# Rational Design of Cu-based Catalysts and Synthetic Systems for Carbon Dioxide Electroreduction

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論 文 名　：Rational Design of Cu-based Catalysts and Synthetic Systems for Carbon Dioxide Electroreduction（電気化学的二酸化炭素還元のための銅触媒と合成システムの合理的な設計）

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<div align="center">論 文 内 容 の 要 旨</div>

With the glowing threat of global climate change, reducing $CO_2$ emissions and achieving sustainable resource use have become urgent priorities. Electrocatalytic $CO_2$ reduction reaction ($CO_2RR$) therefore has significant environmental and economic implications by converting $CO_2$ into organic compounds, fuels, and chemical feedstocks. However, the current limitations of $CO_2RR$ technologies include poor selectivity towards specific products, low reaction rates, insufficient carbon utilization, and a lack of sufficient stability. This study aims to explore catalysts and operating systems for $CO_2RRs$ to convert $CO_2$ into high-value chemicals.

Chapter 1 presents a comprehensive systematic review of $CO_2RR$ research. Chapter 2 focuses on the elucidation of the reaction mechanism and design/optimization of catalysts to develop highly selective electrocatalysts for various specific products. Chapter 3 emphasizes the design and application of operating systems to enhance reaction rates and carbon utilization, with the aim of achieving efficient and stable $CO_2RRs$. Chapter 4 focuses on the exploration and prospecting of the $CO_2RR$ pathway, with the aim of understanding the reaction process at the molecular level and establishing a comprehensive $CO_2RR$ network.

**Chapter 1: General Introduction**

The $CO_2RR$ is an emerging technology with the potential to convert $CO_2$ into valuable products. The successful development and optimization of $CO_2RR$ necessitate a systematic study encompassing the fundamental principles, performance evaluation indicators, and essential experimental components. In this introduction, I systematically introduce the basic principle of $CO_2RR$, the indicators used to evaluate its performance, and the important components required for conducting experiments in $CO_2RR$.

**Chapter 2: Understanding the Roles of Hydroxide in $CO_2$ Electroreduction on a Cu Electrode for Achieving Variable Selectivity**

Hydroxide-derived copper (OH/Cu) electrodes exhibit excellent performance for the electrocatalytic $CO_2RR$. However, the role of hydroxide (OH) in $CO_2RR$ remains controversial and the origin of the selectivity enhancement emerging on OH/Cu has not been fully understood.

In this study, the author synthesized three electrodes characterized by significantly different OH amounts: small (**Cu foil**), moderate (**M-OH/Cu**), and large amounts of OH (**L-OH/Cu**), in which the **M-OH/Cu** and **L-OH/Cu** were prepared by electrooxidation method followed by reduction with different degree. The OH amount on the Cu surface was characterized by electroadsorption technique, which is the first time used for OH amount evaluation. The electroadsorption suggested that the amount of OH and the OH-to-$Cu^0$ ratio on
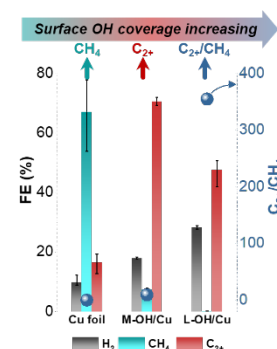


Fig.1. Faradaic efficiency (FE) and the ratio of $C_{2+}$-to-$CH_4$ in $CO_2RR$.

**L-OH/Cu** were 4.7 times and 2.7 times, respectively, larger than those on **M-OH/Cu**, whereas obvious adsorption was not observed on **Cu foil**. Fig. 1 presents Faradaic efficiencies (FE) for $CO_2RR$ on prepared Cu electrodes. **Cu foil** showed a high $CH_4$ selectivity with an average $CH_4$ FE of 67% and **M-OH/Cu** provided a FE of multicarbon products ($C_{2+}$ FE) of 71%. **L-OH/Cu** having large OH amount exhibited a lower $C_{2+}$ FE (54%) than **M-OH/Cu** (71%) but the ratio of $C_{2+}$-to-$CH_4$ on **L-OH/Cu** is higher than 355 (Fig. 1). Density functional theory calculation conducted by Prof. A. Staykov represented that the OH coverage modifies the work function of Cu surfaces and the reaction energetics for the formation of *CHO and *COCHO, which are deeply related to the variable selectivity observed on the Cu electrodes.

## Chapter 3: Designing Enhanced Gas Diffusion Electrode with Ultrathin Super Hydrophobic Macropore Structure for Acidic CO₂ Electroreduction

The development of flow reactors assembled with gas diffusion layer (GDL) electrodes has accelerated the industrial application of $CO_2RR$ technology. Most of $CO_2RR$ to date has focused on alkaline conditions due to the significant selectivity towards carbon products observed under alkaline conditions. However, a major drawback of alkaline electrolytes is their consumption of input $CO_2$ through reactions with hydroxide ions ($OH^-$), leading to reduced carbon utilization efficiency. $CO_2RR$ in acidic electrolytes would weaken carbonate formation, however, its $CO_2RR$ rate is generally limited by the slow $CO_2$ diffusion compared with alkaline electrolytes.

In this study, the author established a model to investigate the factors affecting $CO_2$ diffusion based on a commercially available GDE structure and found that the $CO_2$ diffusion efficiency can be improved by optimizing the thickness, pore size, and hydrophobicity of the GDE. Therefore, a new **Cu-GDL** with an ultra-thin structure, macroporous pores, and superhydrophobicity was newly designed. The preparation method is based on the
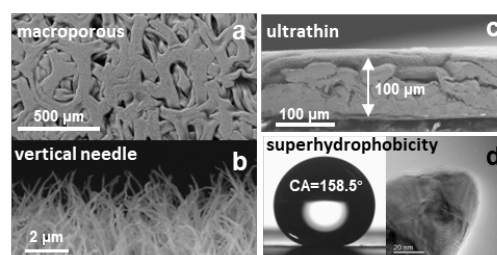


Fig.2. Surface characterization of **Cu-GDL**. a-c SEM, d CA and TEM.

improvement of the chapter 2. Characterization techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and contact angle (CA) measurements revealed the unique structure and superhydrophobic characteristics of the **Cu-GDL** (Fig. 3). By using **Cu-GDL**, the author achieved a Faradaic efficiency ($C_{2+}$ FE) of 87% while achieving a high partial current density ($C_{2+}$ $j$) of up to $-1.6$ A cm$^{-2}$ for multicarbon ($C_{2+}$) product. Furthermore, to assess the potential of $CO_2RR$ technology in practical applications, we systematically evaluated the influence of $CO_2$ concentration on $CO_2RR$ performance. The results demonstrated that diluted $CO_2$ concentrations had minimal impact on $CO_2RR$ selectivity. Even with a diluted 25% $CO_2$ concentration, we achieved a $C_{2+}$ $j$ of $-0.34$ A cm$^{-2}$, meeting industrial standards.

## Chapter 4: Exploration and Prospect of CO₂RR Pathway Based on In Situ Raman Spectroscopy

Although great progress has been made, Cu catalysts remain the only viable option for $CO_2RR$ to form multicarbon ($C_{2+}$) compounds. Catalyst development is largely dependent on the understanding of the $CO_2RR$ pathway, in particular the key step in the construction of carbon skeletons, namely the C–C coupling. Knowledge of the details of the $CO_2RR$ process at the molecular level is therefore critical to success. In this exploration and perspective, we have conducted a preliminary analysis of the $CO_2RR$ pathway based on our observations using in situ Raman spectroscopy, laying the foundation for future exploration of the $CO_2RR$ pathway.