.1%	At-1.0V, in 0.1M $KHCO_3$	1.5h	Provide hydrogenation sites	[94]
$Ce(OH)_x$/Cu/PTFE	Electrochemical	C_2H_6O, 43.0%	At-0.7V, in 1M KOH	6h	Promote the dissociation of water	[99]

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3.1 Wet chemical method

Wet chemical synthesis is the most commonly used methods for the metal oxide nanoparticles, including precipitation, sol-gel, solvothermal, reverse micelle and flow synthesis. The combination utilization of electrochemical methods and wet chemical synthesis for Cu-based catalysts in ECR is mainly related to two paths: Electrodeposition → wet chemical oxidation → electroreduction or Wet chemical synthesis → in-situ electrochemical reconstruction. [107]

David Sinton et al.[63] oxidized electrodeposited copper electrode by using chemical oxidation with H_2O_2 to obtain porous OD-Cu films with high roughness, and the formed oxide layer was reduced to bare Cu at ECR process, giving an oxide-derived Cu reaction surface. The OD-Cu electrode maintains the porosity of the electrodeposited Cu based on the hydrogen bubble dynamic template method (**Figure 9** a-d). The ethylene efficiency of the prepared samples reached more than 30% with the current density of higher than 35mA cm^{-2}. Even if the Cu^+ on the surface are rapidly reduced, the Cu^+ species introduced on the subsurface can also enhance the coupling to a certain extent. Edward H. Sargent et al.[105] reported a series of the electro-redeposited copper (ERD Cu) with in situ reconstitution of the sol-gel $Cu_2(OH)_3Cl$ precursors by applying cathodic current. As the reduction potential increasing from -0.7V to -1.4V (vs. RHE), the content of Cu_2O in the samples gradually decreased, and the nanostructures changed from needle to dendrite. It showed that this electrochemical in-situ reduction method promotes the formation of sharp nanostructure with high curvature surface to stabilize Cu^+, which promotes the C-C coupling and thus the current density of ethylene (160 mA cm^{-2} at - 1.0 V vs. RHE). Similarly, Edward H. Sargent[106] used a wet chemical process, providing uniformity of the electrode morphology and abundant active sites on an initial Cu (I) chloride layer which is subsequently converted to a Cu (I) oxide surface. The reconstructed Cu surface was achieved by electrochemically reducing the formed Cu(I) oxide layer as shown in schematic illustration (**Figure 9** f). The reconstruction process may change the Cu surface from a stable facet such as (111) to a more C_2 selective facet such as (100), leading to a higher selectivity for C_2 products. Yuhan Sun et al.[50] prepared two-dimensional copper phosphate nanosheets by wet chemical method, and obtained three-dimensional nano dendritic polycrystalline copper catalyst after in-situ electrochemical reconstruction by ECR (**Figure 9** e). At a lower initial potential, the yields of ethylene and C_3 (n-PrOH and propionaldehyde) on Cu dendrites were 70-120% and 60-220% higher than those of Cu nanoparticles, respectively.

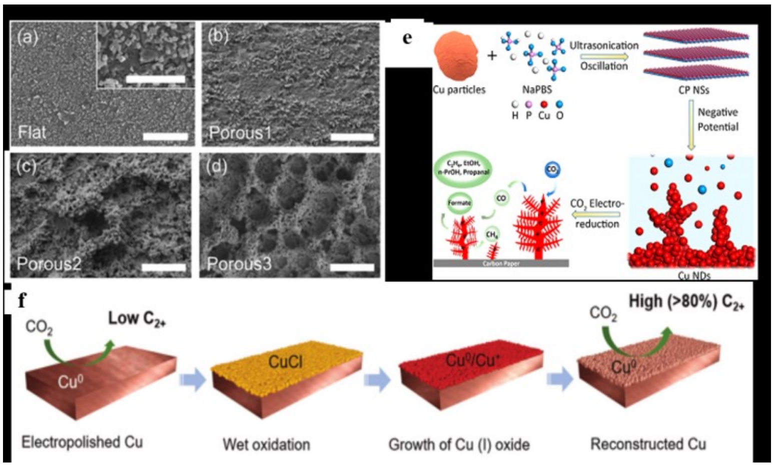

Figure 9. (a-d) SEM Images of four different electrodeposited Cu electrodes that have undergone a wet-chemical oxidation process.[63] Copyright 2017, Royal Society of Chemistry. (e) Schematic illustration of the synthesis of CP NDs and the electrogrowth process of the Cu dendrites, starting from the Cu particles as raw materials.[50] Copyright 2020, American Chemical Society. (f) Schematic illustration of the surface reconstruction process.[106] Copyright 2018, John Wiley and Sons

3.2 Plasma treatment method

Plasma treatment could rapidly change the chemical state and produce highly active defect site on the materials' surface at room temperature, which showed great potential in tailoring the surface structure and compositions of catalysts. Beatriz Roldan Cuenya's group[49] combined electrochemical method and plasma treatment to prepare OD-Cu catalysts. The catalysts with porous oxide surface layer synthesized by electrochemical cycling of Cu foil in KCl solution followed by oxygen plasma treatment of Cu nano cube catalysts.[112] This study showed that the plasma treatment could systematically adjust the shape, ion content and the stability of the copper catalyst under electrochemical conditions. The presence of oxygen in the surface and subsurface regions of the catalyst was pivotal to achieve high activity and hydrocarbon/alcohol selectivity, even more important than the existence of Cu (100) surface, which made the FE of C_{2+} products increase to 73%.[112] The active substances in plasma, including electrons, ions, free radicals and photons, form a large number of low coordination active sites on the catalyst surface and enhance the catalytic performance of copper catalyst in ECR.[117] Furthermore, they developed oxidized copper catalysts displaying lower overpotentials and 60% Faradic efficiency towards ethylene through a facile and tunable plasma treatments [49]. In the O_2 plasma treatment process, the wires merged, forming a highly roughened surface and became highly porous. Then the sample reduced by H_2 plasma and formed Cu, CuO, Cu_2O multilayer structure, based on EDS elemental maps (**Figure 10** a). In general, longer and higher power O_2 plasma treatment increases the roughness factor and the efficiency was limited by mass transfer effect in the research (**Figure 10** b). The multilayer structure can be stable in the ECR process and maintain high catalytic activity due to the continuous Cu^+ supply from the subsurface layer.

3.3 Other methods

The combined utilization of different methods integrates the advantages of the in-situ construction of the electrochemical methods for Cu-based electrode and the flexibility of the other method, which contributes to develop the ideal catalyst with high ECR activity and stability on the electrode. So far, various novel preparation methods were also proposed and combined with the electrochemical methods, which significantly broadens the application of electrochemical methods in synthesizing different types of electrocatalysts.

Xin Wang et al.[111] developed a kind of dealloying method to prepare porous copper catalyst. Firstly, a layer of zinc film was grown on the surface of copper foil by electrodeposition method. Dense copper zinc alloy was formed on the surface of copper foil due to the easy diffusion of zinc atom into copper lattice, and then zinc in alloy was stripped by alkaline solution to obtain porous copper catalyst (**Figure 10** c). With increasing the degree of the dealloying treatment, the crystalline orientation on the surface was altered to Cu (100) and the large amount of exposed crystalline steps and edges were formed, which inhibited the formation of methane and promoted the reaction tendency to produce ethylene.

Ki Tae Nam et al.[113] reported a novel strategy to precisely control the pore structure of copper electrode in order to make clear of the relationship between the pore size and the reaction path of ECR. They prepared a substrate with uniform wavy surface by anodic oxidation of alumina under applied voltage and deposited copper on the wave crest of the substrate to make the surface aperture and the hole depth uniform (**Figure 10** d-g). The pore size and depth of the catalyst are accurately controlled by changing the deposition time. High-depth pore in the catalyst is in favor of increasing the production of ethane, and the low-depth pore is conducive to produce ethylene, while large pore size in the catalyst is adverse to the formation of C_{2+} products (**Figure 10** h).

Liu [114] and Sargent [104] developed the nitrogen atom modified Cu catalyst for ECR via the electrochemical methods and other procedures. Xijun Liu et al.[114] utilized chemical vapor deposition with the nitridation process under NH_3 flow on $Cu(OH)_2$ nanowires to synthesized Cu_3N NWs, and the catalyst (Cu_3N-derived Cu) was obtained by an in-situ electroreduction method. Cu_3N-derived Cu NWs with a high density of grain boundaries exhibited enhanced ECR performance for C_2 products and high stability for more than 28 hours. Edward H. Sargent et al.[104] designed a novel catalyst composed of Cu deposited on Cu_3N with the suppressed reduction of Cu^+, achieving higher selectivity for C_{2+} formation. As shown in **Figure 10** i and j, after the replacement of the long-chain octadecylamine ligands with short-chain azide, the modified Cu_3N crystals went through facile electroreduction process to produce the active Cu-on-Cu_3N catalyst.

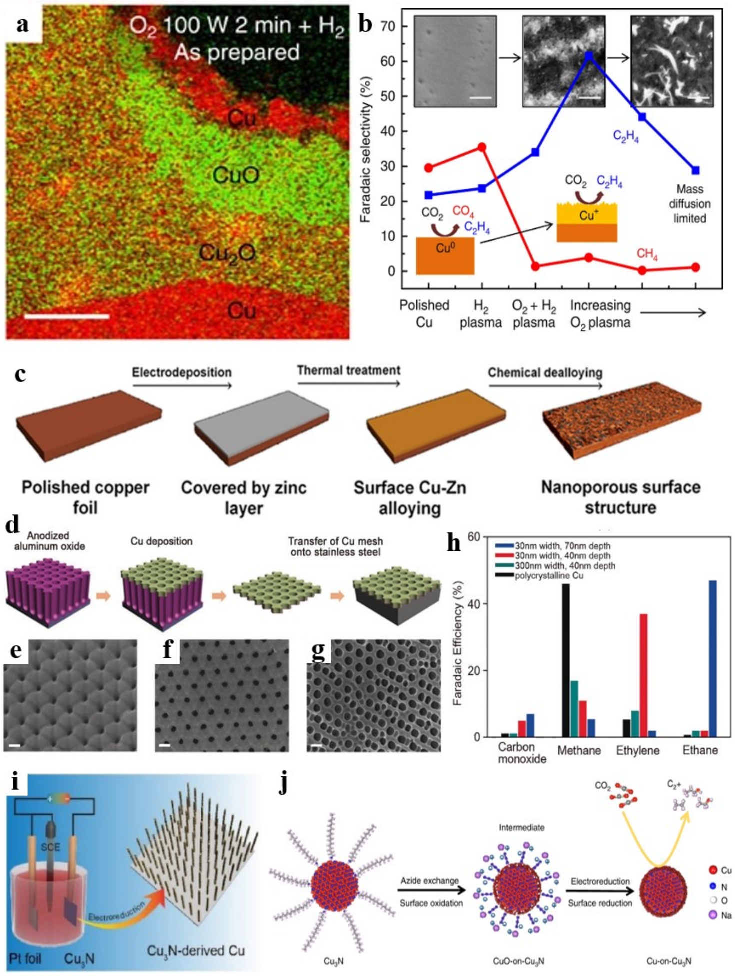

Figure 10. (a) The EDS elemental maps of Cu foils treated with O_2 plasma 100 W 2 min + H_2 plasma.[49] Copyright 2016, Springer Nature (b) Summary of hydrocarbon selectivity of plasma-treated Cu foils.[49] Copyright 2016, Springer Nature (d) Scheme for preparing Cu mesopore electrodes. SEM images of mesopores with e) 30 nm width /40 nm depth, f) 30 nm width /70 nm depth, and g) 300 nm width /40 nm depth. Scale bar=60 nm for (e, f) and scale bar=300 nm for (g). (h) Chemical selectivities for (e-g) at −1.7 V vs. NHE.[113] Copyright 2016, John Wiley and Sons. (i) Schematic illustration of the synthesis of Cu_3N-derived Cu NWs.[114] Copyright 2019, John Wiley and Sons. (j) Schematic of preparing the Cu-on-Cu_3N catalyst.[104] Copyright 2018, Springer Nature.

4. Summary and outlook

In this review, we reviewed the progress of various electrochemical methods in developing Cu-based catalysts for electrochemical reduction of CO_2 to C_{2+} products. Electrochemical method is becoming a widely used technique for electrode synthesis in electrocatalysis. However, there still have huge development potential and cultivation space for the electrochemical synthesized Cu-based catalyst for ECR in aqueous solutions. Based on the current research progress and the blank space in this research field, it is recommended that further research be carried out from the following five aspects:

1) The metalloid dopants (N, B, P, S) were reported to adjust the density of surface vacancies of Cu catalyst and form stable surface defects, which notably affects the CO binding and C_{2+} production.[102,118,119] The electrosynthesis of metalloid-doped Cu catalyst was rarely reported except for the above mentioned CuN_3 derived Cu electrode. Recently, phosphorus-doped Cu (Cu-P) prepared by the electrodeposition method was explored as the C_{2+} products promoters for ECR, due to the more facile conversion of linear bounded *CO intermediate.[46] Thus, further researches are encouraged to focus on developing the electrochemical synthesis methods for different metalloid-doped Cu catalyst and exploring their application potential in ECR.

2) Cu_2O sites could be in situ formed from Cu-based MOF via a facile electroreduction process due to the orderly distributed Cu-O_4 nodes. Considering the synergistic effect of the metal modified Cu catalyst, the controllable electrochemical deposition of the bimetallic Cu/M-MOFs is a promising strategy for further tailoring the MOF-derived Cu catalysts for ECR. Moreover, the electrochemical synthesis of two-dimensional conductive Cu-MOF is also meaningful to be developed due to that the electron conduction channel of two-dimensional framework materials play important role in the electrochemical reaction process.

3) Surface modification is one important strategy to tune the selectivity. For example, Cu nanowire electrodes modified by amino acids and their derivatives stabilized the and facilitated C_{2+} hydrocarbon formation, owning to the strong interaction between the $-NH_2$ groups and intermediate CHO*.[44] Thus, in situ modification of Cu electrodeposit surface with specific functional group is prone to be a feasible and efficient strategy to further enhance the C_{2+} products in ECR.

4) For Cu-based catalyst in ECR, the Cu electrode/electrolyte interface is a very complex reaction involving multiple proton and electron transfers. The electrocatalyst generally undergoes structure reconstruction under the applied potential. Applying advanced operando techniques (optical, X-ray and electron-based techniques) and theoretical calculation methods are highly demanded to characterize the morphology, crystal facet and electronic states of the electrochemical synthesized Cu catalyst under real operating CO2RR process, which would shed light on understanding the reaction mechanism and provide further guidance for the catalyst development.

5) Because of its low synthesis cost and easy scalability, electrochemical synthesis allows the large-scale production of Cu coated electrode, which is particularly attractive for the production of catalyst electrodes for use in electrochemical reduction of CO_2. Therefore, Large-scale experiment related to the scalable Cu-based catalyst needs be performed by choosing appropriate electrochemical conditions and accurately adjusting the parameters of the electrochemical method, for the industrialization of CO_2 electrocatalytic reduction.

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