


Review

A Scientometric Review of CO₂ Electroreduction Research from 2005 to 2022

Hongfei Wang¹, Zhipeng Yu¹, Jie Zhou¹, Chengming Li¹, Ananthanarasimhan Jayanarasimhan²,
Xiqiang Zhao^{1,*} and Hao Zhang^{3,*} 

¹ National Engineering Laboratory for Reducing Emissions from Coal Combustion, Engineering Research Center of Environmental Thermal Technology of Ministry of Education, Shandong Key Laboratory of Energy Carbon Reduction and Resource Utilization, School of Energy and Power Engineering, Shandong University, Jinan 250061, China

² Centre for Sustainable Technologies, Indian Institute of Science, Bengaluru 560012, India

³ State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

* Correspondence: zxq@sdu.edu.cn (X.Z.); zhang_hao@zju.edu.cn (H.Z.)

Abstract: Electrocatalytic CO₂ reduction is regarded as a green and promising technology because it can convert carbon dioxide into value-added fuel or chemicals in a flexible and sustainable way. This research aimed to comprehensively analyze the research hotspots and trends in the field of CO₂ electroreduction from 2005 to 2022 using bibliometric methods based on the core database of Web of Science. The results showed that 4546 papers on CO₂ electroreduction were retrieved from 2005 to 2022, with a clear increasing trend. The research direction was diversified, involving multiple disciplines, and it is a comprehensive research field. *ACS Catalysis* is the journal with the largest number of articles. China is the country with the largest number of documents and has made significant contributions to the development and progress of this field. Copper-based catalysts are still the research focus in recent years. It is of great practical significance to develop copper-based catalysts with high efficiency, low cost, high stability, and high selectivity for the preparation of C₁ products.

Keywords: CO₂ electroreduction; scientometric review; research focus; copper based catalysts; selectivity; C₁



Citation: Wang, H.; Yu, Z.; Zhou, J.; Li, C.; Jayanarasimhan, A.; Zhao, X.; Zhang, H. A Scientometric Review of CO₂ Electroreduction Research from 2005 to 2022. *Energies* **2023**, *16*, 616. <https://doi.org/10.3390/en16020616>

Academic Editor: Adriano Sacco

Received: 6 December 2022

Revised: 29 December 2022

Accepted: 3 January 2023

Published: 4 January 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Demand and supply mismatch in the energy sector and global warming are two major challenges faced by the world. Most of the energy consumed by human society is derived from non-renewable fossil fuels [1,2], and carbon dioxide generated by the continuous burning of fossil fuels is the main cause of global warming [3,4], which is a threat to human survival and development that needs to be addressed immediately. Capturing carbon dioxide emissions (carbon capture) is suitable to alleviate the environmental problems faster than to minimize the emissions (minimizing the use of fossil fuels) [5]. One way using of carbon capture is converting carbon dioxide into value-added fuels or chemicals; converting CO₂ not only captures excessive CO₂ emissions, but it also addresses the energy crisis to a certain extent [6]. CO₂ conversion into value-added chemicals/fuels can be achieved by various methods such as electrocatalysis [7,8], photocatalysis [9], photoelectric catalysis [10,11], and biocatalysis [12,13]. Among these, electrocatalysis has attracted extensive attention due to its unique advantages [14–16], including (1) mild reaction conditions (ambient temperature and pressure); (2) flexible products adjusted by redox potential, reaction temperature, electrolytes, and other parameters; (3) low yields of by-products by optimizing the electrocatalyst; (4) utilization of intermittent renewable energy sources (such as solar energy, wind energy, etc.), which is clean and energy saving.

A wide range of valuable products can be achieved through the transfer of two, four, six, eight, or twelve electrons in the electrocatalytic CO₂ reduction reaction (eCO₂RR) process [4]. The most common products are carbon monoxide (CO), methane (CH₄), formic acid (HCOOH), methanol (CH₃OH), ethylene (C₂H₄), ethanol (C₂H₅OH), etc. [17–21]. Nevertheless, the carbon dioxide molecule is highly chemically stable due to its highly oxidized nature. In addition, the reduction process of CO₂ is challenged by the competitive hydrogen evolution reaction (HER) [22], it poses high thermodynamic and kinetic barriers [23], and it has limited selectivity towards specific products [24]. Significant efforts have been devoted to solve these problems, making great contributions to the development and progress of this process.

Comprehensive review articles [25] are available in the literature, indicating the importance of this research. Nevertheless, no review from the perspective of bibliometrics has been reported. Bibliometrics can identify the annual development trend of the analyzed field and the most influential contributors and journals, and it can analyze research hotspots and development trends in this field. This information can help readers to better understand the current situation and determine the future research direction from the results of bibliometric analysis and is therefore urgently needed.

In this work, the research status of eCO₂RR from 2005 to 2022 was analyzed and discussed based on the core database of Web of Science, involving 4546 articles in terms of literature type, annual trend, discipline category, main institutions, and main researchers. The research focus and future development trend are also discussed, providing valuable insights for future research in this field.

2. Methods

2.1. Data Collection and Processing

The data, i.e., information, on the articles published in the research area of this work, which is eCO₂RR, were obtained from the core database of Web of Science. Web of Science core database is a large comprehensive, multidisciplinary, core journal citation index database, which contains the most relevant, important, and influential academic journals and international conferences in its records. On 28 December 2022, the relevant literature in the field of CO₂ electroreduction from 2005 to 2022 was searched in the Web of Science core database. In order to obtain complete and effective data, this paper used the following search conditions for literature retrieval.

TOPIC: “CO₂ electroreduction”, OR TOPIC: “Electroreduction of carbon dioxide”, OR TOPIC: “CO₂ electrochemical reduction”, OR TOPIC: “Electrochemical reduction of carbon dioxide”, OR TOPIC: “Electrocatalytic reduction of CO₂”, OR TOPIC: “Electrocatalytic reduction of carbon dioxide”, OR TOPIC: “CO₂RR”, OR TOPIC: “eCO₂RR”.

Timespan: 2005 to 2022.

The articles that resulted from the search were considered relevant for the work only if the search term appeared in the title, abstract, or keywords of the publication. The geographical distribution of the document was obtained from the affiliation details provided by the authors in the article. The articles or papers were grouped into single country publications (SP) and international cooperative publications (CP).

Seven types of information were retrieved for further analysis, as follows:

- i. Types of literature and publishing languages;
- ii. Annual trend of published literature during 2005–2022;
- iii. Subject categories and journals;
- iv. Author information;
- v. Geographical distribution;
- vi. Cited frequency;
- vii. Research hotspots and future trends.

2.2. Data Analysis

This paper analyzed the annual publication volume distribution, subject category and journal distribution, author publication volume distribution, geographical distribution, topic category distribution, keywords, and research hotspots through the retrieval result analysis of the core database of Web of Science and the visualization function of VOS viewer to understand the future development trend more clearly and to provide reference for research in the field of eCO₂RR.

3. Results and Discussion

3.1. Types of Literature and Publishing Languages

The literature retrieved from the Web of Science core database were divided into 12 categories. The literature was mainly in the form of research papers, accounting for 83.7% of the total number of published papers, followed by review papers, accounting for 11.8% of the total number of published papers. The third is online publication (3.7%), then conference abstracts (2.3%), and conference proceeding papers (1.3%). Other types of literature were below 1%. The study showed that eCO₂RR is mainly disseminated through scientific papers, both as articles and reviews.

In terms of the language of publication, five languages were used, and 99.1% of the publications were in English, followed by Chinese, accounting for 0.9% of the total publications. The number of articles in other languages was less than 0.1%, and only a few articles have been published.

3.2. Annual Trend of Published Literature during 2005–2022

From 2005 to 2022, 4546 articles were published in the core database of Web of Science. Figure 1 shows the number of published literature per year. It can be seen from the figure that the number of publications increased exponentially from 2005 to 2022, and the number of literature in this field changed only slightly from 2005 to 2016. Nevertheless, since 2016, publications on eCO₂RR increased rapidly. From 2016 to 2018, the average annual growth rate was 48.4%. Especially since 2018, the number of publications increased significantly. The average annual growth rate from 2018 to 2021 increased to 50.4%, and by 2021, the number of publications reached 1108, which fully shows that the research on eCO₂RR has attracted more and more attention.

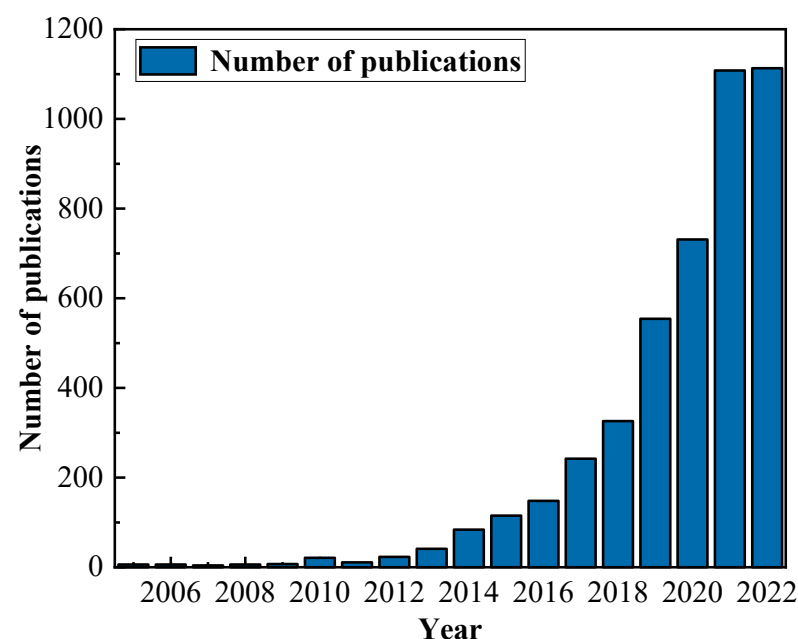


Figure 1. Publication output performance during 2005–2022 (as of December 2022).

3.3. Subject Categories and Journals

According to statistics, related publications in the field of eCO₂RR can be divided into 55 subject categories. As shown in Table 1, most of the published papers belonged to Chemistry Physical, accounting for 42.6% of the total number of published papers. In addition, Chemistry Multidisciplinary accounted for 35.8% of the total number. Following these, there were Material Science Multidisciplinary (33.1%), Nanoscience Nanotechnology (18.6%), Energy Fuels (15.2%), Engineering Chemical (14.0%), Physics Applied (12.0%), Electrochemistry (10.9%), Physics Condensed Matter (7.6%), and Green Sustainable Science Technology (5.0%). This shows that most of the articles involve multiple disciplines such as chemistry, materials, energy, and science, which is a comprehensive research field.

Table 1. Top ten subject categories.

Subject Categories	Publications	Percentage (%)
Chemistry Physical	1938	42.6%
Chemistry Multidisciplinary	1627	35.8%
Materials Science Multidisciplinary	1505	33.1%
Nanoscience Nanotechnology	844	18.6%
Energy Fuels	690	15.2%
Engineering Chemical	637	14.0%
Physics Applied	544	12.0%
Electrochemistry	496	10.9%
Physics Condensed Matter	346	7.6%
Green Sustainable Science Technology	229	5.0%

The results of the journal distribution analysis showed that these 4546 articles were published in 422 different journals. Table 2 lists the top ten journals, among which ACS Catalysis is the most prolific journal, accounting for 5.0% of total publications; the second most prolific journal is *Angewandte Chemie International Edition* (4.4%), then *Journal of Materials Chemistry A* (4.0%), and *Journal of the American Chemical Society* (2.7%) followed. As can be seen, the most published journals are also closely related to chemistry and materials, etc.

Table 2. Top ten most published journals during 2005–2022.

Journal	IF (2021)	TP	%
<i>ACS Catalysis</i>	13.700	227	5.0%
<i>Angewandte Chemie International Edition</i>	16.823	200	4.4%
<i>Journal of Materials Chemistry A</i>	14.511	181	4.0%
<i>Journal of the American Chemical Society</i>	16.383	122	2.7%
<i>Journal of Physical Chemistry C</i>	4.177	118	2.6%
<i>Applied Catalysis B Environmental</i>	24.319	111	2.4%
<i>ACS Applied Materials Interfaces</i>	10.383	108	2.4%
<i>Abstracts of Papers of the American Chemical Society</i>	\	105	2.3%
<i>Journal of CO₂ Utilization</i>	8.321	97	2.1%
<i>Electrochimica Acta</i>	7.336	93	2.0%

IF is the impact factor; TP is the total number of publications; % is the proportion of publications.

3.4. Author Information

According to the results of this analysis, 11,122 authors were involved in the field of eCO₂RR over the past 16 years. Table 3 lists the top ten authors who published the most in the field. According to their productivity rankings, all listed scholars had at least 30 publications. Han, Buxing of the Institute of Chemistry, CAS has published the largest number of papers in the field of eCO₂RR, with 53 articles so far, and he also has a high H-index of 90, which indicates that he has great influence in the field and has made a great contribution to the development of eCO₂RR. He was followed by Roldan Cuenya,

Beatriz, who published 45 articles with an H-index of 64, followed by Sargent, Edward H. (44, H-index of 152), Wang, Guoxiong (43, H-index of 28), Sinton, David (42, H-index of 70), Koper, Marc T.M. (35, H-index 105), Bao, Xin (35, H-index 68), Dinh, Cao Thang (35, H-index 56), Broekmann, Peter (32, H-index 28), and Irabien, Angel (30, H-index 55).

Table 3. Top ten most published authors during 2005–2022.

Authors	Affiliations	Publications	Percentage (%)	H-Index
Han, Buxing	Institute of Chemistry, CAS	53	1.2%	90
Roldan Cuenya, Beatriz	Fritz Haber Institute of the Max Planck Society	45	1.0%	64
Sargent, Edward H.	University of Toronto	44	1.0%	152
Wang, Guoxiong	State Key Laboratory of Catalysis, CAS	43	0.9%	28
Sinton, David	University of Toronto	42	0.9%	70
Koper, Marc T. M.	Leiden University	35	0.8%	105
Bao, Xin	State Key Laboratory of Catalysis, CAS	35	0.8%	68
Dinh, Cao Thang	Queen's University	35	0.8%	56
Broekmann, Peter	University of Bern	32	0.7%	28
Irabien, Angel	Universidad de Cantabria	30	0.7%	55

3.5. Geographical Distribution

In order to determine the cooperative relationships among the major countries or regions involved in eCO₂RR research, the country/region distribution of literature authors was analyzed. Authors from 77 countries/regions have published papers on eCO₂RR. China had the largest number of publications, with 2561, accounting for 56.3% of the total, followed by the United States (20.4%), and Canada (5.4%), indicating that China plays an important role in eCO₂RR research to a large extent. Figure 2 shows the cooperative relationship profile of the author's country or region. As can be seen from Figure 2, China and the United States have the closest international cooperation and are the two countries most closely connected in the field of eCO₂RR research. In addition, China also has closer international cooperation with Germany, Canada, and other countries.

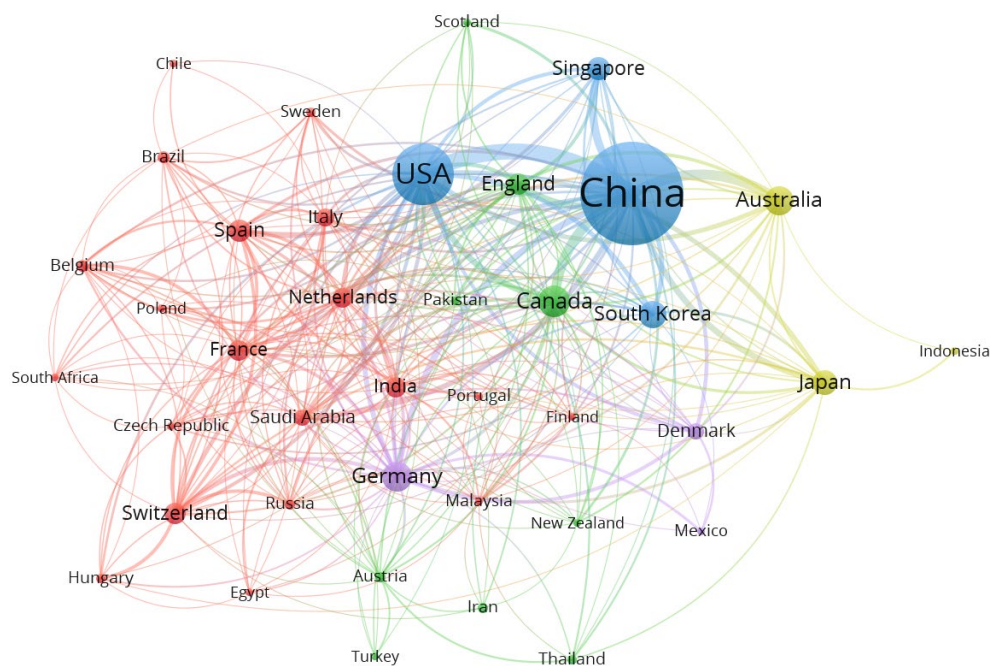


Figure 2. Spectrum of cooperation in different countries or regions from 2005 to 2022.

3.6. Cited Frequency

The citation frequency of the paper reflects its importance in this field. In order to determine the most influential literature in the field of eCO₂RR, the top ten literature with the number of citations were sorted out, as shown in Table 4. Of these articles, three were cited more than 1500 times, and ten were cited more than 1000 times each. China had three articles, followed by the United States (two), Denmark (one), Germany (one), France (one), Netherlands (one) and Canada (one). It can be seen that the literature published by American and Chinese researchers has been cited relatively frequently. The literature with the most citation frequency was “How Copper Catalyzes the Electroreduction of Carbon Dioxide into Hydrocarbon Fuels”, the paper by Peterson, A.A. et al., which described how copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels. The second most cited document was “A Review of Catalysts for the Electroreduction of Carbon Dioxide to Produce Low-Carbon Fuels”, written by Qiao, J.L. et al. The research progress and challenges of catalysts for producing low carbon fuel by electroreduction of carbon dioxide were reviewed. These results indicate the importance of catalysts in the field of eCO₂RR.

Table 4. Top ten most cited articles.

Authors	Title	Affiliations	Total Citation	References
Peterson, A.A. et al.	“How Copper Catalyzes the Electroreduction of Carbon Dioxide into Hydrocarbon Fuels”	Technical University of Denmark	1969	[26]
Qiao, J.L. et al.	“A Review of Catalysts for the Electroreduction of Carbon Dioxide to Produce Low-Carbon Fuels”	Donghua University	1925	[14]
Kuhl, K.P. et al.	“New Insights into the Electrochemical Reduction of Carbon Dioxide on Metallic Copper Surfaces”	Stanford University	1834	[27]
Gao, S. et al.	“Partially Oxidized Atomic Cobalt Layers for Carbon Dioxide Electroreduction to Liquid Fuel”	University of Science and Technology of China	1246	[28]
Kondratenko, E.V. et al.	“Status and Perspectives of CO ₂ Conversion into Fuels and Chemicals by Catalytic, Photocatalytic and Electrocatalytic Processes”	Leibniz Institut für Katalyse e.V. an der Universität Rostock (LIKAT)	1200	[29]
Costentin, C. et al.	“Catalysis of the Electrochemical Reduction of Carbon Dioxide”	Centre National de la Recherche Scientifique (CNRS)	1171	[30]
Kortlever, R. et al.	“Catalysts and Reaction Pathways for the Electrochemical Reduction of Carbon Dioxide”	Leiden University	1154	[31]
Chen, Y.J. et al.	“Single-Atom Catalysts: Synthetic Strategies and Electrochemical Applications”	Tsinghua University	1104	[32]
Dinh, C.T. et al.	“CO ₂ Electroreduction to Ethylene via Hydroxide-Mediated Copper Catalysis at an Abrupt Interface”	Institute of Chemical Process and Environmental Technology, Canada	1076	[33]
Li, C.W. et al.	“Electroreduction of Carbon Monoxide to Liquid Fuel on Oxide-Derived Nanocrystalline Copper”	Stanford University	1057	[34]

3.7. Research Hotspots and Future Trends

According to the keyword statistics from 2019 to 2022, after merging similar keywords and deleting keywords unrelated to eCO₂RR, 7003 keywords were retrieved, and 35 keywords appeared more than 100 times, among which the most common keyword was “CO₂ electroreduction”, which appeared 2861 times. “Electrocatalysts” appeared next with 1720 times, followed by “efficient” with 595 times, and “Cu” with 535 times, with

15 keywords appearing 200 times or more. The results showed that research in the field of eCO₂RR is mainly focused on the study of electrochemical catalysts.

VOSviewer software was used to cluster the keywords and generate a cluster view of keyword co-occurrence (as shown in Figure 3) to obtain the research hotspots in the field of eCO₂RR in recent years. There were five clusters in the keyword clustering in Figure 3, and Table 5 shows the occurrences and proportion of cluster keywords.

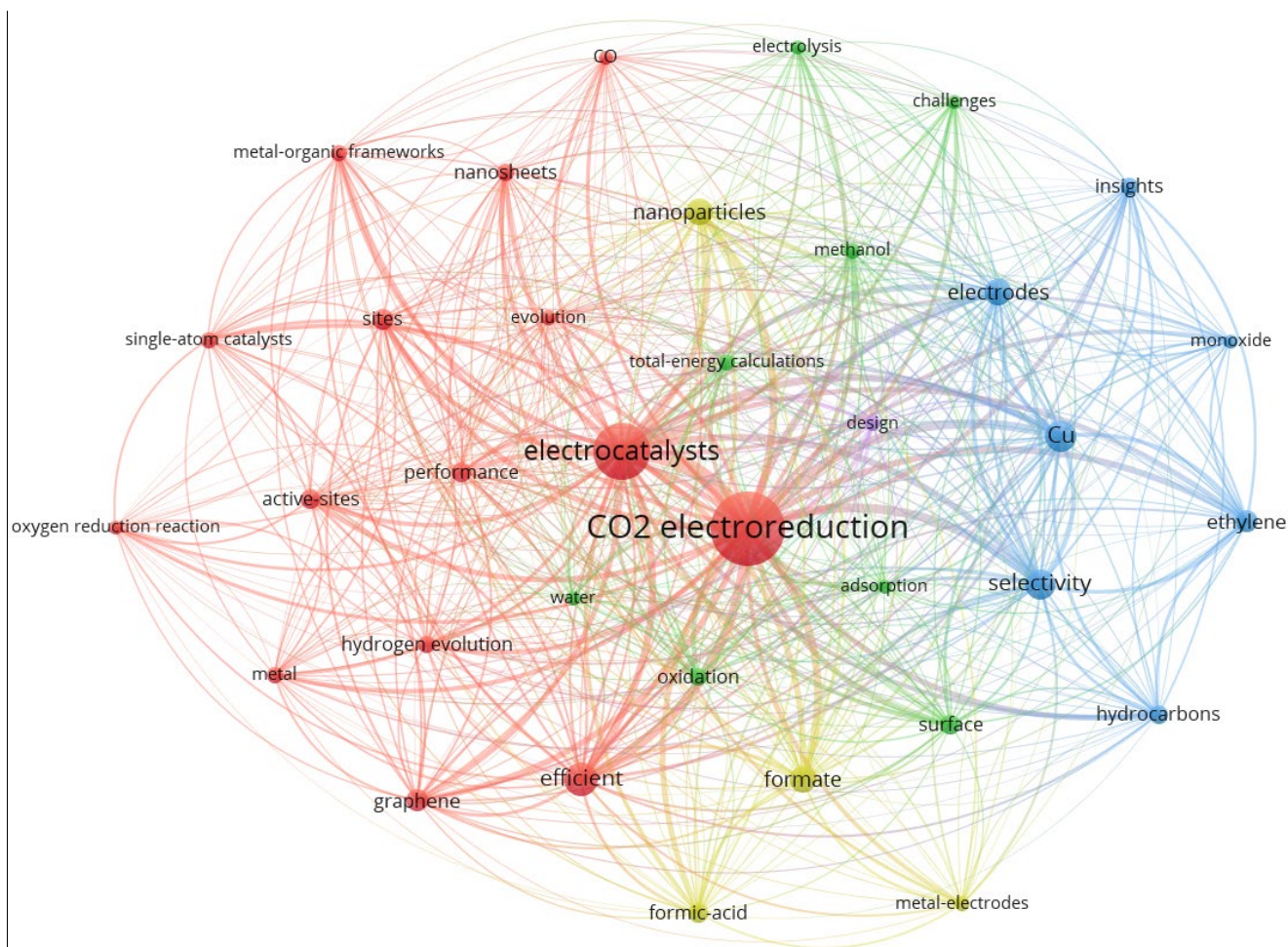


Figure 3. Keyword clustering view of eCO₂RR from 2019 to 2022.

Table 5. The occurrences and proportion of cluster keywords.

Cluster	Occurrences	Percentage
1 (red)	7195	61.5%
2 (blue)	2164	18.5%
3 (green)	1114	9.5%
4 (yellow)	1094	9.3%
5 (purple)	136	1.2%

3.7.1. Cluster 1 (Red): Classification of Catalysts and Product Types

In addition to the general direction of “CO₂ electroreduction”, electrocatalysts appeared the most in this cluster, linking 34 other nodes, which were closely related to the other clusters. Electrochemical catalysts play a very important role in the process of eCO₂RR. There are many kinds of catalysts, and different types of catalysts have different selectivity for the products of eCO₂RR.

As shown in Figure 4, catalysts can be divided into two main categories, namely metallic catalysts and non-metallic catalysts. Metal catalysts include precious metal-based

catalysts and non-precious metal-based catalysts. Non-metallic catalysts are mainly non-metallic carbon material catalysts.

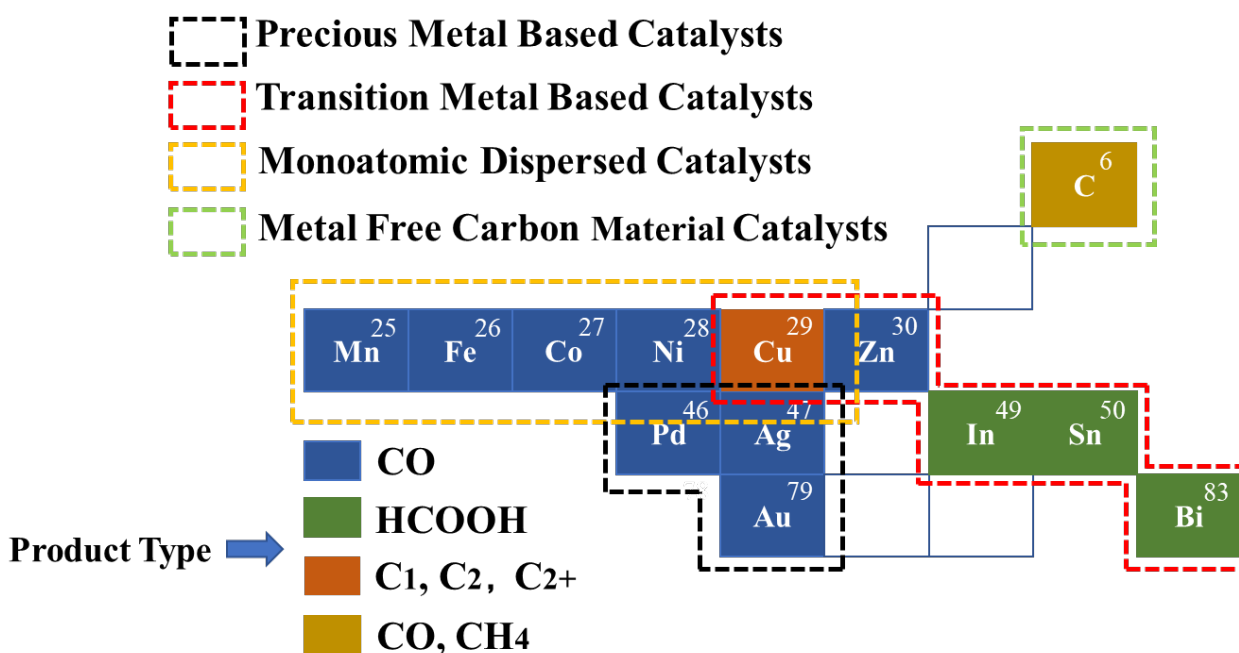


Figure 4. Classification of catalysts and product types.

(1) Metal catalyst

Precious/non-precious metal catalysts are the most used catalysts. Commonly used precious metal-based catalysts mainly include gold (Au), silver (Ag), platinum (Pt), palladium (Pd), etc. Most of the precious metal-based catalysts are involved in the electrocatalytic reduction of CO₂ to CO, showing good conductivity and excellent CO selectivity [35,36].

Gold is one of the most active and selective catalysts for eCO₂RR to produce CO. However, in early studies, the cost of traditional precious metal materials hindered its large-scale application, and its catalytic activity and reaction rate were low, which did not meet the practical needs. At present, most of the traditional precious metal materials are prepared into polymetallic nanoparticles or nanocomposites to reduce production costs and improve catalytic performance [37]. For example, Liu et al. [38] made gold (Au) into nanoneedles for eCO₂RR to produce CO, and its Faraday efficiency reached more than 95% at a low potential of −0.35 V (Figure 5a).

Compared to other precious metals, the cost of silver is relatively low, and silver also has outstanding selectivity for CO generation, which makes silver a suitable catalyst to achieve large-scale production. Thus far, significant improvements have been made in the preparation of silver catalysts with high selectivity and activity [39–41]. As shown in Figure 5b, Lu et al. [42] prepared a nanoporous Ag with a highly curved surface by the two-step dealloying method for eCO₂RR to produce CO. Compared to polycrystalline Ag, the Faradaic efficiency (FE) of CO can reach 92% when the overpotential of nanoporous Ag is less than 0.5 V, which is 3000 times higher than that of polycrystalline Ag.

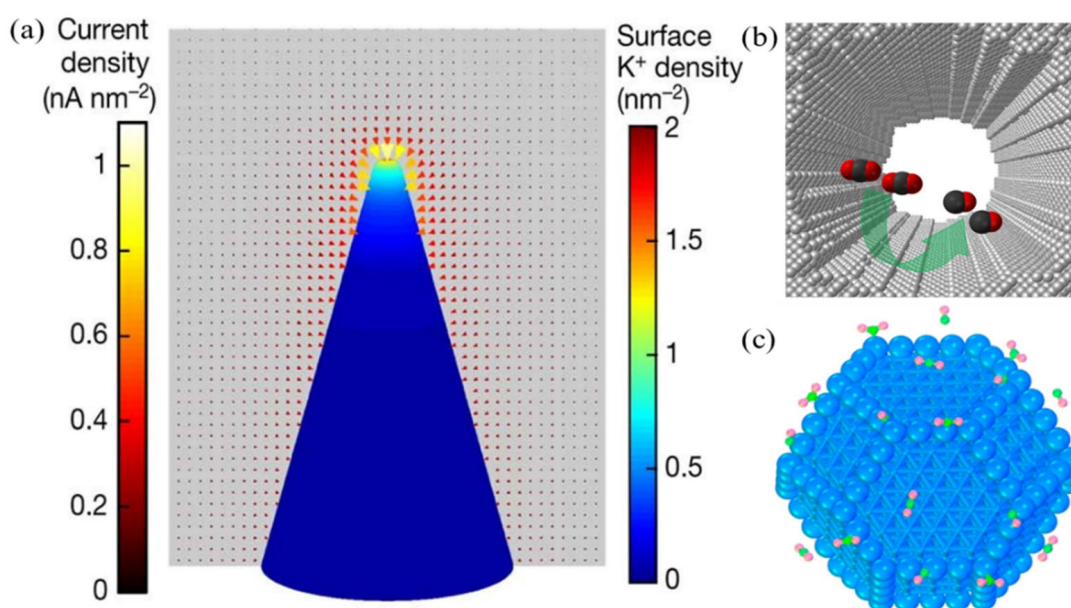


Figure 5. (a) K^+ density and current density distribution on the surface of a gold nanoneedle with a tip radius of 5 nm [38]. (b) Schematic representation of a nanopore for a silver electrocatalyst with a highly curved inner surface [42]. (c) Schematic diagram of CO_2 molecules adsorbing on palladium clusters [43].

Palladium-based electrocatalysts are also considered one of the materials that can be used for CO electrocatalysis from CO_2 . Similarly, due to the poor catalytic activity of polycrystalline Pd, nanostructured Pd was made to improve the catalytic activity and faradaic yield. Nanoparticles of different sizes may correspond to different catalytic activities and product selectivity. For example, Gao et al. [43] prepared Pd nanoparticles of different sizes (2.4–10.3 nm) for CO_2 reduction (Figure 5c) and found that, at the potential of -0.89 V (vs. RHE), the Faradaic efficiency of producing CO from 10.3 nm Pd nanoparticles was only 5.8%, while the Faradaic efficiency of 3.7 nm Pd nanoparticles was 91.2%, and the current density increased by 18.4 times.

Common non-precious metal-based catalysts can also be divided into transition metal-based catalysts and single-atomic dispersed catalysts. Although some of the above precious metal-based catalysts show good catalytic performance, due to the high cost of precious metals, resource shortages, and other characteristics, they cannot be used on a large scale; thus, some non-precious metal catalysts are also widely used in the field of eCO_2RR .

Transition metals have also been used as catalysts for eCO_2RR due to their unique electronic structure. Different transition metals and their oxides catalyze CO_2 to obtain different reduction products. For example, zinc (Zn) and its oxides can catalyze CO_2 reduction to CO. Metal indium (In), tin (Sn), bismuth (Bi), and their oxides mainly catalyze the reduction of CO_2 to formic acid. Copper metal (Cu) and its oxides mostly catalyze the reduction of CO_2 to methane (CH_4), ethanol (C_2H_5OH), methanol (CH_3OH), and other hydrocarbon or polycarbon products [44]. For example, Feng et al. [45] prepared a porous zinc nanoparticle catalyst (P-Zn) and found that the Faradaic efficiency of CO production could reach 98.1% when the electric potential was -0.95 V. Reske et al. [46] prepared copper nanoparticles of different sizes, and the results showed that, with the decrease of nanoparticle size, the selectivity of H_2 and CO increased, while the selectivity of CH_4 and C_2H_4 decreased. This may be because when the size of Cu nanoparticles decreases, the proportion of unsaturated coordination sites on the surface increases, and these surface atoms with low coordination numbers have a stronger binding energy, which increases the selectivity of CO and H_2 , while it decreases the selectivity of hydrocarbons.

In metal-based catalysts, metal size, morphology, roughness, and so on affect the catalytic activity of the catalyst. For example, iron, cobalt, nickel, palladium, and other

metals have good electrocatalytic HER; thus, they are not suitable for eCO₂RR. A single atomic dispersed catalyst is a kind of heterogeneous catalyst with a high utilization rate that disperses atomic metal catalysts on the surface of support. Single-atomic dispersed catalysts are stable, have a high utilization rate of active center atoms and a low coordination number of active center atoms, and they have the advantages of both homogeneous and heterogeneous catalysts. Most of them reduce CO₂ to CO electrocatalytically. At present, there are many carbon materials doped with nitrogen atoms as carriers, and single-atom transition metals are embedded in the carbon matrix to produce metal-nitrogen active site-doped carbon materials [47,48]. For example, Ju et al. [49] used a series of transition metal atoms to coordinate with nitrogen atoms to form a metal-nitrogen atom coordination structure and to stabilize it on the surface of carbon materials. The M-N-C (M = Mn, Fe, Co, Ni, Cu) catalyst was prepared. The results showed that the M-N-C material can catalyze the reduction of CO₂ to CO, and its catalytic activity is related to the type of transition metal atoms, following the Ni > Fe > Mn > Cu > Co.

Due to their multiple active sites and high porosity [50], metal-organic frameworks (MOFs) in non-noble metal based catalysts are also the research focus in recent years. MOFs are crystalline porous materials with a periodic network structure formed by the self-assembly of transition metal ions and organic ligands, such as metal porphyrins and phthalocyanines, which show high eCO₂RR potential [51]. For example, Xin et al. [52] implanted metallocene (MCp₂) with different metal centers into the pores of MOF-545 based on metal porphyrins. MOF-545 has high porosity, large pore diameter, and good thermal stability, and it can interact with MCp₂. The obtained composite material had higher CO₂ adsorption capacity, excellent electron transfer performance, and excellent electrocatalytic activity, which greatly improved the Faraday efficiency of electrocatalytic eCO₂RR active CO by 97%. Xin et al. [50] inserted an electron-conducting polypyrrole (PPy) molecule into the channels of MOFs through in situ low-temperature polymerization and synthesized a series of PPy@MOF-545-M hybrid materials, which exhibit excellent electrocatalytic properties. Among them, PPy@MOF-545-Co increased the selectivity of CO₂ to CO to 98%, almost twice that of MOF-545-Co. In addition, the catalyst can maintain crystallinity and performance within 10 h.

(2) Non-metallic catalysts

Although a large number of metal catalysts are used in the research of eCO₂RR, and some achievements have been made, there are still obvious shortcomings of these catalysts, such as high cost and serious HER, in order to achieve large-scale application. Therefore, more and more attention has been paid to non-metallic catalysts, among which metal-free carbon catalysts have become one of the common electrocatalyst materials for eCO₂RR due to their wide sources, low cost, good conductivity, and high stability. Metal-free carbon material catalysts mostly reduce CO₂ to CO, CH₄, etc. Since Gong et al. [53] proposed that doping heteroatom modification in carbon materials can significantly improve the catalytic activity of carbon materials for electroreduction of oxygen, more and more researchers chose the doping heteroatom modification in carbon materials to improve the catalytic activity of eCO₂RR in CO production [54,55]. For example, Sharma et al. [56] doped nitrogen into carbon nanotubes. Compared to the original carbon nanotubes, this material significantly reduced the overpotential of carbon nanotubes (−0.18V) and increased the Faradaic efficiency of CO production to 80%, showing good catalytic performance.

3.7.2. Cluster 2 (Blue): Copper-Based Catalysts and Methods for Improving Product Selectivity

“Cu” is the largest node in this cluster, which indicates that the catalysts in recent years are still mainly copper-based catalysts. The second is “selectivity”, probably because most researchers are still concerned about selectivity.

Copper-based catalysts are widely used in the field of eCO₂RR due to their good catalytic effect and low cost. In addition, a copper-based catalyst is the only catalyst that can reduce CO₂ to CO, CH₄, HCOOH, C₂H₄, and other hydrocarbons and multi

carbon products. When different copper based catalysts are used for eCO₂RR reaction, the distribution of reduction products is different.

Thus far, most studies on Cu-based catalysts have focused on the production of various C₂ products, such as ethylene, ethanol, and n-propanol, while C₁ products (such as methane) are difficult to obtain directly, and the product selectivity remains low. Copper-based catalysts are still the focus of research because of their unique ability to selectively reduce carbon dioxide to formic acid, CO, methane, and other hydrocarbons [7]. This cluster mainly introduces the selectivity of copper-based catalysts and some common target products (such as ethylene, monoxide, and other hydrocarbons) in recent years.

In this paper, some methods to improve product selectivity are summarized, mainly from the aspects of size, composition, morphology, and structure of copper-based catalysts.

Changes in catalyst size cause changes in catalyst activity, product selectivity, and catalyst stability. For example, Grosse et al. [57] synthesized a copper cube with adjustable size on carbon-based support by a simple electrochemical method and found that the morphology of the Cu cube changed dramatically. More and more researchers chose the doping heteroatom modification in carbon materials to improve the catalytic activity of eCO₂RR in CO production. The selectivity of methane in the product is much higher than that of ethylene, which can be used to produce C₁ product.

Alloying to design the composition of catalysts is also a way to improve product selectivity. For example, Nellaiappan et al. [58] used nanocrystalline high-entropy alloy (HEA: AuAgPtPdCu) to convert CO₂ into gaseous hydrocarbons, which showed limited selectivity due to the large amount of hydrogen produced by copper-based materials. Additionally, nanocrystalline high-entropy alloys still has mainly gas products CO, CH₄, C₂H₄, and H₂, similar to the copper-based catalyst electricity. Although there are many elements in the catalyst, the catalytic effect is only produced by copper, and other elements only produce a synergistic effect; thus, the alloying can not only improve the product selectivity, but it can also significantly enhance the catalytic activity.

The change of copper electrode morphology is also very sensitive to the activity of the eCO₂RR catalyst and the selectivity of products [59]. In the H-type electrolytic cell, single crystal copper was used as a catalyst, and it was found that the surface of Cu (100) had higher C₂H₄ selectivity, while the surface of Cu (111) had higher CH₄ selectivity [60]. The study of Gregorio et al. [61] also showed that, in 1 M KOH, the ethylene selectivity of cubic copper was up to 57%, and the corresponding mass activity was 700 mA/mg. The methane selectivity of octahedral copper was up to 51%, and the corresponding mass activity was 1.45 A/mg.

Changes in catalyst structure (such as surface modification, doping of metals [62–64], metal-organic skeleton regulation [65,66], crystal structure change [67], load [68,69], etc.) also lead to changes in product selectivity. For example, Xie et al. [7] used amino acids to modify the surface of copper to selectively and electrochemically reduce carbon dioxide to hydrocarbons. The results showed that, regardless of the shape of the copper electrode, these modified copper electrodes significantly improved the generation of hydrocarbons.

Ethylene, monoxide, and other hydrocarbons are the most common reduction products used in recent years. Lin et al. [70] proposed a simple, economic, and efficient method of ethylene, which was a kind of by carbon nitride (CN)-coated copper oxide mixed compound (Cu_xO/CN) heterostructure composed of catalysts, and it had a heterogeneous catalyst structure interaction between metal and carbon nitride. The modification of the catalyst can be made at the corner of the Cu and CN membrane enrichment of CO₂. Because the CN membrane can increase the charge density of the Cu_xO active center, the CO₂ adsorption capacity can be enhanced, and then the Faraday efficiency of C₂H₄ can be improved.

Ma et al. [71] prepared a Cu In bimetallic catalyst by the pyrolysis of a Cu In metal organic framework (MOF) material. The structure of the Cu In bimetallic catalyst shows a high CO selectivity of 85% at −0.75 V, which is nearly 7.9 times higher than that of the In/C catalyst.

Zhu et al. [72] proposed a metal-organic skeleton catalyst with a tri-pyramid $\text{Cu}_{(1)}\text{N}_3$ active center, which can generate up to 92% FE of methane. This is the result of strong interplay between Cu (I) and intermediates and the synergistic effect of organic ligands. It plays an important role in stabilizing intermediates and inhibiting the hydrogen evolution reaction.

3.7.3. Cluster 3 (Green) and Cluster 4 (Yellow): Research Status of Preparation of C_1 Product with a Copper-Based Catalyst

Cluster 3 (green) and cluster 4 (yellow) mainly involve C_1 products such as formate (376 occurrences), formic-acid(205 occurrences), and methanol (143 occurrences).

Formate is commonly used as a power stable liquid fuel in fuel cells [73,74], and it is also a key intermediate and important starting material in the chemical synthesis industry [75]. The formation of formate from eCO_2RR is also significant. Liu et al. [76] designed and constructed BiCu bimetallic film on copper foam (BiCu/CF). The synthesized copper foam stabilized the $^*\text{OCHO}$ intermediate and reduced the thermodynamic barrier of eCO_2RR . At the same time, electrons transferred from the catalyst position to the reaction species also accelerated, and the yield of formic acid increased to 85.6%. It produced a record current density of 856 mA cm^{-2} , while having remarkable stability that outperformed state-of-the-art bismuth-based catalysts.

Methanol as an alternative fuel is an ideal energy carrier and is one of the most important commercial chemicals; however, methanol is currently mainly produced by fossil syngas. In addition, it produces huge carbon emissions in the production process; thus, the direct conversion of CO_2 into methanol has great potential to change the mode of methanol production [77]. Zhao et al. [78] prepared uniaxial copper immobilized MXene by selectively etching the hybrid A layer (Al and Cu) in the quaternary MAX phases ($\text{Ti}_3(\text{Al}_{1-x}\text{Cu}_x)\text{C}$). After selectively etching the aluminum layer, copper atoms were well retained and fixed on MXene ($\text{Ti}_3\text{C}_2\text{Cl}_x$). The monatomic Cu with unsaturated electronic structure provided a low energy barrier for the rate-determining step, resulting in a Faradaic efficiency of 59.1% for CH_3OH formation and good electrocatalytic stability.

It can be seen from the first four clusters that the most studied catalysts are still copper-based catalysts, and the reduction products are mostly C_1 products such as CO, CH_4 , methanol, formic acid, and formate. However, most of the Cu-based catalyst research focused on the production of the C_2 product, such as ethylene, ethanol, and normal propyl alcohol, but C_1 products (such as methane, etc.) are difficult to obtain directly. The literature on this subject is relatively small, as shown in Figure 6, and below summarizes some copper-based catalyst preparation and the research status of these products C_1 .

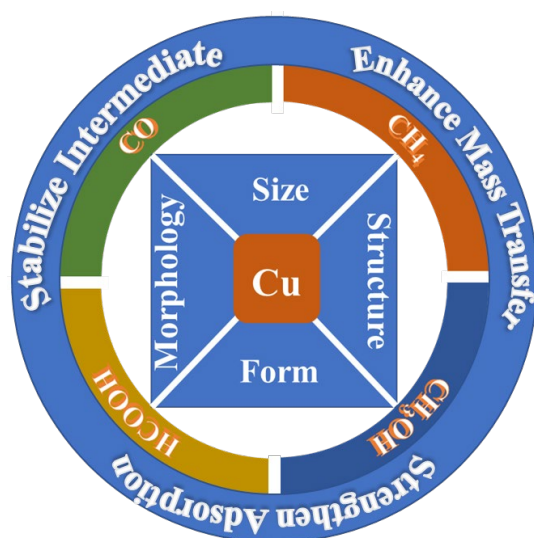


Figure 6. Common C_1 products and key preparation points and optimization strategies for copper-based catalyst preparation.

(a). CO

Carbon monoxide (CO) is an important raw material for the synthesis of various chemicals and fuels. It is the basis of C₁ chemistry, and almost all basic chemicals can be produced by converting CO and H₂. eCO₂RR provides an alternative green route for CO production. In addition to precious metal catalysts such as gold (Au), silver (Ag), and palladium (Pd), copper-based catalysts can also catalyze CO₂ to CO.

Au is one of the effective electrocatalysts for eCO₂RR to CO. However, the cost of gold and the high potential demand hinder its large-scale application. The bimetallic catalyst formed by the combination of gold and copper can effectively solve this problem. In addition, adjusting the exposed crystal plane by controlling the morphology, structure, and composition of the catalyst can also improve the electrocatalytic performance of the catalyst. Among the 3D porous metal nanomaterials, including aerogel [79], nanowires [80], nanoribbons [81], nanosheets [82], nanoparticles [83], hollow nanospheres [84], and aerogel, they have the advantages of hydrophobicity, low density, high porosity, high specific surface area, and good stability [79,85]. This is one of the most attractive catalysts right now. Zhang et al. [86] synthesized Au_{0.95}Cu_{0.05} foam by etching (Figure 7a), which showed the excellent ability of eCO₂RR to CO. At a low overpotential of 240 mV, a Faraday efficiency of 99.5% was achieved for CO, and the current density was 31.3 mA cm⁻². The kinetic study showed that the Cu-modified bimetallic foamed gold interface enhanced the adsorption of CO₂, enhanced mass transfer, promoted the activation of CO₂, and thus improved the production performance of CO.

Alloying has always been an important method to improve the selectivity and catalytic activity of eCO₂RR products [87]. Besides alloying copper with gold or silver, bimetallic Cu-In electrocatalysts are also one of the effective electrocatalysts for eCO₂RR, and they have low cost, high Faradaic efficiency, and good stability of CO [88]. However, the productivity to date has been rather low due to the low current density exhibited in aqueous electrolytes. To solve this problem, Mahyoub et al. [89] prepared a 3D Cu/In NC electrode by electrodeposition. When the CO₂ pressure was 1 atmosphere, the potential was -0.6V--1.1V (vs. RHE), the current density reached -20 mA cm⁻², and FE was 100%. In addition, by increasing the CO₂ pressure, the fractional current density of CO produced reached -229.88 mA cm⁻², which was a new record for most neutral pH electrolytes.

(b). CH₄

Methane (CH₄) is the main component of natural gas, biogas, and so on. It is a kind of fuel with a high calorific value and raw material of hydrogen, carbon monoxide, acetylene, and formaldehyde. eCO₂RR offers a promising method for preparing methane. In eCO₂RR, *CO protonation to *CHO is an important step in the formation of methane, which competes with C-C coupling in the formation of C₂ products [26,90]. In addition, since *CO protonation requires *H, it also competes with hydrogen evolution (HER) [91]. To improve the methane selectivity of eCO₂RR products, both C-C coupling and HER should be inhibited. Cu is a transition metal catalyst for the formation of methane and C₂+ products, but the product selectivity of monometallic catalysts is very low. Therefore, the introduction of the second metal into Cu is a promising way to adjust the product selectivity in eCO₂RR.

The catalyst prepared by Wang et al. [92] by introducing Au into Cu could not only control the C-C coupling under low *CO coverage, which was conducive to *CO protonation, but it also inhibited HER compared to monometallic Cu (Figure 7b). The selectivity ratio of methane to H₂ was improved by 1.6 times compared to the previous best study operating at 100 mA cm⁻² current density, and a Faraday efficiency (FE) of (56 ± 2)% of CO₂ to methane was achieved at a current density of (112 ± 4) mA cm⁻².

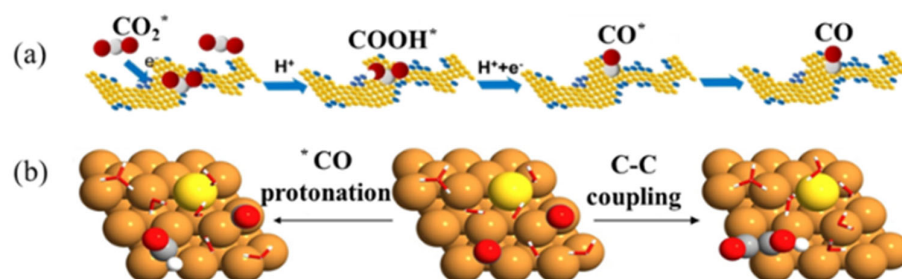


Figure 7. (a) Schematic diagram of the path of electroreduction of CO_2 to CO [86]. (b) Competition between $^*\text{CO}$ protonation and C-C coupling on the Au-Cu surface [92].

To date, most studies on Cu-based catalysts focus on the production of C_2 and C_2+ products, including ethylene, ethanol, ethane, and propanaldehyde, while C_1 products (such as methane) are difficult to obtain directly [93]. The reason is that eCO_2RR is a reduction reaction, and Cu_2+ in the cathode catalyst is inevitably electroreduced to Cu_0 or Cu_1+ [94]. The mixing of Cu_0 and Cu_1+ sites can significantly improve the thermodynamics of $^*\text{CO}$ dimerization, thereby improving the selectivity of C_2 and C_2+ products [95,96]. Therefore, stabilizing Cu_2+ in catalysts is also an important method to improve the selectivity of methane.

Zhou et al. [96] introduced Cu_2+ ions into CeO_2 matrix to form a Cu-Ce-Ox solid solution, wherein CeO_2 can stabilize Cu_2+ during eCO_2RR , and Ce_3+ can inhibit electron accumulation near Cu_2+ sites and protect them from reduction. The results showed that, compared to the Cu-based catalyst with the Cu_0 or Cu_1+ active site, the catalyst containing Cu_2+ in solid solution significantly enhanced the adsorption of $^*\text{CO}$ intermediate and promoted the generation of CH_4 instead of C_2 products.

(c). Methanol

Methanol (CH_3OH), as one of the basic organic raw materials, is not only an important fuel, but it is also a raw material for the preparation of a variety of organic products, such as formaldehyde and acetic acid. eCO_2RR provides a new path for methanol preparation. However, this field still faces two major challenges: competitive hydrogen evolution (HER) and low product selectivity [97,98]. In addition, methanol production from eCO_2RR is a combination of a six-proton and six-electron transfer process [99,100], which means that its reaction kinetics is slower and the methanol production reaction is more difficult compared to the two-electron reaction. Precious metal-based and copper-based catalysts are two promising catalysts for methanol production from eCO_2RR [85]. Among these catalysts, Cu is still a research hotspot due to its low cost. However, the Cu catalytic CO_2 process usually produces a variety of liquid products, which makes methanol have a very low selectivity. In order to improve the selectivity of methanol, it is often adopted to change the morphology [61], structure [101], and oxidation state [102] of copper-based catalysts to improve the selectivity of their products. In particular, Cu_1+ based catalysts have excellent performance in reducing CO_2 to alcohol [103]. However, the Cu_1+ site is extremely unstable in the reduction reaction and is easy to be reduced to Cu_0 site [104]. Therefore, maintaining the stability of the active site of Cu_1+ is the key to achieving the highly selective reduction of CO_2 to CH_3OH . MOFs have the advantages of large specific surface area, high porosity, and adjustable pore diameter, and they are extensively used in the field of eCO_2RR [105,106]. Although MOFs show good performance in eCO_2RR , there are still problems such as low selectivity and poor conductivity and stability in the preparation of methanol [107]. MOFs can be modified by means of calcination and doping to improve the catalytic activity, stability, and selectivity of methanol [108,109].

Yang et al. [109] synthesized a new $\text{Cu@Cu}_2\text{O}$ electrocatalyst by the calcination of Cu-BTC (1,3,5-phthalic acid) MOFs. The electrocatalyst was coated with a nitrogen-doped carbon shell, and the Faradaic efficiency of methanol could reach 45%. This is because the $\text{Cu}(0)/\text{Cu}(I)$ active site of Cu-BTC moderately adsorbed CO^* intermediates, which

contributed to co-catalysis. In addition, the hydroxyl group adsorbed on the catalyst surface was also conducive to the further hydrogenation of CO^* to methanol.

(d). Formic acid and formate

Formic acid (HCOOH) or formate (HCOO^-) is widely used in pharmaceutical, chemical, and other industries, and it is also a promising liquid fuel. Tin (Sn) is an ideal material for large-scale eCO_2RR to HCOOH due to its low price and abundant content [110,111]. Transition metal tin (Sn) and its oxides mainly catalyze CO_2 to formic acid and formate, but their overall activity, catalytic efficiency, and current density are low [112,113]. Cu-based catalysts are favored by many researchers because of their high electro catalytic activity in eCO_2RR [94], selectivity, and ability to produce various hydrocarbons or multi carbon products [114]. However, the poor selectivity of the single product of Cu-based catalysts hinders its commercial application. Therefore, Sn can be introduced into Cu-based catalysts to adjust the selectivity of eCO_2RR [115].

Yan et al. [116] prepared a dendritic Sn/Cu catalyst, and the yield of HCOOH reached $890.4 \mu\text{mol h}^{-1} \text{cm}^{-2}$, which was higher than the yield of most reported Sn catalysts. The results showed that polyethyleneimine enhanced the catalytic performance of the Sn/Cu catalyst, stabilized the CO_2^- intermediate, and thus increased the yield of HCOOH .

The structure and morphology of the catalyst affects the selectivity of the reduction products. Chen et al. [117] electrodeposited Sn on Cu nanowires, showing lower charge transfer resistance and higher specific surface area than the Sn/Cu and Sn foil. At -1.2 V (vs. RHE), the Faraday efficiency of Sn/Nano-Cu electrode was 86.8%, the current density was 38.0 mA cm^{-2} , and the formate yield was $575.1 \pm 24 \mu\text{mol h}^{-1} \text{cm}^{-2}$, which was obviously higher than that of the other two electrodes, and the stability was also good.

3.7.4. Cluster 5 (Purple): Challenges and Future Trend

The only node in this cluster is design (136 times). “Design” is not only for the design of efficient catalysts but also for the design of electrochemical reactors. Although there has been much research on eCO_2RR , there are still many difficulties and challenges in this field. The challenges faced by eCO_2RR mainly come from the following aspects.

- (1) CO_2 is a nonpolar linear molecule with very stable chemical properties, which is difficult to activate and transform. In addition, the CO_2 reduction process is also subject to relatively high thermodynamic and kinetic barriers [118]. In eCO_2RR , the process of CO_2 molecules adsorbing electrons into CO_2 is the first one, which requires a lot of energy. These characteristics of eCO_2RR lead to high overpotential, low selectivity, and competitive hydrogen evolution reaction, resulting in the low energy conversion efficiency of eCO_2RR . At the same time, the products of eCO_2RR are diverse, the selectivity of a single product is low, and the separation is difficult. Therefore, it is still necessary to continue to develop catalysts with high activity, high selectivity, and high stability (especially for a single product), especially copper-based catalysts for C_1 production.

At present, there is still much room for improvement of the copper-based catalyst for C_1 production. The adsorption of CO_2 molecules, the stability of intermediates, and the enhancement of mass transfer can be improved by modifying the size, composition, morphology, and structure of the catalysts to promote the smooth progress of eCO_2RR and obtain chemicals and fuels with high selectivity and high energy density. In addition, improving the stability of catalysts is also the focus of upcoming research. Most of the existing catalysts are stable for tens to hundreds of hours, which is far from meeting the current actual development needs, and researchers still need to continue to work hard.

- (2) At present, although there have been many studies on eCO_2RR , the mechanism of this reaction process is still not clear enough. Most of the studies are still in a relatively simple stage, and researchers need to continue to dig deeply.
- (3) In addition, the low solubility of CO_2 in aqueous solution limits the current density of eCO_2RR . For this problem, in addition to improving the catalyst, it can also be

improved by optimizing the structure of the electrochemical reactor. In addition to the most commonly used H-type reactor, the membrane electrode assembly (MEA) reactor is also the focus of future research. The CO₂ gas in the reactor is not in direct contact with the electrolyte, which can not only enhance mass transfer and reduce ohmic resistance, but it can also effectively avoid hydrogen evolution.

- (4) At present, the research on eCO₂RR is still in the stage of laboratory research, and there is still a long way to go from commercial application. Therefore, it is of great practical significance to develop a CO₂ electrochemical reactor with industrial current density considering the amplification of the CO₂ electroreduction device [119,120].

4. Conclusions

In this study, we conducted a comprehensive scientometric review of the research status and development trends of eCO₂RR from 2005 to 2022 and drew some important conclusions about the development of catalysts in the field of eCO₂RR. Bibliometric research results of eCO₂RR showed that the scientific community has been increasingly interested in the field of eCO₂RR in the past 17 years, and the number of papers increased year by year. Diverse research directions, covering 55 discipline categories, signals a comprehensive research area. From 2005 to 2022, a total of 4546 articles were retrieved and published in 422 different journals. China played an important role in eCO₂RR research, and the cooperation between China and the US was the most frequent.

In addition, as can be seen from keyword clustering, Cu-based catalysts are still the research hotspot in recent years. Most studies on Cu-based catalysts focus on the production of various C₂ products, including ethylene, ethanol, n-propanol, etc. However, C₁ products (such as methane, etc.) are difficult to obtain directly, although the performance of catalysts is constantly optimized. However, at present, most copper-based catalysts for C₁ production still have the problems of low activity, high cost, poor stability, and low product selectivity. Therefore, copper-based catalysts with high efficiency, low cost, high stability, and high selectivity can be developed to produce C₁ products by modifying catalyst size, composition, morphology, and structure.

Author Contributions: Conceptualization, H.W. and X.Z.; methodology, H.W.; software, H.W.; validation, Z.Y., J.Z. and C.L.; formal analysis, H.W.; investigation, H.W.; data curation, H.W.; writing—original draft preparation, H.W.; writing—review and editing, H.W., X.Z., H.Z. and A.J.; visualization, H.W.; supervision, X.Z., H.Z. and A.J.; project administration, X.Z. and H.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key R&D Program of China (2020YFC1910000), National Natural Science Foundation of China (52276214) and National Key R&D Program of China (no. 2018YFE0117300).

Data Availability Statement: Data available on request due to privacy or ethical restrictions. The data presented in this study are available on request from the corresponding author.

Acknowledgments: This work was financially supported by the National Key R&D Program of China (2020YFC1910000), National Natural Science Foundation of China (52276214) and National Key R&D Program of China (no. 2018YFE0117300). The scientific calculations in this paper have been done on the HPC Cloud Platform of Shandong University.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Arora, V.K.; Scinocca, J.F.; Boer, G.J.; Christian, J.R.; Denman, K.L.; Flato, G.M.; Kharin, V.V.; Lee, W.G.; Merryfield, W.J. Carbon emission limits required to satisfy future representative concentration pathways of greenhouse gases. *Geophys. Res. Lett.* **2011**, *38*. [[CrossRef](#)]
2. Shakun, J.D.; Clark, P.U.; He, F.; Marcott, S.A.; Mix, A.C.; Liu, Z.; Otto-Bliesner, B.; Schmittner, A.; Bard, E. Global warming preceded by increasing carbon dioxide concentrations during the last deglaciation. *Nature* **2012**, *484*, 49–54. [[CrossRef](#)] [[PubMed](#)]
3. Anderson, T.R.; Hawkins, E.; Jones, P. CO₂, the greenhouse effect and global warming: From the pioneering work of Arrhenius and Callendar to today's Earth System Models. *Endeavour* **2016**, *40*, 178–187. [[CrossRef](#)] [[PubMed](#)]

4. Eren, E.O.; Ozkar, S. Recent advances in heterogeneous catalysts for the effective electroreduction of carbon dioxide to carbon monoxide. *J. Power Sources* **2021**, *506*, 230215. [[CrossRef](#)]
5. Yuan, X.L.; Sheng, X.R.; Chen, L.P.; Tang, Y.Z.; Li, Y.; Jia, Y.S.; Qu, D.F.; Wang, Q.S.; Ma, Q.; Zuo, J. Carbon footprint and embodied carbon transfer at the provincial level of the Yellow River Basin. *Sci. Total Environ.* **2022**, *803*, 149993. [[CrossRef](#)]
6. De Luna, P.; Hahn, C.; Higgins, D.; Jaffer, S.A.; Jaramillo, T.F.; Sargent, E.H. What would it take for renewably powered electrosynthesis to displace petrochemical processes? *Science* **2019**, *364*, eaav3506. [[CrossRef](#)]
7. Xie, M.S.; Xia, B.Y.; Li, Y.; Yan, Y.; Yang, Y.; Sun, Q.; Chan, S.H.; Fisher, A.; Wang, X. Amino acid modified copper electrodes for the enhanced selective electroreduction of carbon dioxide towards hydrocarbons. *Energy Environ. Sci.* **2016**, *9*, 1687–1695. [[CrossRef](#)]
8. Zhang, T.; Zhong, H.; Qiu, Y.; Li, X.; Zhang, H. Zn electrode with a layer of nanoparticles for selective electroreduction of CO₂ to formate in aqueous solutions. *J. Mater. Chem. A* **2016**, *4*, 16670–16676. [[CrossRef](#)]
9. Hong, D.; Tsukakoshi, Y.; Kotani, H.; Ishizuka, T.; Kojima, T. Visible-Light-Driven Photocatalytic CO₂ Reduction by a Ni(II) Complex Bearing a Bioinspired Tetradentate Ligand for Selective CO Production. *J. Am. Chem. Soc.* **2017**, *139*, 6538–6541. [[CrossRef](#)]
10. Homayoni, H.; Chanmanee, W.; De Tacconi, N.R.; Dennis, B.H.; Rajeshwar, K. Continuous Flow Photoelectrochemical Reactor for Solar Conversion of Carbon Dioxide to Alcohols. *J. Electrochem. Soc.* **2015**, *162*, E115–E122. [[CrossRef](#)]
11. Li, Q.; Rao, X.; Sheng, J.; Xu, J.; Yi, J.; Liu, Y.; Zhang, J. Energy storage through CO₂ electroreduction: A brief review of advanced Sn-based electrocatalysts and electrodes. *J. CO₂ Util.* **2018**, *27*, 48–59. [[CrossRef](#)]
12. Nam, D.H.; Kuk, S.K.; Choe, H.; Lee, S.; Ko, J.W.; Son, E.J.; Choi, E.-G.; Kim, Y.H.; Park, C.B. Enzymatic photosynthesis of formate from carbon dioxide coupled with highly efficient photoelectrochemical regeneration of nicotinamide cofactors. *Green Chem.* **2016**, *18*, 5989–5993. [[CrossRef](#)]
13. Shi, J.; Jiang, Y.; Jiang, Z.; Wang, X.; Wang, X.; Zhang, S.; Han, P.; Yang, C. Enzymatic conversion of carbon dioxide. *Chem. Soc. Rev.* **2015**, *44*, 5981–6000. [[CrossRef](#)]
14. Qiao, J.; Liu, Y.; Hong, F.; Zhang, J. A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels. *Chem. Soc. Rev.* **2014**, *43*, 631–675. [[CrossRef](#)]
15. Zhang, W.; Hu, Y.; Ma, L.; Zhu, G.; Wang, Y.; Xue, X.; Chen, R.; Yang, S.; Jin, Z. Progress and Perspective of Electrocatalytic CO₂ Reduction for Renewable Carbonaceous Fuels and Chemicals. *Adv. Sci.* **2018**, *5*, 1700275. [[CrossRef](#)]
16. Zheng, T.; Jiang, K.; Wang, H. Recent Advances in Electrochemical CO₂-to-CO Conversion on Heterogeneous Catalysts. *Adv. Mater.* **2018**, *30*, e1802066. [[CrossRef](#)]
17. Handoko, A.D.; Wei, F.; Jenndy; Yeo, B.S.; Seh, Z.W. Understanding heterogeneous electrocatalytic carbon dioxide reduction through operando techniques. *Nat. Catal.* **2018**, *1*, 922–934. [[CrossRef](#)]
18. Jiang, K.; Siahrostami, S.; Zheng, T.; Hu, Y.; Hwang, S.; Stavitski, E.; Peng, Y.; Dynes, J.; Gangisetty, M.; Su, D.; et al. Isolated Ni single atoms in graphene nanosheets for high-performance CO₂ reduction. *Energy Environ. Sci.* **2018**, *11*, 893–903. [[CrossRef](#)]
19. Liu, A.; Gao, M.; Ren, X.; Meng, F.; Yang, Y.; Gao, L.; Yang, Q.; Ma, T. Current progress in electrocatalytic carbon dioxide reduction to fuels on heterogeneous catalysts. *J. Mater. Chem. A* **2020**, *8*, 3541–3562. [[CrossRef](#)]
20. Siahrostami, S.; Jiang, K.; Karamad, M.; Chan, K.; Wang, H.; Nørskov, J. Theoretical Investigations into Defected Graphene for Electrochemical Reduction of CO₂. *ACS Sustain. Chem. Eng.* **2017**, *5*, 11080–11085. [[CrossRef](#)]
21. Zheng, T.; Jiang, K.; Ta, N.; Hu, Y.; Zeng, J.; Liu, J.; Wang, H. Large-Scale and Highly Selective CO₂ Electrocatalytic Reduction on Nickel Single-Atom Catalyst. *Joule* **2019**, *3*, 265–278. [[CrossRef](#)]
22. Han, P.; Wang, Z.; Kuang, M.; Wang, Y.; Liu, J.; Hu, L.; Qian, L.; Zheng, G. 2D Assembly of Confined Space toward Enhanced CO₂ Electroreduction. *Adv. Energy Mater.* **2018**, *8*, 1801230. [[CrossRef](#)]
23. Wu, J.; Sharifi, T.; Gao, Y.; Zhang, T.; Ajayan, P.M. Emerging Carbon-Based Heterogeneous Catalysts for Electrochemical Reduction of Carbon Dioxide into Value-Added Chemicals. *Adv. Mater.* **2019**, *31*, e1804257. [[CrossRef](#)] [[PubMed](#)]
24. Mun, Y.; Kim, K.; Kim, S.; Lee, S.; Lee, S.; Kim, S.; Choi, W.; Kim, S.-K.; Han, J.W.; Lee, J. A novel strategy to develop non-noble metal catalyst for CO₂ electroreduction: Hybridization of metal-organic polymer. *Appl. Catal. B Environ.* **2018**, *236*, 154–161. [[CrossRef](#)]
25. Lei, Y.; Wang, Z.; Bao, A.; Tang, X.; Huang, X.; Yi, H.; Zhao, S.; Sun, T.; Wang, J.; Gao, F. Recent advances on electrocatalytic CO₂ reduction to resources: Target products, reaction pathways and typical catalysts. *Chem. Eng. J.* **2023**, *453*, 139663. [[CrossRef](#)]
26. Peterson, A.A.; Abild-Pedersen, F.; Studt, F.; Rossmeisl, J.; Nørskov, J.K. How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels. *Energy Environ. Sci.* **2010**, *3*, 1311–1315. [[CrossRef](#)]
27. Kuhl, K.P.; Cave, E.R.; Abram, D.N.; Jaramillo, T.F. New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energy Environ. Sci.* **2012**, *5*, 7050–7059. [[CrossRef](#)]
28. Gao, S.; Lin, Y.; Jiao, X.; Sun, Y.; Luo, Q.; Zhang, W.; Xie, Y. Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel. *Nature* **2016**, *529*, 68. [[CrossRef](#)]
29. Kondratenko, E.V.; Mul, G.; Baltrusaitis, J.; Larrazabal, G.O.; Perez-Ramirez, J. Status and perspectives of CO₂ conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes. *Energy Environ. Sci.* **2013**, *6*, 3112–3135. [[CrossRef](#)]
30. Costentin, C.; Robert, M.; Saveant, J.M. Catalysis of the electrochemical reduction of carbon dioxide. *Chem. Soc. Rev.* **2013**, *42*, 2423–2436. [[CrossRef](#)] [[PubMed](#)]
31. Kortlever, R.; Shen, J.; Schouten, K.J.P.; Calle-Vallejo, F.; Koper, M.T.M. Catalysts and Reaction Pathways for the Electrochemical Reduction of Carbon Dioxide. *J. Phys. Chem. Lett.* **2015**, *6*, 4073–4082. [[CrossRef](#)] [[PubMed](#)]

32. Chen, Y.; Ji, S.; Chen, C.; Peng, Q.; Wang, D.; Li, Y. Single-Atom Catalysts: Synthetic Strategies and Electrochemical Applications. *Joule* **2018**, *2*, 1242–1264. [[CrossRef](#)]
33. Dinh, C.T.; Burdyny, T.; Kibria, M.G.; Seifitokaldani, A.; Gabardo, C.M.; de Arquer, F.P.G.; Kiani, A.; Edwards, J.P.; De Luna, P.; Bushuyev, O.S.; et al. CO₂ electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. *Science* **2018**, *360*, 783–787. [[CrossRef](#)] [[PubMed](#)]
34. Li, C.W.; Ciston, J.; Kanan, M.W. Electroreduction of carbon monoxide to liquid fuel on oxide-derived nanocrystalline copper. *Nature* **2014**, *508*, 504. [[CrossRef](#)]
35. Chen, C.; Kotyk, J.F.K.; Sheehan, S.W. Progress toward Commercial Application of Electrochemical Carbon Dioxide Reduction. *Chem* **2018**, *4*, 2571–2586. [[CrossRef](#)]
36. Xie, J.; Zhao, X.; Wu, M.; Li, Q.; Wang, Y.; Yao, J. Metal-Free Fluorine-Doped Carbon Electrocatalyst for CO₂ Reduction Outcompeting Hydrogen Evolution. *Angew. Chem. Int. Ed.* **2018**, *57*, 9640–9644. [[CrossRef](#)]
37. Zhao, S.; Jin, R.X.; Jin, R.C. Opportunities and Challenges in CO₂ Reduction by Gold- and Silver-Based Electrocatalysts: From Bulk Metals to Nanoparticles and Atomically Precise Nanoclusters. *ACS Energy Lett.* **2018**, *3*, 452–462. [[CrossRef](#)]
38. Liu, M.; Pang, Y.; Zhang, B.; De Luna, P.; Voznyy, O.; Xu, J.; Zheng, X.; Dinh, C.T.; Fan, F.; Cao, C.; et al. Enhanced electrocatalytic CO₂ reduction via field-induced reagent concentration. *Nature* **2016**, *537*, 382–386. [[CrossRef](#)] [[PubMed](#)]
39. Hsieh, Y.-C.; Betancourt, L.E.; Senanayake, S.D.; Hu, E.; Zhang, Y.; Xu, W.; Polyansky, D.E. Modification of CO₂ Reduction Activity of Nanostructured Silver Electrocatalysts by Surface Halide Anions. *ACS Appl. Energy Mater.* **2018**, *2*, 102–109. [[CrossRef](#)]
40. Luan, C.; Shao, Y.; Lu, Q.; Gao, S.; Huang, K.; Wu, H.; Yao, K. High-Performance Carbon Dioxide Electrocatalytic Reduction by Easily Fabricated Large-Scale Silver Nanowire Arrays. *ACS Appl. Mater. Interfaces* **2018**, *10*, 17950–17956. [[CrossRef](#)]
41. Peng, X.; Karakalos, S.G.; Mustain, W.E. Preferentially Oriented Ag Nanocrystals with Extremely High Activity and Faradaic Efficiency for CO₂ Electrochemical Reduction to CO. *ACS Appl. Mater. Interfaces* **2018**, *10*, 1734–1742. [[CrossRef](#)]
42. Lu, Q.; Rosen, J.; Zhou, Y.; Hutchings, G.; Kimmel, Y.C.; Chen, J.G.; Jiao, F. A selective and efficient electrocatalyst for carbon dioxide reduction. *Nat. Commun.* **2014**, *5*, 3242. [[CrossRef](#)] [[PubMed](#)]
43. Gao, D.; Zhou, H.; Wang, J.; Miao, S.; Yang, F.; Wang, G.; Wang, J.; Bao, X. Size-Dependent Electrocatalytic Reduction of CO₂ over Pd Nanoparticles. *J. Am. Chem. Soc.* **2015**, *137*, 4288–4291. [[CrossRef](#)] [[PubMed](#)]
44. Wakerley, D.; Lamaison, S.; Ozanam, F.; Menguy, N.; Mercier, D.; Marcus, P.; Fontecave, M.; Mougel, V. Bio-inspired hydrophobicity promotes CO₂ reduction on a Cu surface. *Nat. Mater.* **2019**, *18*, 1222–1227. [[CrossRef](#)] [[PubMed](#)]
45. Feng, Y.; Cheng, C.Q.; Zou, C.Q.; Zheng, X.L.; Mao, J.; Liu, H.; Li, Z.; Dong, C.K.; Du, X.W. Electroreduction of Carbon Dioxide in Metallic Nanopores through a Pincer Mechanism. *Angew. Chem. Int. Ed.* **2020**, *59*, 19297–19303. [[CrossRef](#)]
46. Reske, R.; Mistry, H.; Behafarid, F.; Cuenya, B.R.; Strasser, P. Particle Size Effects in the Catalytic Electroreduction of CO₂ on Cu Nanoparticles. *J. Am. Chem. Soc.* **2014**, *136*, 6978–6986. [[CrossRef](#)] [[PubMed](#)]
47. Cheng, Y.; Zhao, S.; Johannessen, B.; Veder, J.; Saunders, M.; Rowles, M.R.; Cheng, M.; Liu, C.; Chisholm, M.F.; De Marco, R.; et al. Atomically Dispersed Transition Metals on Carbon Nanotubes with Ultrahigh Loading for Selective Electrochemical Carbon Dioxide Reduction. *Adv. Mater.* **2018**, *30*, e1706287. [[CrossRef](#)]
48. Yang, H.; Wu, Y.; Li, G.; Lin, Q.; Hu, Q.; Zhang, Q.; Liu, J.; He, C. Scalable Production of Efficient Single-Atom Copper Decorated Carbon Membranes for CO₂ Electroreduction to Methanol. *J. Am. Chem. Soc.* **2019**, *141*, 12717–12723. [[CrossRef](#)]
49. Ju, W.; Bagger, A.; Hao, G.-P.; Varela, A.S.; Sinev, I.; Bon, V.; Cuenya, B.R.; Kaskel, S.; Rossmeisl, J.; Strasser, P. Understanding activity and selectivity of metal-nitrogen-doped carbon catalysts for electrochemical reduction of CO₂. *Nat. Commun.* **2017**, *8*, 944. [[CrossRef](#)]
50. Xin, Z.; Liu, J.; Wang, X.; Shen, K.; Yuan, Z.; Chen, Y.; Lan, Y.-Q. Implanting Polypyrrole in Metal-Porphyrin MOFs: Enhanced Electrocatalytic Performance for CO₂RR. *ACS Appl. Mater. Interfaces* **2021**, *13*, 54959–54966. [[CrossRef](#)]
51. Cheng, Y.; Veder, J.-P.; Thomsen, L.; Zhao, S.; Saunders, M.; Demichelis, R.; Liu, C.; De Marco, R.; Jiang, S.P. Electrochemically substituted metal phthalocyanines, e-MPC (M = Co, Ni), as highly active and selective catalysts for CO₂ reduction. *J. Mater. Chem. A* **2017**, *6*, 1370–1375. [[CrossRef](#)]
52. Xin, Z.; Wang, Y.-R.; Chen, Y.; Li, W.-L.; Dong, L.-Z.; Lan, Y.-Q. Metallocene implanted metalloporphyrin organic framework for highly selective CO₂ electroreduction. *Nano Energy* **2019**, *67*, 104233. [[CrossRef](#)]
53. Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. Nitrogen-Doped Carbon Nanotube Arrays with High Electrocatalytic Activity for Oxygen Reduction. *Science* **2009**, *323*, 760–764. [[CrossRef](#)] [[PubMed](#)]
54. Liu, Y.; Zhang, Y.; Cheng, K.; Quan, X.; Fan, X.; Su, Y.; Chen, S.; Zhao, H.; Zhang, Y.; Yu, H.; et al. Selective Electrochemical Reduction of Carbon Dioxide to Ethanol on a Boron- and Nitrogen-Co-doped Nanodiamond. *Angew. Chem. Int. Ed.* **2017**, *56*, 15607–15611. [[CrossRef](#)]
55. Wang, H.; Jia, J.; Song, P.; Wang, Q.; Li, D.; Min, S.; Qian, C.; Wang, L.; Li, Y.F.; Ma, C.; et al. Efficient Electrocatalytic Reduction of CO₂ by Nitrogen-Doped Nanoporous Carbon/Carbon Nanotube Membranes: A Step Towards the Electrochemical CO₂ Refinery. *Angew. Chem. Int. Ed.* **2017**, *56*, 7847–7852. [[CrossRef](#)]
56. Sharma, P.P.; Wu, J.; Yadav, R.M.; Liu, M.; Wright, C.J.; Tiwary, C.S.; Yakobson, B.I.; Lou, J.; Ajayan, P.M.; Zhou, X.-D. Nitrogen-Doped Carbon Nanotube Arrays for High-Efficiency Electrochemical Reduction of CO₂: On the Understanding of Defects, Defect Density, and Selectivity. *Angew. Chem. Int. Ed.* **2015**, *54*, 13701–13705. [[CrossRef](#)]

57. Grosse, P.; Gao, D.; Scholten, F.; Sinev, I.; Mistry, H.; Cuenya, B.R. Dynamic Changes in the Structure, Chemical State and Catalytic Selectivity of Cu Nanocubes during CO₂ Electroreduction: Size and Support Effects. *Angew. Chem. Int. Ed.* **2018**, *57*, 6192–6197. [[CrossRef](#)]
58. Nellaiappan, S.; Katiyar, N.K.; Kumar, R.; Parui, A.; Malviya, K.D.; Pradeep, K.G.; Singh, A.K.; Sharma, S.; Tiwary, C.S.; Biswas, K. High-Entropy Alloys as Catalysts for the CO₂ and CO Reduction Reactions: Experimental Realization. *ACS Catal.* **2020**, *10*, 3658–3663. [[CrossRef](#)]
59. Luo, W.; Nie, X.; Janik, M.J.; Asthagiri, A. Facet Dependence of CO₂ Reduction Paths on Cu Electrodes. *ACS Catal.* **2016**, *6*, 219–229. [[CrossRef](#)]
60. Jiang, K.; Sandberg, R.B.; Akey, A.J.; Liu, X.; Bell, D.C.; Nørskov, J.K.; Chan, K.; Wang, H. Metal ion cycling of Cu foil for selective C–C coupling in electrochemical CO₂ reduction. *Nat. Catal.* **2018**, *1*, 111–119. [[CrossRef](#)]
61. De Gregorio, G.L.; Burdyny, T.; Loiudice, A.; Iyengar, P.; Smith, W.A.; Buonsanti, R. Facet-Dependent Selectivity of Cu Catalysts in Electrochemical CO₂ Reduction at Commercially Viable Current Densities. *ACS Catal.* **2020**, *10*, 4854–4862. [[CrossRef](#)] [[PubMed](#)]
62. Karapinar, D.; Huan, N.T.; Sahraie, N.R.; Li, J.; Wakerley, D.; Touati, N.; Zanna, S.; Taverna, D.; Tizei, L.H.G.; Zitolo, A.; et al. Electroreduction of CO₂ on Single-Site Copper-Nitrogen-Doped Carbon Material: Selective Formation of Ethanol and Reversible Restructuration of the Metal Sites. *Angew. Chem. Int. Ed.* **2019**, *58*, 15098–15103. [[CrossRef](#)] [[PubMed](#)]
63. Wang, X.; Wang, Z.; de Arquer, F.P.G.; Dinh, C.-T.; Ozden, A.; Li, Y.C.; Nam, D.-H.; Li, J.; Liu, Y.-S.; Wicks, J.; et al. Efficient electrically powered CO₂-to-ethanol via suppression of deoxygenation. *Nat. Energy* **2020**, *5*, 478–486. [[CrossRef](#)]
64. Zhao, K.; Nie, X.; Wang, H.; Chen, S.; Quan, X.; Yu, H.; Choi, W.; Zhang, G.; Kim, B.; Chen, J.G. Selective electroreduction of CO₂ to acetone by single copper atoms anchored on N-doped porous carbon. *Nat. Commun.* **2020**, *11*, 2455. [[CrossRef](#)] [[PubMed](#)]
65. Nam, D.-H.; Bushuyev, O.S.; Li, J.; De Luna, P.; Seifitokaldani, A.; Dinh, C.-T.; de Arquer, F.P.G.; Wang, Y.; Liang, Z.; Proppe, A.H.; et al. Metal–Organic Frameworks Mediate Cu Coordination for Selective CO₂ Electroreduction. *J. Am. Chem. Soc.* **2018**, *140*, 11378–11386. [[CrossRef](#)] [[PubMed](#)]
66. Wu, J.X.; Hou, S.Z.; Zhang, X.D.; Xu, M.; Yang, H.F.; Cao, P.S.; Gu, Z. Cathodized copper porphyrin metal-organic framework nanosheets for selective formate and acetate production from CO₂ electroreduction. *Chem. Sci.* **2019**, *10*, 2199–2205. [[CrossRef](#)] [[PubMed](#)]
67. Huang, J.; Mensi, M.; Oveisi, E.; Mantella, V.; Buonsanti, R. Structural Sensitivities in Bimetallic Catalysts for Electrochemical CO₂ Reduction Revealed by Ag–Cu Nanodimers. *J. Am. Chem. Soc.* **2019**, *141*, 2490–2499. [[CrossRef](#)]
68. Fang, X.; Men, Y.; Wu, F.; Zhao, Q.; Singh, R.; Xiao, P.; Du, T.; Webley, P.A. Improved methanol yield and selectivity from CO₂ hydrogenation using a novel Cu-ZnO-ZrO₂ catalyst supported on Mg-Al layered double hydroxide (LDH). *J. CO₂ Util.* **2019**, *29*, 57–64. [[CrossRef](#)]
69. Liu, J.; Zhang, A.; Jiang, X.; Liu, M.; Sun, Y.; Song, C.; Guo, X. Selective CO₂ Hydrogenation to Hydrocarbons on Cu-Promoted Fe-Based Catalysts: Dependence on Cu-Fe Interaction. *ACS Sustain. Chem. Eng.* **2018**, *6*, 10182–10190. [[CrossRef](#)]
70. Lin, W.; Chen, H.; Li, Z.; Sasaki, K.; Yao, S.; Zhang, Z.; Li, J.; Fu, J. A Cu₂O-derived Polymeric Carbon Nitride Heterostructured Catalyst for the Electrochemical Reduction of Carbon Dioxide to Ethylene. *ChemSuschem* **2021**, *14*, 3190–3197. [[CrossRef](#)]
71. Ma, X.; Tian, J.; Wang, M.; Jin, X.; Shen, M.; Zhang, L. Metal-organic framework derived carbon supported Cu-In nanoparticles for highly selective CO₂ electroreduction to CO. *Catal. Sci. Technol.* **2021**, *11*, 6096–6102. [[CrossRef](#)]
72. Zhu, H.L.; Huang, J.R.; Zhang, X.W.; Wang, C.; Huang, N.Y.; Liao, P.Q.; Chen, X.M. Highly Efficient Electroconversion of CO₂ into CH₄ by a Metal-Organic Framework with Trigonal Pyramidal Cu(I)N₃ Active Sites. *ACS Catal.* **2021**, *11*, 11786–11792. [[CrossRef](#)]
73. Chen, C.; Pang, Y.; Zhang, F.; Zhong, J.; Zhang, B.; Cheng, Z. Sharp Cu@Sn nanocones on Cu foam for highly selective and efficient electrochemical reduction of CO₂ to formate. *J. Mater. Chem. A* **2018**, *6*, 19621–19630. [[CrossRef](#)]
74. Ye, K.; Cao, A.; Shao, J.; Wang, G.; Si, R.; Ta, N.; Xiao, J.; Wang, G. Synergy effects on Sn-Cu alloy catalyst for efficient CO₂ electroreduction to formate with high mass activity. *Sci. Bull.* **2020**, *65*, 711–719. [[CrossRef](#)]
75. Mellmann, D.; Sponholz, P.; Junge, H.; Beller, M. Formic acid as a hydrogen storage material—Development of homogeneous catalysts for selective hydrogen release. *Chem. Soc. Rev.* **2016**, *45*, 3954–3988. [[CrossRef](#)] [[PubMed](#)]
76. Liu, B.; Xie, Y.; Wang, X.; Gao, C.; Chen, Z.; Wu, J.; Meng, H.; Song, Z.; Du, S.; Ren, Z. Copper-triggered delocalization of bismuth p-orbital favours high-throughput CO₂ electroreduction. *Appl. Catal. B Environ.* **2022**, *301*, 120781. [[CrossRef](#)]
77. Liu, X.; Li, B.Q.; Ni, B.; Wang, L.; Peng, H.J. A perspective on the electrocatalytic conversion of carbon dioxide to methanol with metallomacrocyclic catalysts. *J. Energy Chem.* **2022**, *64*, 263–275. [[CrossRef](#)]
78. Zhao, Q.; Zhang, C.; Hu, R.; Du, Z.; Gu, J.; Cui, Y.; Chen, X.; Xu, W.; Cheng, Z.; Li, S.; et al. Selective Etching Quaternary MAX Phase toward Single Atom Copper Immobilized MXene (Ti₃C₂Cl_x) for Efficient CO₂ Electroreduction to Methanol. *ACS Nano* **2021**, *15*, 4927–4936. [[CrossRef](#)]
79. Zhu, C.Z.; Shi, Q.R.; Fu, S.F.; Song, J.H.; Xia, H.B.; Du, D.; Lin, Y.H. Efficient Synthesis of MCu (M = Pd, Pt, and Au) Aerogels with Accelerated Gelation Kinetics and their High Electrocatalytic Activity. *Adv. Mater.* **2016**, *28*, 8779–8783. [[CrossRef](#)]
80. Wang, Y.; Niu, C.; Zhu, Y.; He, D.; Huang, W. Tunable Syngas Formation from Electrochemical CO₂ Reduction on Copper Nanowire Arrays. *ACS Appl. Energy Mater.* **2020**, *3*, 9841–9847. [[CrossRef](#)]
81. Fan, Z.X.; Chen, Y.; Zhu, Y.H.; Wang, J.; Li, B.; Zong, Y.; Han, Y.; Zhang, H. Epitaxial growth of unusual 4H hexagonal Ir, Rh, Os, Ru and Cu nanostructures on 4H Au nanoribbons. *Chem. Sci.* **2017**, *8*, 795–799. [[CrossRef](#)]
82. Yan, S.; Mahyoub, S.A.; Zhong, J.; Chen, C.; Zhang, F.; Cheng, Z. Ultrathin and dense Ag nanosheets synthesis under suppressed face (111) growth and surface diffusion. *J. Power Sources* **2021**, *488*, 229484. [[CrossRef](#)]

83. Ming, M.; Zhang, Y.; He, C.; Zhao, L.; Niu, S.; Fan, G.Y.; Hu, J.S. Room-Temperature Sustainable Synthesis of Selected Platinum Group Metal (PGM = Ir, Rh, and Ru) Nanocatalysts Well-Dispersed on Porous Carbon for Efficient Hydrogen Evolution and Oxidation. *Small* **2019**, *15*, e1903057. [[CrossRef](#)]
84. Sun, Y.; Zhao, Z.; Suematsu, K.; Li, P.; Yu, Z.; Zhang, W.; Hu, J.; Shimano, K. Rapid and Stable Detection of Carbon Monoxide in Changing Humidity Atmospheres Using Clustered $\text{In}_2\text{O}_3/\text{CuO}$ Nanospheres. *ACS Sens.* **2020**, *5*, 1040–1049. [[CrossRef](#)]
85. Lu, L.; Sun, X.; Ma, J.; Yang, D.; Wu, H.; Zhang, B.; Zhang, J.; Han, B. Highly Efficient Electroreduction of CO_2 to Methanol on Palladium-Copper Bimetallic Aerogels. *Angew. Chem. Int. Ed.* **2018**, *57*, 14149–14153. [[CrossRef](#)] [[PubMed](#)]
86. Zhan, P.; Yang, S.; Chu, M.G.; Zhu, Q.; Zhuang, Y.; Ren, C.; Chen, Z.Y.; Lu, L.; Qin, P.Y. Amorphous Copper-modified Gold Interface Promotes Selective CO_2 Electroreduction to CO. *Chemcatchem* **2022**, *14*, e202200109. [[CrossRef](#)]
87. Zhi, X.; Jiao, Y.; Zheng, Y.; Vasileff, A.; Qiao, S.Z. Selectivity roadmap for electrochemical CO_2 reduction on copper-based alloy catalysts. *Nano Energy* **2020**, *71*, 104601. [[CrossRef](#)]
88. Kim, D.; Resasco, J.; Yu, Y.; Asiri, A.M.; Yang, P. Synergistic geometric and electronic effects for electrochemical reduction of carbon dioxide using gold–copper bimetallic nanoparticles. *Nat. Commun.* **2014**, *5*, 4948. [[CrossRef](#)]
89. Mahyoub, S.A.; Qaraah, F.A.; Yan, S.; Hezam, A.; Chen, C.; Zhong, J.; Cheng, Z. 3D Cu/In nanocones by morphological and interface engineering design in achieving a high current density for electroreduction of CO_2 to syngas under elevated pressure. *J. CO₂ Util.* **2022**, *61*, 102033. [[CrossRef](#)]
90. Cheng, T.; Xiao, H.; Goddard, W.A., III. Free-Energy Barriers and Reaction Mechanisms for the Electrochemical Reduction of CO on the Cu(100) Surface, Including Multiple Layers of Explicit Solvent at pH 0. *J. Phys. Chem. Lett.* **2015**, *6*, 4767–4773. [[CrossRef](#)]
91. Gattrell, M.; Gupta, N.; Co, A. A review of the aqueous electrochemical reduction of CO_2 to hydrocarbons at copper. *J. Electroanal. Chem.* **2006**, *594*, 1–19. [[CrossRef](#)]
92. Wang, X.; Ou, P.; Wicks, J.; Xie, Y.; Wang, Y.; Li, J.; Tam, J.; Ren, D.; Howe, J.Y.; Wang, Z.; et al. Gold-in-copper at low *CO coverage enables efficient electromethanation of CO_2 . *Nat. Commun.* **2021**, *12*, 3387. [[CrossRef](#)] [[PubMed](#)]
93. Zhou, X.; Jin, H.; Xia, B.Y.; Davey, K.; Zheng, Y.; Qiao, S.Z. Molecular Cleavage of Metal–Organic Frameworks and Application to Energy Storage and Conversion. *Adv. Mater.* **2021**, *33*, 2104341. [[CrossRef](#)] [[PubMed](#)]
94. Lei, Q.; Zhu, H.; Song, K.; Wei, N.; Liu, L.; Zhang, D.; Yin, J.; Dong, X.; Yao, K.; Wang, N.; et al. Investigating the Origin of Enhanced C_{2+} Selectivity in Oxide-/Hydroxide-Derived Copper Electrodes during CO_2 Electroreduction. *J. Am. Chem. Soc.* **2020**, *142*, 4213–4222. [[CrossRef](#)] [[PubMed](#)]
95. Wang, J.; Tan, H.Y.; Zhu, Y.; Chu, H.; Chen, H.M. Linking the Dynamic Chemical State of Catalysts with the Product Profile of Electrocatalytic CO_2 Reduction. *Angew. Chem. Int. Ed.* **2021**, *60*, 17254–17267. [[CrossRef](#)] [[PubMed](#)]
96. Zhou, X.L.; Shan, J.Q.; Chen, L.; Xia, B.Y.; Ling, T.; Duan, J.J.; Jiao, Y.; Zheng, Y.; Qiao, S.Z. Stabilizing Cu^{2+} Ions by Solid Solutions to Promote CO_2 Electroreduction to Methane. *J. Am. Chem. Soc.* **2022**, *144*, 2079–2084. [[CrossRef](#)]
97. Gao, F.Y.; Hu, S.J.; Zhang, X.L.; Zheng, Y.R.; Wang, H.J.; Niu, Z.Z.; Yang, P.P.; Bao, R.C.; Ma, T.; Dang, Z.; et al. High-Curvature Transition-Metal Chalcogenide Nanostructures with a Pronounced Proximity Effect Enable Fast and Selective CO_2 Electroreduction. *Angew. Chem. Int. Ed.* **2020**, *59*, 8706–8712. [[CrossRef](#)]
98. Yang, P.P.; Zhang, X.L.; Gao, F.Y.; Zheng, Y.R.; Niu, Z.Z.; Yu, X.; Liu, R.; Wu, Z.Z.; Qin, S.; Chi, L.P.; et al. Protecting Copper Oxidation State via Intermediate Confinement for Selective CO_2 Electroreduction to C_{2+} Fuels. *J. Am. Chem. Soc.* **2020**, *142*, 6400–6408. [[CrossRef](#)] [[PubMed](#)]
99. Sun, X.; Zhu, Q.; Kang, X.; Liu, H.; Qian, Q.; Zhang, Z.; Han, B. Molybdenum-Bismuth Bimetallic Chalcogenide Nanosheets for Highly Efficient Electrocatalytic Reduction of Carbon Dioxide to Methanol. *Angew. Chem. Int. Ed.* **2016**, *55*, 6771–6775. [[CrossRef](#)]
100. Yang, H.P.; Yue, Y.N.; Qin, S.; Wang, H.; Lu, J.X. Selective electrochemical reduction of CO_2 to different alcohol products by an organically doped alloy catalyst. *Green Chem.* **2016**, *18*, 3216–3220. [[CrossRef](#)]
101. Li, Y.; Cui, F.; Ross, M.B.; Kim, D.; Sun, Y.; Yang, P. Structure-Sensitive CO_2 Electroreduction to Hydrocarbons on Ultrathin 5-fold Twinned Copper Nanowires. *Nano Lett.* **2017**, *17*, 1312–1317. [[CrossRef](#)] [[PubMed](#)]
102. Lin, S.-C.; Chang, C.-C.; Chiu, S.-Y.; Pai, H.-T.; Liao, T.-Y.; Hsu, C.-S.; Chiang, W.-H.; Tsai, M.-K.; Chen, H.M. Operando time-resolved X-ray absorption spectroscopy reveals the chemical nature enabling highly selective CO_2 reduction. *Nat. Commun.* **2020**, *11*, 3525. [[CrossRef](#)]
103. Tan, X.; Yu, C.; Zhao, C.; Huang, H.; Yao, X.; Han, X.; Guo, W.; Cui, S.; Huang, H.; Qiu, J. Restructuring of Cu_2O to $\text{Cu}_2\text{O}@\text{Cu}$ -Metal-Organic Frameworks for Selective Electrochemical Reduction of CO_2 . *ACS Appl. Mater. Interfaces* **2019**, *11*, 9904–9910. [[CrossRef](#)] [[PubMed](#)]
104. Ren, D.; Deng, Y.; Handoko, A.D.; Chen, C.S.; Malkhandi, S.; Yeo, B.S. Selective Electrochemical Reduction of Carbon Dioxide to Ethylene and Ethanol on Copper(I) Oxide Catalysts. *ACS Catal.* **2015**, *5*, 2814–2821. [[CrossRef](#)]
105. Qiu, Y.L.; Zhong, H.X.; Zhang, T.T.; Xu, W.B.; Su, P.P.; Li, X.F.; Zhang, H.M. Selective Electrochemical Reduction of Carbon Dioxide Using Cu Based Metal Organic Framework for CO_2 Capture. *ACS Appl. Mater. Interfaces* **2018**, *10*, 2480–2489. [[CrossRef](#)] [[PubMed](#)]
106. Zhang, S.; Liu, L.; Yang, J.; Zhang, Y.; Wan, Z.; Zhou, L. Pd-Ru-Bi nanoalloys modified three-dimensional reduced graphene oxide/MOF-199 composites as a highly efficient electrocatalyst for ethylene glycol electrooxidation. *Appl. Surf. Sci.* **2019**, *492*, 617–625. [[CrossRef](#)]
107. Zhao, Y.; Zheng, L.; Jiang, D.; Xia, W.; Xu, X.; Yamauchi, Y.; Ge, J.; Tang, J. Nanoengineering Metal-Organic Framework-Based Materials for Use in Electrochemical CO_2 Reduction Reactions. *Small* **2021**, *17*, 202006590. [[CrossRef](#)]

108. Diercks, C.S.; Liu, Y.; Cordova, K.E.; Yaghi, O.M. The role of reticular chemistry in the design of CO₂ reduction catalysts. *Nat. Mater.* **2018**, *17*, 301–307. [[CrossRef](#)]
109. Yang, X.; Cheng, J.; Yang, X.; Xu, Y.; Sun, W.F.; Zhou, J.H. MOF-derived Cu@Cu₂O heterogeneous electrocatalyst with moderate intermediates adsorption for highly selective reduction of CO₂ to methanol. *Chem. Eng. J.* **2022**, *431*, 134171. [[CrossRef](#)]
110. Gu, J.; Héroguel, F.; Luterbacher, J.; Hu, X. Densely Packed, Ultra Small SnO Nanoparticles for Enhanced Activity and Selectivity in Electrochemical CO₂ Reduction. *Angew. Chem. Int. Ed.* **2018**, *57*, 2943–2947. [[CrossRef](#)]
111. Zhang, A.; Liang, Y.; Li, H.; Wang, S.; Chang, Q.; Peng, K.; Geng, Z.; Zeng, J. Electronic Tuning of SnS₂ Nanosheets by Hydrogen Incorporation for Efficient CO₂ Electroreduction. *Nano Lett.* **2021**, *21*, 7789–7795. [[CrossRef](#)]
112. Hou, X.; Cai, Y.; Zhang, D.; Li, L.; Zhang, X.; Zhu, Z.; Peng, L.; Liu, Y.; Qiao, J. 3D core-shell porous-structured Cu@Sn hybrid electrodes with unprecedented selective CO₂-into-formate electroreduction achieving 100%. *J. Mater. Chem. A* **2019**, *7*, 3197–3205. [[CrossRef](#)]
113. Lu, W.; Zhou, J.; Kong, F.; Fang, H.; Wang, W. Porous tin-based film deposited on copper foil for electrochemical reduction of carbon dioxide to formate. *Int. J. Hydrogen Energy* **2016**, *41*, 1585–1591. [[CrossRef](#)]
114. Jeon, H.S.; Timoshenko, J.; Rettenmaier, C.; Herzog, A.; Yoon, A.; Chee, S.W.; Oener, S.; Hejral, U.; Haase, F.T.; Cuenya, B.R. Selectivity Control of Cu Nanocrystals in a Gas-Fed Flow Cell through CO₂ Pulsed Electroreduction. *J. Am. Chem. Soc.* **2021**, *143*, 7578–7587. [[CrossRef](#)]
115. Chen, D.; Yao, Q.; Cui, P.; Liu, H.; Xie, J.; Yang, J. Tailoring the Selectivity of Bimetallic Copper-Palladium Nanoalloys for Electrocatalytic Reduction of CO₂ to CO. *ACS Appl. Energy Mater.* **2018**, *1*, 883–890. [[CrossRef](#)]
116. Yan, Y.J.; Peng, Y.Y.; Song, Y.C.; Wang, R.Y.; Wang, H.; Bian, Z.Y. Polyethyleneimine-reinforced Sn/Cu foam dendritic self-supporting catalytic cathode for CO₂ reduction to HCOOH. *Chemosphere* **2022**, *301*, 134704. [[CrossRef](#)]
117. Chen, G.Q.; Ye, D.D.; Chen, R.; Li, J.; Zhu, X.; Liao, Q. Enhanced efficiency for carbon dioxide electroreduction to formate by electrodeposition Sn on Cu nanowires. *J. CO₂ Util.* **2021**, *44*, 101409. [[CrossRef](#)]
118. Liu, H.; Zhu, Y.; Ma, J.; Zhang, Z.; Hu, W. Recent Advances in Atomic-Level Engineering of Nanostructured Catalysts for Electrochemical CO₂ Reduction. *Adv. Funct. Mater.* **2020**, *30*, 1910534. [[CrossRef](#)]
119. Liu, C.; Gong, J.; Gao, Z.; Xiao, L.; Wang, G.; Lu, J.; Zhuang, L. Regulation of the activity, selectivity, and durability of Cu-based electrocatalysts for CO₂ reduction. *Sci. China Chem.* **2021**, *64*, 1660–1678. [[CrossRef](#)]
120. Yin, Z.; Peng, H.; Wei, X.; Zhou, H.; Gong, J.; Huai, M.; Xiao, L.; Wang, G.; Lu, J.; Zhuang, L. An alkaline polymer electrolyte CO₂ electrolyzer operated with pure water. *Energy Environ. Sci.* **2019**, *12*, 2455–2462. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.