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Metal-Organic Frameworks-Based Electrocatalytic Reduction of CO_2

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Abstract. Given the increasing emphasis on carbon dioxide (CO_2), diverse approaches have been developed and then used to address the issue. Metal-organic frameworks (MOFs) have shown promise in catalyzing the electrochemical reduction of CO_2. Different types of MOFs have investigated, including Cu-MOFs, Ce-MOFs, and hybrid composites, in order to enhance the catalytic selectivity, activity, and stability of electrocatalysts. MOFs possess distinct structural characteristics such as a large surface area, adjustable pore architectures, and numerous active sites, which provide effective adsorption, activation, and subsequent electrochemical reduction of CO_2. The inclusion of metal centres, such as copper, silver, and cobalt, in MOFs has shown a strong preference for valuable chemical products, such as ethylene, formate, methane, and acetic acid. Incorporating MOFs with carbon-based electrodes or photosensitizers has significantly improved the catalytic efficiency and the speed at which charge is transferred in CO_2 electroreduction processes. Nevertheless, there are still obstacles to overcome, such as the need to optimize the composition of catalysts, manage particle size, and provide scalability for use in industrial applications. Further study is necessary to expand the range of electrochemical techniques and reaction conditions, enhance the longevity of catalysts, and explore the potential of utilizing these types of catalysts for the specific conversion of CO_2 into other valuable liquid fuels.

Keywords: Electrochemical reduction; Metal-organic frameworks; Carbon dioxide.

1. Introduction

The ever-increasing levels of carbon dioxide (CO_2) in the atmosphere have become a pressing global concern, driving the urgent need for sustainable and efficient methods to mitigate CO_2 emissions [1]. As the scientific consensus on anthropogenic climate change grows stronger, the imperative to address the causes and consequences of greenhouse gas emissions becomes increasingly evident [1]. Various creative approaches have emerged, propelled by science and technology, to decrease CO_2 emissions. This encompasses the process of reducing CO_2. CO_2 undergoes transformation into organic compounds or other beneficial chemicals via electrochemical, photocatalytic, biocatalytic, and chemical catalytic processes. Furthermore, carbon capture and utilization technology are capable of capturing CO_2 from industrial emissions sources and transforming it into chemicals, fuel, or building materials, so accomplishing carbon recycling. Simultaneously, the process of plant absorption and forest management converts CO_2 into organic matter by utilizing the photosynthetic activities of plants to absorb and sequester CO_2 [2].

Out of these approaches, electrochemical reduction of CO_2 has great potential. The electrocatalytic reduction of CO_2 involves using catalysts to facilitate the conversion of CO_2 molecules into useful fuels or feedstocks through electrochemical reactions [2]. This process offers several advantages over traditional methods, such as milder reaction conditions, high selectivity, and the utilization of renewable energy sources. By harnessing and utilizing renewable energy sources, such as solar or wind power, electrocatalytic CO_2 reduction offers a pathway to address environmental challenges associated with climate change while simultaneously contributing to the development of sustainable energy storage solutions [3]. There are numerous methods available in this domain to accomplish electrochemical restoration of CO_2. The catalysts encompassed in this category consist of metal-

organic frameworks (MOFs) catalysts, metal ionic catalysts, organic catalysts, carbon-based electrode materials, metal oxide catalysts, and organic-inorganic hybrid materials.

The MOFs are highly effective catalysts for the electroreduction of CO_2, providing viable options to tackle environmental concerns and meet energy requirements. MOFs possess distinctive structural and chemical characteristics that make them very well-suited for CO_2 electroreduction. This allows for the efficient and selective transformation of CO_2 into useful compounds. MOFs have a remarkably large surface area and clearly defined porosity, which means they have a lot of active sites for capturing CO_2 and facilitating catalytic reactions. The extensive surface area facilitates improved CO_2 accessibility and heightened contact with the catalyst, hence facilitating efficient electrochemical conversion [3]. Moreover, MOFs provide the capacity to adjust their metal centres, organic linkers, and pore diameters. This allows for the creation of MOFs that possess customized catalytic characteristics suitable for the electroreduction of CO_2. The catalytic activity, selectivity, and stability of MOFs can be precisely adjusted by carefully choosing suitable metal centres and organic linkers. MOFs possess a wide range of catalytic sites, such as metal centres, unsaturated coordination sites, and defects. These sites enable the activation of CO_2 molecules and facilitate subsequent electrochemical reactions. The existence of diverse catalytic sites inside MOFs boosts the efficiency of catalysis and allows for numerous reaction routes, resulting in a broad spectrum of CO_2 conversion products. Additionally, the integration of several metal centres or the inclusion of co-catalysts in MOFs might generate synergistic effects, hence increasing their catalytic efficiency. The cooperative effects between active sites can promote the transfer of charges, accelerate the speed of reactions, and increase the specificity towards particular products of CO_2 reduction [3]. MOFs exhibit exceptional stability in electrochemical settings, enabling them to endure the challenging circumstances encountered during CO_2 electroreduction, hence assuring long-lasting catalytic activity. MOFs have the capability to be combined with additional materials, such as conductive substrates or nanoparticles, in order to improve their electrocatalytic efficiency. Composite structures that integrate MOFs with conductive materials have the potential to enhance the kinetics of electron transfer, boost catalytic activity, and improve overall efficiency. Computational design and screening approaches allow for the forecasting and enhancement of MOFs catalysts for CO_2 electroreduction. Computational techniques utilize the structural diversity and adjustability of MOFs to gain valuable insights for experimental synthesis and aid in the creation of exceptionally effective catalysts.

Overall, the amalgamation of extensive surface area, adjustable composition, varied catalytic sites, stability, integration capabilities, and computational design of MOFs render them highly effective catalysts for CO_2 electroreduction, so contributing to a more environmentally friendly and enduring future. This research aims to examine the numerous techniques for utilizing MOFs as a catalyst in carbon dioxide restoration. The objective is to analyze the pros and cons of different ways and enhance their effectiveness.

2. Application of MOFs for electrocatalytic reduction of CO_2

Recent research has demonstrated encouraging outcomes in the use of MOFs as catalysts for electroreduction of CO_2, where MOFs can enhance catalytic activity, improved selectivity towards specific products, and extended catalyst lifetimes. For example, MOFs containing specific metal centers, such as copper or silver, have shown high selectivity towards the production of ethylene or formate, respectively, which are valuable chemical products [4]. MOFs possess distinctive structural characteristics, such as a large surface area and customizable pore structures, which enable the adsorption and activation of CO_2 molecules, resulting in enhanced catalytic efficiency.

2.1. Cu/NU-1000 MOF

The process of electrochemical CO_2RR on Cu/NU-1000 MOF catalyst was initially disclosed [5], as shown in Fig. 1. The process of solvothermal growth is used to integrate copper nanoparticles into a thin film of zirconium MOFs, specifically NU-1000. The process involves incorporating individual

Cu (II) ions into the thin film of NU-1000 using solvothermal deposition in MOFs (SIM), followed by reducing the Cu (II) ions to metallic copper using electrochemical methods. The generated Cu nanoparticles exhibit controllability through electrical manipulation and display promising electrocatalytic efficacy for CO_2 reduction in a liquid electrolyte. The thin films of MOFs consist of copper nanoparticles that exhibit enhanced electrocatalytic activity. This makes them suitable for effectively converting CO_2 into fuels. The cost-effectiveness of copper, along with the stability and convenience of separating the catalyst from the product, makes the devised system highly attractive for large-scale industrial use. Nevertheless, there are obstacles that must be addressed, such as the existence of kinetic barriers in the process of reducing CO_2 and the requirement to regulate particle size to achieve the highest level of effectiveness. The current area of application is restricted to the electrocatalytic reduction of CO_2 in aqueous electrolytes, which necessitates additional investigation for wider electrochemical processes and reaction circumstances.

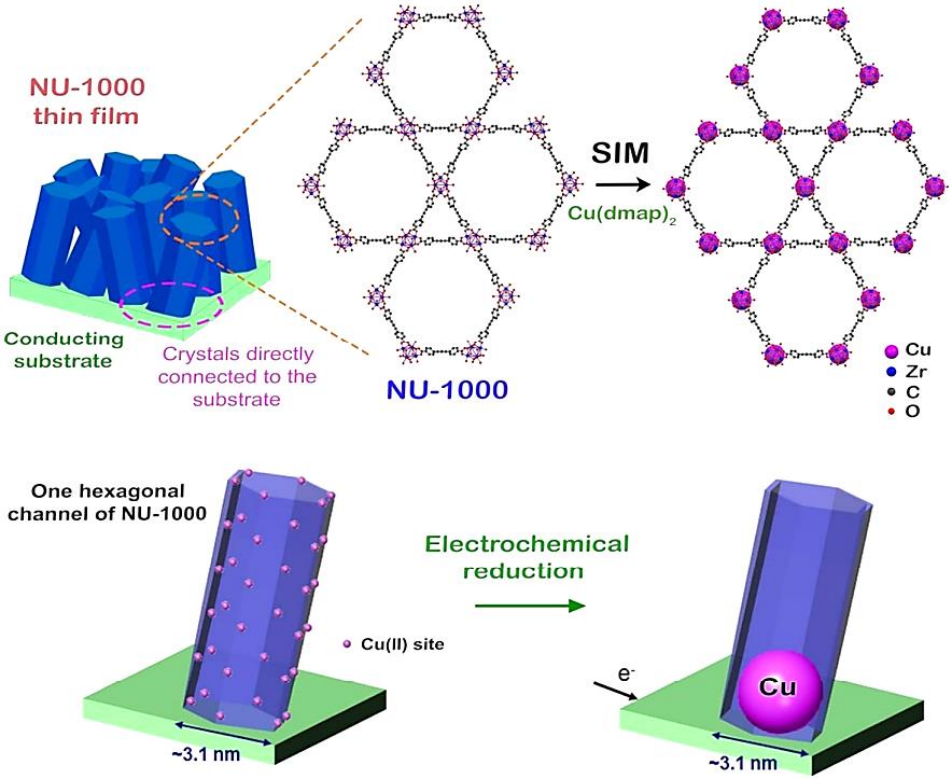

Fig. 1 Schematic representation of SIM to install single-site Cu (II) into the NU-1000 thin film and the electrochemical reduction of Cu (II) to generate metallic Cu nanoparticles [5].

NU-1000 thin films can be evenly coated on transparent conducting FTO platforms via solvothermal growth. These films can be enhanced with Cu (II) sites by utilizing SIM. The film maintains its crystalline structure and shape after the addition of copper, with an approximate loading of 4.0 copper atoms on each Zr6 node. By applying a negative potential to certain Cu sites in the film in a nitrogen-purged, aqueous electrolyte, a portion of them undergoes conversion into metallic Cu. The method results in the creation of Cu electroactive nanoparticles in close proximity to the interface of the MOF/FTO. The pretreated Cu-SIM NU-1000 thin film exhibits good electrocatalytic activity for CO_2 reduction in a CO_2-purged water-based electrolyte. At a voltage of -0.82 V compared to the reversible hydrogen electrode (RHE), the efficiency of converting CO_2 into other substances is around 31%, with formate being the main product of this conversion process. Electrocatalysis does not modify the crystalline structure or shape of the thin layer. This study presents the initial demonstration of the electrochemical properties of metallic copper within MOFs. Through the implementation of the technique proposed in this research, the size of the Cu nanoparticles can be controlled by the dimensions of the channels in the MOFs [5].

2.2. Cu-MOF in GDE

Qiu et al. demonstrated the integration of $Cu_3(BTC)_2$ (Cu-MOF) into a gas diffusion electrode (GDE) made of carbon paper for the purpose of electrochemically reducing CO_2 [6]. The Cu-MOF is employed as a CO_2 adsorbent in the gas diffusion electrode (GDE). The purpose of this design is to overcome the constraints caused by the limited ability of CO_2 to dissolve in water-based solutions. This limitation negatively affects the efficiency of converting CO_2 by electroreduction and the ability to selectively produce desired products. Cu-MOF has CO_2 capture characteristics, rendering it efficient in adsorbing and absorbing CO_2. The inclusion of it in the GDE results in increased faradaic efficiencies of CH_4, which suggests improved selectivity and efficiency in the electrochemical reduction of CO_2. Nevertheless, the lack of detailed information regarding the exact traits and behaviours of Cu-MOF imposes certain constraints. The constraints of production cost and availability of Cu-MOF, as well as the lack of discussion on its stability and lifespan under electrochemical circumstances, may have an impact on its practical implementation. The synthesized Cu-MOF demonstrated superior effectiveness in capturing CO_2, allowing for a continuous supply of CO_2 for future ERC reactions and promoting the creation of ERC products. The onset potential for the GDE using 10 weight percent Cu-MOF was 230 millivolts higher than the onset potential for the GDE without any additives (GDE-Blank). By introducing an adequate amount of Cu-MOF to GDE, the faradaic efficiency for CH_4 can be increased by 2-3 times compared to GDE-Blank, specifically at medium and higher overpotentials. The competitiveness of the HER can be greatly reduced, leading to a decrease of up to 30% in the faradaic efficiency for HER at a potential of -1.8 V (compared to the normal calomel electrode). GDE-CuMOF exhibits a consistently enduring catalytic activity for ERC and a notable preference for CH_4 throughout a continuous stability assessment spanning 6 hours. The improved electrochemical reduction of CO_2 efficiency of the GDE with Cu-MOF is due to the higher concentration of CO_2 at the interface between the GDE and the electrolyte, which is made possible by the CO_2 capturing abilities of Cu-MOF. Nevertheless, incorporating more than 10 weight percent of Cu-MOF can lead to a decrease in the number of active sites in the GDE and an increase in carbon sources for HER [6].

2.3. Cu_2O@Cu-MOF

Tan et al. synthesized a versatile Cu_2O@Cu-MOF electrocatalyst using a process involving in-situ etching, dissolving, and restructuring of Cu_2O [7]. The restructuring process entailed etching, dissolving, oxidizing, and transforming Cu_2O into a Cu-MOF that is bonded to the surface of the remaining undissolved Cu_2O. The inclusion of the 1,3,5-tricarboxylic acid (H_3BTC) ligand enabled the creation of Cu_2O@Cu-MOF. And the hybrid catalyst exhibited variations in its microstructure and morphology in response to changes in treatment time, demonstrating a time-dependent behaviour. The Cu_2O@Cu-MOF, as it is originally produced, demonstrates a notable Faradaic efficiency (FE) in generating hydrocarbon compounds, particularly CH_4, in comparison to Cu_2O and Cu-MOF. The overall fuel efficiency (FE) for hydrocarbons is as high as 79.4%, while the FE ratio of CH_4/C_2H_4 reaches up to 3.89, indicating strong selectivity towards CH_4. The exceptional electrochemical performance is due to the combined effects of the Cu_2O and Cu-MOF, which work together synergistically [7]. The Cu_2O@Cu-MOF, created in its original location, possesses several unsaturated coordination active sites, which gives the hybrid catalyst a high capacity for adsorbing CO_2 and increasing the concentration of CO_2 in the surrounding area. The presence of Cu_2O within the Cu-MOF enhances the process of transferring electric charges. The findings indicate that effectively integrating and balancing the Cu_2O and Cu-MOF can yield a remarkably efficient electrocatalyst for converting CO_2 to CH_4 and potentially other useful liquid fuels. This can be further enhanced by regulating the components and structures in future studies. The conversion of Cu_2O into Cu_2O@Cu-MOF for the purpose of selectively electrochemically reducing CO_2 presents numerous benefits. The Cu_2O@Cu-MOF catalyst, which is custom-made, has a time-dependent response and has a large specific surface area, allowing for a strong ability to adsorb CO_2. This facilitates the optimal utilization of CO_2 in the electrochemical reduction process. The catalyst offers a plentiful supply of active sites, which greatly enhances electrocatalytic activity and leads to superior

performance in comparison to using Cu-MOF alone. Furthermore, the catalytic performance is improved due to the enhanced charge transfer resulting from the Cu_2O core. The distinctive attributes of the Cu_2O@Cu-MOF catalyst result in a remarkable performance, exhibiting a significant hydrocarbon Faradaic efficiency, notably for methane. This makes it a highly attractive contender for selective electrochemical CO_2 reduction.

2.4. Ce-MOF-Ru^{II}-bpy

Karmakar et al. illustrated the process of modifying Ce-MOF after synthesis by attaching $[Ru(bpy)_2]^{2+}$ (a molecular photosensitizer) onto UiO-66-bpydc by grafting [8]. The incorporation of $[Ru(bpy)_2]^{2+}$ onto post-modified Ce-MOF provides numerous benefits for the process of photocatalytic CO_2 reduction. As shown in Fig. 2, it increases the absorption of light by using a wider range of the solar spectrum, leading to enhanced overall efficiency. The Ce-MOF-Ru^{II}-bpy catalyst exhibits exceptional efficiency in the process of visible light-induced CO_2 reduction, resulting in the synthesis of acetic acid at a remarkable rate of 128 millimoles per gramme per hour. This study is the first experimental investigation that shows the successful integration of the Ru^{II}-bipy photosensitizer into a Ce-based MOF (Ce-UiO-66-bpydc-MOF). This integration leads to a highly efficient conversion of CO_2 to C_2 products, with a remarkable production yield of 1133 mmol/g and an impressive selectivity of 99%.

The unoccupied, close-to-the-ground 4f orbital of CeIV facilitates rapid electron transfer, augmenting catalytic efficacy and favouring the creation of specific C_2 products, notably acetic acid. The catalyst has exceptional stability in water, guaranteeing sustained efficiency over an extended period. Nevertheless, the design does possess certain constraints. The focus is mostly on a narrow selection of C_2-based goods, which limits the range of possible outputs. The intricate nature of the catalyst's synthesis process and the precise conditions necessary for maximum performance may provide difficulties [8].

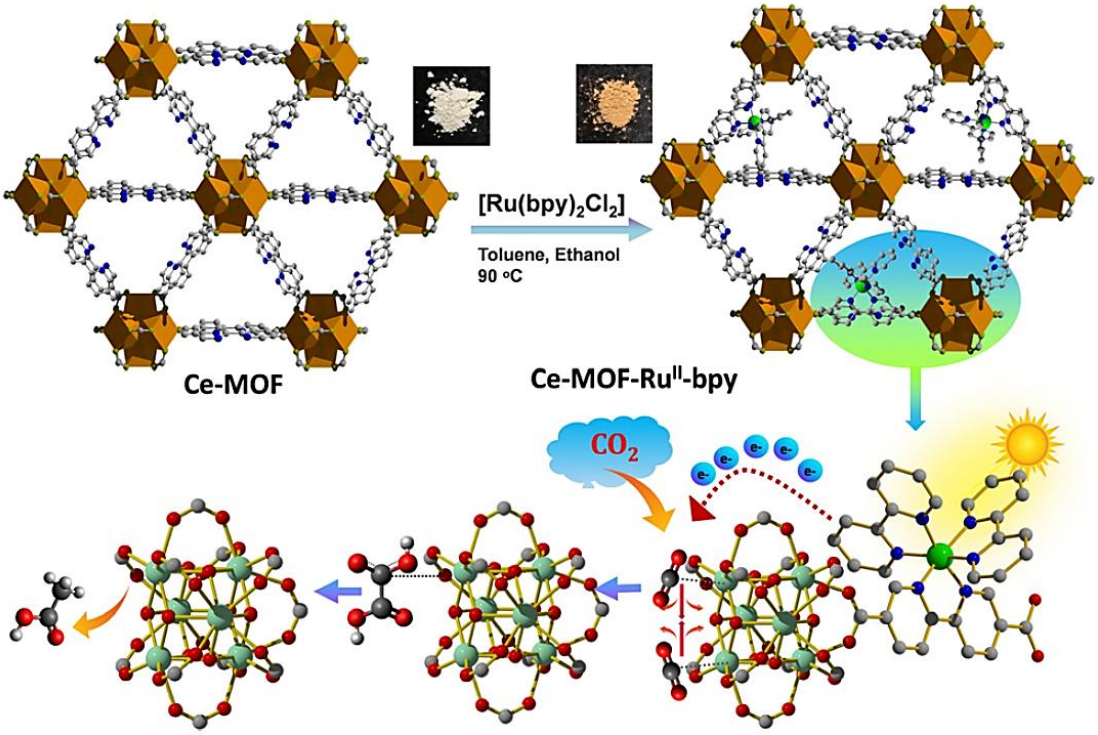

Fig. 2 Schematic for the construction of Ce-MOF-Ru^{II}-bpy and photochemical CO_2 reduction through Ce-MOF-Ru^{II}-bpy under visible light irradiation in pure water [8].

2.5. g-C_3N_4@Co-(Co+Cu) PMOF

Li et al. investigated the synthesis and properties of a novel composite material, g-C_3N_4@Co-(Co+Cu) PMOF, for efficient electrocatalytic reduction of CO_2 [9]. The incorporation of Co-(Co+Cu) PMOF with g-C_3N_4 enhances the magnitude of the electrochemically active surface area and accelerates electron mobility at the interface. Consequently, it exhibits efficient charge transfer and elevated conductivity. The composite material g-C_3N_4@Co-(Co+Cu) PMOF-50% demonstrates a remarkable FE of 97.8%, an exceptionally large current density of -2.1 mA cm^{-2} for CO at -1.4 V vs. RHE, and exceptional long-term durability. The features of these are markedly superior to those of Co-(Co+Cu) PMOF. Density functional theory (DFT) investigations reveal that electrons transfer from carbon atoms in graphene (g-C N) to the interface between Co-(Co+Cu) PMOF. In addition, the Co centres of 34 porphyrin in Co-(Co+Cu) PMOF gather extra electrons, allowing them to function as the main active sites for lowering the Gibbs energy barrier in the production of *COOH. Hence, this composite exhibit enhanced electro-catalytic activity for CO_2RR and effectively inhibits the competing HER, as observed in the experiments, when compared to Co-(Co+Cu) PMOF. This study introduces a novel method for producing 2D porphyrin-based conjugated MOF composites. This method improves the electron transfer capability and facilitates the efficient conversion of CO_2 into valuable chemicals using CO_2RR. The research provides vital insights into the methodical advancement of electrocatalysts for CO_2 reduction and highlights the promising potential of porphyrin-based conjugated MOFs in this specific field of research. The g-C_3N_4@Co-(Co+Cu) PMOF composite demonstrates enhanced catalytic activity in comparison to both the pure Co-(Co+Cu) PMOF and other porphyrin-based MOF analogues, thereby providing several advantages. It demonstrates a notable Faradaic efficiency for CO and a substantial current density, demonstrating its efficacy in the electrocatalytic reduction of CO_2. The research presents a reasonable design approach by merging g-C_3N_4 nanosheets with Co-(Co+Cu) PMOF. This technique exploits the combined effect of the two materials, resulting in enhanced electron transport and conductivity, which are vital for improving the efficiency of electrocatalysis. One drawback is that it only included a partial clip from the research article, which makes it difficult to fully evaluate the study's scope and any potential limits [9].

2.6. Benefits and drawbacks

The benefits and drawbacks of each design are shown in Table 1. To further the progress of electrochemical CO_2 reduction employing MOFs and associated catalysts, it would be feasible to identify many areas that require development and should be the focus of future research. It is essential to prioritize the resolution of kinetic obstacles related to CO_2 reduction reactions. Studying reaction mechanisms, pinpointing the phases that limit the rate of the reaction, and devising methods to overcome these obstacles are crucial for improving the effectiveness and efficiency of catalytic processes. It is crucial to strive for accurate manipulation of particle size, shape, and dispersion of catalysts, specifically copper nanoparticles integrated into MOFs, in order to enhance performance to its maximum potential. It is crucial to enhance the adaptability of MOFs-based catalysts by broadening the scope of electrochemical processes and the variety of products they can selectively produce, going beyond the currently researched CO_2 reduction products such formate, CH_4, acetic acid, and CO. It is imperative to guarantee the enduring stability of these catalysts in challenging environments and to investigate techniques for restoring their catalytic activity, as these factors are crucial for their practical implementation. When transitioning from successful CO_2 reduction procedures at the laboratory scale to large-scale application, it is important to consider scalability, cost-effectiveness, and industrial feasibility. Finally, conducting research to broaden the product range and target a wider range of useful chemicals and fuels shows great promise for future endeavours. By focusing on these specific areas, researchers can enhance their comprehension of the mechanisms involved in reducing CO_2, refine the design of catalysts, and promote the extensive use of MOFs-based catalysts in efforts to reduce CO_2 emissions and combat climate change.

Table 1. The benefits and drawbacks of each design.

Design	Benefits	Drawbacks
Cu/NU-1000 MOF	- Enhanced electrocatalytic activity - Cost-effective and easy separation	- Kinetic barriers in CO_2 reduction - Particle size regulation
Cu-MOF in GDE	- Overcomes CO_2 solubility limitations - Improved faradaic efficiency for CH_4	- Lack of detailed stability information
Cu_2O@Cu-MOF	- High faradaic efficiency for hydrocarbon products, especially CH_4	- Time-dependent variations in microstructure and morphology
Ce-MOF-Ru^{II}-bpy	- Enhanced light absorption and overall efficiency in photocatalytic CO_2 reduction	- Narrow focus on C_2 products - Complex synthesis process
g-C_3N_4@Co-(Co+Cu)PMOF	- Significant Faradaic efficiency and current density for CO synthesis - Excellent long-term durability	- Partial inclusion of information

3. Conclusion

The escalating concentrations of CO_2 in the atmosphere have emerged as a critical worldwide issue, necessitating immediate action to develop sustainable and effective approaches to reduce CO_2 emissions. Using MOFs as catalysts for CO_2 electroreduction shows great potential for reducing CO_2 emissions and effectively using the carbon cycle. The studies addressed emphasize the substantial advancements achieved in improving the catalytic activity, selectivity, and stability by developing and creating MOFs and their composites. The results illustrate the capacity of MOFs, specifically Cu-MOFs, Ce-MOFs, and hybrid composites, to efficiently convert CO_2 into important chemical products, such as ethylene, formate, methane, and acetic acid. MOFs possess distinctive structural characteristics that, when paired with the inclusion of metal centres or the integration of other materials, facilitate the effective adsorption and activation of CO_2, followed by electrochemical reduction. Nevertheless, there are other obstacles that must be overcome in order to achieve practical application, including kinetic barriers, scalability, and catalyst stability. Additional investigation is necessary to refine the design of catalysts, regulate particle size, and optimize reaction conditions in order to improve catalytic efficiency and broaden the scope of electrochemical processes. Overall, the use of MOFs in CO_2 electroreduction has significant potential to help address climate change and achieve sustainable development objectives.

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