# Technologies of CO2 Reduction to Fuels in the Background of "Carbon Neutrality": Current Status, Analytic Comparison and Future Prospect

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**Abstract.** In the background of carbon neutrality, the reduction of $CO_2$ to fuel is a promising and valuable win-win technology that both reduces carbon dioxide emissions which is a major factor in the greenhouse effect and solves the energy crisis of the constant consumption of fossil fuels, enabling a carbon-neutral cycle and sustainable development. This article outlines and categorizes the current research progress and barriers and future perspectives of the main carbon dioxide conversion technologies of enzymatic, electrochemical, and photochemical catalysis, respectively, and introduces the technologies of them in which the products can be used as/converted into fuels (procedures, catalyst synthesis method, efficiency and yield, the corresponding principle and the product for fuel use), then analyzes and compares these technologies including advantages and disadvantages. It is found that although the current carbon dioxide conversion technology has made great achievements, modified enzymes, improved multi-enzyme systems, nanostructures, composite copper electrodes, co-photocatalysts, etc., have played an important role. However, poor product selectivity, poor catalyst stability, low reaction rate, high cost, etc., are still existing problems. Finally, the prospects of $CO_2$-to-fuel technology from technical, economic and policy aspects are presented in this paper to better apply in large-scale industry and commerce.

**Keywords:** $CO_2$ Reduction, Fuels, Enzymatic, Electrochemical, Photochemical.

## 1. Introduction

Global warming is one of the biggest environmental challenges and one of the global issues that people are most concerned about. It has caused more natural disasters, rising sea levels, increasing haze weather and other environmental impacts. The most critical factor leading to this problem is the excessive emission of $CO_2$ in the environment, which is the main gas of greenhouse gases, accounting for about 77% of emissions. The main reasons for the increase in the concentration of $CO_2$ in the environment are the industrial-scale exploitation of fossil fuels and the deforestation of forests for fuel. Therefore, the Intergovernmental Panel on Climate Change (IPCC) study resulted in the Paris Agreement: a global carbon neutrality coalition will be achieved by 2050. Many countries have echoed the call for carbon neutrality. As a result, effective technologies to reduce carbon dioxide emissions have developed rapidly. Carbon capture, storage and utilization (CCSU) is a viable strategy for lowering $CO_2$ levels in the environment. Among them, the technology of converting $CO_2$ into fuel in the utilization of carbon dioxide not only reduces the environmental problems caused by the concentration of carbon dioxide emissions but also solves the fossil fuel reserves dwindling energy crisis problem, which is an attractive way to achieve carbon-neutral cycle and sustainable development.

So far, carbon dioxide reduction technologies include enzymatic catalysis, chemical catalysis, electrochemical catalysis, photochemical catalysis, thermal catalysis, photoelectrochemical catalysis, etc. Some of the products of these technologies are fuels that can be transported and used on-demand and sustain and expand new transportation markets. Although many research results have been reported, carbon dioxide reduction technology is still a highly challenging task, mainly due to poor product selectivity, low yield, poor catalyst stability, low reaction rate, and high cost, which are the main limiting factors for industrial and commercial applications.

This article introduces the three main carbon dioxide conversion technologies of enzymatic reduction, electrochemical reduction, and photochemical reduction. The current status and working principles of these different conversion technologies are comprehensively summarized, of which produce products are fuel or can be converted into fuel; emerging technologies are introduced: procedures, catalyst synthesis method, efficiency and yield, the corresponding principle and the product for fuel use. Besides, the barriers and prospects for these three technologies are summarized, respectively. Furthermore, the introduced technologies, including their Pros and cons, are analyzed and compared, finally making a conclusion of prospect from three aspects of carbon dioxide conversion technology to better apply in industry and commerce in the future, to achieve carbon neutrality and sustainable development.

## 2. Enzymatic technology of CO2 reduction

### 2.1. Introduction of enzymatic technology

The enzymatic $CO_2$ reduction is one of the most effective technologies in $CO_2$ conversion, the metabolic process in cells is a common method for $CO_2$ reduction in nature. Inspired by this, the enzymatic technology in vitro provides a way to reduce $CO_2$.

The enzymatic conversion of CO2 in cells is an important way to reduce greenhouse gas in the atmosphere. In order to achieve this effectively, the Calvin cycle, the reductive citric acid cycle, the reductive acetyl-CoA pathway, the 3-hydroxypropionate cycle, the 3-hydroxypropionate/4-hydroxybutyrate cycle, and the dicarboxylate/4-hydroxybutyrate cycle are the six primary mechanisms used by cells. So far, the Calvin cycle (Figure 1) is the dominant method of CO2 conversion in nature used by photosynthetic organisms.

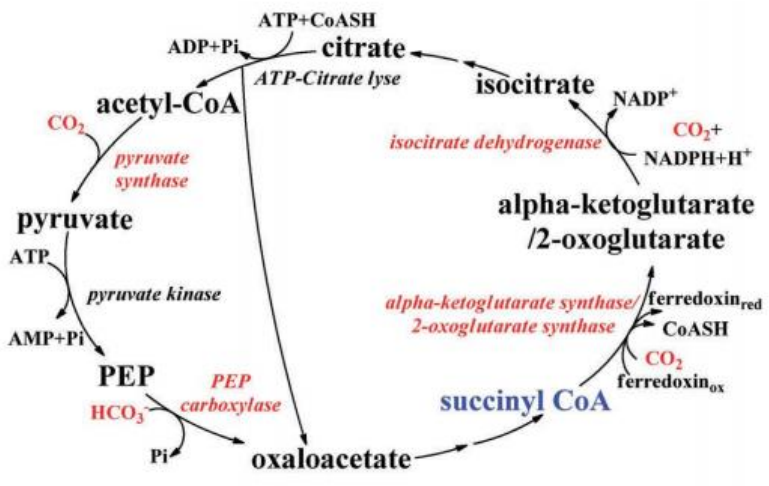



**Figure 1.** Diagram of Calvin cycle process [1].

The enzymatic reduction of carbon dioxide in vitro can be divided into two routes: conversion by a single enzyme and conversion by a multi-enzyme system. In the $CO_2$ reduction by the former way, through the enzymatic property, the enzyme can be summarized into two main categories: (1) oxidoreductases (formate dehydrogenase (FateDH), $CO_2$ reductase, remodeled nitrogenase, carbon monoxide dehydrogenase (CODH), etc.) (2) lyases ( carbonic anhydrase (CA), decarboxylases, etc.) [1].

### 2.2. Enzymatic CO2 reduction to fuel

Methane, a significant fuel, is the major component of natural gas, can also be used as a carbon source for solar cells and vapor chemical deposition of amorphous silicon films, and is widely used in civil and industrial applications produced from $CO_2$ reduction. Research has found that remodeled nitrogenase can produce methane to reduce $CO_2$. Seefeldt and co-workers have demonstrated that

several amino acids such as α-191$^{Gln}$, α-70$^{Val}$ and α-195$^{His}$ have side chains that approach nitrogenase MoFe-cofactor (Figure 2a) and control the substrate binding and the reduction. When α-70$^{Val}$/α-195$^{His}$ were respectively substituted into α-70$^{Ala}$/α-195$^{Gln}$, the MoFe protein catalyzed $CO_2$ to form methane (Equation 1) which produced nearly 16 nmol $CH_4$/nmol MoFe protein in 20 minutes (Figure 2b). The electron flux determines the catalytic rate through the nitrogenase and the partial pressure of $CO_2$ [2].

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (1)$$

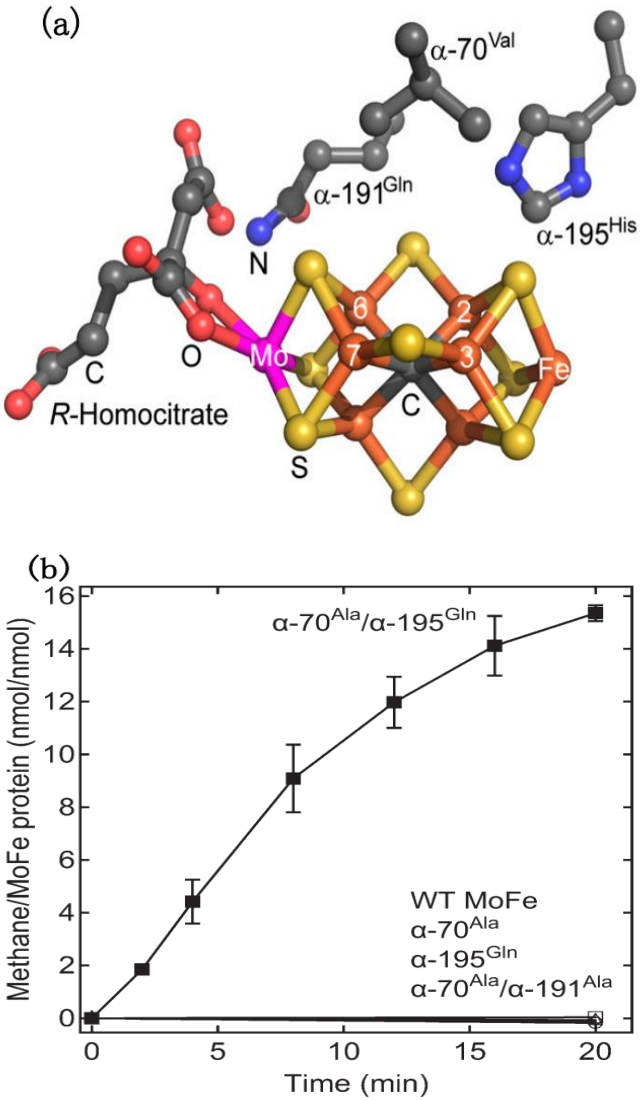



**Figure 2.** (a) Structure of the MoFe-cofactor with vital amino acid residues. (b) $CH_4$ formation for different MoFe proteins: α-70$^{Ala}$/α-195$^{Gln}$ (■) [2].

Methanol can be used as a new type of clean fuel after deep processing, replacing gasoline and diesel for various motor vehicles and boilers. It is an important new alternative energy. Dave and co-workers reported a method that uses formate dehydrogenase ($F_{ate}$DH), formaldehyde dehydrogenase ($F_{ald}$DH) and alcohol dehydrogenase (ADH) to catalyze the reaction in sequence, and the carbon dioxide is finally reduced to methanol through enzymatic coupling. In this process, the terminal electron donor of the catalytic reduction of each dehydrogenase is NADH. The catalytic process is shown in Figure 3 [3].

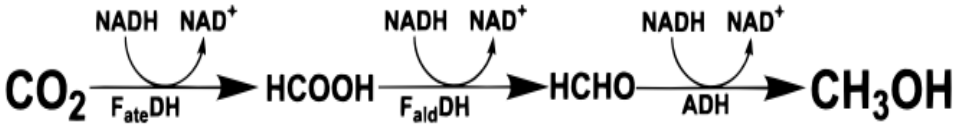
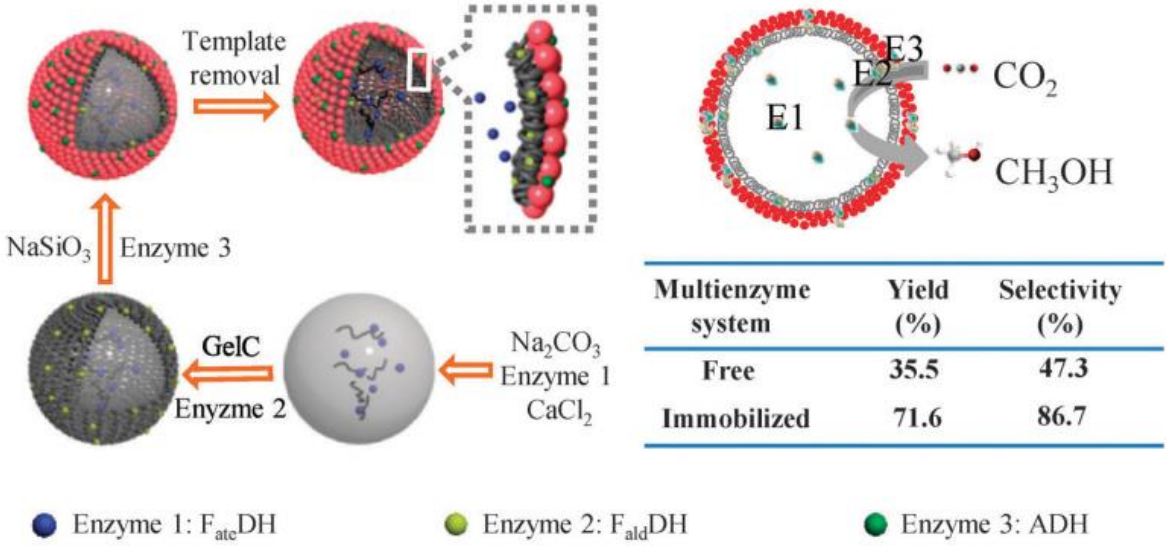



**Figure 3.** The process of three dehydrogenases catalyzes $CO_2$ to methanol [3].

Furthermore, Dave and co-workers also found that for the same concentration of NADH, the methanol yield of the three dehydrogenases in sol-gel (40-90%) was significantly higher than that in the free state (10-20%). They attributed this to confinement and matrix effects [3]. To improve the control of the flexibility of a single enzyme, $F_{ate}DH$, $F_{ald}DH$ and ADH were respectively immobilized in the capsule lumen, the GelC layer and the silica layer to convert $CO_2$ to methanol through biomimetic mineralization and bioadhesion-a multi-enzyme cascade system using hybrid microcapsules (Figure 4). The yield and selectivity of the method were significantly improved (71.6%and 86.7%) [4].




| Multienzyme system | Yield (%) | Selectivity (%) |
|---|---|---|
| Free | 35.5 | 47.3 |
| Immobilized | 71.6 | 86.7 |

**Figure 4.** The multi-enzyme catalytic process of $CO_2$ reduction to $CH_3OH$; The yield and the selectivity for the immobilized enzyme [4].

### 2.3. Barriers and prospects

Enzymes are usually expensive and environmentally sensitive, with poor reusability and low reaction rate, which limit industrial applications. Enzyme technology should be further developed to improve economic feasibility and discover new enzymes to improve catalytic efficiency.

In addition, the in vitro multi-enzyme system has complex reactions and relatively few pathways. A new multi-enzyme route should be constructed to promote the industrial development of enzymes. And simultaneously, it can be combined with photochemical and electrochemical techniques, which show great application potential to improve the reaction yield and selectivity [5].

## 3. Electrochemical technology of CO2 reduction

### 3.1. Introduction of electrochemical technology

Electrochemical $CO_2$ reduction is one of the most active technologies in $CO_2$ conversion. So far, electrolytes of the technology include aqueous, non-aqueous, solid, molten salt and gas, etc.

Typically, most electrochemical reaction is conducted in aqueous media. According to the reaction mechanism, the metal electrodes in aqueous media can divide into three categories (Figure 5): the first one contains Hg, Pb, Bi, etc., which don't combine the $CO_2$RR intermediate and can't reduce

CO, producing formate; the second one contains Au, Ag, Zn, etc. which combine the $CO_2$RR in different level, but still can't reduce CO, producing CO mostly; the last one contains only Cu which combines the $CO_2$RR and reduces CO as well, yielding higher reduction products. Therefore, only copper-based materials can yield hydrocarbon fuels from $CO_2$ reduction and commonly use effective catalysts. However, the product distribution on the electrode can significantly change under different conditions. Furthermore, in this media, the hydrogen evolution reaction (HER) must also be considered, which is easier for most metals to react and can compete with $CO_2$ catalyzed reactions.

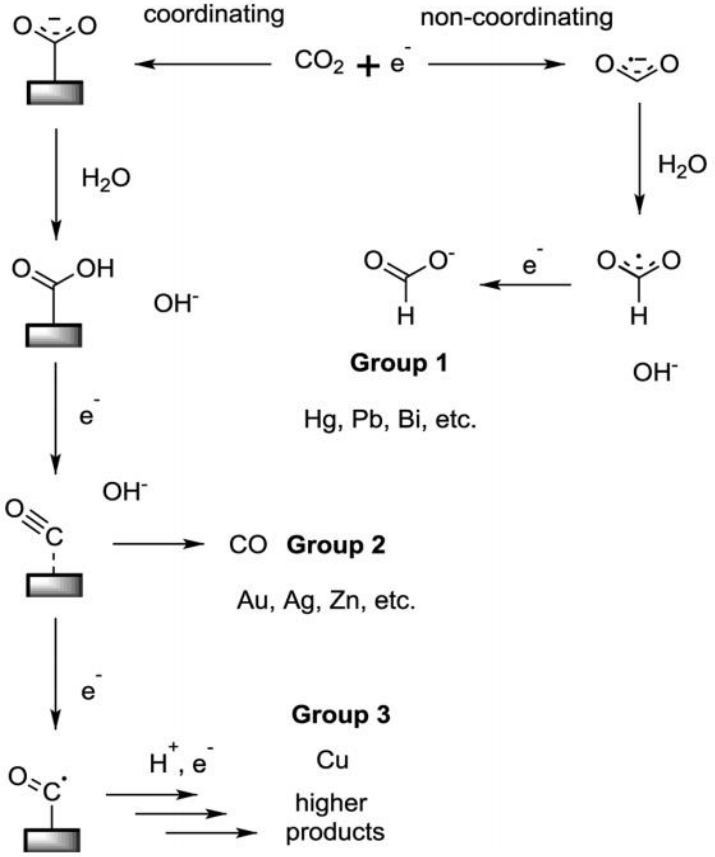



**Figure 5.** Classification of the metal electrodes in aqueous media [6].

The improved electrochemical methods of $CO_2$ reduction generally include reduction in flow cells, high-pressure system and molecular catalyst assisted reaction, etc. In addition, the $CO_2$ reduction efficiency normally uses Faradaic efficiency (FE) and energy efficiency (EE) to calculate [6].

### 3.2. Electrochemical CO2 reduction to fuel

Ethanol, a fuel and one of the ideal clean energy sources, can be added to gasoline as a vehicle fuel-ethanol gasoline to enhance oil product quality and performance while lowering emissions of harmful pollutants, including carbon monoxide and hydrocarbons. Xu and co-workers presented a carbon-supported Cu catalyst that uses an amalgamated Cu-Li method to synthesize (Figure 6). The catalyst demonstrated a high selectivity for ethanol (FE 91% at −0.7 V). They revealed that the key to this high FE is that the Cu single atoms (SA) have a high initial dispersion, which is the key for the dynamic transformation of Cu SA to $Cu_n$ to control the active site to form during the reaction, the hypothesized mechanism is shown in Figure 7 [7].

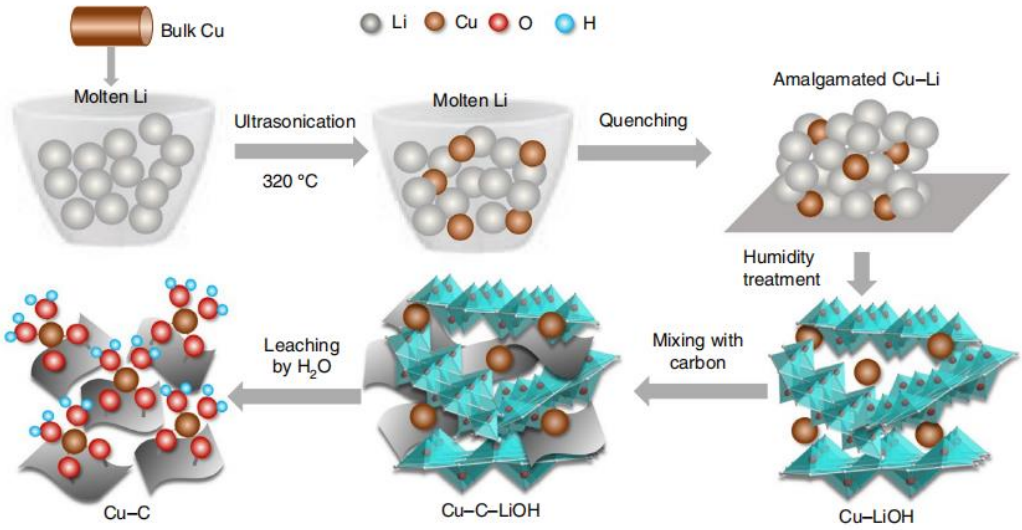



**Figure 6.** Process of the carbon-supported Cu SA catalyst synthesis [7].

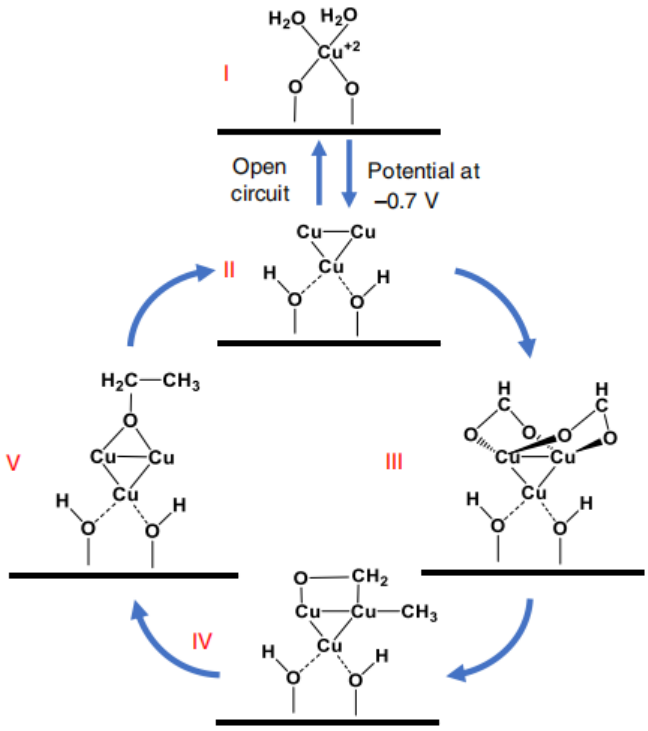



**Figure 7.** Illustration of the hypothesized reaction mechanism [7].

Ethylene, an important organic chemical basic material and one of the most basic materials in the petrochemical industry, is an important raw material for the synthesis of ethanol that can be used as fuel. Chen and co-workers presented polyamine-incorporated Cu electrodes, which can significantly develop the selectivity for ethylene production by co-electroplating. Their research used poly-N-(6-aminohexyl)acrylamide(P1) to prepare the P1-Cu electrode, which contains amine groups through co-electrodeposition on the GDL substrate (Figure 8) when the P1-Cu electrode in 10M KOH and at −0.47V cathode potential, a cell potential of 2.02V, for ethylene, the FE was 87% (Figure 9a). The full-cell energy efficiency was 50% (Figure 9b) higher than those presenting little or no amine electrodes. This behavior is because amino contributes to higher content of CO, higher surface pH and stabilization of intermediates [8].

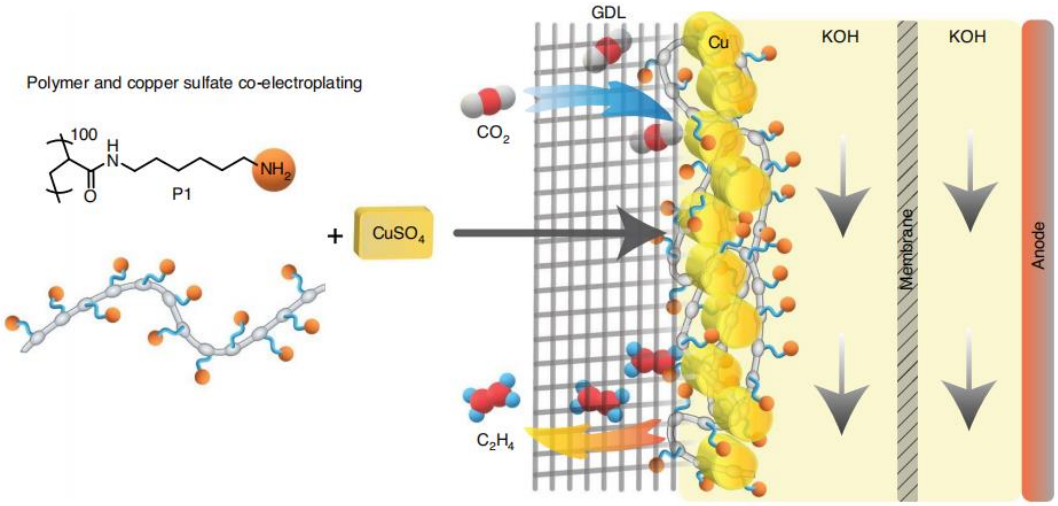



**Figure 8.** Diagram of preparation of P1 and Cu on GDL [8].

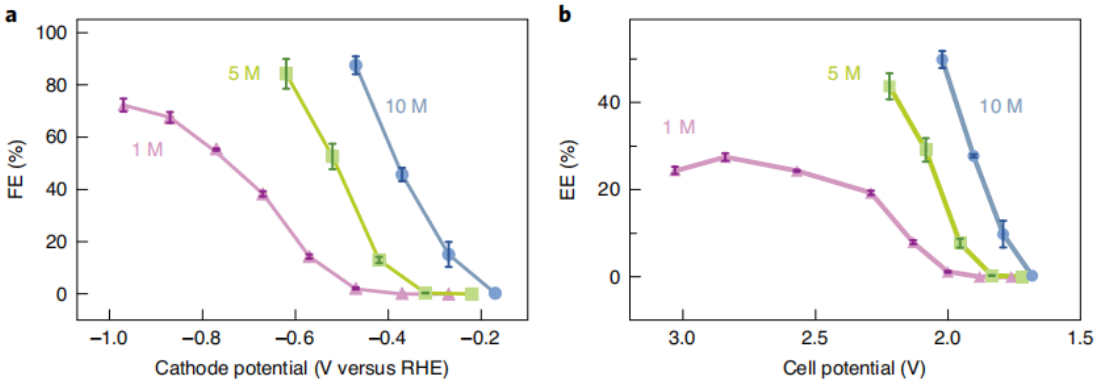



**Figure 9.** (a) The plot of FE of ethylene for different cathode potentials. (b) The plot of EE of ethylene for different cell potentials [8].

Methane, as introduced above, can also be produced in electrochemical $CO_2$ reduction. Cai and co-workers presented a carbon dots (CDs)-Cu SA catalyst with unique $CuN_2O_2$ sites anchored at the graphitic carbons' edges, which was synthesized by calcining at a low temperature from copper disodium EDTA (Figure 10). This catalyst exhibited extraordinary selectivity (99%) and high FE (78%. at −1.44V) for $CO_2$ reduction to methane which, due to the new electronic structure of the $CuN_2O_2$ site, in this structure, the HER is greatly suppressed and requires lower energy [9].

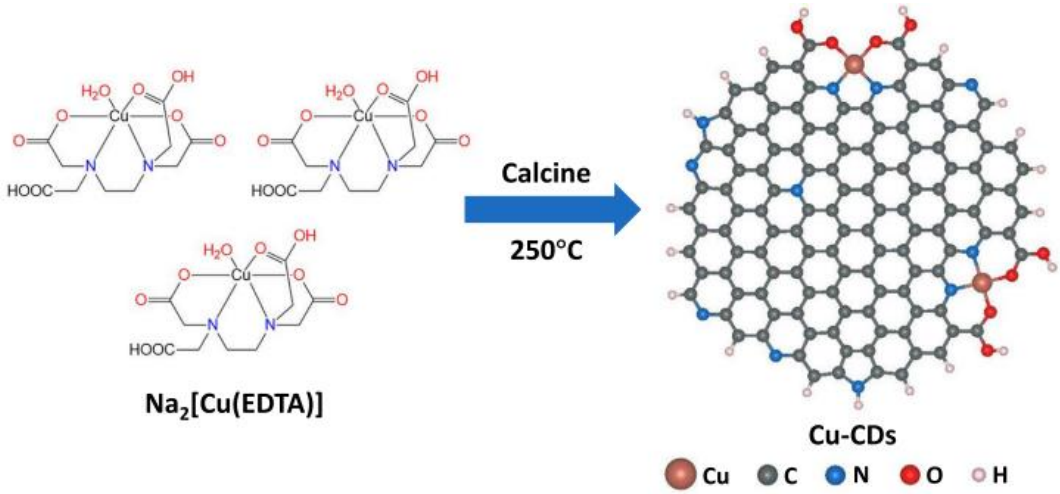



**Figure 10.** Illustration of synthesis of the Cu-CD catalysts [9].

### 3.3. Barriers and prospects

In electrochemical $CO_2$ reduction, the catalyst activity is generally low, and the product selectivity is relatively poor. Also, the product is usually a mixture, which is more difficult to separate. It is possible to fully use the synergistic effects between the components of catalytic materials and continue exploring the special morphology and structure of materials to develop new catalysts.

Additionally, the low stability and easy deactivation of catalysts, especially copper-based catalysts, seriously hinder the commercial application of electrochemical technology. It is essential to deeply research the electrochemical catalytic mechanism and material structure to analyze the factors affecting the stability. Moreover, catalysts' structural design and preparation should focus more on energy and economic considerations [10].

## 4. Photochemical technology of CO2 reduction

### 4.1. Introduction of photochemical technology

Photochemical $CO_2$ reduction is one of the most common technologies in $CO_2$ conversion. The basic mechanism is shown in Figure 11. Under the irradiation of incident light, when the photocatalyst absorbs photons, electrons are excited from the valence band (VB) to the conduction band (CB) and simultaneously generate the same number of electron-hole pairs in CB which are separated from each other and move to the photocatalyst surface's active sites. Electrons reduce the $CO_2$ adsorbed on the photocatalyst surface with $H_2O$. The process includes light absorption, excitation, photoelectron-hole separation and transfer, $CO_2$ adsorption, surface $CO_2$ reduction reaction, and product desorption. All the processes together affect the reaction efficiency. Furthermore, the product is determined by the number of electrons and protons involved in the reaction. Its selectivity may be determined by photocatalysts, reaction conditions, etc. [11,12].

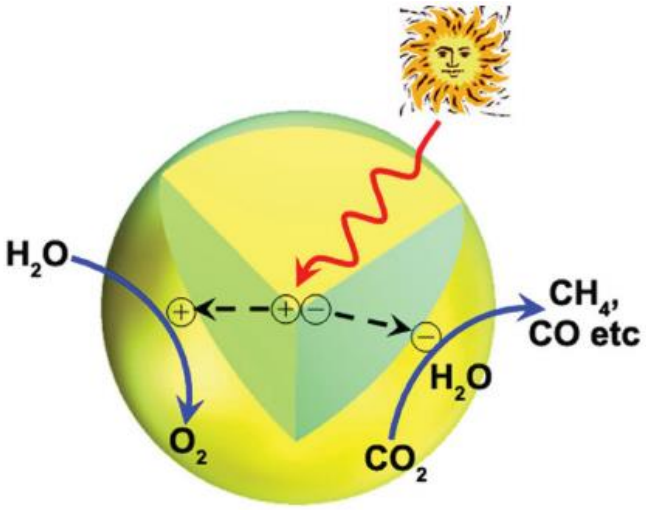



**Figure 11.** Diagram of the basic mechanism of photochemical $CO_2$ conversion [11].

Recently, different photocatalyst structures and surface characteristics have been explored, including bandgap engineering, nanostructuralization, surface oxygen vacancy engineering, macro/meso/microporous structurization, co-catalysts, exposure of highly active crystal facets, and Z-scheme construction, etc. [11].

### 4.2. Photochemical CO2 reduction to fuel

Methanol, as introduced above, a new type of clean fuel, can also be produced in photochemical $CO_2$ reduction. Penumaka and co-workers designed and synthesized photocatalytic nanostructure $Ni_2P$/CdS for the $CO_2$ conversion to $CH_3OH$. The reaction mechanism is shown in Equations 2-4, and the conversion process is shown in Figure 12. With sacrificial donor triethylamine (TEA) and 1.5ml

of hydrogen peroxide, $CO_2$ was converted to methanol using 5wt% $Ni_2P$/CdS as a catalyst. The analysis showed that no by-products were produced, and the yield of $CH_3OH$ was excellent (2843μmol/g cat). Moreover, the catalytic efficiency and morphology of the $Ni_2P$/CdS did not change in three cycles within one hour (Figure 13). They attributed the high photocatalytic activity to the effective separation of the electrons and holes in CdS and the homogenous dispersion of the co-catalyst [13].

$$H_2O_2 - 2e^- \rightarrow O_2 + 2H^+ \quad (2)$$

$$CO_2 + e^- \rightarrow CO_2^- \quad (3)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad (4)$$

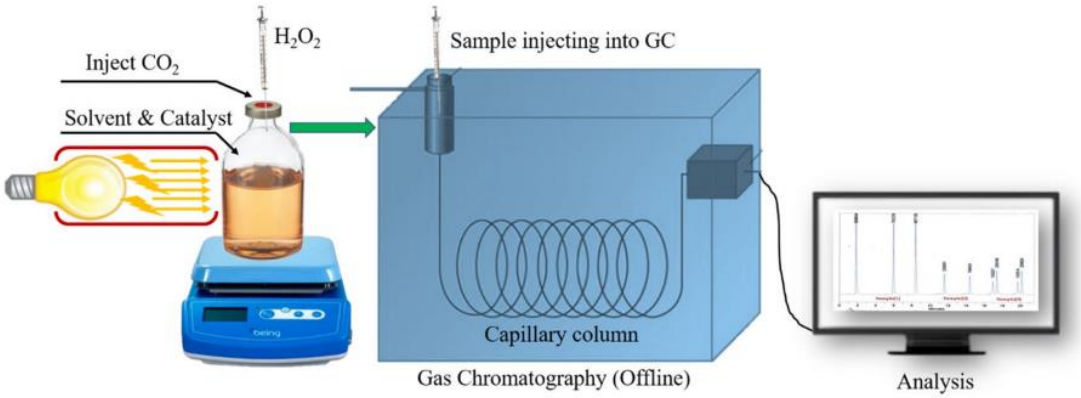



**Figure 12.** Process of photochemical $CO_2$ reduction to $CH_3OH$ [13].

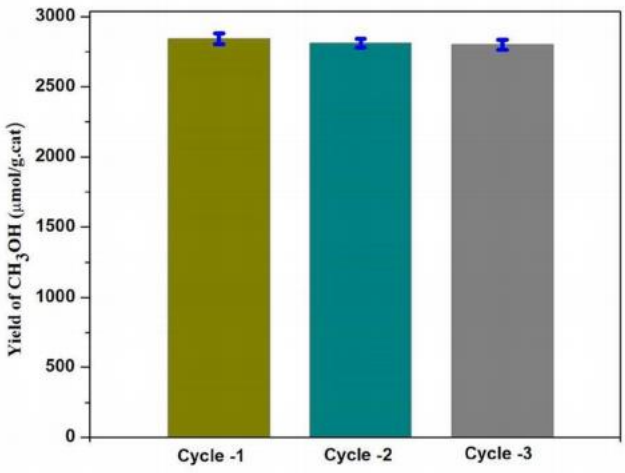



**Figure 13.** The yield of methanol of $Ni_2P$/CdS for 3 cycles in 1h [13].

Furthermore, another group also reported a technique for reducing $CO_2$ to methanol. They presented that using industrial steel slag by-product through modified with nanostructured palladium on its surface as a catalyst for $CO_2$ conversion which has two steps: the photocatalytic reaction of $CO_2$ and water to formic acid as intermediate, and then its thermal decomposition to $H_2$ and methanol (Figure 14), the formic acid conversion is 98%, and the yield of methanol is 43% [14].

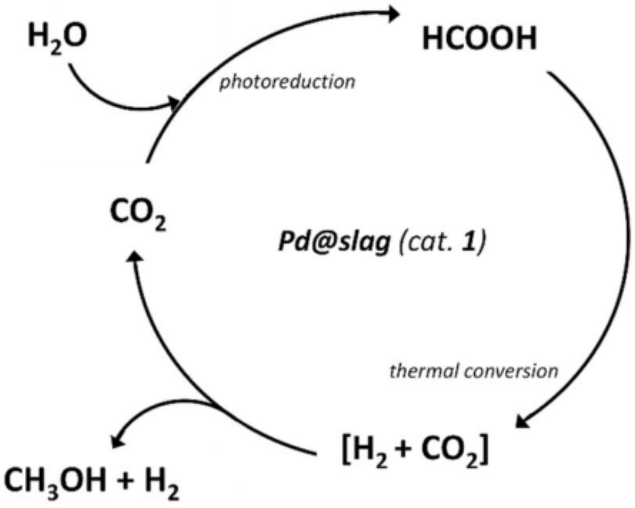



**Figure 14.** Schematic of the overall process [14].

CO, a common gas fuel mixed with hydrogen to form water gas, can also be used in chemical and metallurgical industries. Rui and co-workers reported that an Ag@Cr-decorated mixture of $CaGa_4O_7$-loaded $Ga_2O_3$ and the CaO catalyst shows an excellent selectivity (95%) and high formation rate (>835μmol $h^{-1}$) per 0.5g cat for CO. They demonstrated the presence of CA species is beneficial to improve the stability of the conversion process. The existence of CaO on the $Ga_2O_3$ surface improves the catalyst selectivity and activity. They enhance carbon dioxide adsorption at the basic sites to improve the catalytic efficiency, and the plausible mechanism is shown in Figure 15 [15].

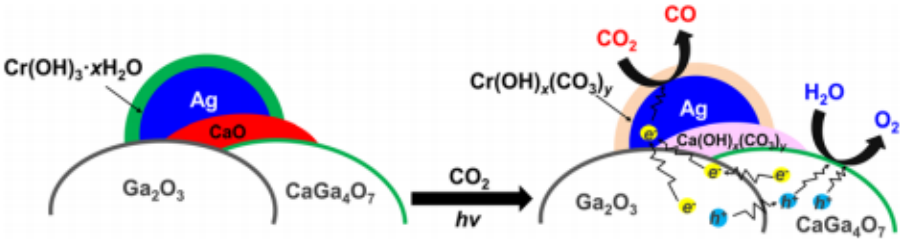



**Figure 15.** Diagram of the plausible reaction mechanism [15].

### 4.3. Barriers and prospects

Photocatalysts are deactivated after long-term light irradiation, so the reduction efficiency is reduced. It is necessary to study further the reasons for the deactivation of semiconductors to prolong the use time to increase economic benefits [11].

Besides, some semiconductors have the problem of low quantum yield, and improving the quantum efficiency of photoreaction is the key to the breakthrough of photochemical reduction of $CO_2$ technology. Additionally, the photothermal synergy technology has the development prospect of reduction to fuel, but the yield is low, so further understanding of the mechanism is needed to improve the reaction efficiency [12].

## 5. Comparison of enzymatic, electrochemical and photochemical technology

Through analyzing the technologies introduced above, Table.1 presents a comparison of the nine different technologies, including fuel products or products that can be converted into fuels, catalytic efficiency/product yield, and advantages and disadvantages in terms of industrial and commerce application.

**Table.1.** Comparison of enzymatic, electrochemical and photochemical technology

| Technology | | Product | Catalytic efficiency/ Product yield | Advantages | Disadvantages | Ref |
|---|---|---|---|---|---|---|
| Enzymatic technology | Remodeled nitrogenase MoFe protein catalyst | Methane | 16nmol/nmol cat within 20 min | ● Controllable catalytic rate<br>● Unique single enzyme catalyze $CO_2$ conversion to $CH_4$ | ● Contains intermediates<br>● Slow reaction rate over 20 minutes | [2] |
| | Three dehydrogenases coupling reaction in silica sol-gel | Methanol | 40-90% yield | ● A facile pathway | ● Difficult to manipulate the catalytic behavior of the individual enzyme<br>● High cost of NADH | [1,3] |
| | Three dehydrogenases coupling reaction immobilized on the GelCSi microcapsules | Methanol | 71.6% yield 86.7% selectivity | ● High activity and stability<br>● Regulable for individual enzyme<br>● Easy to recycle enzymes | ● Complicated operation steps<br>● High cost of NADH | [4] |
| Electrochemical technology | $Cu_n$ dynamically formed from carbon-supported Cu SA | Ethanol | 91% FE | ● Clean Energy Product<br>● Low onset potential | ● Short stabilization time<br>● High cost of catalyst synthesis | [7] |
| | Polyamine-incorporated Cu electrodes | Ethylene | 87% FE | ● High stabilization of intermediates<br>● Higher full-cell energetic efficiency | ● Poor stability of electrodes on GDL<br>● The product needs to be further processed into fuel | [8] |
| | Carbon dots(CDs)-Cu SA catalyst with unique $CuN_2O_2$ sites | Methane | 99% selectivity 78% FE | ● High selectivity<br>● Well-controlled single atomic active sites<br>● Low energy input | ● Synthesis temperature needs to be precisely controlled | [9] |
| Photochemical technology | $Ni_2P$/CdS nanostructure photocatalyst | Methanol | 2843μmol/g cat | ● High selectivity<br>● Stable performance of the catalyst | ● The use of sacrificial donors limits the process scale | [13] |
| | Modified steel slag with nanostructured | Methanol | 43% yield | ● Low‑cost catalyst<br>● Relatively mild conditions | ● Low yield of product | [14] |

| | | | | | | |
|---|---|---|---|---|---|---|
| | palladium photocatalyst | | | | ● Contains intermediate reactions<br>● Low stability of the catalyst | |
| | Ag@Cr-decorated mixture of $CaGa_4O_7$-loaded $Ga_2O_3$ and the CaO photocatalyst | CO | 95% selectivity | ● High formation rate for the product<br>● A simple and convenient technique | ● Difficult to separate other gas by-products | [15] |

## 6. Conclusions

The biggest contributor to global warming is the increasing carbon dioxide in the atmosphere, which brings many environmental problems that endanger human survival and ecosystems, and has generated significant alarm in various countries. The technology of converting carbon dioxide into fuel can not only reduce carbon dioxide emissions to promote the realization of carbon neutrality but also solve the problem of the energy crisis to achieve sustainable development, which is a greatly promising technology.

This article summarizes and classifies the research progress of enzymatical, electrochemical and photochemical carbon dioxide conversion technologies and the obstacles of these technologies, then introduces the current technologies whose product can be used as/converted to fuel, as well as their advantages and disadvantages. Despite the great achievements in $CO_2$-to-fuel technology, with the important roles of modified enzymes, improved multi-enzyme systems, nanostructures, composite copper electrodes, co-photocatalysts, etc., there are still widespread challenges such as high costs, poor stability of catalysts, accompanying by-product formation that is difficult to separate, which seriously hinder the large-scale utilization.

In order to better apply to industry and commerce, attention should be paid to these aspects in the future:

Technically: an in-depth study of the reaction mechanism, understanding of the influencing factors of catalysis, optimization of existing technologies to improve catalyst selectivity, stability, and efficiency; development and exploration of new advanced materials and technologies to improve the yield, selectivity and activity of fuel products; studying technologies that combine these three technologies to greatly improve the yield, reaction rate, and catalytic efficiency of fuel products.

Economically: explore low-cost materials as catalysts, research new technologies to reduce catalyst synthesis costs, improve technical methods to reduce energy input, and find low-cost materials suppliers.

In policy: government agencies and industries strongly support the research and development of carbon dioxide-to-fuel technology, regulate its development, provide financial assistance, and international cooperation is conducive to applying technology.

## References

[1] Shi Jiafu, Jiang Yanjun, Jiang Zhongyi, et al. Enzymatic conversion of carbon dioxide [J]. Royal Society of Chemistry, 2015, 44(17): 5981-6000.

[2] Yang Zhiyong, Vivian R. Moure, Dennis R. Dean, et al. Carbon dioxide reduction to methane and coupling with acetylene to form propylene catalyzed by remodeled nitrogenase [J]. Proc Natl Acad Sci USA, 2012, 109(48): 19644-8.

[3] Robyn Obert, Bakul C. Dave. Enzymatic conversion of carbon dioxide to methanol: Enhanced methanol production in silica sol-gel matrices [J]. Journal of the American Chemical Society, 1999, 121(51): 12192-12193.

[4] Wang Xiaoli, Zheng Li, Shi Jiafu, et al. Bioinspired Approach to Multienzyme Cascade System Construction for Efficient Carbon Dioxide Reduction [J]. ACS Catalysis, 2014, 4: 962-972.

[5] Long, Nguyen V.D., Jintae Lee, Kee-Kahb Koo, et al. Recent Progress and Novel Applications in Enzymatic Conversion of Carbon Dioxide [J]. Energies, 2017, 10(4): 473.

[6] John-Paul Jones, G. K. Surya Prakash, George A. Olah. Electrochemical $CO_2$ Reduction: Recent Advances and Current Trends [J]. Israel Journal of Chemistry, 2014, 54: 1451-1466.

[7] Xu Haiping, Dominic Rebollar, He Haiying, et al. Highly selective electrocatalytic $CO_2$ reduction to ethanol by metallic clusters dynamically formed from atomically dispersed copper [J]. Nature Energy, 2020, 5: 623-632.

[8] Chen Xinyi, Chen Junfeng, Nawal M. Alghoraibi, et al. Electrochemical $CO_2$-to-ethylene conversion on polyamine-incorporated Cu electrodes [J]. Nature Catalysis, 2021, 4: 20-27.

[9] Cai Yanming, Fu Jiaju, Zhou Yang, et al. Insights on forming N,O-coordinated Cu single-atom catalysts for electrochemical reduction $CO_2$ to methane [J]. Nature Communications, 2021, 12: 586.

[10] Lei Wen, Xiao Weiping, Wang Deli. Research Progress of Copper-based Catalysts for Electrochemical Reduction of Carbon Dioxide [J]. Journal of Electrochemistry, 2019,25(04): 455-466.

[11] Tu Wenguang, Zhou Yong, Zou Zhigang. Photocatalytic Conversion of $CO_2$ into Renewable Hydrocarbon Fuels: State-of-the-Art Accomplishment, Challenges, and Prospects [J]. Advanced Materials, 2014, 26(27): 4607-26.

[12] Tong Zhenwei, Zhong Zhencheng. Review on photocatalytic $CO_2$ reduction reaction [J]. Clean Coal Technology, 2022, 28(6): 91-102.

[13] Penumaka Nagababu, Sehba Anjum Mumtaz Ahmed, Y.Taraka Prabhu, et al. Synthesis of $Ni_2P$/CdS and Pt/$TiO_2$ nanocomposite for photoreduction of $CO_2$ into methanol [J]. Scientific Reports, 2021, 11: 8084.

[14] Caterina Fusco, Michele Casiello, Pasquale Pisani, et al. Steel slag as low-cost catalyst for artificial photosynthesis to convert $CO_2$ and water into hydrogen and methanol [J]. Scientific Reports, 2022, 12: 11378.

[15] Rui Pang, Kentaro Teramura, Masashige Morishita, et al. Enhanced CO evolution for photocatalytic conversion of $CO_2$ by $H_2O$ over Ca modified $Ga_2O_3$ [J]. Communications Chemistry, 2020, 3: 137.