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Development of Advanced Catalysts for Electrochemical CO₂ Reduction Reaction to Value-added Products

Zeyu Guo (20473775), BEng, MSc

Supervised by

Dr. Mengxia Xu ¹

Dr. Kam Loon Fow ¹

Dr. Hainam Do ¹

Prof. Jonathan Hirst ²

¹ Department of Chemical and Environmental Engineering, and New Materials Institute, University of Nottingham Ningbo China, Ningbo 315100, China

² School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, U.K

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Abstract

The carbon dioxide electroreduction reaction (CO₂RR), driven by low-carbon electricity, represents a promising approach for achieving sustainable carbon-neutral energy conversion. However, CO₂RR involves the sequential or simultaneous occurrence of multiple proton and electron transfer processes, normally accompanied by the competitive hydrogen evolution reaction (HER). These complex processes with unclear mechanisms can lead to diminished selectivity for desired carbonaceous products. Therefore, this research focuses on the development of advanced electrocatalysts, particularly single-atom catalysts (SACs) and copper (Cu)-based catalysts for CO₂ electroreduction to C₁ products (carbon monoxide, CO and methane, CH₄) and C₂₊ products (ethylene, C₂H₄). Furthermore, the corresponding structure-function relationships and related reaction mechanisms are systematically investigated.

Firstly, SACs have emerged as attractive materials for CO₂RR. Dual-atom catalysts (DACs), an extension of SACs, exhibit more compelling functionalities due to the synergistic effects between adjacent metal atoms. However, the rational design, clear coordination mode, and in-depth understanding of heteronuclear dual-atom synergistic mechanisms remain elusive. Therefore, a heteronuclear Ni-Ag dual-atom catalyst loaded on defective nitrogen-rich porous carbon, denoted as Ni-Ag/PC-N, is synthesized through cascade pyrolysis. The configuration of Ni-Ag dual-atom sites is confirmed as N₃-Ni-Ag-N₃. Ni-Ag/PC-N demonstrates a remarkable CO Faradaic efficiency (FE_{CO}) exceeding 90% over a broad range of applied potentials, i.e., from −0.7 to −1.3 V versus reversible hydrogen electrode (RHE). The peak FE_{CO} of 99.2% is observed at −0.8 V vs. RHE. Tafel

analysis reveals that the rate-determining step of CO₂RR-to-CO is the formation of the *COOH intermediate, and Ni-Ag/PC-N exhibits optimal electrokinetics. *In situ* Fourier-transform infrared spectroscopy (FTIR) and *in situ* Raman spectra indicate accelerated production of *COOH intermediates during the CO₂RR-to-CO process. Density functional theory (DFT) calculations demonstrate that the coordinated Ni atom lowers the energy barrier of *COOH intermediates formation over the Ni-Ag/PC-N surface, while the adjacent Ag atom mitigates the catalyst poisoning caused by the strong *CO affinity on the Ni atomic site. These findings establish a solid foundation for the practical applications of dual-atom catalyst in CO₂RR and potentially other fields, contributing to the development of more efficient and sustainable energy solutions.

Secondly, while CO₂RR is extensively researched for generating valuable C₁ and C₂₊ products, the influence of adsorbed hydrogen (*H) on product distribution remains inadequately understood. This work explores the effect by developing bimetallic Cu-based electrocatalysts with varied lanthanum (La) doping ratios. The as-prepared oxide-derived (OD)-La_{0.10}-CuO_x catalyst exhibits a FE over 80% for C₂₊ products at 300 mA cm⁻², whereas OD-La_{0.40}-CuO_x achieves a 61.4% FE_{CH₄} at 400 mA cm⁻². Kinetic isotope experiments reveal distinct dependencies of the rate-determining steps on *H transfer for CO₂RR in OD-La_{0.10}-CuO_x and OD-La_{0.40}-CuO_x. *In situ* attenuated total reflectance–surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) and DFT calculations demonstrate that the moderate H₂O dissociation capability of OD-La_{0.10}-CuO_x lowers the energy barrier for *CHO → *OCCHO conversion, thus increasing the FE_{C₂₊}. Conversely, OD-La_{0.40}-CuO_x, with its strong H₂O dissociation capability, favours *CHO → *CH₂O, thereby promoting CO₂RR-to-CH₄. These findings advance the understanding of the role

of *H in CO₂ electroreduction at industrial current densities and present avenues for tailored CO₂RR products via doping engineering.

Thirdly, under industrial current density ($> 300 \text{ mA cm}^{-2}$), the insufficient *CO coverage on the catalyst surface induces the competitive HER and sluggish kinetics of C–C coupling, which hinders CO₂RR-to-C₂₊ products. Herein, this work reports europium hydroxide modified oxide-derived CuO nanosheets (Eu(OH)₃-Cu NSs) that could effectively optimize the local *CO coverage and C-C coupling, achieves efficient CO₂RR-to-C₂₊ products. The Eu(OH)₃-Cu electrocatalyst demonstrates significantly enhanced selectivity for C₂₊ products, achieving an optimal FE of 81.4% with partial current density of 326 mA cm^{-2} , in contrast to bare CuO NSs. Additionally, compared to CuO component with fast cathodic corrosion, Eu(OH)₃ component can be well maintained at current density of 400 mA cm^{-2} within the flow cell system in hybrid Eu(OH)₃-Cu. *In situ* electrochemical impedance spectroscopy and infrared spectroscopy reveal that the hybrid Eu(OH)₃-Cu demonstrates lower onset potential and enrichment of asymmetric *OCCHO intermediates. This hydroxide-metal interface engineering marks a convenient and immensely promising paradigm to enhance the selectivity and stability for CO₂RR-to-C₂₊ products.

To summarize, this thesis provides new insights into high-performance CO₂RR electrocatalysts design, including synergistic heteronuclear Ni-Ag dual-atom catalysts, lanthanum-modified CuO_x with controllable adsorbed hydrogen, and europium hydroxide modified Cu with optimal *CO affinity. These advancements contribute to improving the activity, selectivity and stability of CO₂RR.

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List of Publications

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Abbreviations

^1H NMR	Proton nuclear magnetic resonance
*COOH	Carboxylate radical
*H	Adsorbed hydrogen
φ	Phase angle
2D	Two-dimensional
AC	Aberration-corrected
AEM	Anion exchange membrane
ATR	Attenuated total reflectance
BET	Brunauer-Emmett-Teller
C ₂₊	Multi-carbon products
C ₂ H ₄	Ethylene
C ₂ H ₅ OH	Ethanol
C ₂ H ₆	Ethane
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
CCUS	Carbon capture, utilization, and storage
C _{dl}	Double-layer capacitance
CE	Counter electrode
CEM	Cation exchange membrane
CH ₃ CHO	Acetaldehyde
CH ₃ COOH	Acetate
CH ₃ OH	Methanol
CH ₄	Methane
CHE	Computational hydrogen electrode

ClO_4^-	Perchlorate
CO	Carbon monoxide
CO ₂	Carbon dioxide
CO ₂ RR	Carbon dioxide electroreduction reaction
CP	Chronoamperometry
CPE	Constant phase angle element
CTAB	Cetyltrimethylammonium bromide
Cu _{cub}	Cu cubes
Cu _{oh}	Cu octahedra
Cu _{sph}	Cu spheres
CV	Cyclic voltammetry
C ϕ	Proton-adsorption pseudo-capacitance
DACs	Dual-atom catalysts
DFT	Density functional theory
E	Applied potentials
DMSO	Dimethyl sulfoxide
ECSA	Electrochemically active specific surface area
EDS	Energy dispersive X-ray spectroscopy
EE	Energy efficiency
EELS	Electron energy loss spectroscopy
E _f	Fermi level
EIS	Electrochemical impedance spectroscopy
EPR	Electron paramagnetic resonance
ET	Electron transfer step
Eu(OH) ₃ -Cu	Europium hydroxide modified oxide-derived copper oxide
EXAFS	Extended X-ray absorption fine structure

fcc	Face-centred cubic
FE	Faradaic efficiency
FID	Flame ionization detectors
FT	Fourier transform
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
g-C ₃ N ₄	Graphite nitride
GDE	Gas diffusion electrode
HAADF	High-angle annular dark-field
HCO ₃ ⁻	Carbonate groups
HCOOH	Formic acid
HER	Hydrogen evolution reaction
HOMO	Highest occupied molecular orbital
ICP-MS	Inductively coupled plasma mass spectrometry
j	Current density
KIE	Kinetic isotope effect
La-CuO _x	Lanthanum-copper bimetallic oxide catalysts
LC-TEM	Liquid cell TEM
LSV	Linear sweep voltammetry
LUMO	Lowest unoccupied molecular orbital
MEA	Membrane electrode assembly
MEMS	Microelectromechanical system
ML	Machine learning
M-N-C	Metal-Nitrogen-Carbon
MOF	Metal organic frameworks
Ni-Ag/PC-N	Nickel and silver anchored onto nitrogen-rich porous carbon

Ni-Pc	Nickel phthalocyanine
NLDFT	Non-local density functional theory
NSs	Nanosheets
OCP	Open circuit potential
OD	Oxide-derived
OER	Oxygen evolution reactions
OH _{ads}	Hydroxide electrosorption
PAW	Projector augmented wave
PBE	Perdew-Burke-Ernzerhof
PC	Porous carbon
PC-N	Nitrogen-doped porous carbon
pDOS	Partial densities of state
PT	Proton transfer step
R _{ct}	Charge transfer resistance
RDS	Rate-determining step
RE	Rare earth
RF	Roughness factor
RHE	Reversible hydrogen electrode
R _s	Solution resistance
SACs	Single-atom catalysts
SAED	Selected area electron diffraction
SCE	Saturated calomel electrode
SEIRAS	Surface-enhanced infrared absorption spectroscopy
SEM	Scanning electron microscopy
SO ₄ ²⁻	Sulphate
SPCE	Single-pass carbon conversion efficiency

STEM	Scanning transmission electron microscopy
TBs	Twinning boundaries
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TM	Transition metal
TOF	Turnover frequency
TPB	Triple-phase boundary
vdW	van der Waals
WE	Working electrode
WTs	Wavelet transforms
XAFS	X-ray absorption fine structure
XANES	X-ray absorption near edge structure
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZIFs	Zeolitic imidazolate frameworks
ΔG	The Gibbs free energy change
η	Overpotential
ε_d	d-band centre

Chapter 1 Introduction

1.1 Background

1.1.1 Climate change and energy crisis

Since the onset of the first industrial revolution in 1750, rapid economic and population growth, along with human activities such as the excessive use of fossil fuels, industrial processes, and deforestation, have collectively led to significant increases in carbon dioxide (CO₂) emissions. These activities have resulted in severe negative impacts on the Earth's environment, intensifying both the rate and extent of global climate change. Consequently, they pose substantial threats to the living environment, as well as to the life and health of human beings. Based on projected future emissions, the Intergovernmental Panel on Climate Change estimates that global surface temperatures could increase by between 1.4 °C and 4.5 °C above pre-industrial levels by the year 2100 [1]. In light of these considerations, at the 21st Conference of the Parties in December 2015, 195 countries committed to limiting the increase in global average temperature to 2°C above pre-industrial levels, while also working towards the more ambitious goal of restricting the temperature increase to 1.5 °C above pre-industrial levels [2]. This commitment is vital because exceeding 2 °C could melt northern glaciers, threaten coastal cities and island nations, disrupt global food supplies, and endanger ecosystems like coral reefs [3].

To avoid the severe impacts of climate change, gigatons of CO₂ must be removed from the atmosphere. As shown in the **Figure 1.1**, since data collection began in 1960, atmospheric CO₂ concentrations have consistently risen. Specifically, the global monthly average concentration increased from an annual average of 280 ppm in 1950 to 418 ppm

in 2023, with a projected rise to 422 ppm in 2024, which represents an increase of more than 20% over this recording period [4]. This concentration and the rate of emissions are unacceptable relative to the standard atmospheric CO₂ concentration of 300 ppm [5]. Thus, the uncontrolled emission of CO₂ and its accumulation is the main contributor to global warming. For mitigating the rising global temperature trend, there is an urgent need to develop promising CO₂ conversion technologies for reducing atmospheric CO₂ levels.

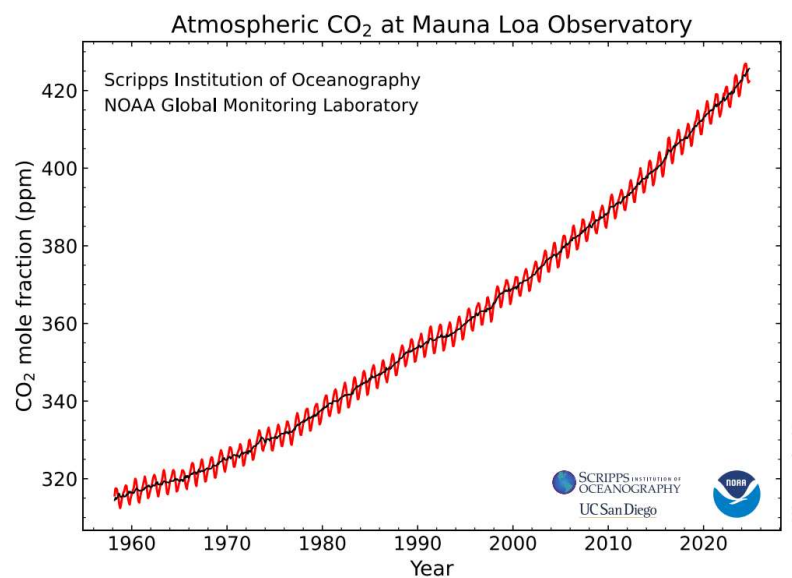


Figure 1.1: The atmospheric CO₂ concentration at Mauna Loa Observatory from 1960 to October 2024. The jagged pattern in atmospheric CO₂ concentrations reflects seasonal fluctuations driven by the terrestrial biosphere, with lower levels during growing season and higher levels in the dormant season. Reprinted from Scripps Institution of Oceanography, UC San Diego. Reproduced from reference [4].

Apart from climate change, as the industrialization accelerates, energy demand and CO₂ emissions are increasing significantly. Fossil fuels currently account for over 80% of global primary energy due to the advantages of low development costs and mature conversion technologies [6]. Along with the rapid increase in the world's population, global demand for fossil energy is expected to triple in the next three decades [7]. This surging energy crisis will undoubtedly lead to an imbalance between supply and demand for

resources. Therefore, there is a consensus to accelerate the decarbonization of the energy system and the transition to green energy. As shown in **Figure 1.2**, the main alternatives to fossil fuels are nuclear, hydro, biofuels, wind and solar energy. However, wind and solar energy are intermittent due to weather variations and daily and seasonal cycles. Therefore, the mismatch between electricity production and consumption has created an urgent need for energy storage solutions. Electricity serves as a crucial energy carrier, facilitating the transmission of energy from major sources to end users, enabling efficient energy use and providing flexibility in meeting diverse energy demands. Electricity only accounts for about 19% of global energy demand, while the rest is fulfilled by various fuels [8]. Thus, developing electricity powered technologies is crucial for ensuring stable energy supply and promoting sustainable development.

Additionally, the CO₂ emissions accompanying fossil energy consumption are also a critical environmental problem. Two-thirds of global CO₂ emissions come from the indiscriminate use of non-renewable fossil fuels [9]. Therefore, to some extent, the green energy transition can alleviate the energy and environmental crisis. As energy transition proceeds, electrochemical energy storage has become an essential technology [10]. Electrochemistry offers an opportunity to convert electrical and chemical energy into each other. Electrocatalysis plays a key role in the energy conversion process that is at the heart of renewable energy technologies, including fuel cells and electrolyzers [11]. Typical strategies for sustainable fuel synthesis by means of electrocatalysis include the electrolytic reduction of CO₂ to polycarbonate products [12], the electrocatalytic reduction of nitrogen to ammonia [13] and the electrocatalytic conversion of light alkanes to high value-added chemicals [14]. The inadequate catalyst performance significantly contributes to efficiency

losses in energy conversion units. The limited understanding of catalytic mechanisms and catalyst design principles poses a substantial challenge to the development of efficient electrocatalysts for renewable energy conversion. Addressing these issues is crucial for improving energy efficiency and advancing sustainable technologies.

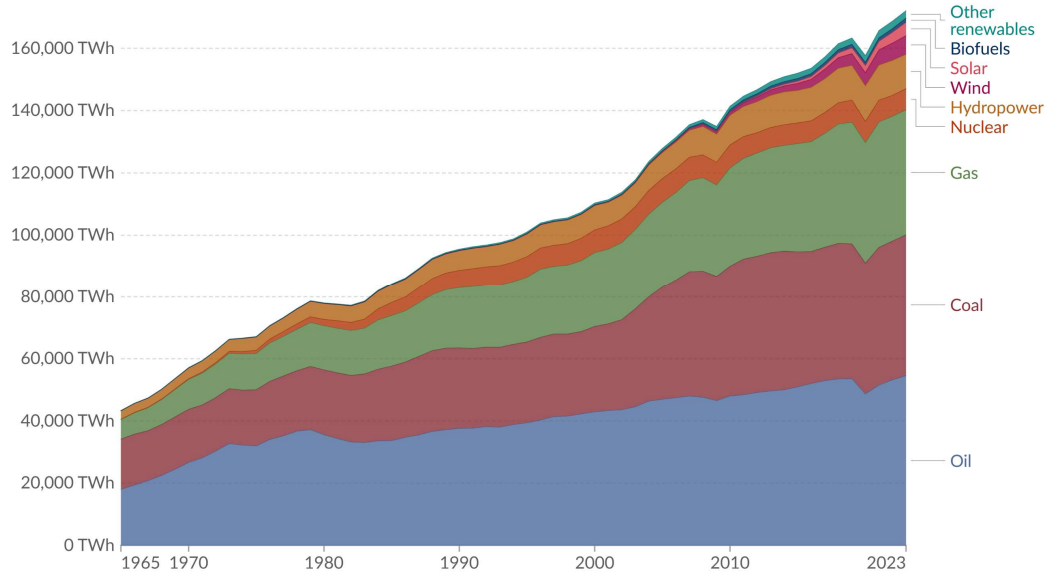


Figure 1.2: World Energy Consumption by source from 1965 to 2023 measured in terms of primary energy using the substitution method. Data source: Energy Institute-Statistical Review of World Energy (2024). Note: "Other renewables" include geothermal, biomass, and waste energy. Reproduced from the website (<https://ourworldindata.org/energy-mix>) and reference [15].

1.1.2 CO₂ utilization

The International Energy Agency estimates that carbon capture, utilization, and storage (CCUS) technologies will cumulatively reduce CO₂ emissions by 15% by 2070, with 92% of the captured CO₂ sequestered underground and the remaining 8% converted into industrial products [16]. Within CCUS technology, carbon capture and storage (CCS) technology holds promise for achieving net-zero emissions [17]. However, its widespread adoption is hindered by its substantial energy requirements, elevated costs, and unfavourable economic viability. Carbon capture and utilization (CCU) technology has

been developed to convert captured CO₂ into value-added products, achieve sequestration, and generate economic value. Compared to CCS, CCU technology not only facilitates long-term CO₂ storage but also possesses significant economic potential, thereby robustly enhancing the feasibility of CO₂ capture, storage, and utilization technologies [18]. As a crucial component of CCUS technology, CCU has the capacity to transform approximately 230 million tons of CO₂ into industrial products in 2019 [18-21].

Thus, developing renewable energy driven CO₂ conversion technologies are crucial for lowering atmospheric CO₂ levels and enabling decarbonized production of high value-added chemicals. They help mitigate climate change, address the energy crisis, and support a circular economy and sustainable development. Currently, CO₂ conversion has been achieved through various methods, including thermal catalysis [22], biocatalysis [23], photocatalysis [24], and electrocatalysis [5]. However, thermal catalytic processes typically require high-temperature conditions, leading to significant energy consumption that may negate their environmental benefits, and thermal catalysis can also introduce additional pollutants or increase emissions of certain harmful gases. Furthermore, the reaction rates in biocatalysis and photocatalysis are often slow, which limits their effectiveness for industrial applications. Additionally, maintaining selectivity and efficiency during scale-up to industrial levels poses significant challenges for biocatalytic and photocatalytic processes.

1.1.3 Electrochemical CO₂ conversion

Among these approaches, electrochemical CO₂ reduction reaction (CO₂RR) has emerged as a highly promising technology for efficient conversion with a higher step and atomic economy, and lower energy costs. The advantages of CO₂RR include: (1) a

relatively mild energy conversion process that does not necessitate significant additional heat input [25, 26]; (2) minimal usage of chemicals, with water or wastewater as the primary byproducts [27]; (3) compact and adaptable reactors can be easily designed and scaled up as per requirement [28, 29]; (4) utilization of renewable sources of electricity such as solar, tidal and geothermal energy, without further CO₂ emissions [30, 31]. The pioneering work by Hori et al. shows that CO₂RR can produce a wide range of products depending on the catalyst used (**Figure 1.3**) [32]. The process of CO₂RR can convert CO₂ into valuable chemicals and fuels, specifically C₁ compounds such as carbon monoxide (CO), methane (CH₄), and multi-carbon (C₂₊) products like ethylene (C₂H₄) and ethanol (C₂H₅OH) (**Table A 1**) [33]. Through in-depth research and technological innovation, it is promising that CO₂ can be effectively converted from emission sources into valuable compounds. This approach will reduce dependence on conventional energy sources while promoting global environmental protection and sustainable development.

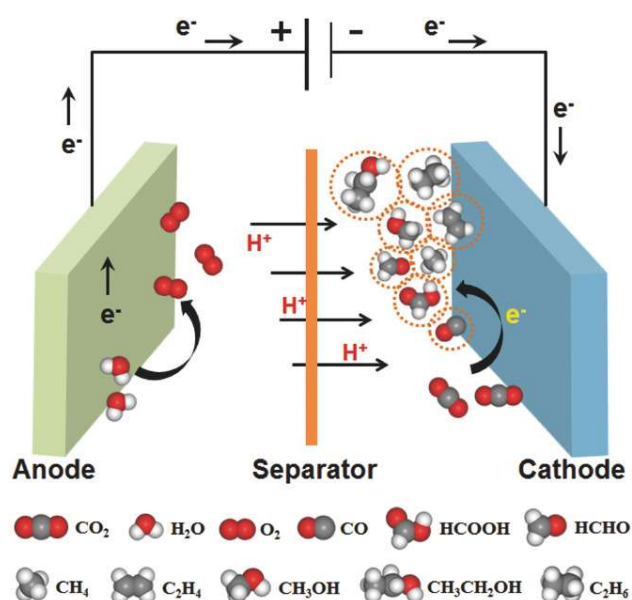


Figure 1.3: An illustration of electrochemical CO₂ reduction reaction process showing the various potential products generated within an electrochemical reaction cell. Reproduced from reference [34].

However, CO₂RR to value added products is a sophisticated process that involves multiple proton-coupled electron transfer steps [31, 33, 35]. Moreover, during the CO₂RR process, the presence of H₂O in the electrolyte enables competition between HER and CO₂RR. This competition can lead to H₂ as a by-product, consequently impacting the selectivity for the desired carbon-containing products [36]. Therefore, when designing and optimizing electrocatalysts for CO₂RR, it is essential to focus on strategies that inhibit the HER while promoting the CO₂RR to enhance the yield and selectivity of the target products. Additionally, the products of CO₂RR exhibit minimal differences in thermodynamic potential, resulting in low selectivity for specific desired products (**Table A 1**). These issues pose a challenge in developing electrocatalysts with high current density, FE and stability toward CO₂RR to desired products. Current strategies for developing high-performance electrocatalysts for the selective electrochemical conversion of carbon dioxide to C₁ and C₂₊ products include single-atom site construction [37, 38], heteroatom doping [39], and hybrid interface engineering [40]. For instance, Jiang's research team successfully loaded ordered compartmentalized Ni single atoms into graphene vacancies. Electrochemical tests demonstrated that the Ni atomic sites dispersed in graphene can achieve a CO production FE of up to 93.2% [38]. Besides, Yin et al. prepared Cu-modified CeO₂ composites (Cu_y/CeO₂) with different Cu loadings for CO₂RR. Strong adsorption sites for CO₂ molecules exist at the interface between Cu and CeO₂, which serve to activate CO₂ molecules and subsequently facilitate the generation of *CO at the interface of adjacent Cu nanoparticles [41]. These design strategies are anticipated to accelerate the development of robust cathode catalysts for electrochemical carbon dioxide conversion.

Additionally, the lack of understanding of reaction mechanism and active site further complicates the optimization of catalysts structure and their performance [42]. Specifically, it is essential to reveal the relationship between key reaction intermediates, such as $^*\text{COOH}$, $^*\text{CO}$, $^*\text{H}$, and $^*\text{OCCHO}$, and their electrochemical properties. In light of this, researchers have employed a range of advanced techniques, including electrochemical *in situ* spectroscopy and DFT calculations, to conduct related studies on CO_2RR . These methods enable researchers to precisely understand reaction pathways, monitor real-time changes in electrocatalytic materials, and visualize formation and transformation of intermediates [43-45]. They also facilitate molecular-scale analysis of catalytic materials and reaction barriers, leading to insights into detailed reaction pathways and the development of high-performance electrocatalysts. For instance, *in situ* surface-enhanced infrared absorption spectroscopy can investigate the surface adsorption processes of electrocatalysts and effectively capture information about the changes in intermediates on the electrode surface during CO_2RR [46]. This provides direct experimental evidence that elucidates the reaction mechanism. Besides, Zhu et al. used DFT combined with a machine learning algorithm (ML) to effectively predict and screen highly active bimetallic site catalysts toward CO_2RR to HCOOH [47]. The application of these technologies enhances understanding of the CO_2RR mechanism and structure-function relationship while significantly influencing the development of related electrocatalytic materials.

1.2 Aim and Objectives

Recent studies have demonstrated significant progress in the CO_2RR to generate higher value-added products at the lab-scale [42]. However, the commercial application of

CO₂RR still faces several challenges, including limitations in electron selectivity, catalytic activity, and operation stability. Numerous explorations on improving CO₂RR selectivity and activity have been conducted in this research area. The development of new materials, including single-atom catalysts [48], copper-based catalysts [5] and lanthanide catalysts [49], offers new insights for designing advanced electrocatalysts. Meanwhile, the understanding of the CO₂RR mechanism through combining electrochemical *in situ* spectroscopy and DFT also provides theoretical support for optimizing the catalytic system.

The overall research aim is to develop advanced catalysts for the electrocatalytic conversion of CO₂ molecules into high-value-added chemicals, ranging from CO to C₂H₄. As illustrated in **Figure 1.4**, the first PhD research project focuses on the enhanced CO₂RR-to-CO process by designing single-atom catalysts. This work aims to enhance the understanding of the structure-function relationship between the engineered active sites and their catalytic performance in CO₂RR, setting the stage for subsequent research on optimizing the CO₂RR process for C₁ and C₂₊ products. Following this, the second PhD research project focuses on enhanced CO₂RR-to-C₁/C₂₊ process by optimizing adsorbed hydrogen. This work aims to deepen the understanding of correlations among various products, especially C₁ and C₂₊ products, increasing the conversion efficiency of desired CO₂RR products. Finally, the third PhD research project focuses on enhanced CO₂RR-to-C₂H₄ process by constructing hybrid structures. This work aims to reveal the understanding of synergistic effects, especially for C-C coupling and intermediates adsorption. Among three projects, the design and optimisation of catalysts is essentially the construction of bimetallic system. Compared with single-metal materials, the introduction of an additional

metal element can form an active interface and create a synergistic effect, thereby improving catalytic performance [50].

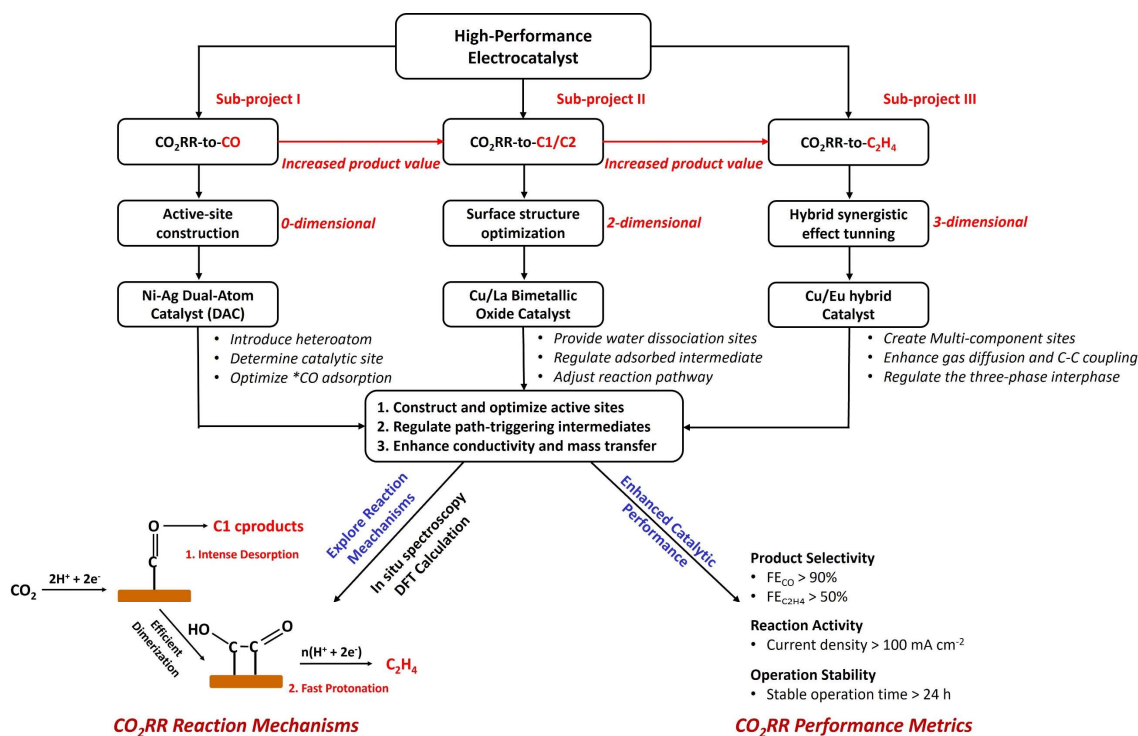


Figure 1.4: The research roadmap of this PhD project on development of advanced catalysts for electrochemical CO_2 reduction reaction to value-added products.

Research objective 1. Achieving electrochemical conversion of CO_2 to CO through the construction of atomic active sites in Ni-Ag dual-atom catalysts

Atomically dispersed metal atoms are suitable for individual or coupled proton-electron transfer due to enhanced adsorption and activation of CO_2 , leading to the high selectivity for CO production [51-54]. Therefore, the first research objective is to construct atomic active sites on dual-atom electrocatalysts to reveal the synergistic effect on the catalytic conversion of CO_2 in the $\text{CO}_2\text{RR-to-CO}$ system and the mechanism of CO formation.

Research objective 2. Achieving tuneable electrochemical conversion of CO_2 to C_1 or C_{2+} products through the optimization of surface adsorption in Cu/La bimetallic oxide catalyst

*The introduced rare-earth element provides an effective way to regulate the electronic structure and microenvironment of CO₂RR, leading to the controllable electron selectivity towards C₁ or C₂₊ products formation [39, 55-58]. Therefore, the second research objective is to optimize the adsorption of *H on the surface of the lanthanum-doped Cu-based catalyst and to reveal the correlations between C₁ and C₂₊ products.*

Research objective 3. Achieving electrochemical conversion of CO₂ to C₂H₄ through the creation of hybrid hydroxide-metal interface in Eu(OH)₃/Cu catalyst

*The existence of hybrid structure can enhance proton and electron transfer, increasing reactant activation and improving catalytic performance by stabilizing intermediates and lowering energy barriers of CO₂RR [40, 55, 59-61]. Therefore, the third research objective is to achieve highly selective C₂H₄ production by facilitating *CO adsorption and asymmetric C-C coupling on Eu(OH)₃/Cu catalyst.*

1.3 Overview of thesis

This chapter (Chapter 1) highlights the status of the CO₂ issue, including climate change and the energy crisis, while exploring potential mitigation strategies, particularly through electrochemical CO₂ reduction. Additionally, the research advancements and shortcomings of CO₂RR are presented. This chapter offers a concise overview of the research background and motivation for this PhD project. It clearly outlines the research aim and objectives and provides a framework for the thesis, thereby establishing a solid foundation for the subsequent chapters to develop.

Chapter 2 provides a comprehensive review of recent advancements in the field of electrochemical CO₂ reduction reaction. This chapter encompasses an overview of the processes and products associated with CO₂RR, identifies key factors influencing the reaction, and discusses the development of transition metal-based electrocatalysts.

Chapter 3 systematically describes methodologies employed in the study, detailing the chemicals used, the electrochemical procedures followed, and the techniques for *ex situ* characterization of electrocatalysts. Furthermore, it includes a detailed discussion of *in situ* electrochemical spectroscopies and the application of density functional theory to enhance the understanding of the mechanism studied.

Chapter 4 investigates heteronuclear dual-atom catalysts consisting of nickel (Ni) and silver (Ag) anchored onto a nitrogen-rich porous carbon matrix (Ni-Ag/PC-N) toward CO₂RR-to-CO. The configuration of as-prepared dual-atom catalyst has been accurately determined. Besides, the electrocatalytic performance, kinetics in CO₂RR-to-CO and synergistic effects of Ni-Ag/PC-N are examined by *in situ* FTIR, *in situ* Raman and DFT calculation. As a first research work, it has established a platform for electrochemical performance evaluation, reduction product analysis, electrocatalyst characterisation and reaction mechanism exploration, and laid a foundation for follow-up research projects.

Chapter 5 explores the correlation between the branching pathways of C₁ and C₂₊ products and surface-adsorbed hydrogen (*H) in CO₂RR by synthesized La-Cu bimetallic oxide catalysts (La-CuO_x). The water dissociation capacity and *H abundance of the catalyst surface is thoroughly evaluated. Moreover, the electrocatalytic performance of La-CuO_x catalysts with varying La-doping amounts for CO₂RR, as well as their reaction mechanisms for various products formation are revealed by *in situ* FTIR and DFT

calculation. As an extension of Chapter 4, this work achieves an improvement in CO₂RR product value from CO to CH₄ and C₂H₄, and current density from 10 to 300 mA cm⁻².

Chapter 6 examines the structure-function relationship between hybrid hydroxide-metal interface and CO₂RR-to-C₂H₄ by prepared Europium hydroxide modified oxide-derived copper oxide catalysts (Eu(OH)₃-Cu). The composition and phase of Eu(OH)₃-Cu evolution before and after different CO₂RR time are carefully assessed. Furthermore, the electrocatalytic performance, reaction pathways and asymmetric C-C coupling mechanism are explored by *in situ* FTIR and DFT calculation. As an extension of Chapter 4 and Chapter 5, this project further enhanced the electron selectivity and current density of C₂H₄ and C₂₊ products, approaching them to industrial application standards.

Finally, Chapter 7 summarizes the key findings and conclusions from this PhD research project. Apart from this, the limitations of current research and proposed future work on electrochemical CO₂ reduction reaction from lab to fab have been listed and discussed in this section.

Chapter 2 Literature Review

*Parts of **Chapter 2** have been adapted with permission from the following publication:*

Z. Guo, F. Yang, X. Li, H. Zhu, H. Do, K. Loon Fow, J.D. Hirst, T. Wu, Q. Ye, Y. Peng, H. Bin Wu, A. Wu, M. Xu, Electrocatalytic CO₂ reduction to C₂H₄: From lab to fab, *Journal of Energy Chemistry*, **2024**, 90, 540-564.

Considering global warming and the need for alternative energy sources, green energy technologies have emerged as a viable solution. As the transition to sustainable energy progresses, the efficient operation of power systems relies heavily on electrochemical energy storage [10]. The interconnectedness between various forms of energy is essential for adjusting the social energy structure and facilitating energy transformation. Electrochemistry offers an opportunity to convert electrical and chemical energy interchangeably. In the realm of renewable energy technologies, electrocatalysis plays a crucial role in the energy conversion process, particularly in electrocatalytic CO₂ conversion to multicarbon products [5, 62, 63]. The electrochemical reduction of carbon dioxide powered by renewable electricity represents a promising strategy for converting CO₂ into high-value carbon-based chemicals and fuels (**Figure 2.1**). This approach not only enables a closed-loop anthropogenic carbon cycle but also converts intermittent energy into chemical energy for the storage of surplus renewable electricity [64].

This chapter begins by reviewing current research on the CO₂RR process and detailing the value of electroreduction products and their technological advantages. Subsequently, this chapter provides a comprehensive review of the factors influencing the CO₂RR process, including electrocatalysts, ion exchange membranes, electrolytes, and electrochemical cells. Finally, this chapter presents a detailed review of transition metal catalysts toward high-performance CO₂RR, focusing on Ni-based single-atom electrocatalysts, Cu-based electrocatalysts, and rare earth electrocatalysts.

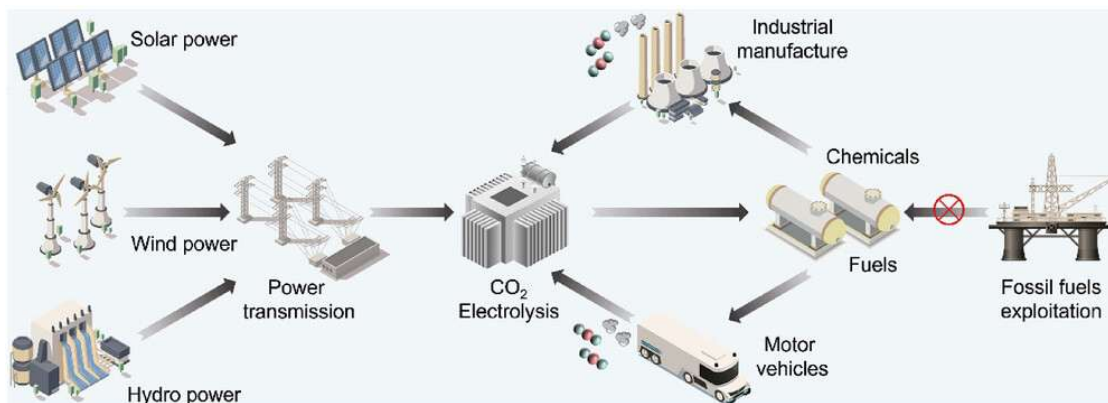


Figure 2.1: The electrochemical CO₂ reduction reaction technology and the corresponding sustainable carbon energy cycle. Reproduced from reference [64].

2.1 Electrochemical CO₂ reduction reaction

2.1.1 CO₂ properties

Understanding the fundamentals of the CO₂RR is crucial for the development of stable and efficient electrocatalysts. Electrode materials for CO₂RR are designed based on the orbital properties of the CO₂ molecule. CO₂ is a linear triatomic molecule characterized by a centre of symmetry, cylindrical axial symmetry, and a horizontal plane of symmetry [65]. As observed in the equilibrium molecular geometry, CO₂ is a central and linearly symmetric stable molecule. Within the linear triatomic molecule CO₂, C=O has a bond energy of 750 kJ mol⁻¹ and a bond length of 1.12 Å. Therefore, this is considered a highly stable molecule without an electric dipole moment [66-68].

As shown in **Figure 2.2**, hybridization of the 2s and 2p_x orbitals in the CO₂ molecule results in the formation of two σ bonds and two π bonds, along with two sp hybridized orbitals. Among them, each sp hybridized orbital of carbon forms a σ-bond with a 2p_z orbital of one oxygen, while each π(π^{3/4}) bond consists of a 2p_y/2p_z orbital, two 2p_x orbitals, and a 2p_y orbital. These structures confer a high bond energy stability to CO₂ molecules. In the CO₂ molecule, the lowest unoccupied molecular orbital (LUMO) is situated at the

carbon centre, which exhibits Lewis's acidity and possesses the highest oxidation state, while the highest occupied molecular orbital (HOMO) is located at the more electronegative oxygen atom. The LUMO is a C-O σ orbital, whereas LUMO+1 represents a straightforward combination of in-plane and out-of-plane C-O π orbitals [69]. These orbitals need to be filled to facilitate the acquisition of the necessary electrons from the active centre of the catalyst during CO₂RR. This process is crucial for effective CO₂ transformation into reduced products. Therefore, to effectively activate CO₂, the electron donor orbitals of the catalyst's active centre must overlap with the acceptor orbitals of CO₂. Additionally, the electronic chemical potential at this juncture must exceed the free energy required to drive the reaction. Typically, the electrocatalyst should form a chemical bond with CO₂ to stabilize the $^*\text{CO}_2^{\cdot-}$ radical or reaction intermediate [69, 70]. This stabilization is essential for facilitating further reaction steps for converting CO₂ into valuable products.

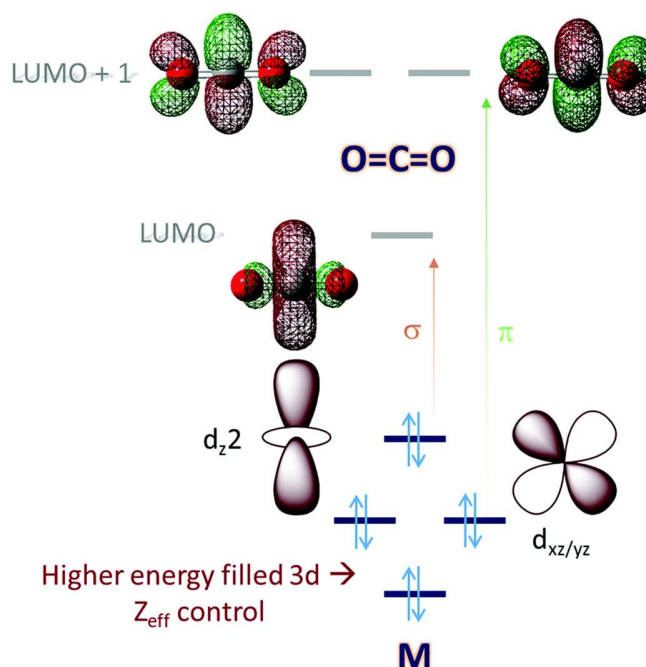


Figure 2.2: Electronic structure consideration of CO₂ activation and reduction using a 3d metal site. Reproduced from reference [69].

2.1.2 Reaction pathways of CO₂ reduction

The CO₂ electroreduction typically occurs at the electrode-electrolyte interface, where the commonly used electrolyte is high-quality proton-donor H₂O, and the electrodes are solid electrocatalysts integrated within H-type electrolytic cell or gas-fed flow cell. As mentioned above, during the CO₂RR process, CO₂ are first adsorbed onto the catalyst surface to form *CO₂^{•−} species, which are subsequently converted into a variety of reaction intermediates. As illustrated in the **Table A 1**, CO₂ has the potential to produce up to 16 distinct products depending on the number of electrons and protons transferred during the reaction. Recent research efforts have focused on enhancing the selectivity of C₁ and C₂₊ products, with their reaction pathways being thoroughly investigated. Below, several representative reaction pathways for C₁ and C₂₊ product formation are outlined.

(1) Basic pathways for CO₂RR to C₁ product

As shown in **Figure 2.3**, in the CO₂RR process, varying adsorption states of the reaction intermediate influence the reaction pathways, thereby yielding distinct product types. For instance, the carbon adsorption state (*COOH) and the oxygen adsorption state (*OCHO) of a reaction intermediate are commonly associated with pathways that produce the two-electron reduction products carbon monoxide (CO) and formic acid (HCOOH), respectively. *COOH can yield *CO through electron and proton transfer, followed by dehydration reactions, which can subsequently produce *CHO or *COH via hydrogenation. The *CHOH species generated from the further hydrogenation of *CHO and *COH can be converted to *CH₂OH via protonation. This intermediate subsequently diverges into two reaction pathways, leading to the formation of the six-electron reduction product methanol (CH₃OH) and the eight-electron reduction product methane (CH₄). Moreover, *CHO can

be protonated to produce $^*\text{CH}_2\text{O}$ and $^*\text{CH}_3\text{O}$, which are important intermediates in the formation of CH_4 and CH_3OH . However, the selectivity of CH_3OH in the CO_2RR process is much lower than that of CH_4 , which is mainly due to the presence of high energy barriers in the conversion of $^*\text{CH}_2\text{OH}$ and $^*\text{CH}_3\text{O}$ to methanol, resulting in kinetically limited CH_3OH production.

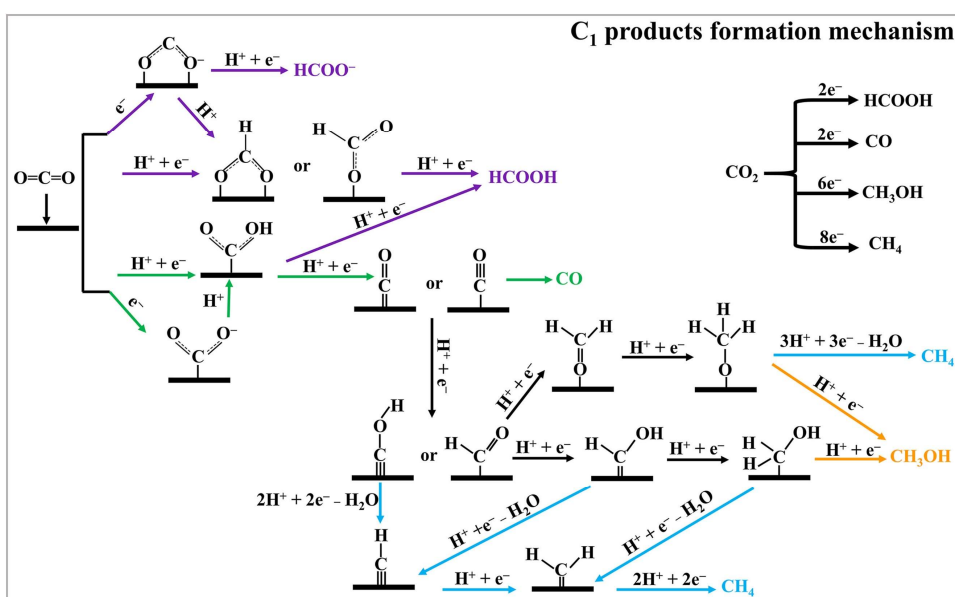


Figure 2.3: The formation mechanism of various C_1 products. Reproduced from reference [71].

(2) Basic pathways for CO₂RR to C₂+ product

Dimerization of carbon-containing intermediates is essential for C₂₊ product formation and is a rate-determining step in the CO₂RR process. Here, the dimerization of *CO serves as a key example of C₂₊ product formation. Similarly, other protonation coupling pathways can be formed, including *CO-*CHO, *CO-*COH, *CHO-*CHO, and *CO-*CH₂, among others. The various pathways for producing different C₂₊ products are illustrated in the **Figure 2.4**, highlighting *CO as a crucial intermediate in the synthesis of multicarbon products through C-C coupling. The dimerization of *CO leads to proton and

electron transfer, resulting in the formation of $^*\text{COCHO}$. This intermediate is then further protonated to yield the 8-electron reduced product acetate (CH_3COOH). The CO dimer or $^*\text{COCO}$ species can undergo proton transfer to form $^*\text{COCO}$ H. This intermediate then proceeds through a series of proton-electron transfer steps, ultimately yielding the 12-electron reduced product C_2H_4 . Ethanol ($\text{C}_2\text{H}_5\text{OH}$) is another 12-electron reduced product that can be further reduced by intermediates such as $\text{CH}_3\text{CH}_2\text{O}^*$ or $^*\text{CHCOH}$. Additionally, the species CH_2CHO^* and $\text{CH}_3\text{CH}_2\text{O}^*$ can undergo further proton-electron transfer steps, leading to the formation of the 10-electron reduced product acetaldehyde (CH_3CHO) and the 12-electron reduced product ethane (C_2H_6), respectively.

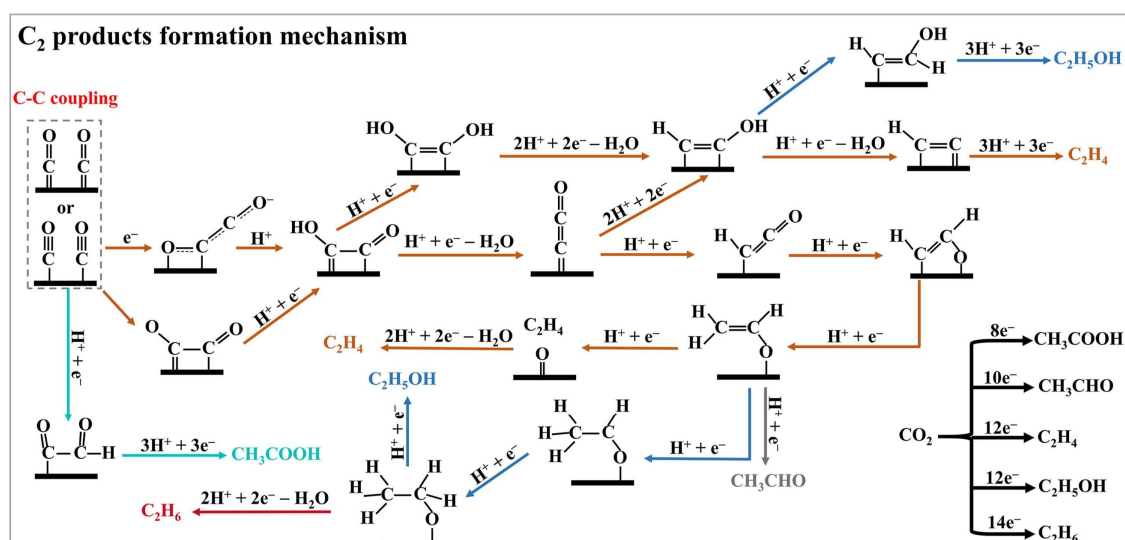


Figure 2.4: The formation mechanism of various C₂ products. Reproduced from reference [71].

2.1.3 Product values of CO₂ reduction

While numerous products emerge from the electrocatalytic CO₂ conversion, many studies have identified CO and C₂H₄ as the most promising candidates for industrial application, considering both the efficiency of current catalysts and the costs associated with product separation and market demand [62, 72]. This thesis focuses on CO₂RR-to-CO

and CO₂RR-to-C₂H₄. These two processes have great potential for combating climate warming and energy crisis among the CO₂RR series, which are discussed below.

(1) CO₂RR-to-CO

The electrochemical CO₂RR-to-CO segment is the most fundamental and critical aspect of the CO₂ electroreduction series. This is primarily because CO serves as a key component of syngas (a crucial industrial gas feedstock consisting of a mixture of CO and H₂) and is frequently utilized as a reactant in Fischer-Tropsch chemistry for the synthesis of various organic compounds [72].

Conventional CO synthesis is a high-temperature endothermic process characterized by low reaction rates, low energy efficiency, and high production costs. Consequently, replacing these traditional high-temperature methods with green electrochemical conversion represents a critical strategy for facilitating the energy transition [73]. Moreover, CO₂RR-to-CO process is the most readily achievable among all CO₂RR-to-C_x compound processes due to the lower operating costs (CO₂ feedstock and input power, product separation) and hardware costs (CO₂ electrolyzer and associated components) during commercialization. Besides, the CO₂RR-to-CO process involves only two electrons (The standard electrode potential for CO is -0.11V vs. RHE). As opposed to the conversion processes listed in **Figure 2.5**, CO₂RR-to-CO has the lowest cost of electricity. Considering that the price of electricity for industrial use is US\$ 0.05/kWh, the minimum cost of recycling CO₂ to CO is only US\$ 0.13/kg [72]. Besides, CO₂RR-to-CO offers significant operating cost advantages over other two-electron reactions, such as CO₂RR-to-HCOOH, primarily because liquid products typically require separation from the electrolyte solution. This liquid-phase separation incurs higher costs compared to the separation of gas-phase

CO from a liquid electrolyte. Hence, industrial-scale CO₂RR-to-CO process emerges as the most economically competitive strategy for CO₂ conversion [72-75].

(2) CO₂RR-to-C₂H₄

The electrochemical CO₂RR-to-C₂H₄ is a highly complex and valuable segment of the CO₂ electroreduction series. Among the hydrocarbon products from CO₂RR, ethylene (C₂H₄) is particularly noteworthy as it serves as a primary raw material to produce plastics, catalysts, and cleaning agents. The production of C₂H₄ is usually closely integrated with refineries, forming a large industrial chain. The annual global production capacity of C₂H₄ currently stands at nearly 200 million tonnes [76-78]. As the most significant organic chemical, C₂H₄ has the highest market price (1.04 \$/kg) (**Figure 2.5**) [72]. Given the significant market size and high prices of C₂H₄, ranging from 600 to 1200 dollars per ton (depending on region), it is a highly promising target for CO₂RR [31, 79-81].

However, at present, the traditional industrial route for ethylene production is steam cracking (800 to 900°C) [82]. This is a process in which hydrocarbons are broken down by refining petroleum or ethane in the presence of steam. Thermal cracking generates substantial amounts of CO₂ and other harmful gases, leading to environmental pollution. Furthermore, it depends on finite fossil fuels like oil and natural gas, exacerbating resource constraints [83]. Besides, as a conventional high-temperature steam cracking process, it is a non-selective and non-catalytic conversion reaction [84-88]. This also implies that the variety of products from cracking is complex and requires high operational costs for further separation and purification. Hence, the development and implementation of CO₂RR-to-C₂H₄ is a crucial and promising aspect of the strategy to promote the transformation of the traditional energy mix [62, 66].

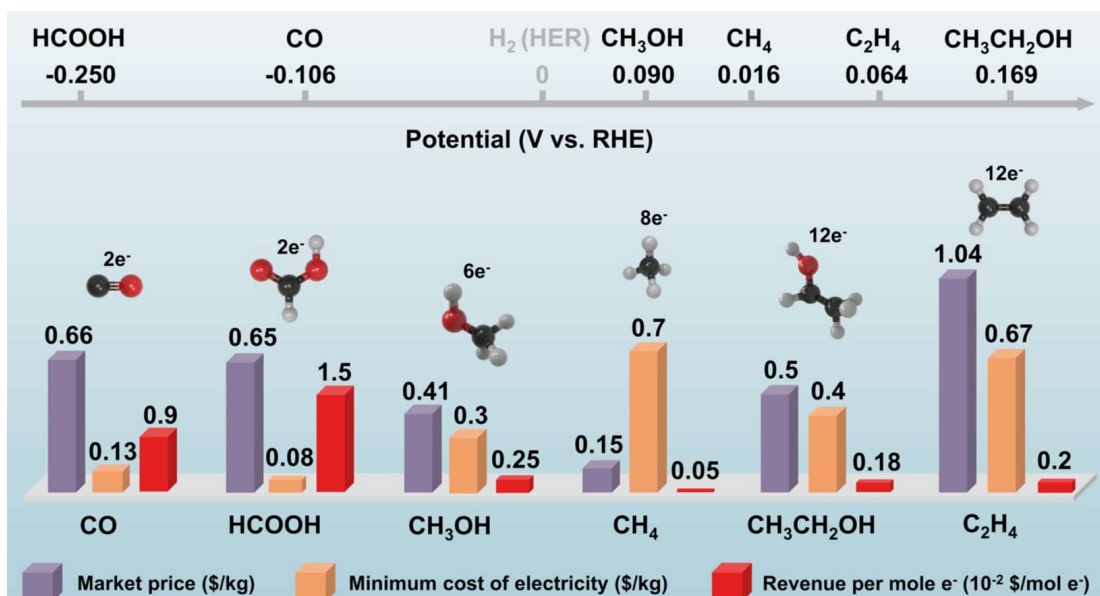


Figure 2.5: The standard reduction potentials for products of CO₂ electrolysis are illustrated in the upper panel, while the lower panel presents an economic analysis that includes market prices, minimum electricity costs per kilogram, and revenue generated per mole of electrons for each product, based on 2017 US commodity prices. Reproduced from reference [72].

2.2 Factors influencing the electrochemical CO₂ reduction reaction

2.2.1 Electrocatalyst effect

The electrocatalyst is the fundamental component of CO₂RR system, playing a critical role in influencing both the reaction rate and product selectivity. According to Sabatier's principle, optimal catalytic activity is anticipated when the adsorption energy of key reaction intermediates on the catalyst surface is at an ideal strength [42]. Adsorption energies that are too weak hinder the formation of intermediates by inadequately activating reactants, whereas adsorption energies that are excessively strong impede the conversion of stabilized intermediates into target products for desorption [89]. Therefore, the interaction between the reactants and the catalyst surface significantly influences its electrochemical performance. The performance of electrocatalysts primarily depends on

several factors, including the chemical structure (composition and valence), geometrical structure (morphology), atomic arrangement, and electronic structure. Therefore, the design of the electrocatalyst is critical for achieving optimal performance in CO₂RR.

Currently, metal-based catalysts in CO₂RR are extensively studied, encompassing both transition metals and main group metals. These catalysts are categorized based on their surface binding strength to CO₂ reduction intermediates and the types of generated products, as illustrated in **Figure 2.6** [90]. Metal-based catalysts, including Titanium (Ti), Manganese (Mn), Iron (Fe), Nickel (Ni), and Platinum (Pt), exhibit low activity for the reduction of CO₂ and primarily facilitate the production of H₂. In contrast, catalysts such as Cadmium (Cd), Indium (In), Tin (Sn), Mercury (Hg), and Bismuth (Bi) enable the conversion of CO₂ to *OCHO or *COOH, leading to the formation of HCOOH or HCOO⁻. Additionally, catalysts like Palladium (Pd), Silver (Ag), Gold (Au), Zinc (Zn), and Chromium (Cr) are capable of reducing *COOH intermediates to *CO. However, due to the weak binding of *CO to the metal surface, these catalysts are unable to continue the reduction process to yield other products, resulting in the formation of CO. Copper (Cu) is unique among metals in that Cu-based catalysts can reduce CO₂ to form HCOOH and CO or a wide range of C₂₊ products through further reduction and *CO dimerization.

As previously discussed in Section 2.1.3, the target products of this thesis are CO and C₂H₄. However, main-group metal-based materials (such as Sn [91], Bi [92], In [93], etc.) demonstrate promising potential in CO₂RR for the production of HCOOH or HCOO⁻, owing to their thermodynamically more favourable adsorption of *OCOH compared to *COOH. Therefore, this thesis will focus on transition metal-based electrocatalysts, and their development will be reviewed in detail in the following Section 2.3.

										III A	IV A	V A
										B	C	N
	IV B	V B	VI B	VII B	VIII			I B	II B	Al	Si	P
	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
	Zr	Nb	Mo	Td	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi

	H ₂		CO		HCOOH		CO, HCOOH, C ₂ + products
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Figure 2.6: Schematic classification of metal catalysts for electrocatalytic CO₂ reduction and their corresponding main products. Reproduced from reference [90].

2.2.2 Electrolyte effect

The electrolyte effect is another critical factor influencing the CO₂RR. Its primary role is to facilitate ion conduction between the electrodes, thereby establishing a closed circuit within the electrochemical system [94, 95]. The ideal electrolyte should possess, but is not limited to, the following characteristics: high solubility for CO₂, high ionic conductivity, strong electrochemical stability, good chemical compatibility with the electrode material to facilitate efficient mass transfer of CO₂ molecules from the electrolyte to the electrode surface, low viscosity, ease of handling and storage, as well as being environmentally friendly and safe [96]. Therefore, the selection of an appropriate electrolyte is critical.

As shown in **Figure 2.7**, there are two main types of electrolytes: aqueous electrolytes and non-aqueous electrolytes. Non-aqueous electrolytes can be further divided into three categories: organic solvents, ionic liquids, and the mixture of them. However, non-aqueous system electrolytes still face many difficulties in CO₂RR. Organic electrolytes are characterized by their high cost, non-consumable nature, and difficulty in recycling. The complex structure of ionic liquids has limited their in-depth study in electrocatalysis and

large-scale applications [96, 97]. Despite the superior conductivity of ionic liquids, the current density has not been significantly improved, and these problems also exist in hybrid electrolytes. Aqueous electrolytes, including acidic, neutral, alkaline, and water-in-salt solutions are the most widely studied and utilized electrolyte systems due to several advantages. These include low cost, scalability, wide availability, relatively simple preparation methods, safe handling and storage, and stable ionic conductivity. Moreover, aqueous solutions serve as both proton donors and acceptors, enabling the formation of various electrochemically active species [98, 99]. Factors such as pH [100, 101], anions [102, 103] and cations [104, 105] present in aqueous electrolyte, significantly influence the performance of CO₂RR.

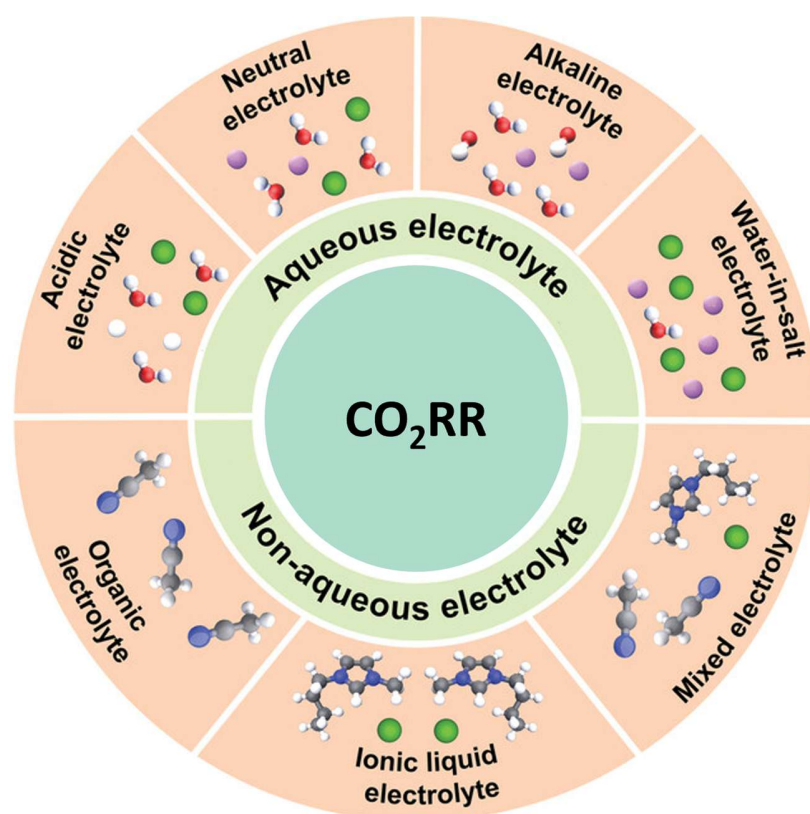


Figure 2.7: Schematic overview of categories of electrolytes applied in electrocatalytic CO₂RR. Reproduced from reference [96].

The local pH at the electrode interface is a crucial parameter for regulating electrocatalytic selectivity [106]. Both CO₂ reduction and competitive HER contribute to an increase in OH⁻ concentration, resulting in a significant disparity between the local pH near the electrode surface and the pH of the broader catalytic system. To mitigate this issue, a buffer electrolyte can be employed to maintain a relatively stable pH, thereby optimizing the selectivity and efficiency of CO₂RR [107]. Additionally, the implementation of buffered electrolytes can effectively regulate the local environment, improve reaction conditions, and enhance catalytic performance.

However, the influence of solution pH is multifaceted, and conclusions cannot be universally applied to various electrocatalyst systems and different target products. Generally, lower pH values favour the production of H₂ in competitive reactions. Simultaneously, a lower pH enhances the formation of hydrogenated reduction products of CO₂, such as formate and methanol. In contrast, higher pH levels promote the production of carbon monoxide and multi-carbon products. As shown in **Figure 2.8**, Liu et al. developed a microkinetic model to examine the influence of electrolyte pH on the kinetics of CO₂RR on the surface of the Cu (211) catalyst. Their findings indicated that both the Tafel slope and polarization curves of CO₂RR changed with varying pH values [108]. Further, both theoretical and experimental findings highlight that the pH value of the electrolyte significantly influences the activity and selectivity of C₁ and C₂₊ products. Specifically, the free energy of the C₁ and C₂₊ product pathway is lower at pH = 13 compared to pH = 7 at -0.5 V vs. RHE, indicating that higher pH levels favour the formation of C₁ and C₂₊ products.

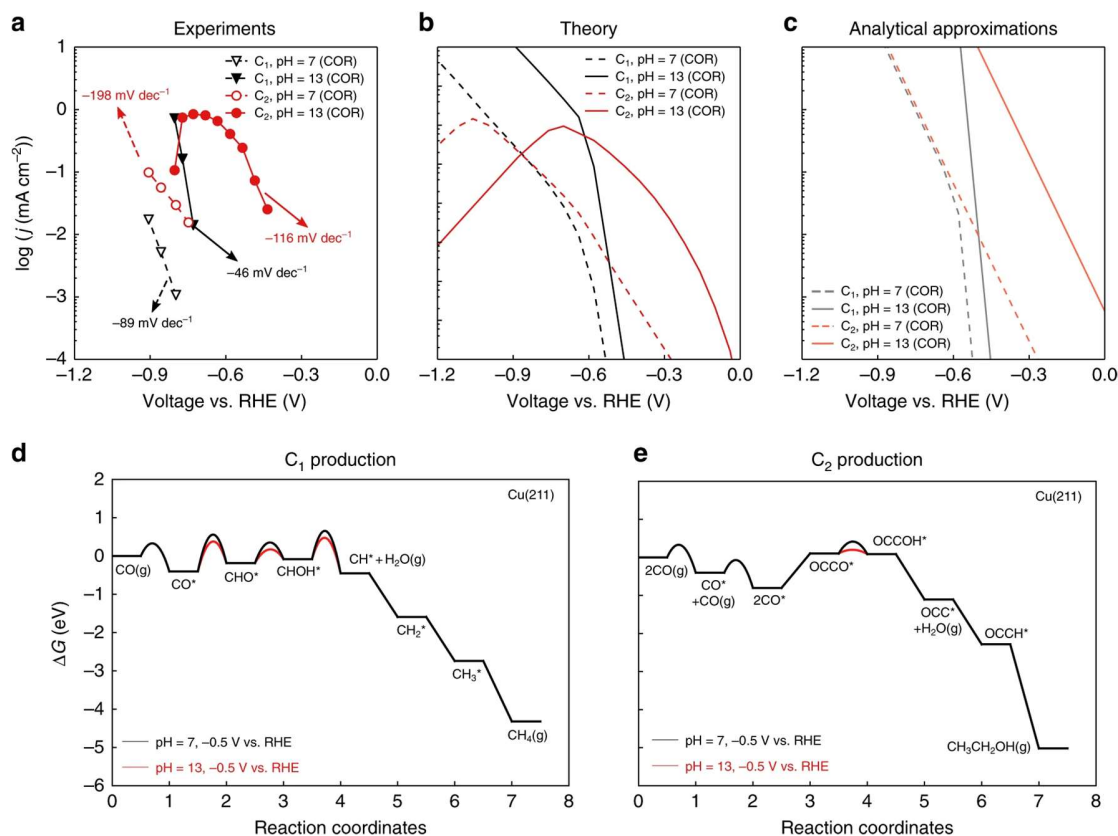


Figure 2.8: The effect of pH on C₁ and C₂ product activities. (a) Measured CO₂RR activities toward C₁ and C₂ at pH = 7 and 13. (b) Predicted CO₂RR polarization curves from the microkinetic model at pH = 7 and pH = 13. (c) Approximated CO₂RR polarization curves. Free energy diagram of the dominant pathway at low coverage for (d) C₁ formation and (e) C₂ formation at -0.5 V vs. RHE at pH = 7 and pH = 13 on Cu (211). Reproduced from reference [108].

Anions in the electrolyte can also modulate the performance of CO₂RR. Generally, the presence of halides, sulphate (SO₄²⁻), and perchlorate (ClO₄⁻) on the surface of the Cu catalyst is effective in promoting the formation of C₂H₄ and C₂H₅OH [109-111], whereas the presence of HCO₃⁻ facilitates the generation of C₁ products [112]. Cuernya et al. demonstrated that halogen ions can induce the reconstruction of nanostructured CuO. Furthermore, the introduction of halide ions into the electrolyte can lower the overpotential for CO₂RR, following the order of Cl⁻ < Br⁻ < I⁻. This effect arises from the adsorption of

halide ions on the surface of Cu, which facilitates the transfer of charge to CO₂ molecules, thereby promoting the formation and stabilization of *COOH intermediates [113].

Cations within the electrolyte, particularly those of alkali metals, can engage with reaction intermediates via non-covalent interactions or through electrostatic field effects, thereby influencing the characteristics of the CO₂RR [114, 115]. Distinctive adsorption of various intermediates is an essential factor that modulate the observed differences in catalytic selectivity. Hori et al. demonstrated a positive correlation between the selectivity for C₂H₄ and the size of the cations, with electron selectivity following the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ [116]. These insights imply that the selection of cation is intricately linked to the activity and selectivity of the CO₂RR.

2.2.3 Electrochemical cell

Electrolyzers encompass both solid oxide electrolyzers operating at high temperatures (above 600 °C) and low-temperature (room-temperature) electrolyzers. While significant progress has been made in the electrolysis of CO₂ into CO using solid oxide electrolyzers, waste heat from high-temperature electrolysis may cause environmental pollution or waste of resources [117]. Consequently, the production of CO, C₂H₄ and other compounds primarily takes place in room-temperature CO₂ electrolysis. Therefore, this section focuses on the room-temperature electrochemical system [118, 119]. To achieve the formation of target products at room-temperature, three primary electrochemical systems are employed: the H-cell, flow-cell, and membrane electrode assembly (MEA). These electrochemical systems offer distinct approaches for operating CO₂RR process, each possessing unique advantages and considerations. The H-cell configuration utilizes a liquid electrolyte, while the flow-cell operates with a continuous flow of electrolyte. On the other hand, the MEA

system incorporates a membrane electrode assembly, which facilitates selective ion transport and catalytic reactions [120].

(1) H-cell

In the H-cell configuration, the integration of the cathode and anode compartments within the electrolyte are seamless (**Figure 2.9a**). The ion-exchange membrane plays a crucial role as a selective barrier, effectively separating the distinct reaction environments of the cathode and anode. However, achieving high current densities exceeding 200 mA cm^{-2} in H-cell is a significant challenge primarily due to gas diffusion limitations. The sluggish diffusion characteristics, especially the relatively low diffusion coefficient ($D_{\text{CO}_2} = 1.94 \times 10^{-3} \text{ mm}^2 \text{ s}^{-1}$ at 25°C) and limited solubility (34 mM, standard situation) of CO_2 , restrict the mass transfer rate during the CO_2RR process [119]. Consequently, these diffusion limitations hinder the attainment of higher current densities in the CO_2RR process [118, 119]. Another limitation of the H-cell configuration is its incompatibility with alkaline electrolytes, as hydroxide ions readily react with dissolved CO_2 , resulting in the formation of carbonates [81, 121, 122]. Besides, the application of non-alkaline electrolytes exacerbates the occurrence of ohmic overpotential [123]. Therefore, H-cells are generally employed in laboratories for fundamental research.

(2) Flow-cell

Gas-fed flow-cells are the most extensively studied reactors in the CO_2RR process. This electrolyzer can achieve industrial currents readily and potentials can be monitored by inserting reference electrodes for CO_2RR fundamental research (**Figure 2.9b**) [124, 125]. The flow-cell configuration offers a viable solution to address the challenges associated with the liquid-based systems. Instead of relying on liquid, the flow-cell diffuses

the gas directly onto the electrode surface [126-129]. In this setup, gaseous CO₂ is fed directly into the interface between the catalyst and the electrolyte, promoting efficient mass transfer of CO₂ to the catalyst layer. This design enables swift diffusion of CO₂, thereby enhancing the overall performance of the flow-cell electrolyzer [130, 131]. The use of gas diffusion electrode (GDE) in flow-cells introduces new design concepts and operating principles in the field of CO₂ abatement, and improves the feasibility of gas-fed reactors for commercial applications [132, 133]. As reported, a gas-fed flow-cell with an alkaline electrolyte (10 M KOH) can operate at a constant voltage of -0.55 V (vs. RHE) for 150 hours, producing C₂H₄. Furthermore, increasing the electrolyte's concentration enhances conductivity, improves reaction kinetics, and enables current densities over 200 mA cm^{-2} to be achieved at an overpotential of less than 0.7 V [123].

(3) MEA

The membrane electrode assembly (MEA), depicted in **Figure 2.9c**, is a significant advancement in gas-fed flow-cell technology. This cell configuration eliminates the need for cathode flowing electrolyte by directly placing the cathode GDE in close proximity to the ion exchange membrane [28, 134]. Referred to as the zero-gap design structure, this arrangement offers a distinct advantage by greatly enhancing the rate of the CO₂RR. Zhuang's group reported the first pure water MEA for CO₂RR-to-CO in 2019, reaching an industrial-scale current density of 500 mA cm^{-2} [135]. However, the use of these two gas-fed electrolyzer results in the reaction of CO₂ with the strong alkaline electrolyte, leading to the formation of (bi)carbonates and the precipitation of salts on the GDE and ion exchange membranes. This situation can cause a decrease in the conductivity of the entire system [136]. Additionally, the liquid product can be diluted into the bulk electrolyte,

thereby increasing downstream separation costs. Urgent issues to be addressed include catholyte stability, ohmic loss of electrolyte, consumption of CO_2 due to its reaction with the electrolyte, catalyst contamination caused by electrolyte impurities, and flooding of the GDE. Therefore, the design of an electrolytic cell capable of overcoming these challenges is of utmost importance for the industrial application of CO_2RR [137].

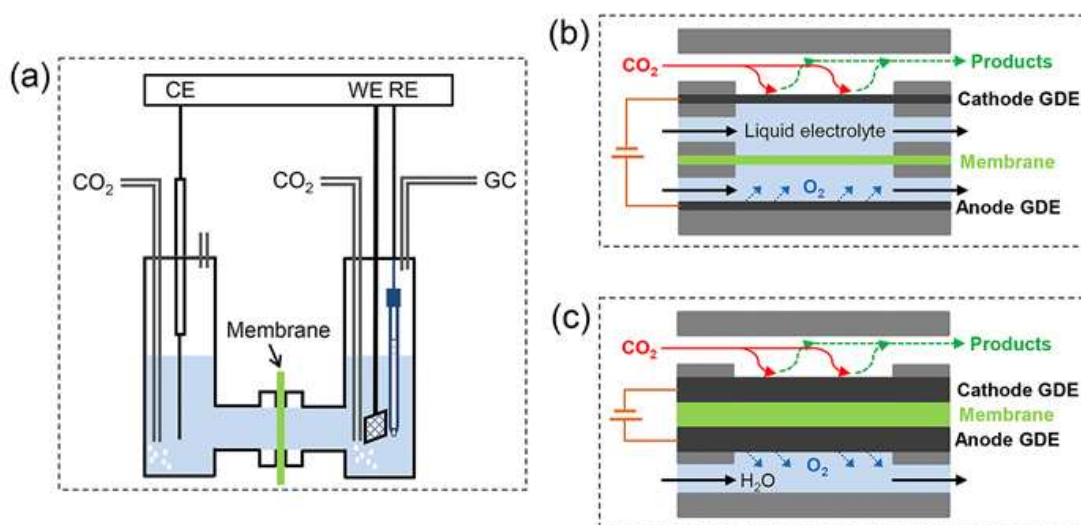


Figure 2.9: Schematic diagram of CO_2 electrolyzers (a) H-cell, (b) Flow-cell and (c) MEA. Reproduced from reference [138].

2.3 Development of CO_2RR electrocatalysts

As mentioned in section 2.2, transition metal-based electrocatalysts, with their high activity, tuneable selectivity towards various desired products (e.g., CO , C_2H_4), cost-effectiveness, and robust stability, are well-suited for CO_2RR . Directed by the increased value of products, Ni-based single atom electrocatalysts toward CO_2RR -to- C_1 products, Cu-based and rare-earth element-doped electrocatalysts toward CO_2RR -to- C_{2+} products are reviewed respectively. Beyond this, bimetallic materials can construct unique electronic structures through the synergy of heterogeneous metal components, thereby

regulating the electronic distribution of active sites and optimising the active interface, thus improving the catalyst activity [50]. Herein, more specifically, sub-sections highlight Ni-based dual atom catalyst, alloy and rare-earth element-doped materials.

2.3.1 Ni-based single atom electrocatalyst

Single atom electrocatalysts (SACs) have so far attracted widespread interest in the field of electrocatalytic CO₂RR due to their separated and well-defined active sites. The experimental strategy of reducing the metal nanoparticle size to nanoclusters or even individual atoms can significantly improve the reactivity and selectivity of electrocatalysis toward the target product. For example, metallic Ni catalysts showed a significant size-dependent effect on CO₂RR-to-CO. As shown in **Figure 2.10**, bulk metallic Ni catalysts are mainly for HER and have low CO selectivity. When the size of Ni catalysts is reduced to the nanoscale, changes in the coordination number of active centres and the local electronic structure of catalysts can affect the activity and selectivity of the catalysts through facets and defects. The Ni single atom catalysts exhibited high selectivity for CO₂RR-to-CO with 97% FE and less than 3% FE for HER [139].

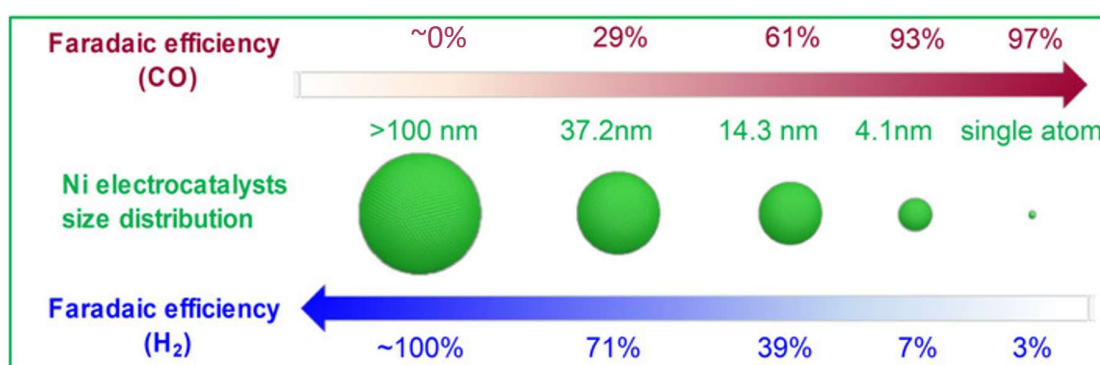


Figure 2.10: Ni metal supported on nitrogen doped carbon demonstrates remarkable size dependent effect on CO₂RR-to-CO. Reproduced from reference [139].

Generally, the atomically dispersed metal sites on the SAC generally act as the main active centres during electrocatalysis [38, 51, 140-145]. However, the high surface free energy of the atomic sites makes them easy to aggregate and difficult to obtain. Consequently, the separated atoms are anchored to the various substrates to form a stable configuration and to maintain a suitable distance. The high dispersion of metal atoms in SACs highlights the advantages of individual atoms with extremely high activity and allows for increased atom utilization and reduced feedstock costs in large-scale applications. Apart from this, the unsaturated coordination environment of SACs can enhance CO₂RR performance. This is because the unsaturated coordination environment can play an important role in the activation, adsorption and desorption of CO₂ on the catalyst surface, aiming to reduce the whole reaction energy barrier. Moreover, the synergy between the single atom and the carrier can lead to a tuning of electronic structure, resulting in the optimal CO₂RR performance [144, 146-148]. Therefore, various carriers, including metals, metal oxides, carbon materials, and their derivatives, have been developed [149].

(1) M-N-C carriers

Among these carriers, atomically dispersed M-N-C catalysts utilize nitrogen-doped carbon-based materials as carriers to anchor single atom. These catalysts offer advantages such as a hierarchical pore structure, large specific surface area, and high electrical conductivity [149]. Thus, atomically dispersed M-N-C catalysts, as a typical class of SACs, have outstanding performance in terms of activity, selectivity, and stability, and show promising prospects in the field of CO₂RR [150]. Atomically dispersed M-N-C catalysts are typically synthesized by combining inorganic metal salts with organic materials containing nitrogen and carbon. This mixture is then subjected to high-temperature

pyrolysis in an inert atmosphere. During the synthesis process, nitrogen atoms are incorporated into the carbon structure, allowing for the formation of M-N coordination, which effectively anchors the metal atoms [149, 150]. This approach significantly enhances the dispersion and stability of the metal atoms within the catalyst matrix [151]. Chen et al. pyrolyzed the precursor formed by mixing graphene, cyanamide and iron salt under nitrogen atmosphere at high temperature. The separated Fe atoms in the catalyst were coordinated with N in graphene to form a stable Fe-N-NG structure, thus obtaining Fe SACs (**Figure 2.11**) [152]. Deng et al. realized the controlled preparation of cobalt (Co) single atoms loaded on N-doped carbon by pyrolysis of Zn-Co zeolitic imidazolate frameworks (ZnCo-ZIFs) precursors [153]. The high-temperature pyrolysis method has broad industrial application prospects for the synthesis of atomically dispersed M-N-C and provides a feasible method for large-scale preparation of high-performance catalysts.

Meanwhile, the local coordination environment in atomically dispersed M-N-C catalysts has crucial effects on the electrocatalytic performance, and the local electron density and the configuration of the active metal sites can be adjusted to affect the charge transfer rate and the adsorption of reaction intermediates, thus modulating the activity and selectivity of CO₂RR [154, 155]. Geng et al. prepared Co₁-N₄ and Co₁-N_{4-x}C_x catalysts with different active sites by pyrolysis assisted by metal organic frameworks (MOFs). It was shown that the active sites of Co₁-N₄ could increase the binding strength of CO₂ and promote the activation of CO₂, which resulted in better catalytic performance than that of Co₁-N_{4-x}C_x [156]. Additionally, the M-N_x coordination formed by the metal and nitrogen species is commonly considered to be the catalytic activity centre, and several studies have demonstrated that differences in the number of N coordination sites also affect the

performance of M-N-C catalysts in electrochemical reforming processes. Liu et al. obtained Ni-N-C catalysts with different Ni-N coordination numbers by high-temperature pyrolysis, in which the N atoms of polypyrrole were doped into porous carbon, which functioned as an anchor to stabilize the Ni atoms. The reduction of Ni-N coordination number facilitates the COOH* formation, which improves the activity of CO₂RR, as demonstrated by DFT calculations [157].

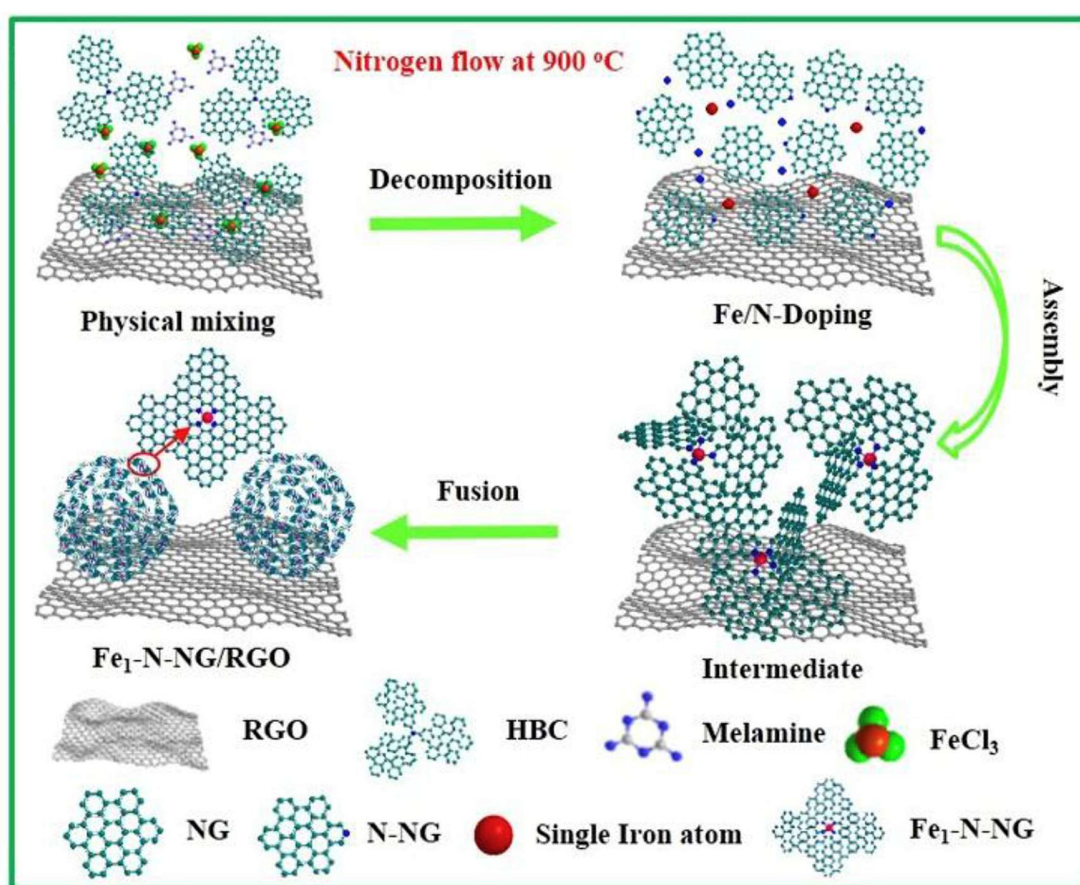


Figure 2.11: Schematic illustration of the Fe SACs formation. Reproduced from reference [152].

(2) Metal atom

Apart from that, the type of metal element is crucial for SAC design. As shown below, the metal elements used to construct the SAC for electrochemical CO₂RR are categorized

into three types, which are transition metals (TM) (Ni, Cu, Zn, Fe, Co and Mo), precious metals (Ag, Pd and Ir) and p-block elements (Sb, Sn and Bi). Commonly reported TM-SACs are used to convert CO₂ to CO through an electrocatalytic strategy. Besides, Cu, Mo, Sb, Co and Sn SACs are reported to convert CO₂ into liquid products (e.g. methanol, methanol, etc.) (**Figure 2.12**) [144, 145]. However, the determinants of product selectivity on SACs remain unclear. Thus, researchers need to further develop and count SACs with higher product selectivity to elaborate the corresponding structure-function relationships.

										B	C	N	O
										Al	Si	P	S
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po

Figure 2.12: The metals using as single atomic sites for CO₂RR. Reproduced from reference [51].

(3) Ni-based single atom catalyst

Importantly, electrocatalysis materials with Ni as the atomically active site show significant advantages. Ni, as a well-stocked group VIII-B metal, has valence states ranging from 0 to +4 [158]. In addition, its moderate CO₂ adsorption capacity and d-band close to the Fermi energy level makes it an ideal alternative to precious metals in the design of catalysts for CO₂RR [159]. The rich redox properties and diverse coordination geometries of nickel make it possible to endow Ni-based materials with specific catalytic functions by rationally designing ligand frameworks to coordinate with Ni centres [160].

In light of this, previous work found that the bulk Ni (111) crystalline surface exhibits strong adsorption energy for CO, resulting in the Ni surface being poisoned by CO*. This property leads to the poor electrocatalytic activity of Ni-based materials even at high application potentials, e.g. Ni-based hydrides/metal oxides usually exhibit excellent HER performance [51, 144]. However, it has been shown that Ni atoms loaded on porous carbon-based materials are potential candidates for CO₂RR due to their high catalytic efficiency and low cost. Firstly, porous carbon-based materials can enhance the diffusion of CO₂ to the active site. In addition, the Ni-N-C coordination has catalytic activity for CO₂RR-to-CO. Jiang's research team has succeeded in loading ordered compartmentalized Ni single atoms into graphene vacancies. Electrochemical tests have shown that in 0.5 M KHCO₃, Ni atomic sites dispersed in graphene carriers can produce CO with a Faradaic efficiency (FE) of up to 93.2% (**Figure 2.13a**) [38]. DFT calculations demonstrate that the characteristic electronic configuration at the Ni single-atom site differs from that of a typical metal Ni catalyst. The former electronic configuration leads to a noticeable reduction of the energy barrier for CO₂ conversion.

Moreover, considering the cost of graphene, some researchers are trying to use cheaper carbon black as an alternative to expensive graphene. For example, Wang et al. employed low-cost carbon black to replace graphene as a carrier for single-atom Ni. This low-cost catalyst achieved a CO Faradaic efficiency of 99% in 0.5 M KHCO₃ (**Figure 2.13b**) [145]. Recent research has reported that stepwise pyrolysis of mixtures of melamine, amino acids and nickel acetate under an Ar atmosphere can give Ni SACs suitable for CO₂RR-to-CO. During pyrolysis at high temperatures in an Ar atmosphere, the melamine undergoes a condensation reaction to form the graphite nitride (g-C₃N₄) that is used as the

base material for the SAC. The voids on the surface of g-C₃N₄ can effectively anchor Ni(II) atoms. The spectroscopy data indicate that this strategy yields a Ni SAC valence of +1 and is coordinated to four pyridine-N. Electrochemical test data show that the synthesized Ni SAC can achieve a current density of 350 A g⁻¹. Furthermore, the Faradaic efficiency of CO reaches 97% at an applied potential of 0.61 V [144].

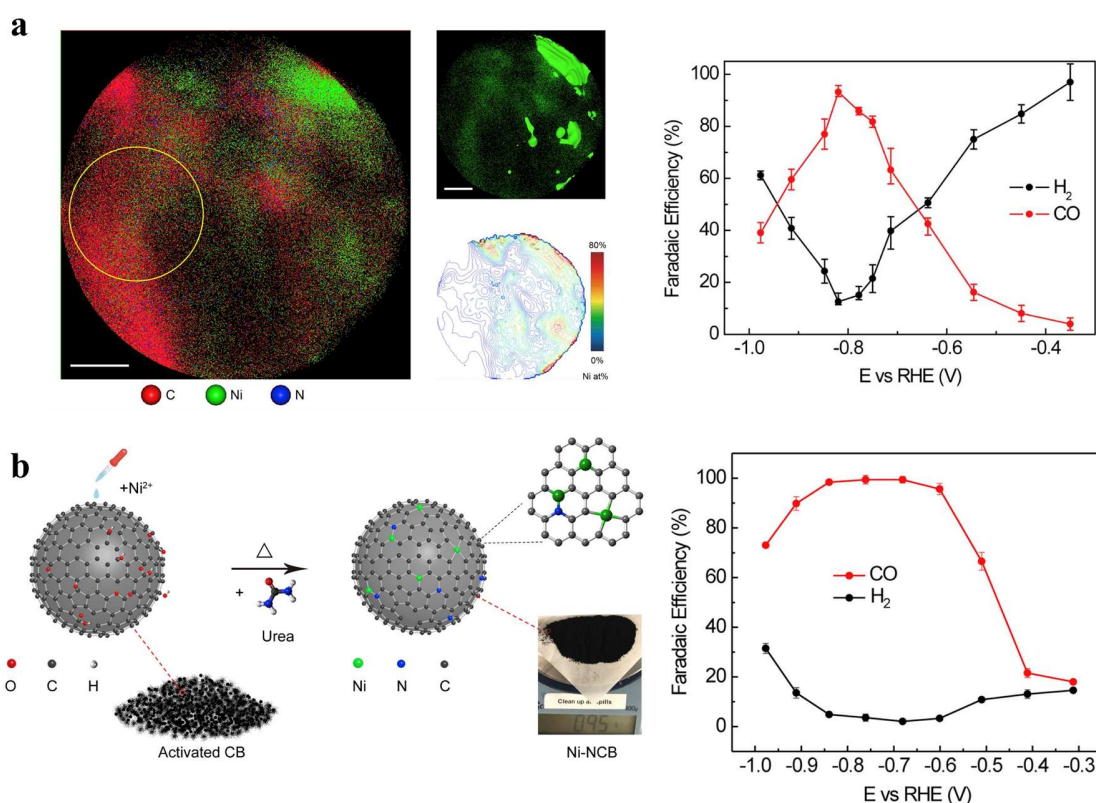


Figure 2.13: (a) 2D atom map of NiN-GS. Scale bar, 10 nm. 2D projected view of Ni atoms. The green areas represent Ni-rich areas (>50 at%). Scale bar, 10 nm. Contour map of Ni concentration with an interval of 2 at%. Reproduced from reference [38]. (b) Schematic of the synthesis of large-scale single-atom Ni-NCB catalyst and its CO₂RR-to-CO performance. Reproduced from reference [145].

Further research has shown that mechanistic studies on the highly selective generation of CO over single-atom catalysts can provide further guidance for the design of efficient catalysts. Strasser et al. revealed the origin of CO₂RR activity and response mechanisms in different SACs [161]. From determined turnover frequency (TOF) maps of CO formation

and DFT theoretical energy maps, they constructed three different reaction kinetic regions (**Figure 2.14**). The Fe, Mn, and Co catalysts among them start CO₂RR at about -0.4 V vs. RHE, while the Ni-N_x and Cu-N_x species, which are weakly bound to *COOH, require a larger overpotential to drive this reaction compared to the other catalysts. The Fe and Co catalysts reach their maximum activity when the overpotential reaches about -0.6 V vs. RHE, while the Ni catalyst is just starting the CO₂RR, and the intermediate controlling the rate of reaction in this region changes from *COOH to *CO. However, as the overpotential continues to increase, the catalytic activity of Fe and Co begins to decline, whereas the Faraday efficiency of the Ni catalyst for CO continues to rise. DFT calculations show that the HER side reactions at this potential are dominated by Fe, Co and Mn catalysts due to the strong binding of H*. In contrast, Ni and Cu catalysts exhibit significantly weaker binding energy for H*, which impedes HER activity on their surfaces. It is noteworthy that the reactivity of the Cu-N_x catalysts observed in the experiments was not as high as that of Ni-N_x. This disparity arises from the thermodynamic instability of Cu-N_x under strong reducing conditions at slightly higher overpotentials (< -0.7 V vs. RHE), where the Cu species are prone to aggregate into metallic Cu nanoparticles, resulting in reduced FE_{CO}.

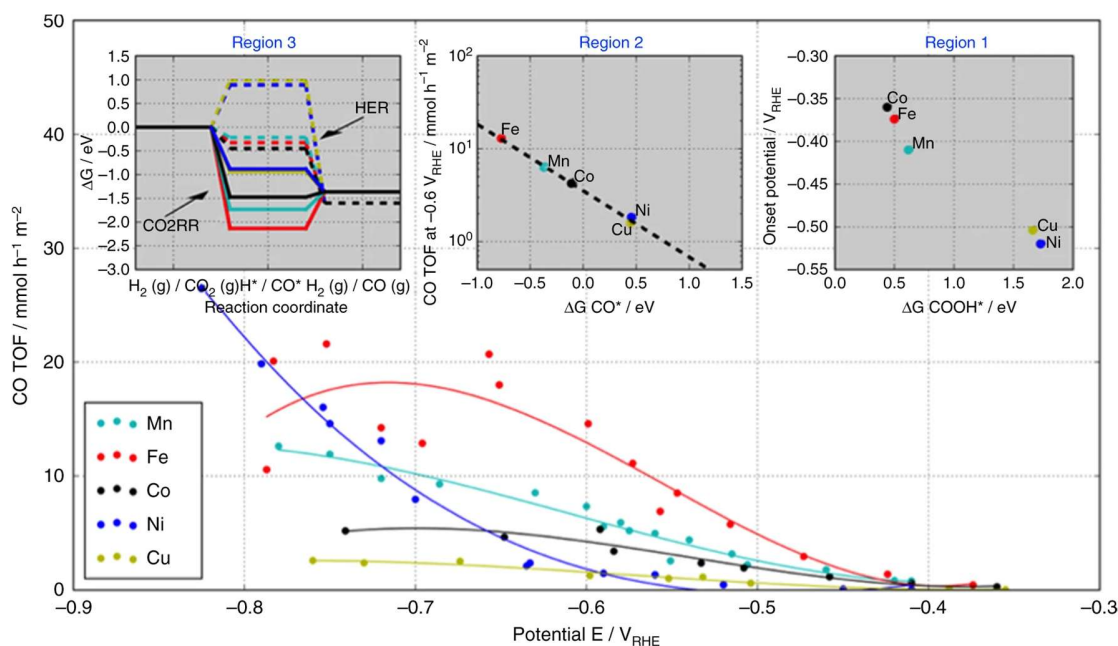


Figure 2.14: Experimental CO₂RR-to-CO generation TOF of M-N-C catalysts versus applied infrared-corrected electrode potential. Reproduced from reference [161].

(4) Ni-based dual atom catalyst

Although SACs exhibit many distinct advantages in CO₂RR, all intermediates (*COOH, *CHO, *CO, etc.) bind to the same metal site results in catalytic activity being limited by the linear relationship between the adsorption energies of various reaction intermediates and atomic sites [162]. Taking CO₂RR-to-CO as an example, the related key intermediates are *COOH and *CO. For CO production, a catalyst must possess a good desorption capacity for *CO; however, the facile desorption of *CO can lead to instability in the intermediate *COOH. This interplay between the adsorption and desorption dynamics of intermediates is crucial for optimizing the overall catalytic performance. The formation of CO requires electrocatalyst with effective desorption ability for *CO. However, excessive desorption of *CO may result in the instability of the *COOH [163]. To disrupt this linear relationship, researchers have developed dual-atom catalysts (DACs)

with bimetallic active sites. Apart from disrupting the linear relationship, DACs retain all the advantages of SACs, increase the metal loading, and further adjust the electronic structure of catalysts [164-166]. According to the relative position of the dual-atom sites, DACs can be divided into isolated dual-atom site catalysts and binuclear dual-atom site catalysts. An isolated dual-atom site consists of two distinct central metal atoms that are anchored to surrounding chelating atoms without forming a metal-metal bond. A binuclear dual-atom site comprises two central metal atoms that are bonded together to create a bimetallic atom pair.

Ren et al. reported a Ni/Fe-N-C catalyst featuring isolated bimetallic Ni-Fe sites. The Ni/Fe-N-C catalyst demonstrated superior performance for CO₂RR-to-CO and achieved a higher current density compared to both Ni-N-C and Fe-N-C [167]. DFT calculations show that the adjacent Ni-Fe centres lower the energy barriers for *COOH formation and *CO desorption through synergistic effects, thereby enhancing the electrocatalytic activity of the bimetallic Ni-Fe DACs for CO₂RR. Moreover, Li et al. developed dual-metal sites (Ni-Fe, Fe-Co, and Ni-Co) in nitrogen-doped carbon derived from ZIF-8 (ZIF-NC) [168]. Compared to other dual-metal atomic site configurations, the Ni-Fe catalyst demonstrates the highest CO₂RR activity and stability. Structural characterization and theoretical calculations reveal that the most active configuration of the N-coordinated bimetallic site is 2N-bridged (Fe-Ni)-N₆, where Fe-N₄ and Ni-N₄ partially share two N atoms. As shown in **Figure 2.15**, the synergistic effect between the two metals (Fe and Ni) contributes to improved adsorption of *COOH and enhanced desorption of *CO compared to the single metallic sites (Fe-N₄ or Ni-N₄), thereby enhancing both intrinsic activity and selectivity.

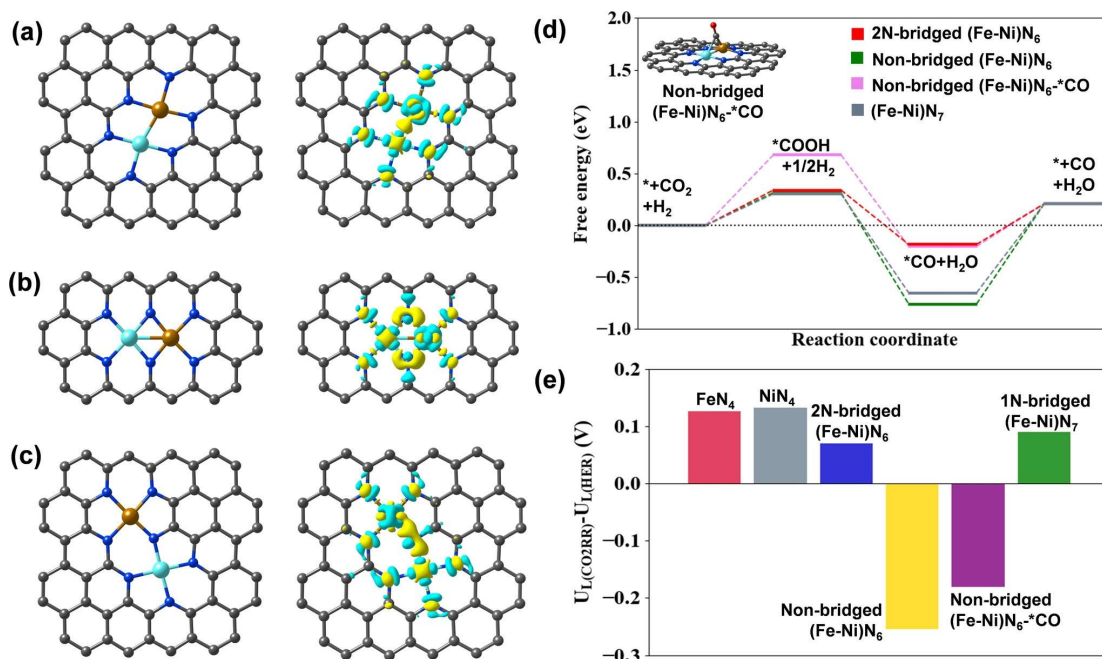


Figure 2.15: Atomic structure (left panel) and electronic structure (right panel) of dual metal a) non-bridged (Fe-Ni)N₆, b) 2N-bridged (Fe-Ni)N₆, and c) 1N-bridged (Fe-Ni)N₇ sites, d) Calculated free energy evolution of CO₂RR on various dual metal Fe-Ni sites, e) Calculated limiting potential difference between the CO₂RR and the HER on various single metal and dual-metal sites. Reproduced from reference [168].

2.3.2 Cu-based electrocatalyst

As shown in **Figure 2.6**, Cu-based materials are highly regarded as the most promising electrocatalyst for the CO₂RR-to-C₂₊ products. One advantageous characteristic of Cu is its abundance, as the U.S. Geological Survey estimates a vast reserve of 210 million tons of exploited Cu resources [169]. Moreover, Cu is economically favourable, with a market price of only \$9 per kilogram [170, 171]. Further, previous studies have indicated that among metallic materials, Cu-based materials possess the moderate adsorption strength for *CO and *H [172-174]. This property makes Cu the most promising material for electrochemical CO₂ conversion to C₂₊ products. This is because too weak and too strong *CO binding strength will lead to C₁ compounds and H₂ production, inhibiting the C-C coupling to proceed [175-179]. Nevertheless, the current lack of commercially

viable cathodic catalysts arises from the low catalytic activity, selectivity and durability of Cu-based electrocatalysts. Currently, the design strategies for Cu-based catalytic sites primarily encompass surface functionalization, morphology control, alloy system construction, and oxidation state regulation, among others [42].

(1) Surface functionalization

Surface functionalization has been proven to be an essential approach in stabilizing microstructures, optimizing the adsorption of reaction intermediates, and accelerating the mass transfer [87, 88]. Various surface additives, such as polyquinone [180], cysteamine [181-183], polypyrrole [184], polyaniline [185], and N-aryl-pyridinium organics [31], have been reported as effective in achieving these objectives. Previous studies have shown that organohalide salt additives in electrolytes can achieve a reductive electro-dimerization process through generating organic films on the surface of Cu. For instance, N, N'-ethylene-phenanthroline dibromide has been observed to optimize the dimerization mechanism on the Cu surface [186]. Furthermore, *in situ* electrodeposited organic film provides additional protection to the nanostructure of the Cu surface during the electrocatalytic process. Consequently, the combination of the molecular additive with the Cu electrode has resulted in a significant enhancement of C_{2+} products ($FE_{C_{2+}} > 78\%$, $FE_{C_2H_4} > 45\%$), as illustrated in **Figure 2.16a** [187]. Moreover, the modification of Cu with N-aryl-substituted tetrahydrobipyridine films and derived oligomeric films has been found to greatly enhance C_2H_4 selectivity, as demonstrated by $FE_{C_2H_4}$ of 72% (**Figure 2.16b**). Through electrodeposition, the organic film stabilizes the atop-bound $*CO$ intermediate and promotes the coupling process of bridge-atop bound $*CO$, thereby facilitating the CO_2RR -to- C_2H_4 process. As a result of these properties, the N-aryl pyridine salt-modified

Cu electrode retains high selectivity and reactivity towards C_2H_4 , with long-term operating stability of up to 190 h in the membrane-electrode-assembly-based system [31].

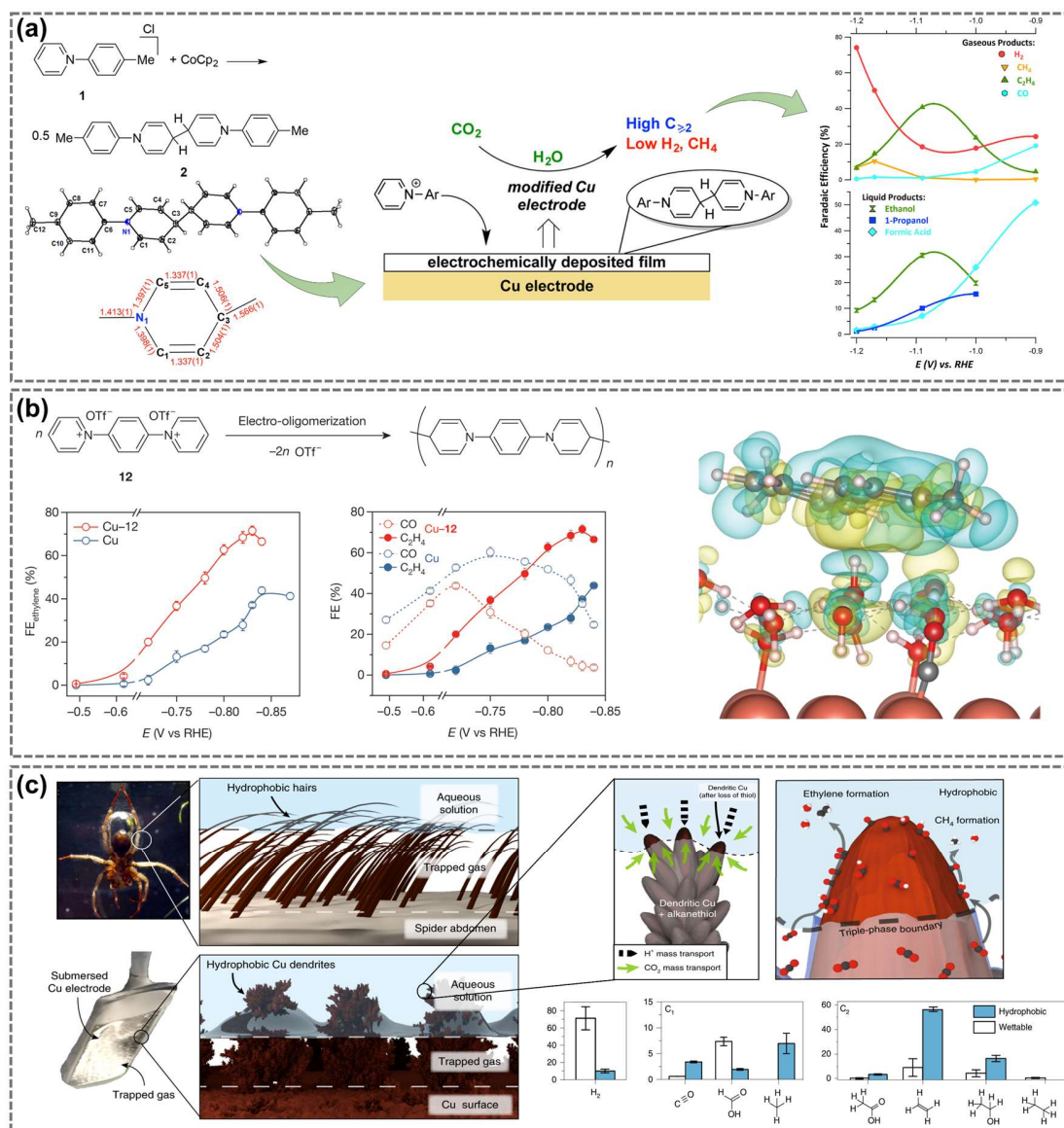


Figure 2.16: (a) Synthesis, crystal structure, and selected structural parameters (Å) of surfactant. Schematic illustration of FEs towards gas products on Cu electrode depositing with N-substituted pyridinium additives. Reproduced from reference [187]. (b) Synthesis pathway of the N-aryl-pyridinium organics and FE toward C_2H_4 . Plots of electron density difference for the CO adsorption with one water layer and the tetrahydro-bipyridine. Reproduced from reference [31]. (c) Diagram of mass transport of reactants and product formation on the electrode surface during CO_2RR -to- C_2H_4 process by wettable and hydrophobic dendrite. FEs toward H_2 , C_1 and C_2 products. Reproduced from reference [188].

Moreover, researchers have explored the use of hydrophobic polymers [189-191] and functional organic layers [192] to restrict water diffusion to the electrode surface, while also stabilizing electrode structure and optimizing adsorption energy. A promising design strategy involves the combination of Cu dendrites with 1-octadecanethiol to create superhydrophobic surfaces that can significantly reduce FE of HER (from 71% to 10%) while improving the selectivity of CO₂RR-to-C₂H₄ (**Figure 2.16c**) [188]. This strategy restricts water transport and forms the triple-phase boundary (TPB), effectively trapping CO₂ gas and increasing the local CO₂ concentration on the cathode surface. Consequently, there is a notable increase in Cu-*COOH and the subsequent formation of Cu-*CO, resulting in enhanced efficiency in C-C coupling and further C₂H₄ formation [188].

(2) Morphology control

Numerous studies have confirmed the significant role that the morphology of electrocatalysts plays in the heterogeneous catalytic reactions [193-195]. Material morphologies are commonly created by introducing defects and utilizing different facets [196-198]. Therefore, this part places particular emphasis on defects and crystal facets to explore their structure-function relationships during the CO₂RR-to-C₂H₄ process.

In metallic crystalline materials, defects serve as indicators of disorder within the periodic structure [196, 199]. Recent research has explored the relationship between the stability of CO₂RR-to-C₂H₄ and the density of defects in catalyst materials [200]. It has been observed that the incorporation of crystal defects can enhance catalytic stability by circumventing carbon deposition, which in turn leads to the generation of CH₄ (**Figure 2.17a**). Furthermore, the presence of defects not only prevents catalyst poisoning but also increases the coverage of *CO and improves the efficiency of C-C coupling (FE_{C₂H₄} > 62%)

[200]. Moreover, the stability of the Cu nanoneedles during the reaction is positively correlated with the density of externally introduced crystal defects. Beyond this, the surface of the Cu foil after pulse potential treatment exhibits abundant defects (Figure 2.17 b), leading to increased adsorption of $\ast\text{CO}$ on the catalyst surface, and a higher roughness factor and electrochemically active surface area of the electrode (Figure 2.17b, left panel). Remarkably, the cathodic catalyst treated with pulse potentials achieves a high FE of C_2H_4 (FE > 60%) at a potential of -1.0 V, and it exhibits unprecedented working stability, operating reliably for over 6 months (Figure 2.17b, right panel) [201].

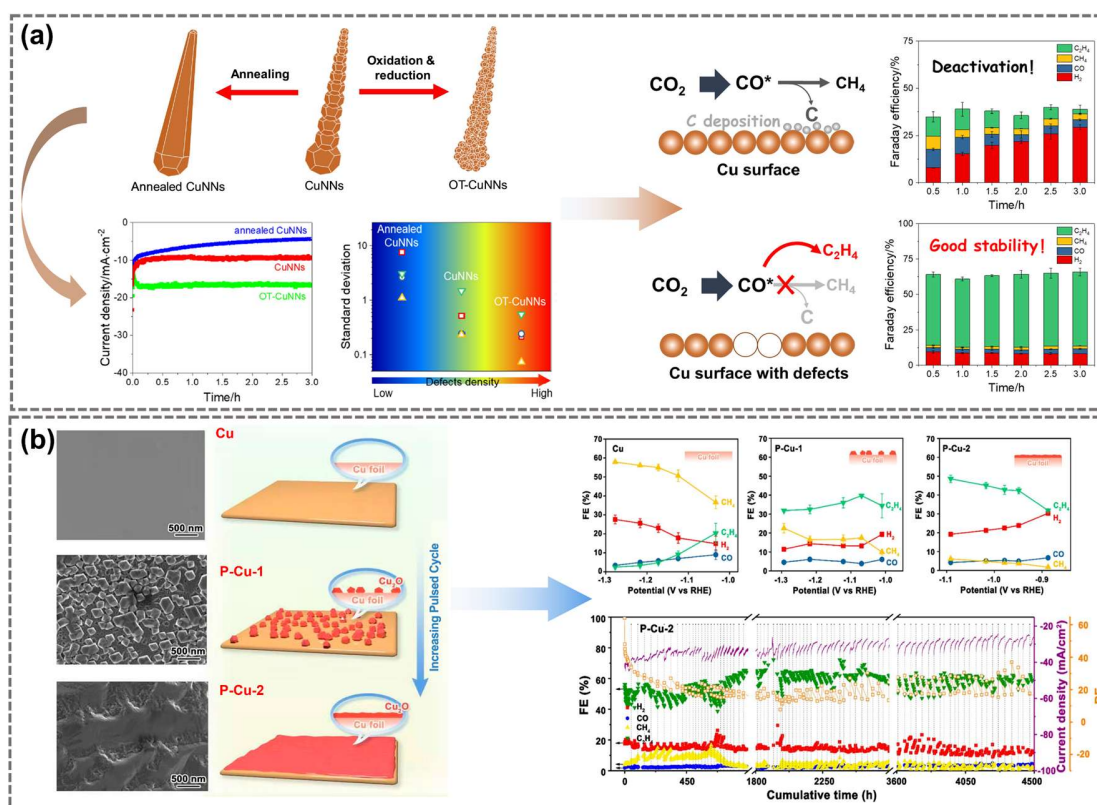


Figure 2.17: (a) Schematic illustration of treatments to eliminate or increase the number of defects in Cu nanoneedles. Proposed mechanism and obtained FEs toward gas products for different Cu electrodes. Reproduced from reference [200]. (b) Schematic diagram of electrochemical pulsed potential treatment. FEs of gaseous products on P-Cu-2 (pulsed synthesis with 900 cycles) and comparison of $\text{C}_2\text{H}_4/\text{CH}_4$ ratios and roughness factor (RF) for as-prepared catalysts. Reproduced from reference [201].

Recent studies have revealed that different facets of Cu-based catalysts possess distinct atom arrangements and surface energy, which significantly influence the activity and selectivity of the CO₂RR [202-205]. For instance, Gregorio et al. synthesized catalysts in various shapes, such as spherical, cubic, and octahedral shapes, which exposed distinct Cu facets (**Figure 2.18a**) [204]. The CO₂RR performance of different Cu nano-catalysts were subsequently assessed using a flow-cell at ampere-level current densities in a 1 M KOH solution. The results indicate that the cubic Cu NCs with exposed (100) facets display an improved C₂H₄ selectivity (up to ~57%) and a mass activity of 700 mA mg⁻¹. Conversely, the octahedral Cu NCs with exposed (111) facets exhibit enhanced methane selectivity (up to ~51%) with a mass activity of 1.45 A mg⁻¹ (**Figure 2.18b**). Hence, an increase in the proportion of Cu (100) facets among the exposed facets proves effective in promoting C₂H₄ formation. To achieve this, Li et al. designed a Cu NC with a higher ratio of Cu (100) facets to Cu(111) facets by selectively coating the Cu (111) surface with an ultrathin Al₂O₃ layer (**Figure 2.18c**), resulting in a higher FE_{C₂H₄} of 60.4%. The FE ratio of C₂H₄ to CH₄ for Al₂O₃-coated Cu NCs is 22 times greater than that of pristine Cu NCs (**Figure 2.18d**) [205].

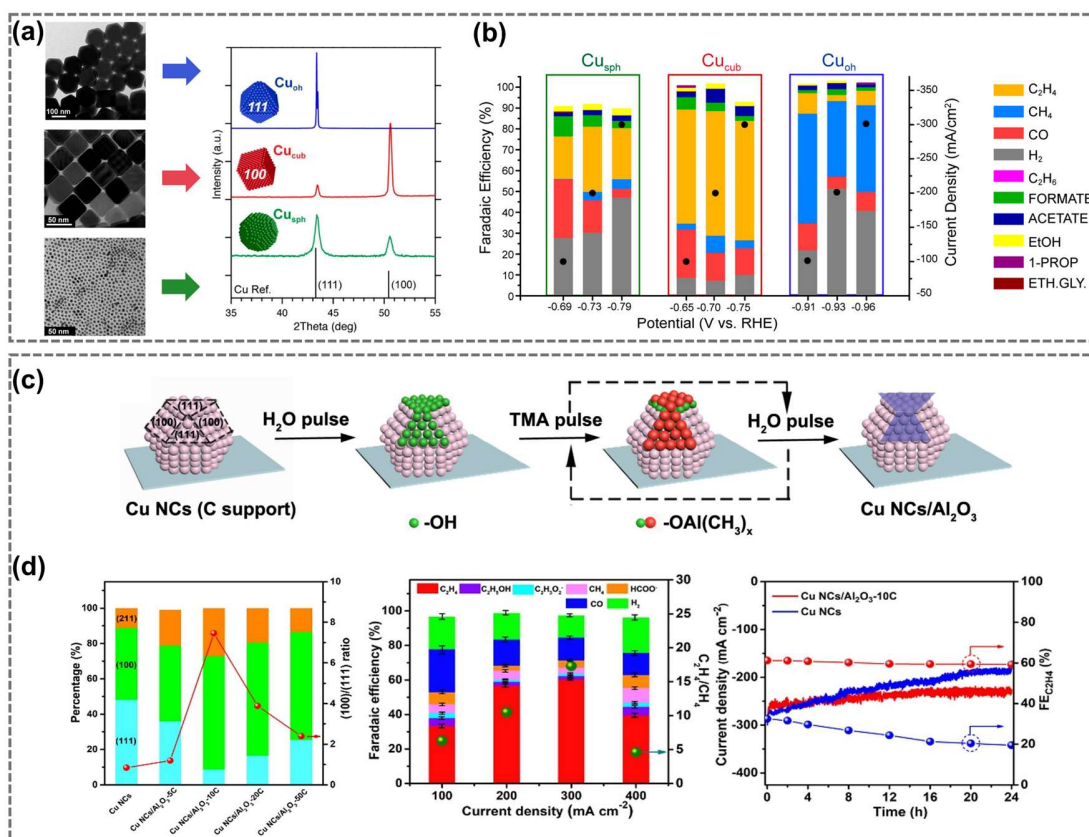


Figure 2.18: (a) Morphology and X-ray diffraction (XRD) patterns of Cu spheres (Cu_{sph}), Cu cubes (Cu_{cub}) and Cu octahedra (Cu_{oh}) with different facets, and (b) The product distribution over three Cu catalysts with different facets exposure. Reproduced from reference [204]. (c) Schematic diagram of selectively covering Cu(111) of Cu nanocrystals with ultrathin Al₂O₃ layer. (d) The product distribution of CO₂RR over Al₂O₃ selectively covered Cu NCs catalyst. Reproduced from reference [205].

(3) Alloy system construction

The utilization of nanostructured alloys has proven effective in catalysing heterogeneous electrocatalytic reactions. This efficacy can be attributed to various factors, such as the alloy's capacity to enhance product selectivity and to lower the overall energy barrier of the reaction [206-209]. This improved performance is a result of the elemental bifunctionality, electronic structure, and geometric strain present in the alloy material [206, 208, 210]. Within the realm of CO₂RR research, the incorporation of other elements into Cu-based catalysts has proven to be advantageous in attaining enhanced performance. This

approach can significantly alter the surface binding energy and optimize the adsorption mode of intermediates on the electrode surface through the single-atom alloy construction, strain regulation, among others [211, 212].

In recent years, researchers have utilized Cu-based poly-alloy catalysts with confined nanostructures in their research on CO₂RR [206, 210, 213]. These alloy catalysts have been the subject of investigation in order to understand the relationship between their physical characteristics, such as mixture patterns (disordered, ordered, and phase-separated atomic mode), and their electrocatalytic performance. Experimental findings using Cu-Pd catalysts indicate that bimetallic alloy catalysts with disordered atomic arrangements have a relatively high HER selectivity. Interestingly, alloys with an ordered atomic arrangement (Cu:Pd = 1:1) displayed the highest selectivity (FE > 80%) for C₁. Furthermore, the phase-separated alloy material (Cu:Pd = 1:1), which consists of three separate phases (face centered cubic type Cu, Cu₂O, and face centered cubic type Pd), demonstrated the highest total current density and the highest selectivity for C₂H₄ (370 mA cm⁻², FE > 45%) (**Figure 2.19a**) [214]. These experimental results indicate that the geometric arrangement of the materials can influence the selectivity of CO₂RR products.

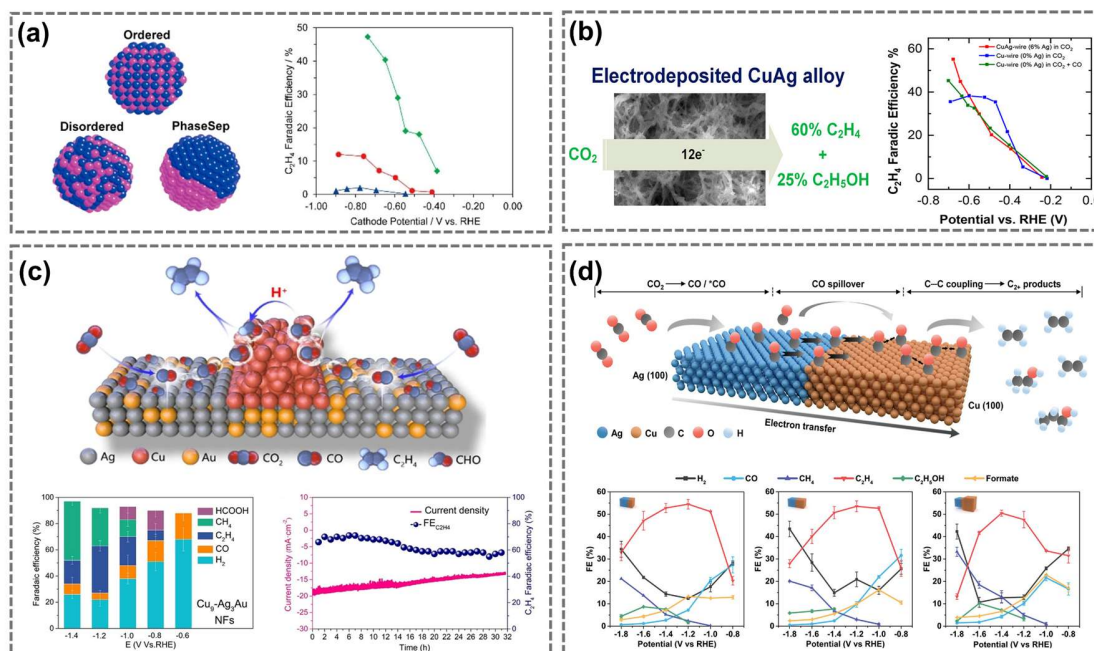


Figure 2.19: (a) Schematic illustration of prepared Cu-Pd nanoalloys with different structures. FE_{C₂H₄} for bimetallic Cu-Pd catalysts with different mixing patterns: ordered, disordered, and phase-separated. Reproduced from reference [214]. (b) Schematic diagram of a porous Cu-Ag alloy and CO₂RR-to-C₂H₄ performance. FE_{C₂H₄} from Cu wire and CuAg wire in different gas feeding. Reproduced from reference [215]. (c) General mechanistic overview, selectivity, and stability of C₂H₄ production of Cu₃-Ag₃Au catalyst. Reproduced from reference [216]. (d) Illustration of a plausible CO₂RR mechanism on Ag₆₅-Cu₃₅ JNS-100 (Ag-Cu Janus nanostructures with 100 facets) and FEs toward different products. Reproduced from reference [217].

The utilization of tandem catalysts consisting of Cu and noble metals like Au, Ag, and Pd effectively enhances the CO₂RR-to-C₂H₄ process. The inclusion of Ag or Au in the Cu-Au, Cu-Ag, or Cu-Au-Ag alloy systems increases the probability of C-C coupling on the adjacent Cu, resulting in a higher local concentration of *CO. An example of this is the electrodeposited Cu-Ag catalyst, which demonstrates FE_{C₂H₄} of 60% at low potentials (−0.7 V vs RHE) and a total current density of approximately 300 mA cm^{−2} (Figure 2.19b). Similarly, the polynary Cu-Au/Ag nano-framework materials exhibit significant selectivity for C₂H₄, with percentages of 69±5% and 77±2% in H-cell and flow-cell setups,

respectively (**Figure 2.19c**). Furthermore, mechanistic investigations suggest that Cu with a positive charge and a highly distorted lattice effectively lowers the energy barrier for the rate-determining step. This is due to the strong lattice mismatches and electronic interactions between the Ag/Au substrate and the Cu complement. Moreover, Ag-Cu Janus nanostructures with (100) facets, as depicted in **Figure 2.19c**, exhibit superior performance of CO₂RR-to-C₂₊ products, particularly with FE_{C₂H₄} of 54%. This can be attributed to their optimized electronic structure and the tandem electrocatalytic reduction of CO₂ [217].

(4) Oxidation state regulation

Determination of the oxidation states can reveal the chemical state of the elements and rationalize the design of electrocatalysts. By regulating the oxidation state, the number of valence electrons can be modified, leading to changes in electron distribution. For transition metal atoms, adjusting the oxidation state can alter the arrangement of empty d-orbitals and unpaired d-electrons, which is crucial for electron transfer to reactants [176]. In the process of CO₂RR, controlling the oxidation state can facilitate the activation of CO₂ molecules, the adsorption of reaction intermediates, and the promotion of C-C coupling, thereby lowering the energy barrier of the overall reaction [176, 218]. It has been reported that Cu^{δ+} (0 < δ < 1) plays a critical role in directing the CO₂RR pathway towards efficient C₂₊ formation. However, Cu^{δ+} species experience *in situ* self-reduction during long-term electrolysis, especially under industrial current densities [219, 220]. Therefore, optimizing the oxidation state of Cu-based electrodes to achieve high selectivity and stable operation of CO₂RR-to-C₂H₄ has become a priority [220-222].

Various Cu-based catalysts with different oxidation levels have been prepared using different treatments such as as-prepared, cyclic voltammetry (CV), and electrodeposition.

These treatments lead to OD-Cu catalysts dominated by Cu(0), coexistence of Cu(I) and Cu(0) states, and Cu(I), respectively [223]. Data gathered from CO₂RR experiments suggest that among the three OD-Cu catalysts, the CV-treated Cu electrode, containing both Cu(I) and Cu(0) regions, exhibit the highest increase in C₂H₄ generation with FE exceeding 40% (**Figure 2.20a**). The application of *in situ* surface-enhanced infrared absorption spectroscopy (SEIRAS) has facilitated the identification of both atop-bound and bridge-bound *CO during CO₂RR on the CV-treated Cu electrode (**Figure 2.20b**). This treatment has been shown to enhance the dimerization of CO and improve the selectivity of C₂H₄ product. This study demonstrates that the design of Cu valence states is an effective strategy for investigating their impact on the selectivity of C₂H₄ in CO₂RR.

Xia and co-workers have developed Cu-based catalysts with different oxidation levels by adjusting the amounts of reducing agents. The catalysts with the optimal oxidation level are capable of inhibiting the formation of CH₄ and promoting C-C coupling, resulting in FE_{C₂H₄} of 53% (**Figure 2.20c**) [222]. Additionally, Cu-based catalysts with varying valence states (Cu-pC, Cu₂O-pC, and Cu₂O/Cu-pC, where pC denotes porous carbon) have been obtained by manipulating the gas type and oxygen concentration during the annealing process. Among these Cu-based materials with different oxidation states, Cu₂O/CuO-pC displays the highest selectivity for C₂H₄, achieving FE of 65.1% at current densities up to 578 mA cm⁻² in a 1 M KOH electrolyte (**Figure 2.20d**) [175, 221].

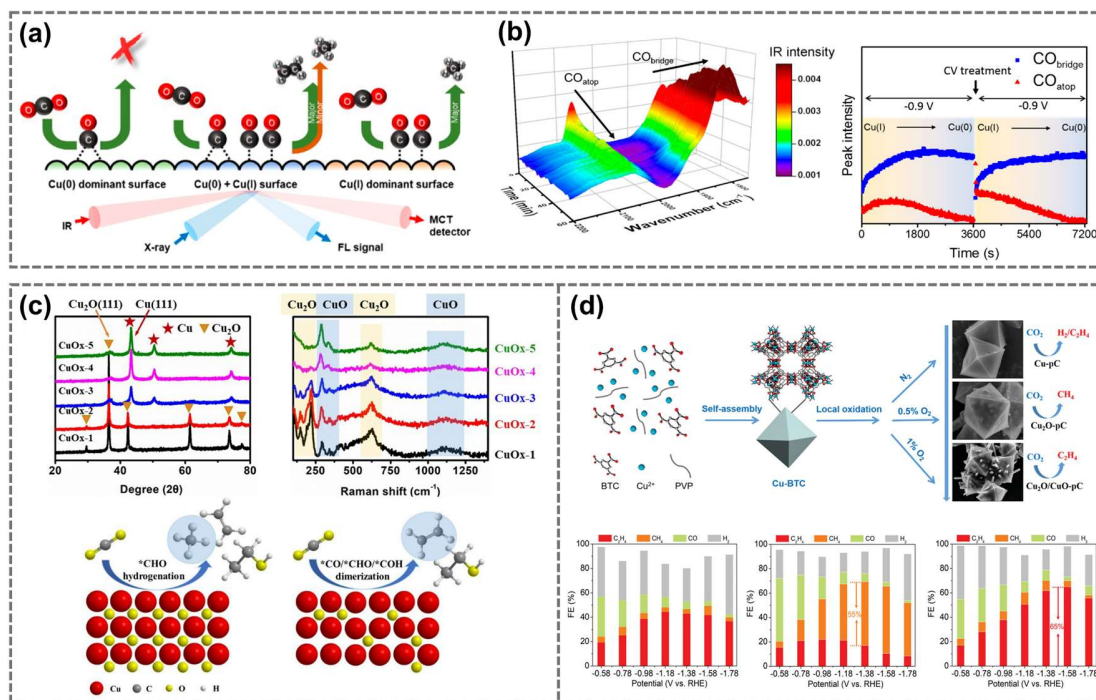


Figure 2.20: (a) Schematic illustration of the CO₂RR-to-C₂H₄ on the three Cu surfaces with different amounts of Cu(I) and Cu(0) states. (b) *In situ* SEIRAS of CV-treated electrode and time-dependent CO_{bridge} and CO_{atop}-associated peak intensities. Reproduced from reference [223]. (c) XRD pattern and Raman spectra of CuO_x catalysts (top part). Schematic illustration of the CO₂RR-to-C₂H₄ on high/low oxidation CuO_x catalysts (bottom part). Reproduced from reference [222]. (d) Schematic flowchart of the fabrication of catalysts with adjustable morphology. FEs of different products for Cu-pC, Cu₂O-pC, and Cu₂O/CuO-pC, respectively (bottom part, from left to right). Reproduced from reference [221].

2.3.3 Rare-earth element-doped electrocatalyst

In the energy conversion process, the electronic structure of catalysts plays a decisive role in their CO₂RR performance. By employing two or more metals for doping, the electronic structure of the catalyst can be tuned to the properties of the different metals [50]. Compared to single-metal catalysts, doped catalysts have demonstrated significantly enhanced activity and selectivity while operating at a reduced cost [224]. Charge transfer between atoms on different surfaces alters the electronic structure of the catalyst and the adsorption energy of reaction intermediates, significantly enhancing CO₂RR activity. Therefore, the performance and stability of catalysts can be improved by introducing other elements and adjusting doping ratios to achieve demanding application conditions [50].

Rare earth (RE) metals, known as “industrial vitamins” due to their ability to provide prolonged service and multifunctional capabilities in harsh environments [225], have attracted much academic attention as doping elements for electrocatalysts [49]. The RE elements consist of 15 lanthanides, ranging from lanthanum (La) to lutetium (Lu), along with two group IIIB elements: scandium (Sc) and yttrium (Y). Due to their placement in the same group, these elements share similar ground-state electronic structures (**Figure 2.21**). Sc and Y have the following electronic configurations: Sc is represented as ([Ar] 3d¹ 4s²), and Y is represented as ([Kr] 4d¹ 5s²). Among the 15 lanthanides, La, cerium (Ce), gadolinium (Gd), and Lu display ([Xe] 4fⁿ⁻¹ 5d¹ 6s²) configurations, while the other lanthanides follow the ([Xe] 4fⁿ 6s²) configuration [49, 226].

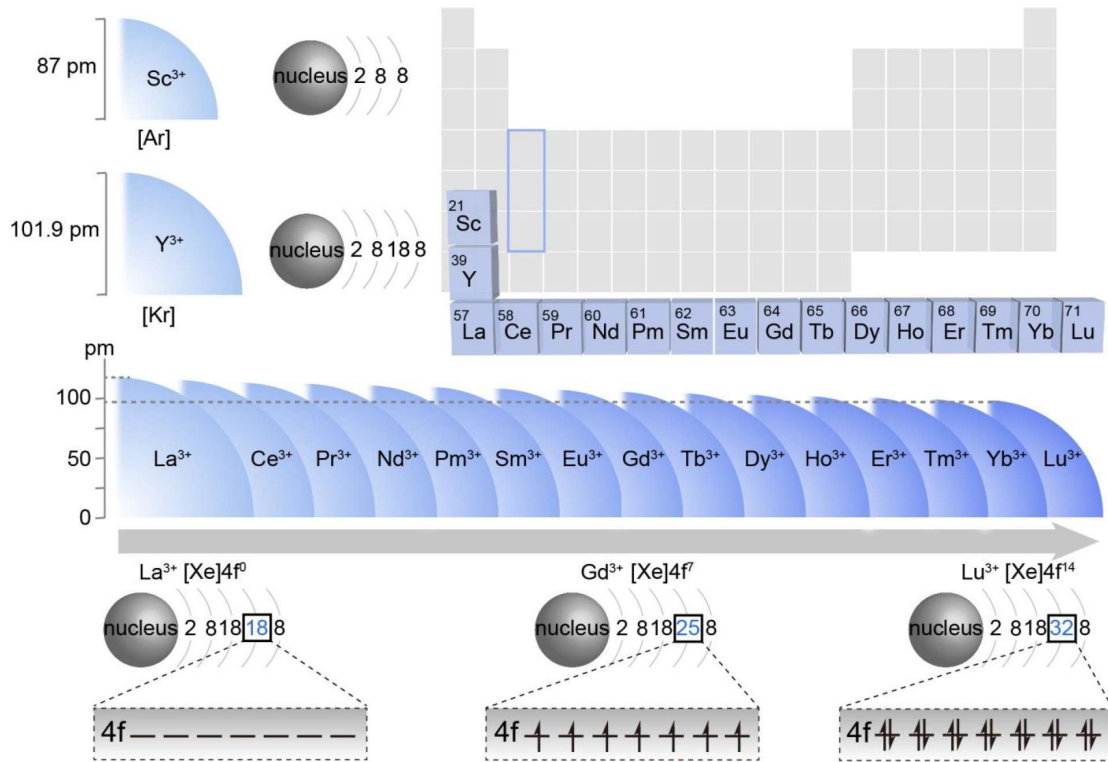


Figure 2.21: The ionic radius and valence configuration of RE elements vary across the series. From La³⁺ to Lu³⁺, the number of electrons in the 4f orbital grows with the increasing atomic number. Specifically, the electron configurations of La³⁺, Gd³⁺, and Lu³⁺ illustrate an empty, half-filled, and fully filled 4f orbital, respectively. Reproduced from reference [226].

RE metals exhibit low electronegativity due to their unique 4f electronic structure and unfilled 5d orbitals. The external 5s and 5p sublayer electrons can effectively shield the 4f sublayer electrons, which makes the RE metals have significant spin-orbit coupling effects and lanthanide contraction phenomena [226]. Theoretically, when RE metals are doped into the host material, due to the difference in electronegativity between them and the elements of the host material, the RE metals are able to provide electrons and change the electronic environment around the atoms of the host material. Therefore, this doping can effectively adjust the local electron density of the surrounding atoms to a higher valence chemical state [49, 226].

Recent studies have shown that RE can be effectively doped into various carriers and are extensively utilized in a range of catalytic reactions. This RE doping has increasingly drawn attention for its applications in CO₂RR (**Figure 2.22**) [49, 227]. First, the distinctive electronic structure and chemical properties of RE metals can alter the local electron density of surrounding atoms, optimizing the electronic state of the carriers. This modification enhances the adsorption capacity on the catalyst surface, ultimately leading to increased electron transfer and improved catalytic performance [228]. Second, the incorporation of RE elements can inhibit the precipitation of lattice oxygen from the cathodic catalyst by facilitating the formation of unconventional orbitals, such as 3d-2p-4f hybridization. This offers promising new avenues for stabilizing active Cu⁺ species and improving the operation stability in CO₂RR process [57, 58]. Third, given the unique physicochemical properties of RE elements, their larger ionic radius can induce tensile strain in the catalytic substrate. This induced strain is beneficial for fine-tuning the binding energy of *CO intermediates, thereby improving the CO₂RR performance [229]. Fourth, RE doping is also an effective strategy for modulating the activation and dissociation of water, facilitating the formation of adsorbed hydrogen (*H) that are essential for providing protons in CO₂RR process [230]. Therefore, the introduction of RE elements into Cu-based catalysts optimizes the local electronic states, stabilizes active sites, and facilitates proton transfer, resulting in high-performance CO₂RR.

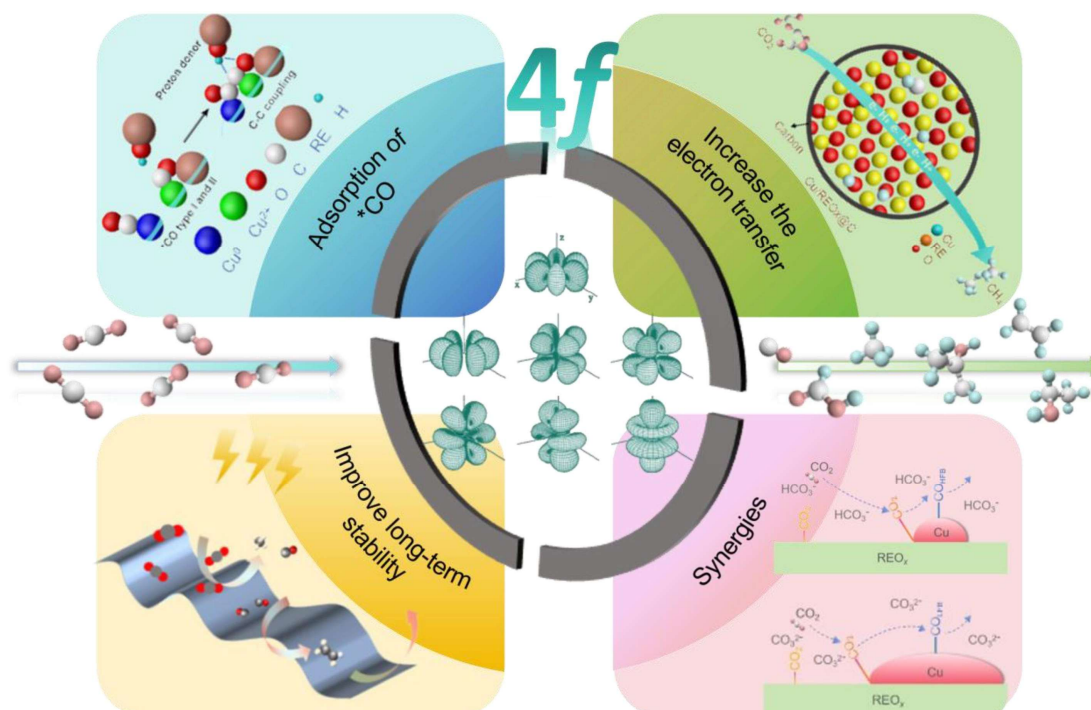


Figure 2.22: The function of RE-based electrocatalysts in CO₂RR. Reproduced from reference [227].

However, the significant difference in atomic radius between RE elements and other transition metal elements presents challenges in doping RE atoms into Cu-based catalysts. So far, the application of RE in Cu-based electrocatalysts toward CO₂RR has been infrequently reported. Therefore, effective strategies for precise control of RE metal doping in catalysts are lacking. It is essential to elucidate the structure-function relationship between doped electrocatalysts structure and their CO₂RR performance.

(1) Enhanced electron transfer

Recent literature reports that rare earth metal-doped CuO_x catalysts enhance the performance of CO₂ electroreduction to C₂₊ products. Feng et al. developed the single-atom Gd-doped Cu₂O (Gd₁/CuO_x) catalyst, leveraging the unique electronic structure and large ionic radius of Gd to stabilize Cu⁺ species and enhance the electron transfer during CO₂RR. This design also induces tensile strain in Gd₁/CuO_x, resulting in exceptional

performance for CO₂RR-to-C₂₊ products. As illustrated in **Figure 2.23**, at -0.8 V vs. RHE, the Faradaic efficiency of C₂₊ products reached 81.4%, accompanied by the partial current density of -444 mA cm⁻². Experimental and theoretical results indicate that the doped Gd enhances CO₂ activation, stabilizes the key intermediate O*CCO, and reduces the energy barrier for CO₂RR-to-C₂₊ [229]. Besides, Song et al. synthesized CeO₂/Bi₃NbO₇ using electrospinning technology [231]. The incorporation of CeO₂ resulted in reduced crystallinity of the CeO₂/Bi₃NbO₇ composite, leading to a strong atomic coupling at the interface. This interface effect decreases the energy barrier between the valence band and conduction band of the catalyst, altering the electronic structure of both CeO₂ and Bi₃NbO₇. As a result, this promotes electron transfer on the surface of CeO₂/Bi₃NbO₇, which is advantageous to produce HCOOH.

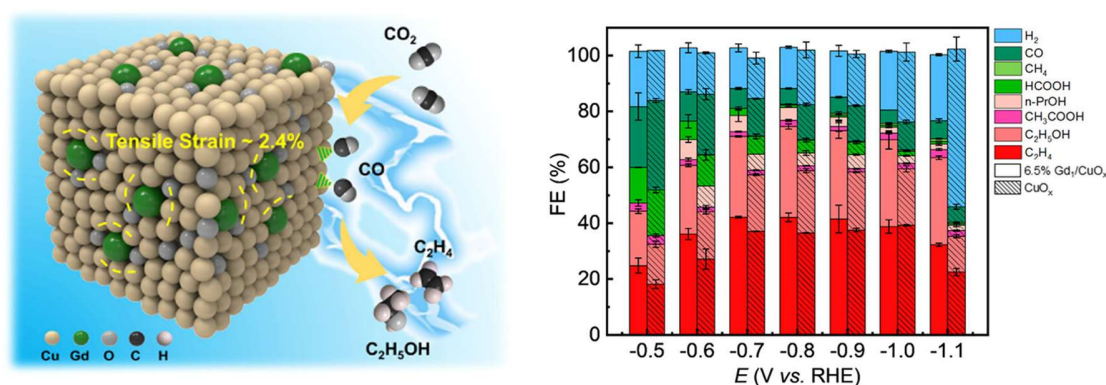


Figure 2.23: Schematic diagram of CO₂RR-to-C₂₊ products on Gd₁/CuO_x with tensile strain. Product distribution over 6.5% Gd₁/CuO_x and CuO_x under different potentials. Reproduced from reference [229].

(2) Synergy effect

Compared to doping with a single RE element, co-doping with RE elements and another element may create a synergistic effect. Jia et al. synthesized a series of Cu-X-Y catalysts (where X and Y denote different metals) using a co-electrodeposition process. When the electrocatalyst composition is Cu₁₀La₁Cs₁, the Faradaic efficiency for C₂H₄ in

an H-cell reaches 56.9% at a current density of 37.4 mA cm^{-2} . Furthermore, this catalyst attains a Faradaic efficiency of 70.5% for C_{2+} products, with the partial current density reaching as high as -486 mA cm^{-2} in a flow cell. Experimental results and DFT calculations demonstrate that doping Cu with La and Cs significantly enhances reaction efficiency through a series of effects, including the introduction of defects, alterations in electronic structure, and improvements in charge transport rates [232]. Apart from this, the use of CeO_2 as a carrier to generate oxygen vacancies not only enhances the catalysts' adsorption capacity for intermediates but also lowers the reaction energy barrier, while simultaneously protecting other metals and improving the selectivity of CO_2RR through synergy effect. Zhou et al. employed electrospinning technology to incorporate Cu^{2+} into the CeO_2 lattice, resulting in the formation of a Cu-Ce-O_x solid solution [233]. Due to the greater reducibility of Ce^{4+} in CeO_2 compared to Cu^{2+} , electrons are prevented from accumulating at the active sites of Cu^{2+} , thereby stabilizing its presence. The Cu-Ce-O_x solid solution achieved a FE_{CH_4} of 67.8% and $\text{FE}_{\text{C}_2\text{H}_4}$ of 3.6%.

(3) Adsorption of $\ast\text{CO}$

Furthermore, Liu et al. have developed a series of RE and Cu mixed-phase catalysts, specifically CuSm_2O_4 , by adjusting the composition and structure of these electrocatalysts (**Figure 2.24**) [234]. This allows for the modulation of product distribution in CO_2 electrolysis, facilitating the conversion between C_{2+} products and CH_4 . In particular, when the atomic ratio of Cu to Samarium (Sm) is 9:1 (i.e., $\text{Cu}_9\text{Sm}_1\text{-O}_x$), the Faradaic efficiency of C_{2+} products can reach 81%, with the generation of CH_4 being nearly negligible at the applied current density of 700 mA cm^{-2} . However, at the applied current density of 500 mA cm^{-2} , the Faradaic efficiency of CH_4 on the $\text{Cu}_1\text{Sm}_9\text{-O}_x$ (with a Cu/Sm ratio of 1:9)

reaches 65%, while the electron selectivity for the C_{2+} products is relatively low. As the Cu content increases, the electrocatalyst consists of mixed phase of $CuSm_2O_4$ and Cu, and the Cu phase accounts for a relatively large proportion. A small amount of Sm can enhance the $*CO$ binding strength and facilitates the $*OCCO$ formation. Conversely, increasing the Sm content leads to the presence of both $CuSm_2O_4$ and Sm_2O_3 in the catalyst, and the Sm_2O_3 phase accounts for a relatively large proportion. Meanwhile, introduced Sm can stabilize Cu^{2+} , enhance the supply of protons, and lower the energy barrier for $*CO$ hydrogenation to $*CHO$, $*CH_2O$ and $*CH_3O$, ultimately resulting in CH_4 formation [234].

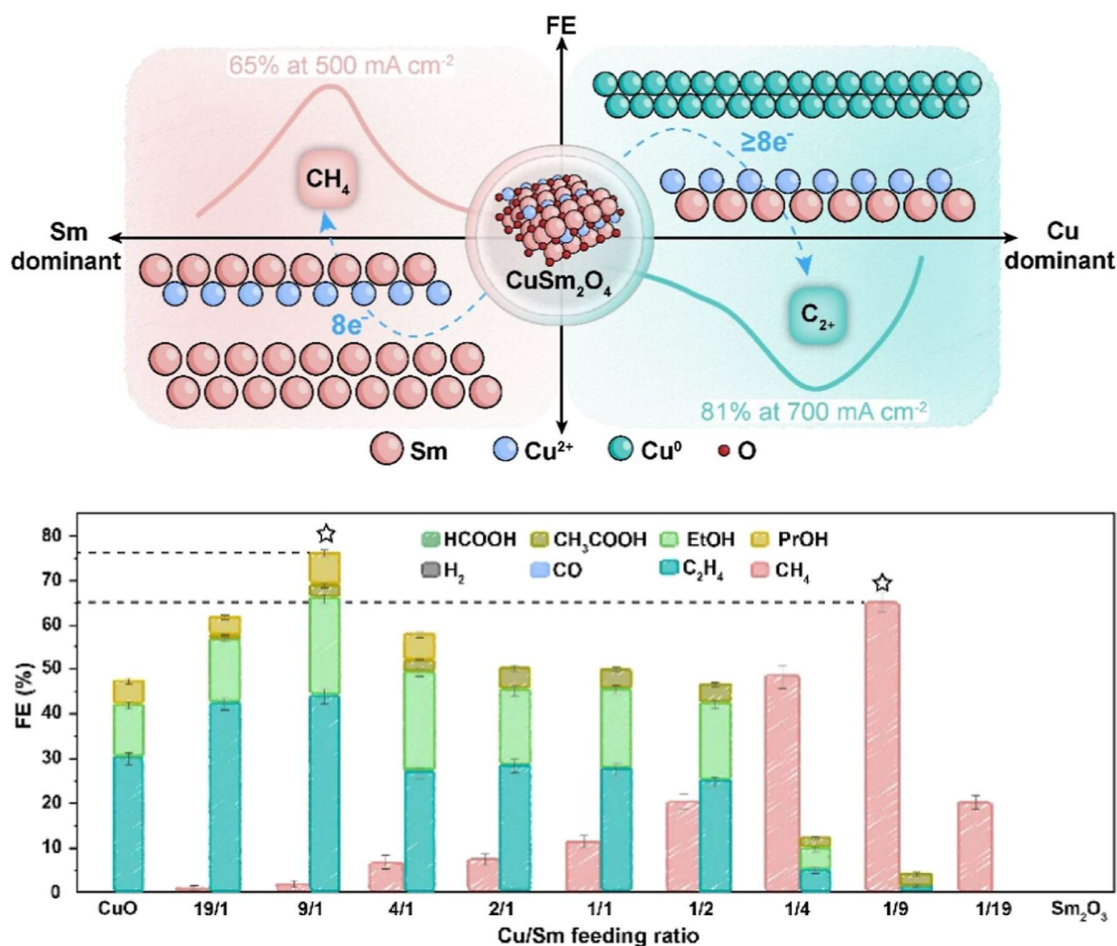


Figure 2.24: Schematic diagram of modulating the CO_2RR -to- C_{2+} products or CH_4 by Cu-Sm oxide mixed-phase electrocatalysts. The FEs of CH_4 and C_{2+} products at the applied current density of 500 mA cm^{-2} over different doping ratios of as-prepared Cu/Sm catalysts. Reproduced from reference [234].

(4) Orbital coupling for long-term stability

In contrast to conventional d-p and d-d orbital hybridizations, the incorporation of the 4f orbitals from RE elements enables the formation of higher-order 4f and 2p atypical orbital hybridizations, which mitigate lattice oxygen leaching during CO₂RR and enhance the desired durability and activity [49, 227]. Recently, Sun et al. proposed a strategy to stabilize Cu⁺ species by designing a hybridization structure of Ce⁴⁺ 4f-O 2p-Cu⁺ 3d orbitals in Ce-doped Cu₂O [39]. The introduction of the high-order Ce⁴⁺ 4f and O 2p orbital hybridization near E_f can effectively maintain Cu–O covalency and inhibit the leaching of lattice oxygen, thereby stabilizing Cu⁺ species (**Figure 2.25**). Compared to Cu₂O, the synthesized Ce-Cu₂O enhanced the C₂H₄/CO ratio by 1.69 times at –1.3 V vs RHE through enhanced CO₂ activation and *OCCO formation. Furthermore, it demonstrated stability throughout the 7-hour CO₂RR-to-C₂H₄ process, with *in situ* characterization techniques confirming the presence of stable Cu⁺ species in the Ce-Cu₂O during the electroreduction process.

Moreover, Wang et al. constructed Sm³⁺ 4f-O 2p-Cu⁺ 3d orbital hybridization by introducing Sm atoms to achieve enhanced selectivity and stability of CO₂RR [57]. Experimental results and DFT calculations demonstrated that unconventional higher-order orbital hybridization not only stabilized the Cu⁺ species, but also promoted the activation of CO₂, the adsorption of *CO, and the decrease of the C-C coupling energy barrier. Similarly, the incorporation of Gd into Cu₂O has been reported to enhance Cu–O interactions and promote the retention of Cu⁺ species [58]. Further, the electron enrichment of Cu sites in Gd-doped Cu₂O strengthens the interaction between Cu and *OCHCH₂, leading to improved CO₂RR-to-C₂H₄ performance.

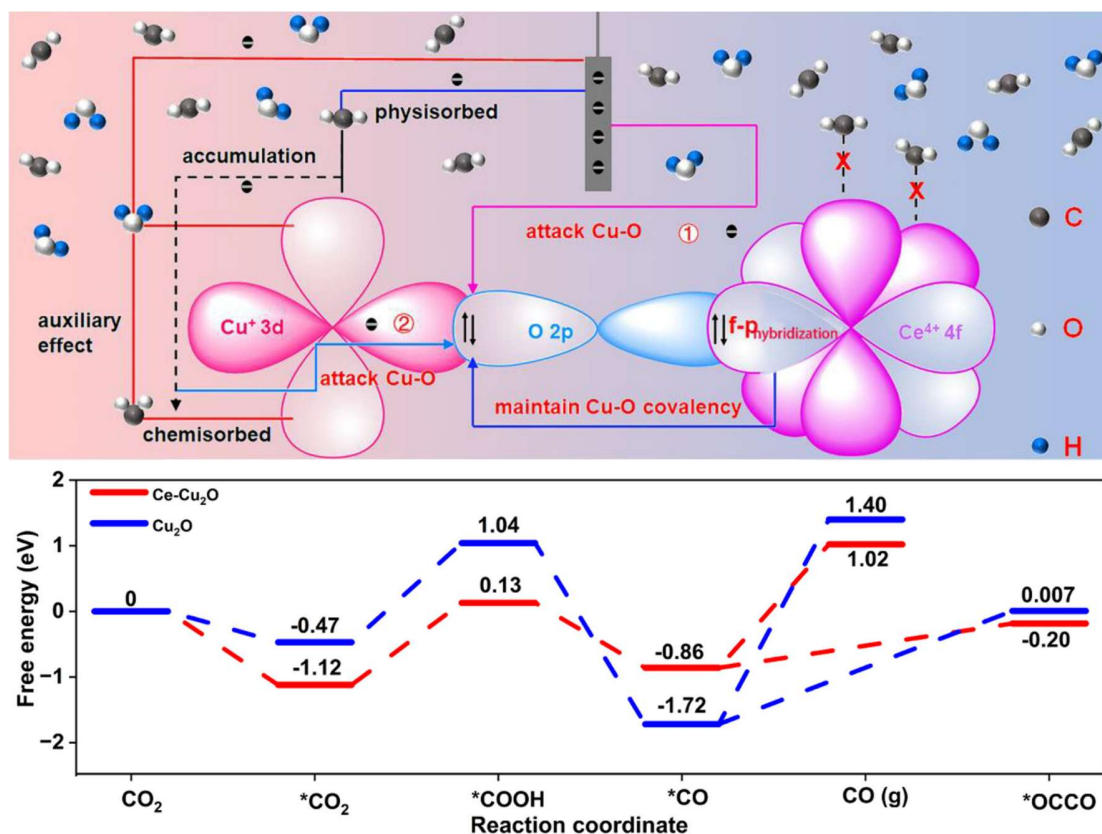


Figure 2.25: The reason for active Cu^+ deactivation and a schematic diagram showing the high-order $\text{Ce}^{4+} 4f\text{-O } 2p\text{-Cu}^{+} 3d$ orbitals in $\text{Ce-Cu}_2\text{O}$. The free energy diagrams for each step during CO_2RR -to- C_2H_4 process on the surface of $\text{Ce-Cu}_2\text{O}$ and Cu_2O . Reproduced from reference [39].

To summarize, this chapter provides the introduction of fundamentals of electrochemical CO_2 reduction reaction, including CO_2 properties, reaction pathways, product values of CO_2RR . Furthermore, this chapter also discusses the key factors influencing the CO_2RR , such as electrocatalyst effect, electrolyte effect and electrochemical cell. Additionally, the development of high-performance CO_2RR electrocatalysts was systematically reviewed. Based on the literature review, this PhD research project has successfully established an operation and evaluation device for the electrochemical performance of CO_2RR (see Chapter 3 for details). This includes the manipulation of the electrochemical workstation, the assembly and operation of the

electrolyzer, and the detection and quantification of gas-phase and liquid-phase products. For instance, two types of electrolyzers, H-cell and flow-cell, were utilized to evaluate the performance of CO₂RR at laboratory-scale and industrial-scale current densities, respectively. Moreover, based on the above review of CO₂RR electrocatalyst developments, Ni-Ag dual-atom catalysts, La-doped CuO_x catalysts, and hybrid Eu(OH)₃-Cu catalysts were employed in three research sub-projects focused on CO₂RR studies and corresponding reaction mechanisms.

However, while reviewing the existing research, some research gaps were revealed, including electron selectivity deficiencies toward desired product formation, insufficient operation current density and stability, ambiguous specific reaction pathway, and limited exploration of the relationship between different reaction intermediates (such as *H, *CO, *COOH and *OCCHO) and electrocatalytic performance. Therefore, this comprehensive review and presented research gaps offers significant theoretical support and strong motivation for the subsequent experimental work, which includes the design and synthesis of electrodes, the optimization of electrochemical conditions, and the investigation of the structure-activity relationship of catalysts.

Chapter 3 Methodologies

This chapter offers a detailed description of the chemicals, the electrochemical procedures, the electrocatalysts characterization techniques, and the computational simulations methods. Section 3.1 presents information on the chemicals utilized in electrocatalyst synthesis and electrochemical experiments. Section 3.2 discusses the involved electrochemical procedures, detailing the preparation of electrodes for both H-cell and flow-cell, the electrocatalysis experiments, and the detection and quantification of CO₂RR products. Subsequently, Section 3.3 outlines the characterization techniques employed, encompassing both *ex situ* and *in situ* characterization methods, which are crucial for understanding the physical and chemical properties of the prepared samples and for gaining mechanistic insights into CO₂RR. Finally, Section 3.4 describes the DFT calculation methods implemented in this study to investigate the relationships between structure function relationship and related reaction mechanisms.

3.1 Chemicals

The source and specifications of chemicals were listed in the following **Table 3.1**. Unless otherwise specified, all chemicals are used as received and not purified.

Table 3.1: Details of chemicals used in this research.

Chemical name	Specification	Source
Alpha-D-glucose	99.7%	Macklin Biochemical Technology Co., Ltd.
Anion exchange membrane	Fumasep FAA-3-PK-130	Sinero-Tech Co., Ltd.
Carbon paper	YLS-30T	Sinero-Tech Co., Ltd.

Cation exchange membrane	Nafion 117	Sinero-Tech Co., Ltd.
Copper nitrate trihydrate	99.9%	Sinopharm Chemical Reagent Co., Ltd.
Cupric acetate monohydrate	99.9%	Sinopharm Chemical Reagent Co., Ltd.
Deuterium oxide	99.9%	Ningbo Cuiying Scientific Co. Ltd.
Dimethyl sulfoxide	99%	J&K Scientific Co. Ltd.
Ethanol	99.5%	Sinopharm Chemical Reagent Co., Ltd.
Europium nitrate hexahydrate	99.9%	Sinopharm Chemical Reagent Co., Ltd.
Hexadecyl trimethyl ammonium bromide	99%	Sinopharm Chemical Reagent Co., Ltd.
Isopropyl alcohol	99.7%	Sinopharm Chemical Reagent Co., Ltd.
Lanthanum nitrate hexahydrate	99.9%	Sinopharm Chemical Reagent Co., Ltd.
Melamine	99%	Macklin Biochemical Technology Co., Ltd.
Nafion solution	5 wt.%	Macklin Biochemical Technology Co., Ltd.
Nickel nitrate hexahydrate	99.7%	Sinopharm Chemical Reagent Co., Ltd.
Potassium bicarbonate	97%	Macklin Biochemical Technology Co., Ltd.
Potassium chloride	99.5%	Macklin Biochemical Technology Co., Ltd.
Potassium hydroxide	85%	Macklin Biochemical Technology Co., Ltd.
Silver nitrate	99.7%	Sinopharm Chemical Reagent Co., Ltd.
Sodium citrate tribasic hydrate	99.7%	Macklin Biochemical Technology Co., Ltd.
Sodium hydroxide	99.9%	Macklin Biochemical Technology Co., Ltd.
Sulfuric acid	99.8%	Macklin Biochemical Technology Co., Ltd.
Ar	99.999%	Linde Gas (Ningbo) Co., Ltd.
CO ₂	99.999%	Linde Gas (Ningbo) Co., Ltd.

3.2 Electrochemical measurements

3.2.1 Preparation of electrodes

For the electrode preparation for H-cell, as shown in **Figure 3.1**, a total of 10 mg of catalyst was dispersed within a mixture containing 50 μL of Nafion solution (5 wt.%) and 1950 μL of isopropanol and sonicated for over 1 hour. The resulting catalyst slurry, amounting to 100 μL , was then added dropwise on a pre-cleaned carbon paper measuring 1×1 cm and thoroughly dried in a vacuum oven set at 60°C for 20 minutes. The catalyst loading of as-prepared electrode is approximately 0.5 mg cm^{-2} .

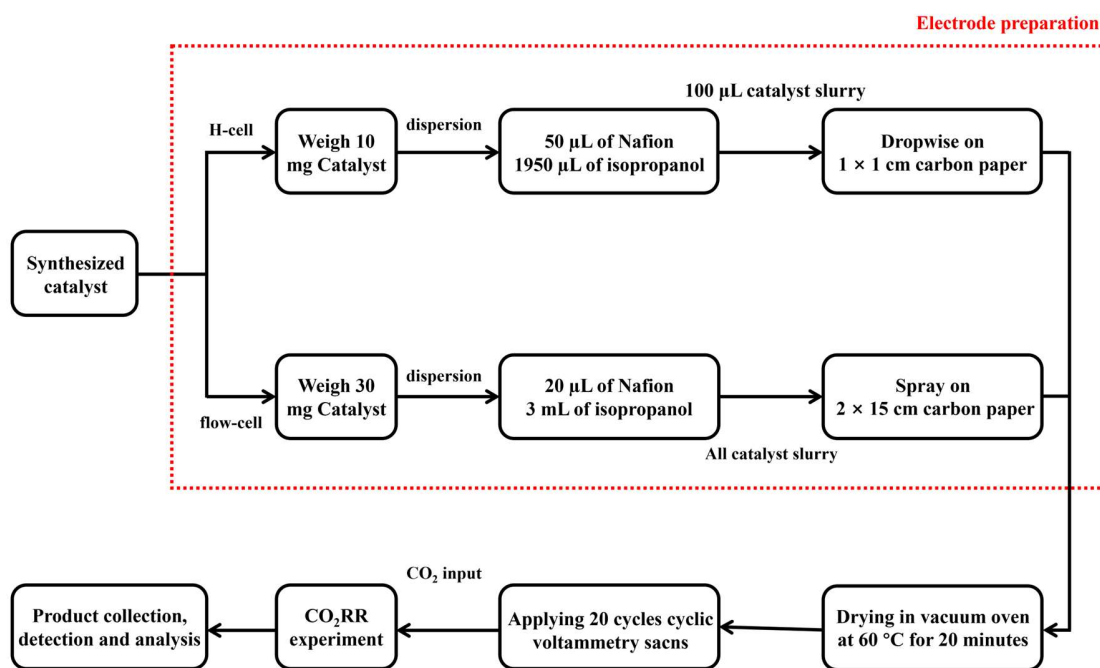


Figure 3.1: The roadmap of electrode preparation and CO₂RR experimental procedure.

For the electrode preparation for flow-cell, a commercially available carbon paper, utilized as a GDE, was precisely cut to dimensions of $2.0 \text{ cm} \times 15.0 \text{ cm}$ and thoroughly rinsed with deionized water. A catalyst weighing 30 mg, was dispersed in a mixture containing 20 μL of Nafion solution (5 wt.%) and 3 mL of isopropanol, followed by

sonication for over 1 hour. This prepared catalyst slurry was sprayed onto the cleaned GDE using a handheld airbrush, achieving a catalyst loading of approximately 1 mg cm^{-2} . After drying the cathode electrodes in a vacuum oven at 60°C for 20 minutes, they were sectioned into seven squares, each measuring approximately $2.0 \text{ cm} \times 2.0 \text{ cm}$.

3.2.2 Electrocatalytic experiments

(1) Electrolysis experiment

For the first research project, all electrolysis experiments were conducted within a hermetically sealed H-type cell (**Figure 2.9a** and **Figure 3.2**). The cell consists of two compartments, namely the anode chamber and cathode chamber, both with a volume of 50 mL. These compartments were separated by a proton exchange membrane (Nafion-117) which allows only hydrated hydrogen ions to pass through. The electrolysis process employed a three-electrode configuration. In the cathode chamber, the working electrode (WE) was a treated carbon paper measuring $1 \times 1 \text{ cm}$, while the reference electrode was an Ag/AgCl electrode saturated with 3 M KCl. Additionally, platinum sheet electrodes measuring $2 \times 2 \text{ cm}$ served as the counter electrode (CE) in the anode chamber. Both chambers contained a 30 mL aqueous solution of 0.1 M KHCO_3 , which was saturated with CO_2 and had a pH of approximately 6.8. To prevent air bubbles from adhering to the electrode surface, a stirrer maintained a speed of 800 rpm in the cathode chamber. An electrochemical workstation was used to monitor the electrolysis processes and collect electrochemical data. Prior to each electrolysis, a high-purity CO_2 was fed into the chamber at a flow rate of 30 sccm for at least 40 minutes to ensure a saturated electrolyte.

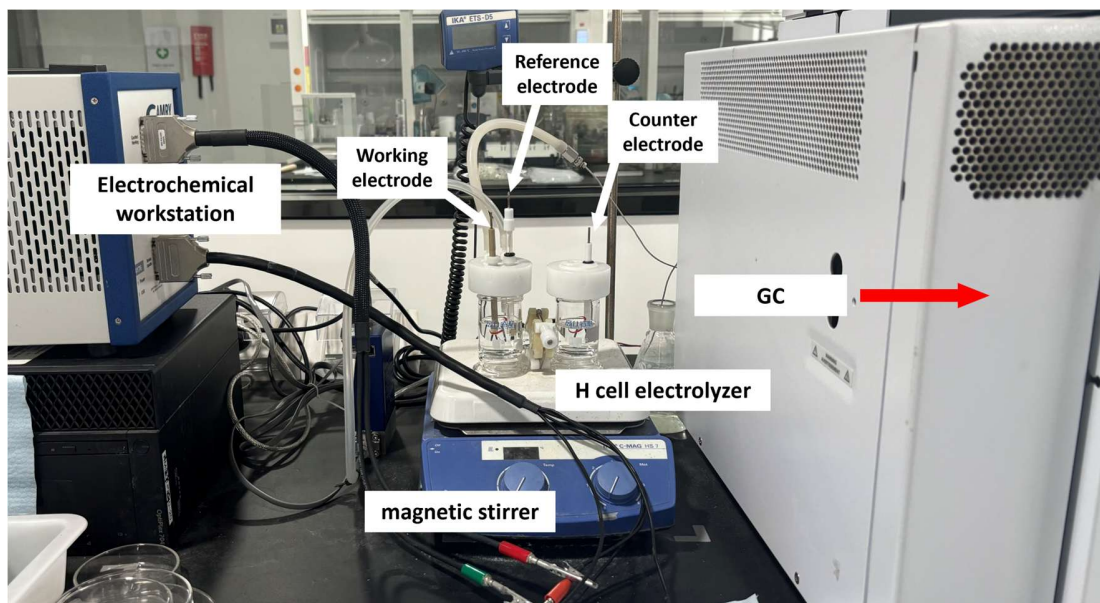


Figure 3.2: The photograph of the used H-type cell device in this study.

For the second and third research project, the electrochemical performance tests were conducted in a gas-fed flow cell configured with either an anion exchange membrane (AEM) or a cation exchange membrane (CEM), depending on the electrolyte used (1 M KOH and 1 M KCl) to satisfy the industrial requirement (**Figure 2.9b** and **Figure 3.3**). The electrolyzer comprised three chambers: the airflow chamber (1.0 cm × 1.0 cm), the cathode chamber with the WE (2.0 cm × 2.0 cm) and an Ag/AgCl reference electrode (saturated with 3 M KCl), and the anode chamber containing nickel foam (2.0 cm × 2.0 cm). The active area of the catholyte chamber was 1.0 cm². A high-purity CO₂ gas stream was passed through the gas chamber at a rate of 50 sccm, controlled by a mass flow meter. The cathode chamber was supplied with 10 mL min⁻¹ of 1 M KOH (pH = 13.6) and 1 M KCl (pH = 6.4) aqueous electrolytes via a peristaltic pump, while the anode chamber was fed with 10 mL min⁻¹ 1 M KOH aqueous electrolyte using another peristaltic pump. The gas flow rate between the gas-fed flow cell and the gas chromatography (GC, Agilent 8890B) inlet was verified by a soap film flow meter (Sensidyne Gilibrator-2).

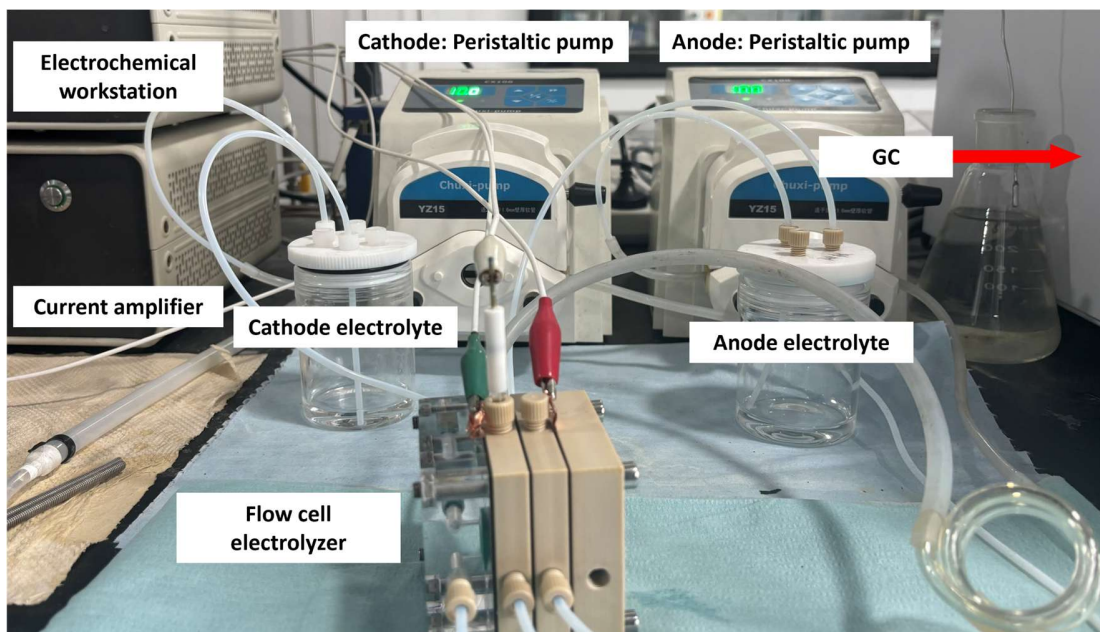


Figure 3.3: The photograph of the used flow cell device in this study.

All electrolysis experiments were conducted using an electrochemical workstation (CHI 660E) equipped with a current booster (CHI 680D). CV scans were performed prior to each CO₂RR experiment to pre-activate the electrocatalyst and remove organic residues present on the electrode surface, using 20 cycles over a potential range of -0.6 to -2.0 V relative to Ag/AgCl. Potentials were converted to values relative to RHE with manual iR_u compensation, following **Eq. 1** below [37]:

$$E \text{ (vs. RHE)} = E \text{ (vs. AgCl)} + 0.0591 \times pH + 0.210 - iRu \times 0.85 \quad \text{Eq. 1}$$

where i represents the current in the electrolysis and Ru is the solution resistance.

(2) ECSA measurement

The electrochemically active specific surface area (ECSA) was found to be directly proportional to the double-layer capacitance (C_{dl}). To determine the C_{dl} , CV scans were initially performed within the non-Faradaic interval ($E_{\text{open-circuit}} \pm 0.05$ V) at various scan

rates (20, 40, 60, 80, 100 and 120 mV s⁻¹). Subsequently, the non-Faradaic currents ($\Delta j = (j_a - j_c)/2$) were plotted at open-circuit potential against the scan rate to obtain the C_{dl} , where j_c and j_a represents cathodic and anodic current, respectively, following **Eq. 2** below [37]:

$$C_{dl} = \frac{\Delta j}{v} = \frac{j_a - j_c}{2v} \quad \text{Eq. 2}$$

where j_a and j_c are anodic and cathodic current densities, v is the scan rate in mV/s.

(3) Tafel slope measurement

The Tafel slope was determined by fitting a straight line using the logarithm of the CO partial current density (j_{CO}) as the horizontal coordinate and the overpotential (η) as the vertical coordinate, following **Eq. 3** below [37]:

$$\eta = a \log \left(\frac{j}{j_0} \right) \quad \text{Eq. 3}$$

where η is the overpotential, a is the Tafel slope, j is the current density (mA cm⁻²), and j_0 is the exchange current density.

(4) Energy efficiency measurement

The cathodic energy efficiency (EE) was computed on the basis of the cathodic CO₂RR coupled with the anodic water oxidation reaction ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$; 1.23 V versus RHE), following **Eq. 4** below [235]:

$$EE = \frac{E_{oxo} - E_{redo}}{E_{ox} - E_{red}} \times FE \quad \text{Eq. 4}$$

where E_{oxo} and E_{redo} are the thermodynamic potentials for water oxidation and CO₂RR to various products, respectively:

1.15 V (derived from 1.23 – 0.08 V) for C₂H₄,

1.06 V (derived from 1.23 – 0.17 V) for CH₄.

E_{ox} and E_{red} are the applied potentials at the anode and cathode, respectively. For calculating the $EE_{1/2}$, zero overpotential for the anodic reaction, implying $E_{ox} = 1.23$ V.

3.2.3 Detection and quantification of CO₂ reduction products

Gas products (H₂, CO, CH₄ and C₂H₄ etc.) were monitored in real-time by connecting a GC inlet directly to the cathode chamber. The GC system is equipped with two flame ionization detectors (FID, the back FID for CO and CH₄ detection; the front FID for C₂-C₃ hydrocarbons detection) and a thermal conductivity detector (TCD for H₂ detection) for the identification and quantitative analysis of these products (**Figure 3.4** and **Figure 3.5**). The Faradaic efficiency of the gas product was calculated using the following **Eq. 5** below:

$$FE_{gas} = \frac{Z_{product} \times V \times x_i \times F \times P_o}{RT \times j_{total}} \times 100\% \quad \text{Eq. 5}$$

where $Z_{product}$ is the number of electrons needed to produce one molecule of the target product (2e⁻ for CO, 8 e⁻ for CH₄ and 12 e⁻ for C₂H₄), V is the outlet gas flow rate in standard cubic centimetres per minute (sccm), x_i is the concentration (ppm) of the gas product detected by GC. F is the Faraday constant (96485 C mol⁻¹), P_o is the atmospheric pressure (1.01×10⁵ Pa), R is the ideal gas constant, T is the absolute temperature (273.15 K), and j_{total} is the total current [236].

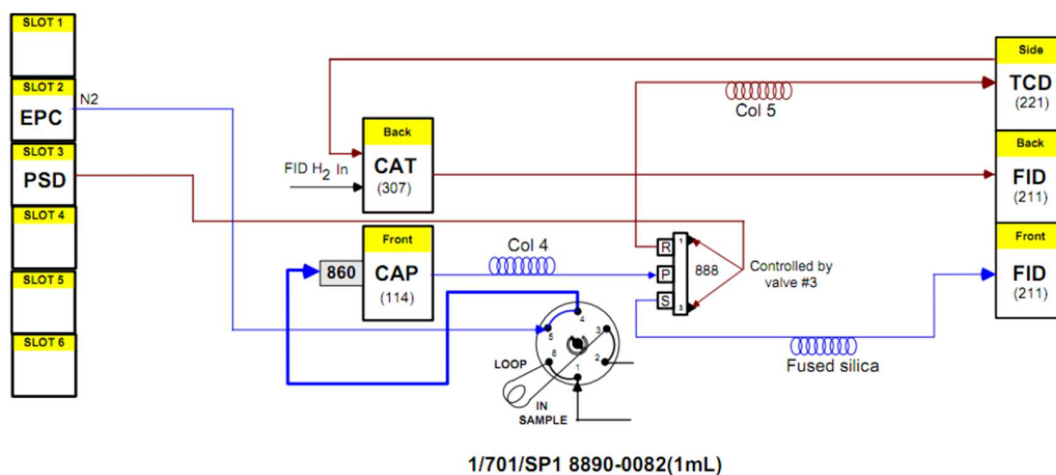


Figure 3.4: The GC configuration in this work.

Liquid products (HCOOH, CH₃OH and C₂H₅OH etc.) were quantified using proton nuclear magnetic resonance (¹H NMR, Bruker DPX 400 MHz) with a water suppression technique. An internal standard was prepared by mixing 150 μL of dimethyl sulfoxide (DMSO) with 300 mL of ultrapure water (**Figure A 1**). The NMR test solution consisted of 500 μL spent electrolyte, 100 μL D₂O, and 100 μL of aqueous DMSO (containing 0.05 μL DMSO). The FE of liquid products was calculated using the following **Eq. 6** below:

$$FE_{liquid} = n_i \times \frac{z_i F}{Q} \times 100\% \quad \text{Eq. 6}$$

where n_i represents the number of moles of liquid product i ($2e^-$ for HCOOH, $6e^-$ for CH₃OH and $12e^-$ for C₂H₅OH); z_i represents the number of electrons required to produce one molecule of product i ; F represents the Faradaic constant; Q represents the total charge passed through the WE.

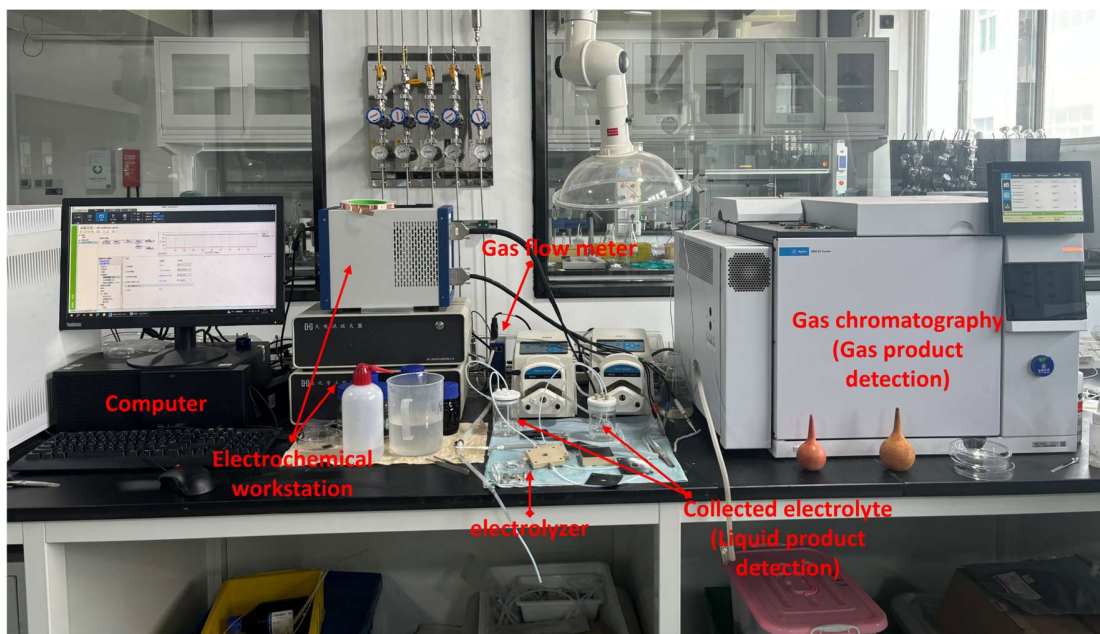


Figure 3.5: The photograph of experimental set-up in this project.

3.3 Electrocatalyst characterisation techniques

3.3.1 *Ex situ* characterizations

The prepared electrocatalysts were characterized systematically in this thesis. The surface morphology of the as-prepared catalysts was observed using transmission electron microscopy (TEM, FEI Tecnai G2 F20) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, JEOL ARM 200F, Japan). Besides, AC-HADDF-STEM experiments were performed on a Thermo Fisher Themis Z spherical aberration-corrected transmission electron microscope with an electron acceleration voltage of 300 kV.

The crystallographic information of the materials was analysed by using an X-Ray Diffraction (XRD, Bruker D8 Advance) with Cu K α radiation in the 2θ range from 10° to 90° . The chemical and electronic states of elements in the catalysts were also analysed

using an X-ray photoelectron spectroscopy (Thermo Escalab 250). The C1s peak at 284.8 eV was applied for the calibration of binding energies. Raman spectrometer equipped with a 325 nm Ar-ion laser beam under ambient conditions (Renishaw RM2000) was used. The electron paramagnetic resonance (EPR) spectra were recorded on a Bruker A300 EPR spectrometer at room temperature. The Brunauer-Emmett-Teller (BET) method conducted by Micromeritics ASAP 2460 instrument was utilized to calculate the specific surface areas. The pore volume was derived from the sorption curve by the non-local density functional theory (NLDFT) model.

The X-ray absorption fine structure (XAFS) spectra on Ni and Ag K-edge were collected at 44A beamline of National Synchrotron Radiation Research Centre in Taiwan. XAFS spectra on Cu K-edge was conducted using the RapidXAFS 2M (Anhui Absorption Spectroscopy Analysis Instrument Co., Ltd.) in transmission mode at 20 kV and 40 mA. The data were collected in fluorescence mode using a Lytle detector while the corresponding reference sample were collected in transmission mode. The reference sample was grinded and uniformly dubbed on the special adhesive tape. The acquired extended X-ray absorption fine structure (EXAFS) data were processed according to the standard procedures using the ATHENA module of Demeter software packages.

3.3.2 *In situ*/operando characterizations

(1) *In situ* ATR-SEIRAS measurements

In situ ATR-SEIRAS were acquired using a Nicolet iS50 FT-IR spectrometer, equipped with a liquid nitrogen-cooled mercury cadmium telluride detector and a PIKE VeeMAX III variable angle ATR sampling accessory. The IR spectra were recorded at a resolution of 8 cm⁻¹, and 64 interferograms were co-added for each spectrum. Absorption

units of the spectra were defined as $A = -\log(R/R_0)$, where R and R_0 represent the reflected IR intensities of the sample and reference single-beam spectra, respectively. A 60° Si face-angled crystal was served as the reflection accessory, with the incident angle set to approximately 70°. A thin layer of gold (Au) film was chemically deposited on the Si crystal surface to enhance the IR signal and aid electron conduction. Initial *in situ* ATR-SEIRAS measurements of the Au film were conducted to mitigate interference with the CO₂RR signal. Catalyst ink was deposited onto the Au film, acting as the WE (0.05 mg cm⁻²), and was evenly distributed across the surface to further minimize the influence of the Au film. A platinum (Pt) wire and a saturated calomel electrode (SCE) were served as the CE and RE, respectively. A CO₂-saturated 1 M KHCO₃ or 1 M KCl solution was utilized as an electrolyte. The chronopotentiometry method was employed during *in situ* experiments under various potentials (vs. RHE without *iR* correction), with SEIRAS spectra collected concurrently during each potential test. The reference background for the SEIRAS spectrum was obtained at open circuit potential.

(2) *In situ* Raman measurements

In situ Raman spectroscopy was performed in a homemade single-chamber cell equipped with a three-electrode system. CO₂ electrolysis was carried out on the electrochemical workstation in the CO₂-saturated 0.1 M KHCO₃. During the electrolysis, the Raman signals were recorded on an inVia Reflex Raman microscope (Renishaw) equipped with a water immersion objective (50×) and diode lasers (532 and 633 nm). Each spectrum was derived using 10% laser power, 20 s exposure time and averaging 3 scans in extended mode. *In situ* Raman spectroscopy was recorded at open circuit potential and different potentials within -0.2 to -0.8 V (vs. RHE) with 0.1 V potential interval. Prior to

testing, a pre-electrolysis (CV) procedure was applied to activate the cathodic catalyst. Each spectrum was captured after 5 minutes of consecutive CO₂RR.

3.4 Density functional theory calculations

In this thesis, DFT calculations were performed using the spin-polarized DFT method as implemented in the Vienna Ab-initio Simulation Package (VASP 5.4.4) [237, 238]. VASP facilitates accurate first-principles calculations based on DFT for a variety of scientific applications, and is known for its efficiency, reliability, and versatility. The package offers a comprehensive set of algorithms and numerical methods for simulating properties such as energies, forces, and excited electron states, providing valuable insights into the fundamental behaviours of materials. The projector augmented wave (PAW) method was adopted to describe the electron-ion interactions and the Perdew-Burke-Ernzerhof (PBE) functional was employed for the electronic exchange and correlation effects [239-241]. The semi-empirical correction scheme of Grimme (DFT-D3) was implemented in all calculations to address van der Waals (vdW) interactions [242]. A 500-eV plane-wave cut-off energy and $3 \times 3 \times 1$ Monkhorst-Pack k -point grid was applied for structure optimization. All the geometric structures were fully relaxed until the energy and force met the criteria of 10^{-5} eV and $0.02 \text{ eV } \text{\AA}^{-1}$, respectively. The solvent effect was simulated by an implicit solvent model, VASPsol, as implemented in VASP, with the dielectric constant of water set to 78.4 [243, 244]. VASPKIT was used to analyse the calculation results from VASP [245].

The Gibbs free energy change (ΔG) of each electrochemical step was calculated based on the computational hydrogen electrode (CHE) model [246], following **Eq. 7** below:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S \quad \text{Eq. 7}$$

where ΔE is the electronic energy difference directly obtained from DFT calculations, ΔZPE is the zero point energy difference, T is the room temperature (300 K) and ΔS is the entropy change.

The entropies of free gases are taken from standard values. For adsorbates, all 3N degrees of freedom were treated as frustrating harmonic vibrations with negligible contributions from the catalysts' surfaces. In the CHE model, each reaction step was treated as a simultaneous transfer of the proton-electron pair as a function of the applied potential [247], following **Eq. 8** below:

$$G(H^+ + e^-) = 1/2G(H_2) - eU \quad \text{Eq. 8}$$

where U is the applied bias potential and e is the elementary charge.

The transition state search was conducted with climbing image nudged elastic band (CI-NEB) method [248], followed by the dimer method to converge the saddle point within 0.05 eV Å⁻¹.

Chapter 4 Ni-Ag dual atom electrocatalyst for CO₂RR to CO

*Parts of **Chapter 4** have been adapted with permission from the following publication:*

Z. Guo, H. Zhu, G. Yang, A. Wu, Q. Chen, Z. Yan, K. Loon Fow, H. Do, J.D. Hirst, T. Wu, M. Xu, Synergistic Engineering of Heteronuclear Ni-Ag Dual-Atom Catalysts for High-Efficiency CO₂ Electroreduction with Nearly 100% CO Selectivity. *Chemical Engineering Journal*, **2023**, 476, 146556.

In this chapter, a meticulous synthesis of heteronuclear dual-atom catalysts consisting of nickel (Ni) and silver (Ag) anchored onto a nitrogen-rich porous carbon matrix, denoted as Ni-Ag/PC-N, were conducted. The precise configuration of the dual-atom sites has been accurately determined as N₃-Ni-Ag-N₃. The Ni-Ag/PC-N catalyst has demonstrated an exceptional CO Faradaic efficiency (FE_{CO}) exceeding 90% over a wider range of applied potentials (−0.7 to −1.3 V). Particularly noteworthy is the peak FE_{CO} of 99.2% achieved at −0.8 V versus the RHE. The Tafel analysis has revealed that the rate-determining step in the process is the formation of the *COOH intermediates, and the Ni-Ag/PC-N catalyst has exhibited the most favourable electrokinetic. *In situ* Fourier-transform infrared and *in situ* Raman spectra analyses have provided insights into an accelerated production of *COOH intermediates and an enhancement in mass transfer during CO₂ electroreduction. DFT calculations have further elucidated the exceptional catalytic activity and the synergistic mechanisms resulting from the interaction between heteronuclear dual atoms. The findings have demonstrated that the presence of a neighbouring Ni atom effectively lowers the energy barrier for *COOH intermediates formation and enhanced the rate-determining step. Meanwhile, the adjacent Ag atom serves to mitigate the detrimental effects caused by the strong affinity of *CO for single Ni atom adsorption sites, effectively preventing its poisoning.

4.1 Introduction

As discussed in Section 2.3.1, transition metals such as Ni, Ag, Co, Fe, when dispersed atomically and anchored on nitrogen-rich porous carbon, have gained significant attention as a novel type of SACs for CO₂ recycling [167, 236, 249-258]. These catalysts are favoured for their efficient atomic utilization and the presence of uniform catalytic sites. Among the various Metal-Nitrogen-Carbon (M-N-C) catalysts reported, Ni₁-N_x-C_y sites have demonstrated high FEs towards CO (FE_{CO}) at low applied potentials, e.g., Ni-NG: 95.0% at -0.73 V *vs* RHE [259] and Ni-N₃-V: 96.1% at -0.66 V *vs* RHE [260]. However, the strong binding of *CO on Ni atomic site poses challenges for CO desorption and catalyst poisoning [261, 262], leading to a sharp decrease in selectivity at higher applied potentials (over -1.0 V *vs* RHE) [161, 263]. Meanwhile, previous studies have reported that Ag₁-N_x-C_y can effectively suppress HER and enhance CO disruption owing to its unique electronic structure [264, 265]. However, it has lower-than-desired selectivity and a high energy barrier for *COOH formation during CO₂RR-to-CO, e.g., FE_{CO} of Ag₁-G: 79.2% at -0.70V *vs* RHE [266]; FE_{CO} of Ag-N-C-1: ~70% at -0.85 V *vs* RHE [267].

In comparison to SACs, dual-atom catalysts (DACs) show greater potential for improved activity and selectivity in CO₂RR due to the synergistic interactions between adjacent metal atoms [236, 252-254, 257, 268]. To optimize the performance of DACs in terms of activity and FEs, it is essential to establish the relationship between the catalysts' active site and its CO₂RR-to-CO performance. Accordingly, real-time detection of reaction intermediates and products during CO₂RR plays a crucial role in elucidating this structure-function relationship [269-272]. Traditional characterization techniques are unable to capture the reaction intermediates on the catalyst surface due to the rapid reaction kinetics

of CO₂RR and the complexity and low concentration of these intermediates. Therefore, *in situ* spectroscopy and DFT have been employed to monitor the intermediate states in real-time and calculate the energy of absorbed intermediates [271, 273, 274].

In this work, a cascade-anchored pyrolysis strategy was employed to precisely synthesize efficient electrocatalyst for CO₂RR-to-CO. The constructed catalyst, denoted as Ni-Ag/PC-N, consists of atomically dispersed Ni-Ag sites embedded in a defective nitrogen-rich porous carbon matrix. To validate the specific coordination model of the catalytic sites on Ni-Ag/PC-N, X-ray absorption near-edge structure (XANES) and EXAFS spectroscopy were conducted. The results indicate that the active site consists of two adjacent Ni and Ag atoms, each is coordinated to three nitrogen atoms and firmly anchored to the defective PC-N matrix, forming the N₃-Ni-Ag-N₃ coordination. Remarkably, Ni-Ag/PC-N exhibits superior CO₂RR performance over a wide potential window (600 mV), reaching a peak FE_{CO} of 99.2% at -0.8 V vs RHE, with a partial current density of ~13 mA cm⁻². To understand the mechanisms, *in situ* FTIR and *in situ* Raman spectra were used to confirm that the Ni-Ag/PC-N surface effectively stabilizes *COOH intermediates, leading to the production of CO via synergistic effects. Further, DFT calculations provided insights into synergistic effects of the coordinated Ni-Ag pairs. These effects not only lower the energy barrier for *COOH formation on single Ag atoms but also prevent the potential catalyst poisoning effect caused by the high *CO affinity on single Ni atoms. This synergistic facilitation of DACs addresses the common issues associated with SACs and offers promising ways for the precise design and synergetic engineering of atomically dispersed catalysts for CO₂RR.

4.2 Experimental

4.2.1 Synthesis of porous carbon carriers

The porous carbon samples were prepared via a typical synthesis procedure [275]. Initially, a total of 800 mg of sodium citrate tribasic hydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 3\text{H}_2\text{O}$, AR) underwent pyrolysis in a porcelain boat. This process was conducted within a tube furnace that operated under an argon atmosphere at a flow rate of 100 sccm. The temperature gradually increased at a rate of 10 °C per minute, and the pyrolysis occurred at a temperature of 800 °C for a duration of one hour. The resulting black solid was rinsed using dilute H_2SO_4 (0.5 M) to remove the sodium carbonate until no bubbles were observed. The black carbon was then filtered and washed three times with deionized water. Subsequently, the PC sample with a 3-D honeycomb structure was prepared by drying it at 80 °C for a period of 6 hours.

4.2.2 Synthesis of diatomic Ni-Ag/PC-N catalyst

All catalyst samples were prepared using a previously reported synthesis procedure, with a minor modification [275]. In brief, 1.2 g of freshly prepared PC, along with 1.5 mmol of silver nitrate, 67 mmol of α -D-glucose, and 1.5 mmol of nickel nitrate hexahydrate, were mixed with 50 mL deionized water and subjected to ultrasonic treatment for a duration of 2 hours. Following this, the resulting solid-liquid mixture was centrifuged twice at 7000 rpm and the remaining solution was slowly decanted off. The moist solids were placed in an oven at 70 °C to dry overnight. The dehydrated mixture was then blended with melamine in a mass ratio of $M(\text{mixture}):M(\text{melamine}) = 1:5$. Finally, the mixture was pyrolyzed under an Ar atmosphere at a flowrate of 100 sccm, with a heating rate of 10 °C per min, at a temperature of 800 °C for 2 hours, resulting in the formation of Ni-Ag/PC-N.

4.2.3 Synthesis of control catalysts

In order to conduct controlled experiments, catalysts of Ni/PC-N and Ag/PC-N were fabricated in the same manner as described above, with the exception of adding only 3.0 mmol of nickel nitrate hexahydrate and 3.0 mmol of silver nitrate, respectively. Additionally, PC-N and Ni-Ag/PC were prepared following a similar procedure, excluding the addition of metal salts and melamine, respectively.

4.2.4 DFT calculation details

Apart from the DFT calculation details discussed in section 3.4, the dual metal Ni-Ag/PC-N (coordination: N₃-Ni-Ag-N₃), single metal Ni/PC-N (coordination: Ni-N₃) and Ag/PC-N (coordination: Ag-N₃) models were built based on a 6 × 6 supercell of primitive graphene with a vacuum separation of 20 Å to avoid possible interactions between the periodic replicas along the *z* direction.

4.3 Results and discussion

4.3.1 Synthesis and characterization of Ni-Ag/PC-N catalyst

The desired Ni-Ag/PC-N materials were synthesized applying a sequential pyrolysis approach with anchoring in a cascade manner [275, 276]. **Figure 4.1a** demonstrates the production of porous carbon (PC) with a high specific surface area and abundant defects through the pyrolysis of carbon substrates, specifically sodium citrate, which is a more cost-effective alternative to graphene. The PC material was subjected to sulfuric acid washing to eliminate any inorganic impurities, resulting in a 3-D honeycomb-like morphology with ample oxygen-containing groups (**Figure 4.1b**) [275]. Subsequently, the

metal salt solution and chelating agent, α -D-glucose, were ultrasonically mixed to effectively separate and sequester each metal ion using the domain-limiting effect.

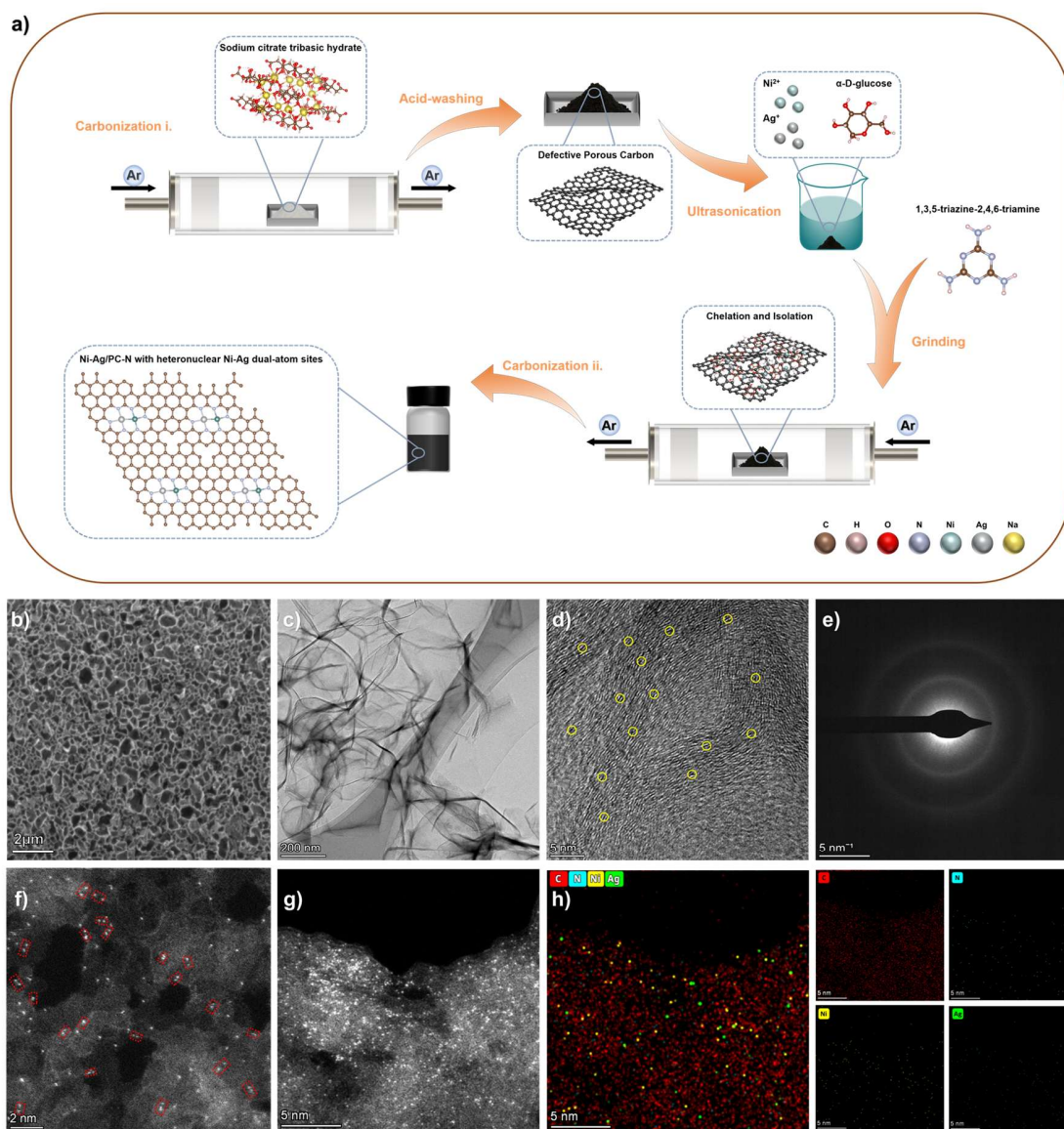


Figure 4.1: a) Schematic illustration of the synthesis process of Ni-Ag/PC-N; b) SEM image of PC, c) TEM and d) HRTEM image of Ni-Ag/PC-N. Several lattice distortions are marked with yellow circles; e) SAED pattern of Ni-Ag/PC-N; f) AC-HAADF-STEM images of Ni-Ag/PC-N. Some observed atom pairs are highlighted with red dashed lines; g) AC-HAADF-STEM and h) Corresponding elemental mapping of Ni, Ag, C and N for Ni-Ag/PC-N.

It is worth mentioning that the controlled molar ratio of Ni ions to silver ions in the precursor impregnation solution was set at 1:1, aiming to promote the formation of as many Ni-Ag dual-atom pairs as possible to maximize their synergistic effect. The as-prepared PC material was introduced to the mixed solution, allowing the chelated metal ions to be chemically anchored to the PC's oxygen-rich and defect-rich surface. The resulting solid-liquid mixture underwent sequential ultrasonic dispersion, high-speed centrifugation, and decanting, followed by thorough drying in a vacuum. Prior to the second pyrolysis step, the PC material, anchored with metal complexes, was physically ground and thoroughly mixed with the nitrogen source material, melamine. During pyrolysis, the chelated metal complexes decomposed at approximately 500 °C, forming residues that prevented the aggregation of metal atoms. Furthermore, these protected metal atoms combined with the carbon-nitrogen species (PC-N) from melamine decomposition at around 800 °C, resulting in the formation of the M-N-C coordination.

Based on the powder X-ray diffraction (PXRD) pattern (**Figure 4.2**), it can be observed that the PC, Ni/PC-N, and Ni-Ag/PC-N samples all exhibit only two broad peaks at approximately 24.1° and 44.1°, indicating the presence of graphitic carbon and absence of any crystalline impurities or metal particles. However, in the PXRD pattern of Ag/PC-N, characteristic diffraction peaks of Ag are observed. The excessive concentration of Ag precursor solution results in the formation of Ag clusters under the same synthesis conditions. This phenomenon is evident in the tendency of free Ag atoms generated during pyrolysis to diffuse and aggregate into clusters on the PC-N surface. Conversely, when the concentration of AgNO₃ is reduced and Ni atoms are introduced to achieve their coexistence and distribution on PC-N, the diffusion of Ag atoms is restricted, and they are

stabilized by the nearby Ni atoms [236, 267]. The PC (**Figure 4.3**), PC-N (**Figure 4.4**), Ag/PC-N (**Figure 4.5**) and Ni-Ag/PC-N (**Figure 4.1b**) samples show a three-dimensional honeycomb-like porous structure, as observed in the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images. This porous structure facilitates mass transfer during CO₂RR [262].

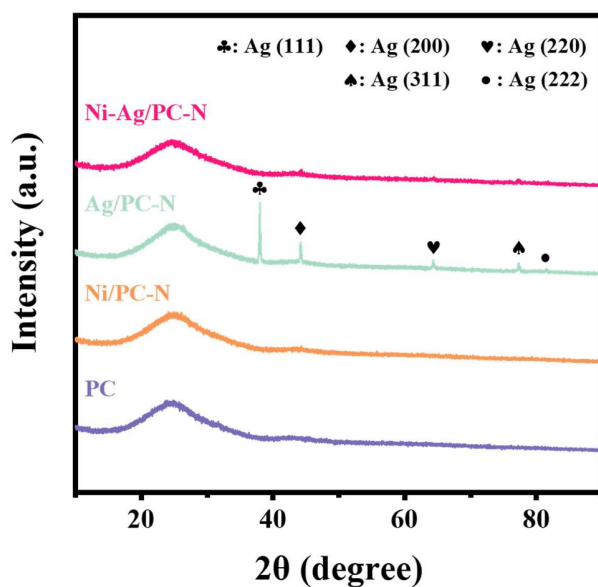


Figure 4.2: PXRD patterns of Ni-Ag/PC-N, Ag/PC-N, Ni/PC-N and PC materials.

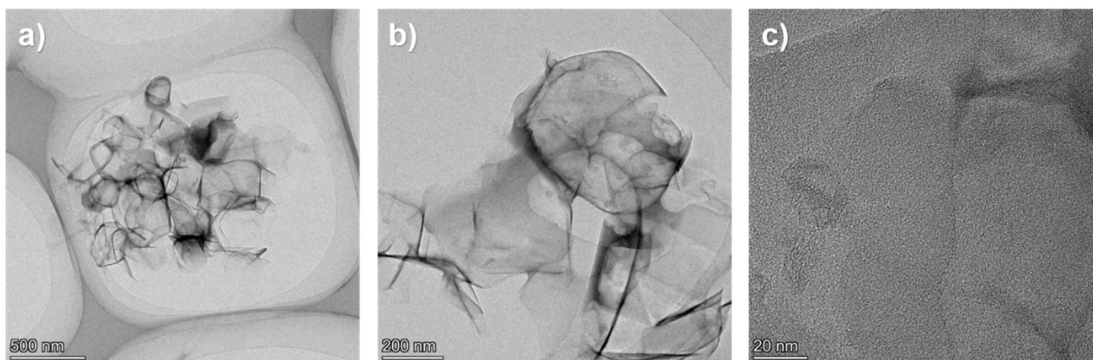


Figure 4.3: (a-c) TEM images of PC materials at different magnifications.

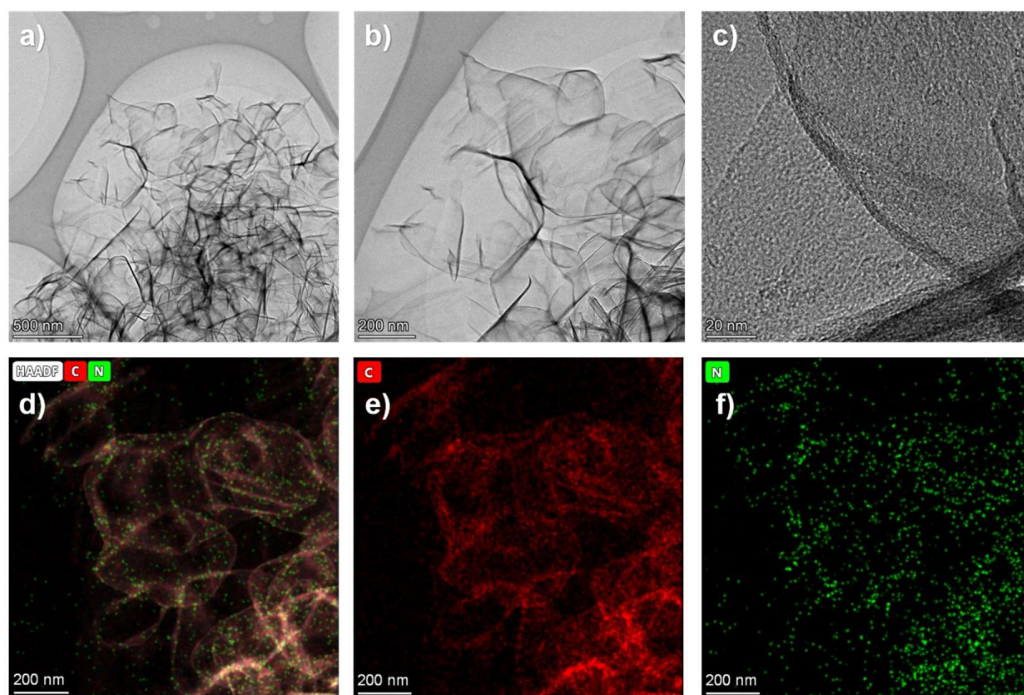


Figure 4.4: (a-c) TEM images of PC-N materials at different magnifications; (d-f) HAADF-STEM and the corresponding elemental mapping images of C, N for PC-N materials.

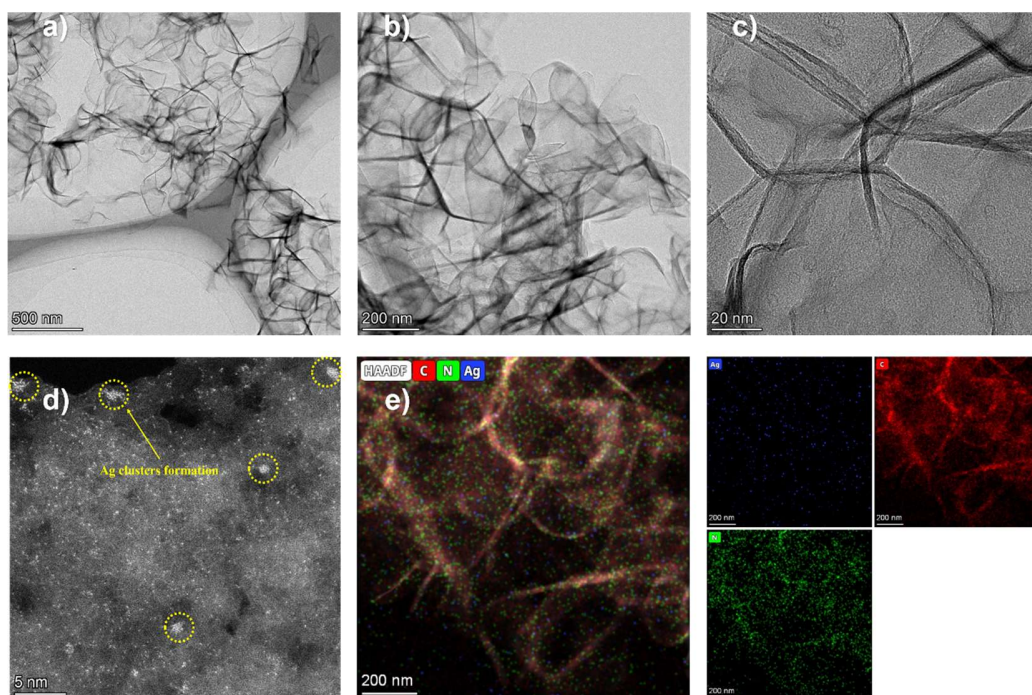


Figure 4.5: (a-c) TEM images of Ag/PC-N materials at different magnifications; (d) HAADF-STEM images of Ag/PC-N materials, Some observed Ag clusters are circled in yellow dashed lines, and (e) the corresponding elemental mapping images of Ag, C and N for Ag/PC-N materials.

Furthermore, the lamellar morphology of the dispersed Ni-Ag/PC-N, which is characteristic of pyrolyzed carbonaceous materials and favours single-atom loading, is evident in the high-resolution TEM (HRTEM) images (**Figure 4.1c** and **Figure 4.6**). Notably, the HRTEM image (**Figure 4.1d**) reveals distinct lattice-distortion defects in the carbon substrate, marked by yellow circles, possibly attributed to the coordination of dispersed Ni/Ag hetero-diatomic pairs with N atoms during the stepwise carbonization process.

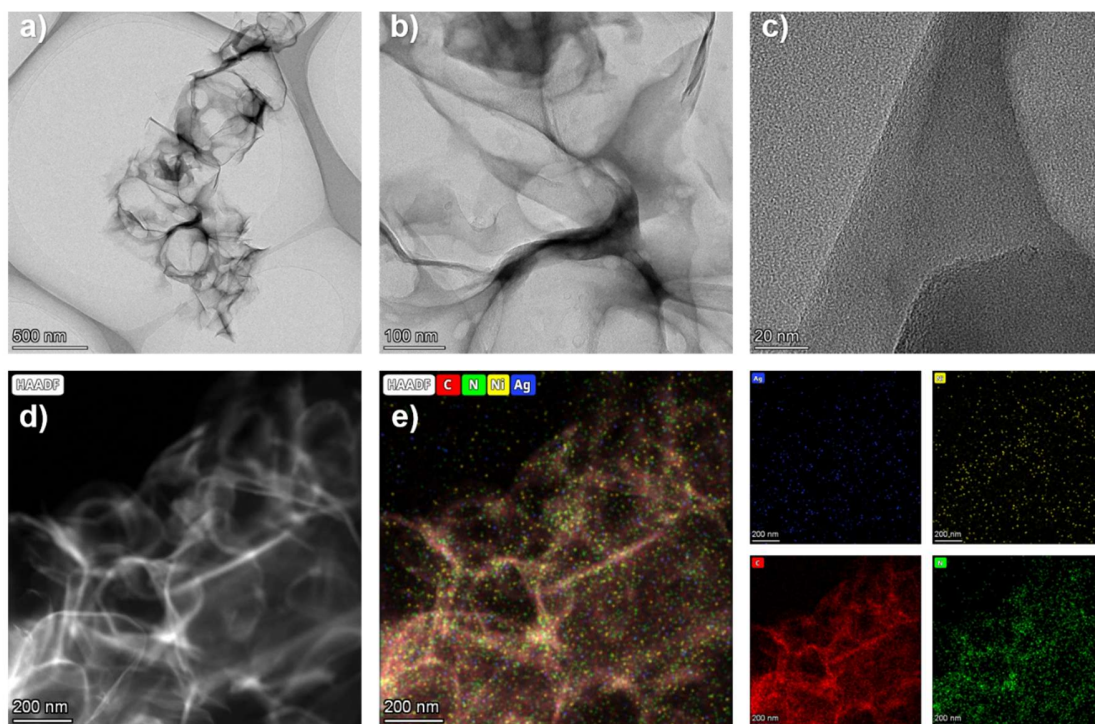


Figure 4.6: (a-c) TEM images of Ni-Ag/PC-N materials at different magnifications; (d, e) HAADF-STEM and the corresponding elemental mapping images of Ag, Ni, C and N for Ni-Ag/PC-N materials.

Additionally, **Figure 4.1e** presents selected area electron diffraction (SAED) image of the Ni-Ag/PC-N, displaying a ring pattern indicative of amorphous carbon, consistent with the PXRD pattern. For a closer examination of the distribution of metal single-atoms, aberration-corrected high-angle annular dark field scanning transmission electron

microscopy (AC-HAADF-STEM) images confirm the uniform dispersion of Ni and Ag sites, measuring approximately 0.15 nm in size, in the Ni-Ag/PC-N (**Figure 4.7**).

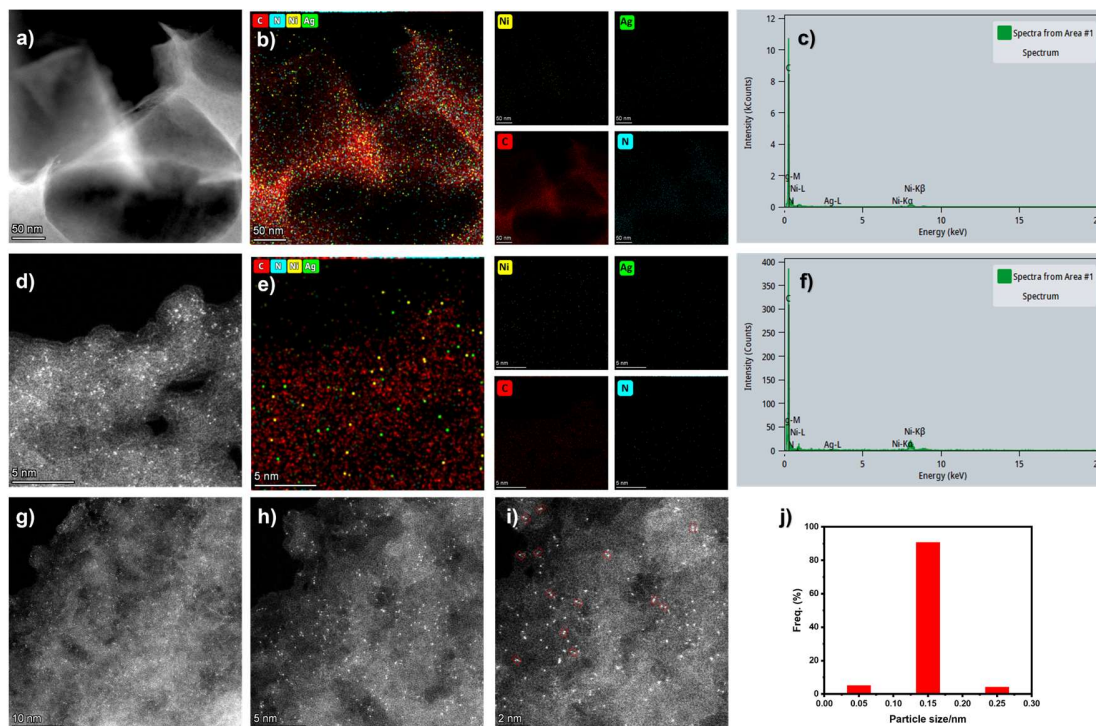


Figure 4.7: (a&b, d&e) AC-HAADF-STEM and the corresponding elemental mapping images of Ag, Ni, C and N for Ni-Ag/PC-N materials; (c, f) EDS-AC-HAADF-STEM-spectra from selected area of Ni-Ag/PC-N materials; (g-i) AC-HAADF-STEM images of Ni-Ag/PC-N materials at different magnifications. Some atom pairs are highlighted with red dashed lines; (j) diagram on the metal atoms size distribution of Ni-Ag/PC-N sample, data are selected from figures g to i.

Interestingly, the presence of neighbouring dual-dot sites is observed and circled by the red dashed line, providing indications of the existence of diatomic sites (**Figure 4.1f** and **Figure 4.7**). Energy dispersive X-ray spectroscopy (EDS) analysis further confirms the uniform distribution of Ni, Ag and N elements on the carbon matrix without any aggregation (**Figure 4.1g, h**). Besides, inductively coupled plasma mass spectrometry (ICP-MS) results demonstrate that the mass percentages of Ni and Ag in Ni-Ag/PC-N are 0.46% and 6.60% (7.06% in total), respectively, which are higher than those of Ni/PC-N

(0.69%) and Ag/PC-N (2.96%) (**Table 4.1**). This higher metal loading capacity of Ni-Ag/PC-N can be attributed to the interaction between Ni and Ag species, which stabilize each other, and form coordinated heteronuclear dual-metal sites [167, 277]. Additionally, the intensity ratio of the D-band to G-band (I_D/I_G) obtained from Raman spectroscopy serves as an indicator for structural imperfections in carbon materials. The Raman spectra display two prominent peaks at around 1338 and 1589 cm⁻¹, corresponding to the in-plane stretching vibration of C-atoms sp² hybridization and defects within the C-atom lattice, respectively [161, 267, 278].

Table 4.1: ICP-MS analysis results of the as-prepared electrocatalysts.

Catalyst	Ni (wt.%)	Ag (wt.%)
PC	0	0
PC-N	0	0
Ni/PC-N	0.69	0
Ag/PC-N	0	2.96
Ni-Ag/PC-N	0.46	6.60

Figure 4.8a indicates that the concentration of inner defects in PC, PC-N and Ni-Ag/PC-N significantly increases during cascade pyrolysis processes ($I_D/I_G = 0.97, 1.01$ and 1.08 , respectively). This indicates that the abundance of defects in the carbon matrix facilitates the reaction kinetics during electrocatalytic reactions [279]. Furthermore, the Ni-Ag/PC-N sample possesses a high BET specific surface area of 303 m² g⁻¹ compared to the other samples (**Table 4.2**) due to its porous and defective structure formed during the stepwise carbonization process [267]. The N₂ adsorption isotherms confirm the presence of layered mesopores and micropores in the sample, which greatly enhances mass transfer during the CO₂RR process (**Figure 4.8b**) [280].

Table 4.2: BET surface areas, external surface area and micropore volume of the as-synthesized samples.

Sample	BET surface areas (m ² g ⁻¹)	External surface area (m ² g ⁻¹)	Micropore volume (cm ³ g ⁻¹)
PC	110	71	0.02
PC-N	195	127	0.03
Ni/PC-N	259	198	0.03
Ag/PC-N	199	116	0.04
Ni-Ag/PC	157	91	0.03
Ni-Ag/PC-N	303	157	0.08

Additionally, the CO₂ adsorption isotherms demonstrate that the Ni-Ag/PC-N catalyst has a higher CO₂ adsorption capacity of 1.02 mmol g⁻¹ compared to PC (0.60 mmol g⁻¹) and PC-N (0.55 mmol g⁻¹), indicating more CO₂ molecules can be adsorbed on its surface (**Figure 4.8c**) [267]. Electron paramagnetic resonance (EPR) spectroscopy is commonly utilized to characterize the defect properties of M-N-C materials. All four samples exhibit similar characteristic peaks in their EPR spectra, with a g factor of 2.002. These peaks are associated with unpaired electrons on the conjugated CN aromatic ring [281]. The source of these unpaired electrons can be attributed to C-vacancies, with the highest concentration of C-vacancies observed in the Ni-Ag/PC-N samples (**Figure 4.8d**). The presence of an abundance of unpaired electrons from C-vacancies at the interface enhances the electronic properties of Ni-Ag/PC-N and creates potential catalytic sites for CO₂RR, thereby leading to its exceptional catalytic performance [282].

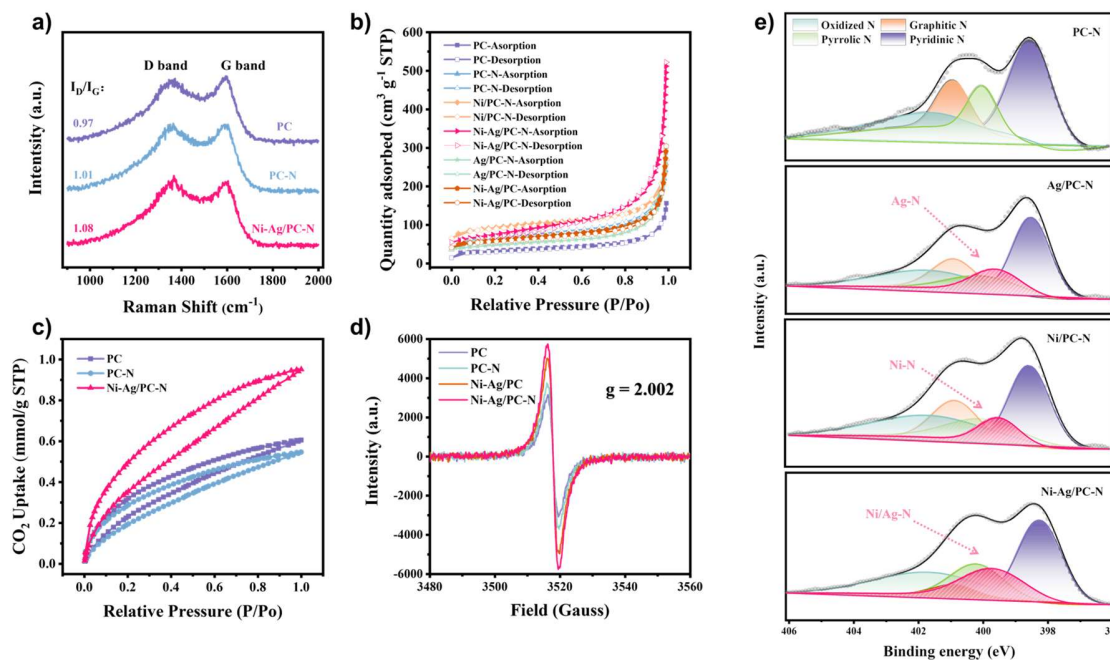


Figure 4.8: a) Raman spectra of PC, PC-N and Ni-Ag/PC-N; b) N₂ adsorption-desorption isotherms of PC, PC-N, Ni/PC-N, Ni-Ag/PC-N, Ag/PC-N and Ni-Ag/PC; c) CO₂ adsorption measurements of PC, PC-N and Ni-Ag/PC-N; d) EPR spectra of C-vacancies in PC, PC-N, Ni-Ag/PC and Ni-Ag/PC-N; e) High-resolution XPS N 1s spectrum of PC-N, Ag/PC-N, Ni/PC-N and Ni-Ag/PC-N.

4.3.2 Atomic structure of Ni-Ag/PC-N catalyst

X-ray photoelectron spectroscopy (XPS), XANES and EXAFS spectroscopy techniques provide valuable insights into the valence information and coordination environment of the metal centres in Ni-Ag/PC-N. The N 1s spectrum obtained from the high-resolution XPS analysis of Ni-Ag/PC-N (**Figure 4.8e**) reveals five distinct peaks representing different nitrogen species: pyridinic-N (398.3 eV), metal-N (399.6 eV), pyrrolic-N (400.0 eV), graphitic-N (400.9 eV) and oxidized-N (401.7 eV) [236, 252, 254]. Notably, as-prepared materials show porphyrin-like moieties at 399.6 eV, which are assigned to metal-nitrogen (M-N) coordination. Moreover, the area proportion of characteristic M-N peaks (399.6 eV) increases with the higher mass percentage of the metal element in the catalyst (**Figure 4.8e** and **Table 4.1**) [257], suggesting the coexistence and

stabilization of Ag and Ni species are primarily coordinated to nitrogen rather than forming nanoparticles or clusters [167]. This observation, combined with the high density of atomic pairs observed (**Figure 4.1f**), supports the postulation of the formation of Ni/Ag dual-metal sites in the Ni-Ag/PC-N sample. Further analysis of the XPS curves of Ni 2p and Ag 3d reveals that the Ni 2p_{3/2} peak in the Ni-Ag/PC-N sample appears at around 854.90 eV, between the Ni⁰ 2p_{3/2} (~852.9 eV) and Ni²⁺ 2p_{3/2} (~856.0 eV) peaks. Similarly, the Ni 2p_{1/2} peak (~872.48 eV) falls within the interval of Ni⁰ 2p_{1/2} (~870.5 eV) and Ni²⁺ 2p_{1/2} (~873.5 eV) (**Figure 4.9a**) [144, 161, 269]. The Ag 3d XPS spectrum exhibits two peaks at approximately 374.08 eV and 368.2 eV, corresponding to Ag 3p_{3/2} and Ag 3p_{5/2}, respectively (**Figure 4.9b**). These peaks have higher binding energies compared to Ag⁰ 3d_{3/2} (~373.4 eV) and Ag⁰ 3d_{5/2} (~368.0 eV) and are close to Ag⁺ 3d_{3/2} (~374.3 eV) and Ag⁺ 3d_{5/2} (~368.3 eV) [265, 266]. In summary, the chemical state of Ni 2p in the Ni-Ag/PC-N sample lies between 0 and +1, while Ag 3d exhibits a chemical state above 0 and close to +1, which aligns with the commonly estimated valence state of SACs (**Figure 4.10** and **Figure 4.11**).

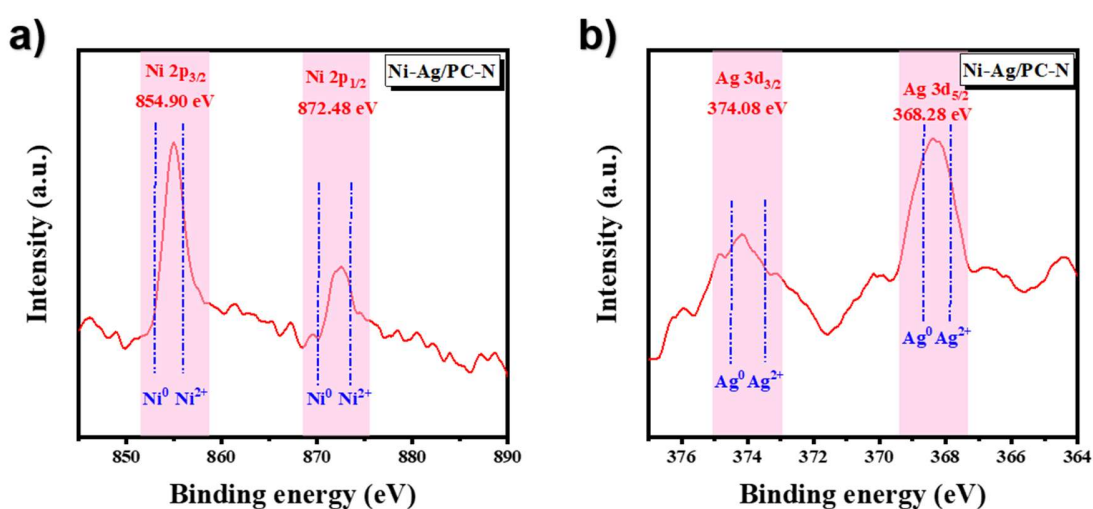


Figure 4.9: The XPS spectra of Ni-Ag/PC-N for the Ni 2p (a) and Ag 3d (b) regions.

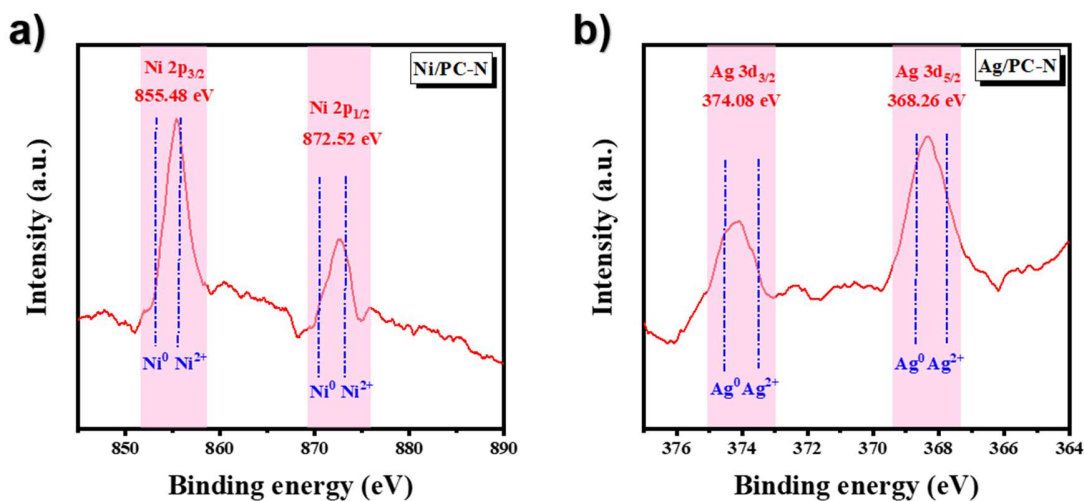


Figure 4.10: The XPS spectra of (a) Ni/PC-N for the Ni 2p region; and (b) Ag/PC-N for Ag 3d region.

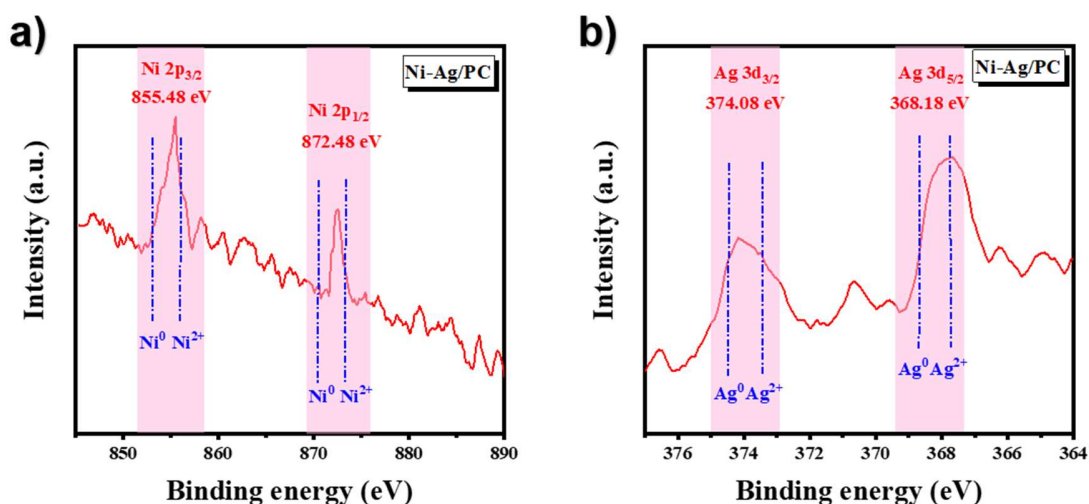


Figure 4.11: The XPS spectra of Ni-Ag/PC for the Ni 2p (a) and Ag 3d (b) regions.

In order to gain a comprehensive understanding of the coordination modes and chemical states of the Ni and Ag centres in Ni-Ag/PC-N, additional XANES and EXAFS measurements were conducted. The Ni K-edge XANES results (**Figure 4.12a**) show that the adsorption threshold of the Ni-Ag/PC-N sample lies between that of the Ni foil and the NiO standard samples. This observation provides valence information for Ni^{δ+} ($0 < \delta < 2$) in the Ni-Ag/PC-N samples, which aligns with the previously obtained XPS results [161, 262].

Additionally, the inset of **Figure 4.12a** highlights the leading edge feature at approximately 8336 eV, indicating the hybridization of the 3p and 4p orbital of the Ni central atom [144]. The higher peak intensity in Ni-Ag/PC-N, resulting from the distorted D_{4h} symmetry, is comparable to the nickel phthalocyanine (Ni-Pc) standard sample [144]. These observations suggest that the Ni centre in Ni-Ag/PC-N exhibits a typical metal-nitrogen (M-N_x) coordination similar to that of the Ni-Pc standard, but with the distortion of the D_{4h} symmetry attributed to another metal-metal (M₁-M₂) coordination [277].

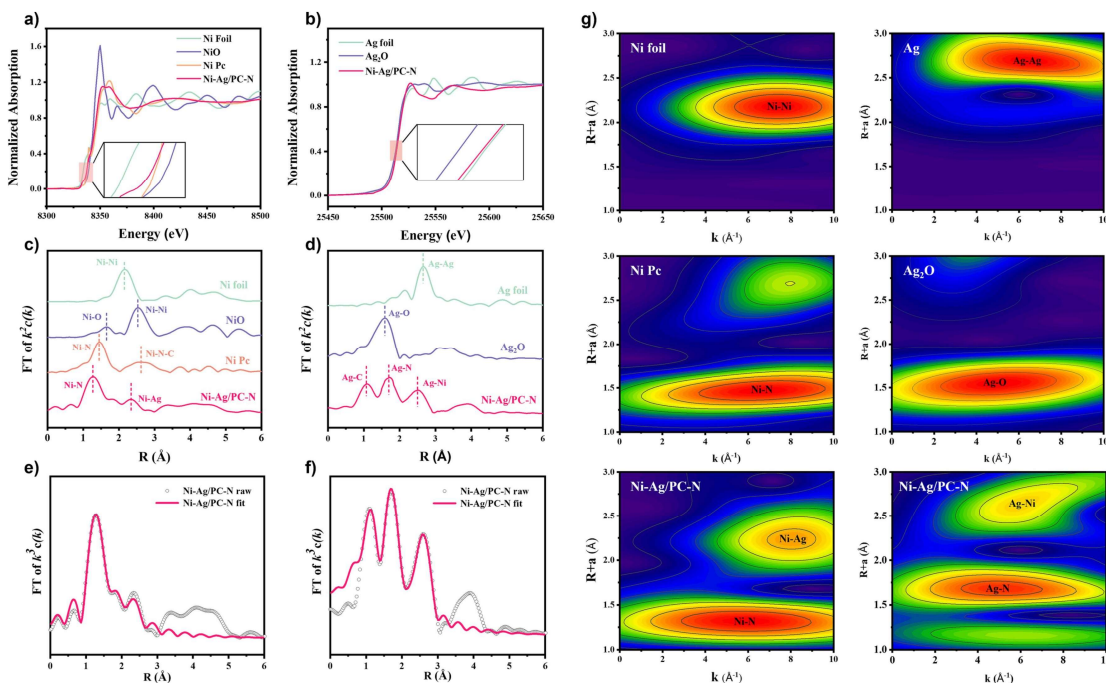


Figure 4.12: a) Ni K-edge XANES spectra of Ni foil, NiO, Ni PC, and Ni-Ag/PC-N; b) Ag K-edge XANES profiles of Ag foil, Ag₂O, and Ni-Ag/PC-N. Fourier transformation of c) Ni K-edge XANES and d) Ag K-edge XANES spectra at R space. The corresponding Ni K-edge e) and Ag K-edge f) EXAFS fitting curves for Ni-Ag/PC-N at R space, respectively; g) WTs k^3 -weighted EXAFS contour plots of Ni K-edge for Ni Foil, Ni Pc, Ni-Ag/PC-N and Ag K-edge for Ag foil, Ag₂O, and Ni-Ag/PC-N.

Furthermore, the Ag K-edge XANES results on the same samples demonstrate that the intensity of the Ni-Ag/PC-N samples is greater than that of the Ag foil and slightly less intense than the Ag₂O standard samples (**Figure 4.12b**). This indicates that the valence

information of Ag^{γ+} (0<γ<1) in the Ni-Ag/PC-N is consistent with the results obtained from the XPS analysis.

The comparison between Ag foil and Ni-Ag/PC-N reveals that the absorption edge position of Ni-Ag/PC-N is skewed towards the higher energy side. This indicates that the Ag species are positively charged and firmly attached to the surface of the PC-N carrier as electron donors, thus forming M-N_x sites [267]. The Fourier transform (FT) k^2 weighted EXAFS spectra were employed to provide more detailed information about the M-N_x and M₁-M₂ coordination mentioned earlier. Through comparison with other standard samples (**Figure 4.12c**), it is observed that the peaks at 1.30 Å and 2.33 Å in the k^2 -weight FT spectra from Ni K-edge EXAFS can be attributed to M-N_x and M₁-M₂ coordination, respectively. Notably, the characteristic peak at 1.30 Å may be ascribed to Ni-N, as evidenced by the comparison with the FT curve of the Ni Pc sample. Interestingly, the M₁-M₂ peak observed for Ni-Ag/PC-N at 2.33 Å is not found in the Ni foil and NiO standard samples, providing further evidence for the presence of Ni-Ag coordination. Similarly, the k^3 -weight FT spectra from Ag K-edge EXAFS of the same Ni-Ag/PC-N samples exhibit peaks at 1.10Å, 1.68Å and 2.57Å, which can be assigned to Ag-C, Ag-N and Ag-M coordination, respectively (**Figure 4.12d**). In contrast to the Ag foil reference spectrum, the peak at 2.70 Å for the Ag-Ag coordination is not detected in Ni-Ag/PC-N, thereby confirming that the coordination mode of M₁-M₂ as an Ag-Ni coordination.

To support the arrangement of Ni-Ag dual-atom sites on PC-N, wavelet transforms (WTs) were performed using high-resolution in R -space and k -space (**Figure 4.12e and f**). The WT-EXAFS contour plots of the Ni-Ag/PC-N sample, both at the Ni K-edge and Ag K-edge, show peak intensities at approximately 4.3 Å⁻¹, which corresponds to the Ni-N

and Ag-N coordination [254, 266]. Furthermore, a sub-maximal intensity at around $6.2 \text{ \AA}^{-1}$ indicates the presence of heteronuclear dual-atom Ni-Ag coordination in Ni-Ag/PC-N, which is noticeably different from the Ni-Ni coordination ($7.6 \text{ \AA}^{-1}$) and Ag-Ag ($7.2 \text{ \AA}^{-1}$) coordination in Ni foil and Ag standards (**Figure 4.12g** and **Figure 4.13**) [144, 267].

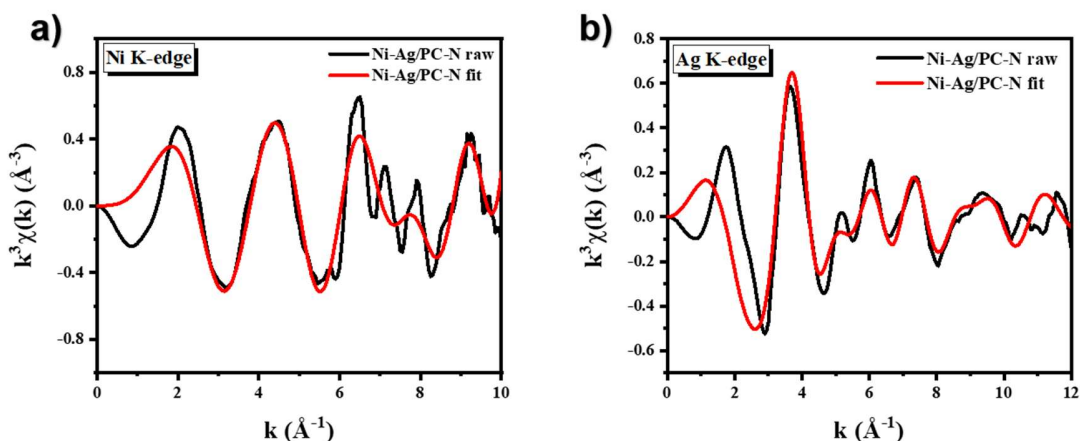


Figure 4.13: FT-EXAFS fitting curves of (a) Ni and (b) Ag K-edge of Ni-Ag/PC-N in k space.

By fitting the results to Ni K-edge EXAFS and Ag K-edge EXAFS, quantitative coordination information regarding Ni and Ag atoms in Ni-Ag/PC-N is obtained. The analysis of Ni K-edge EXAFS reveals a coordination number of 3.1 for Ni-N bonding and a coordination number of 1.0 for Ni-Ag bonding (**Figure 4.12e** and **Table 4.3**). Similarly, fitting results of Ag K-edge EXAFS confirm Ag-N coordination number of 3.3 and Ag-Ni coordination number of 1.5 (**Figure 4.12f** and **Table 4.4**). In summary, local coordination conformation of heteronuclear Ni/Ag dual-atom site in Ni-Ag/PC-N is quantitatively determined as N₃-Ni-Ag-N₃ coordination. Both the Ni foil and Ag standard samples exhibit a coordination number of 12, indicating the atomic dispersion of Ni and Ag species in the Ni-Ag/PC-N samples. This observation aligns with the previously discussed characterization findings, including XRD, HADDF-STEM, XPS, and other relevant analyses.

Table 4.3: EXAFS fitting parameters at the Ni K-edge of various samples ($S_0^2 = 0.96$)

Samples	Path	C. N.	R (Å)	$\sigma^2 (\times 10^{-3} \text{ Å}^2)$	ΔE (eV)	R factor
Ni foil	Ni-Ni	12*	2.49*	5.6±2.4	6.3±2.4	0.01
NiO	Ni-O	6*	2.11*	7.3±2.5	5.6±1.7	0.01
	Ni-Ni	12*	2.98*	8.6±1.1		
Ni Pc	Ni-N	4*	1.93*	4.1±3.1	6.1±2.8	0.02
	Ni-C	12*	2.95*	5.3±1.7		
Ni-Ag/PC-N	Ni-N	3.1	1.86±0.02	7.9±2.7	8.4±2.9	0.02
	Ni-Ag	1.0	2.56±0.02	5.2±2.6		

Table 4.4: EXAFS fitting parameters at the Ag K-edge of Ni-Ag/PC-N sample, Ag foil and Ag₂O

Samples	Path	C. N.	R (Å)	$\sigma^2 (\times 10^{-3} \text{ Å}^2)$	ΔE (eV)	R factor
Ag foil	Ag-Ag	12*	2.88*	10.9	2.98	0.003
Ag ₂ O	Ag-O	4*	1.8*	19.9	4.81	0.01
Ni-Ag/PC-N	Ag-N	3.3	1.87±0.02	6.8±5.3	8.4±2.9	0.02
	Ni-Ag	1.5	2.87±0.02	9.9±0.8		

Notes: *The experimental EXAFS fits by fixing C. N. as the known crystallographic value. C. N.: coordination numbers; R: distance between the absorber and backscatter atoms; σ^2 : Debye-Waller factors; ΔE_0 : the inner potential correction. R factor: goodness of fit.

4.3.3 Electrochemical performance of CO₂RR on Ni-Ag/PC-N catalyst

The electrocatalytic performance of the catalysts (Ni-Ag/PC-N, Ni-Ag/PC, Ni/PC-N, Ag/PC-N, PC-N, PC) was initially evaluated by linear sweep voltammetry (LSV) in a conventional gastight H-cell reactor in a CO₂- and Ar-saturated 0.1 M KHCO₃ solution (**Figure A 2**). The current density in this study is standardized to the electrode's geometric surface area. Among the synthesized catalysts, Ni-Ag/PC-N exhibits the lowest applied potential of −0.72 V to achieve a current density of 10 mA cm^{−2} in a CO₂-saturated

electrolyte. In comparison, the applied potentials required to maintain the same current density for Ni/PC-N, Ni-Ag/PC, Ag/PC-N, PC-N, and PC are -0.82 , -0.98 , -1.06 , -1.07 , and -1.08 V, respectively (**Figure 4.15a**). Notably, when comparing the LSV curves of Ni-Ag/PC-N in Ar- and CO₂-saturated electrolytes, a significant increase in current density and onset potential are observed ((**Figure 4.15a**). This suggests that the Ni-Ag/PC-N catalyst demonstrates sensitivity to the presence of CO₂ molecules in the electrolyte and exhibits effective electrocatalysis for CO₂ reduction rather than HER [167]. To gain a more comprehensive understanding of the CO₂RR activity and the product distribution across six as-prepared catalysts, potentiostatic CO₂ electrolysis was conducted at potentials ranging from -0.7 V to -1.3 V (*vs* RHE) for 2 hours at 0.1 V intervals. The calibration curves for the various gas products and the original chromatograms are included below (**Figure 4.14**).

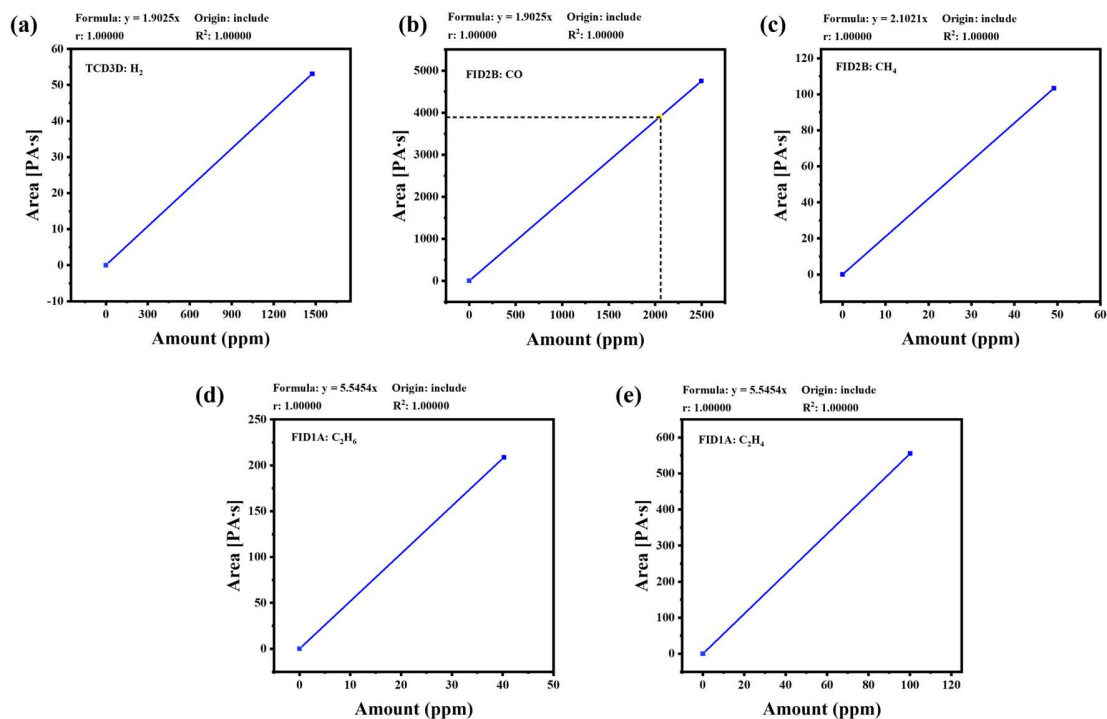


Figure 4.14: Calibration curves and corresponding formulas for various gas products, (a) H₂, (b) CO, (c) CH₄, (d) C₂H₆ and (e) C₂H₄.

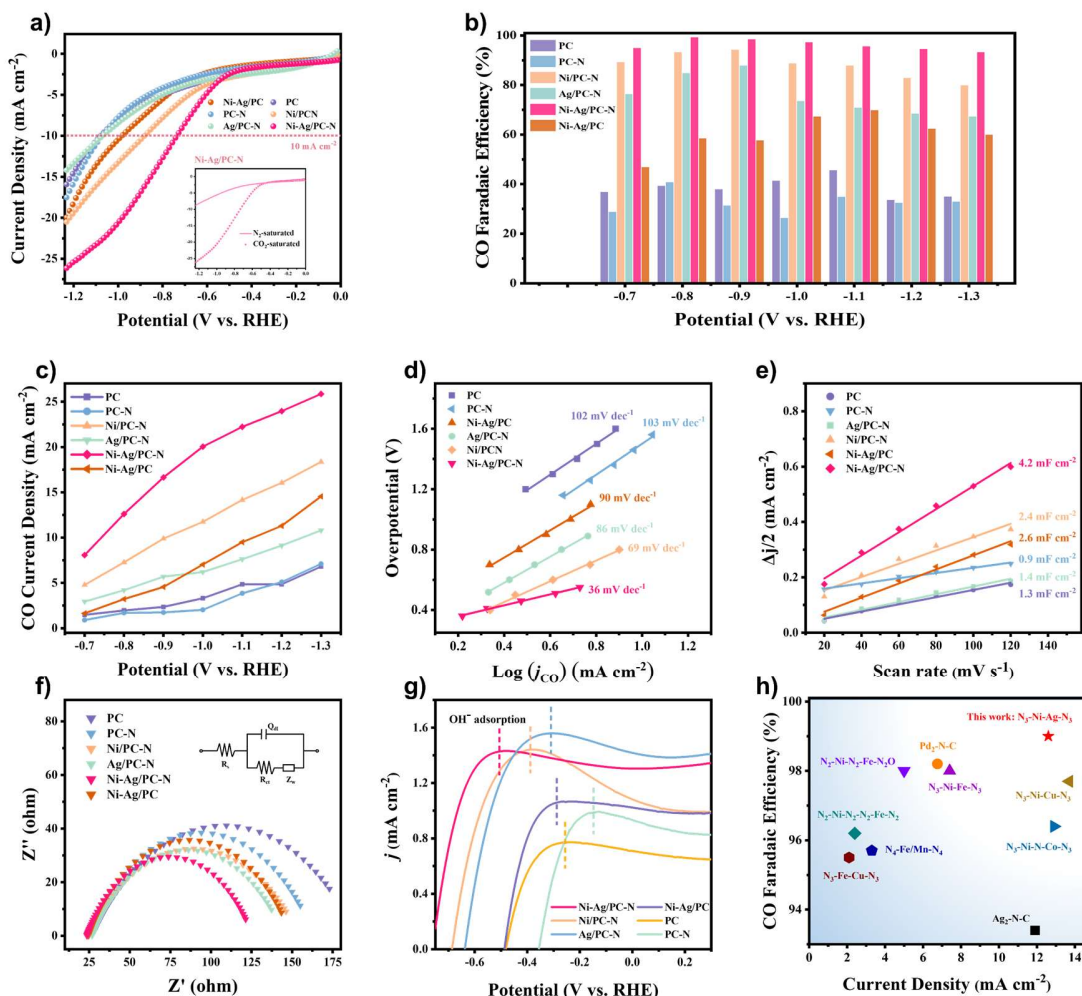


Figure 4.15: Electrocatalytic performances of CO₂RR over PC, PC-N, Ni/PC-N, Ag/PC-N, Ni-Ag/PC, and Ni-Ag/PC-N. a) LSV curves in CO₂-saturated 0.1 M KHCO₃ solution. The inset figure is LSV curves of Ni-Ag/PC-N in Ar-saturated 0.1 M KHCO₃ solution; b) CO Faradaic efficiency of CO₂RR from -0.7 V to -1.3 V vs RHE, c) CO partial current density, d) Tafel curves for the CO partial current density, e) ECSA curves and f) EIS curves of as-prepared catalysts; g) Single oxidative LSV scans in Ar-saturated 0.1 M KOH of different catalysts; h) FE_{CO} value of Ni-Ag/PC-N in this work and other reported dual-atom catalysts for CO₂RR-to-CO [167, 236, 252-254, 256, 257, 268, 283].

Moreover, the results depicted in **Figure 4.15b** and **Figure 4.16** exhibit that Ni-Ag/PC-N maintains a high FE_{CO} above 90% within the potential range of -0.7 V to -1.3 V (vs RHE). Notably, at a potential of -0.7 V, Ni-Ag/PC-N achieved a FE_{CO} of 94.8%. As the potential becomes more negative, Ni-Ag/PC-N reaches its peak FE_{CO} of 99.2% at -0.8

V. However, at an applied potential of -1.3 V, its FE_{CO} decreases slightly to 93.1%. This decrease can be attributed to the limitation of CO₂ dissolution in the 0.1 M KHCO₃ solution, which hinders mass transfer, and the increased participation of electrons in HER [271].

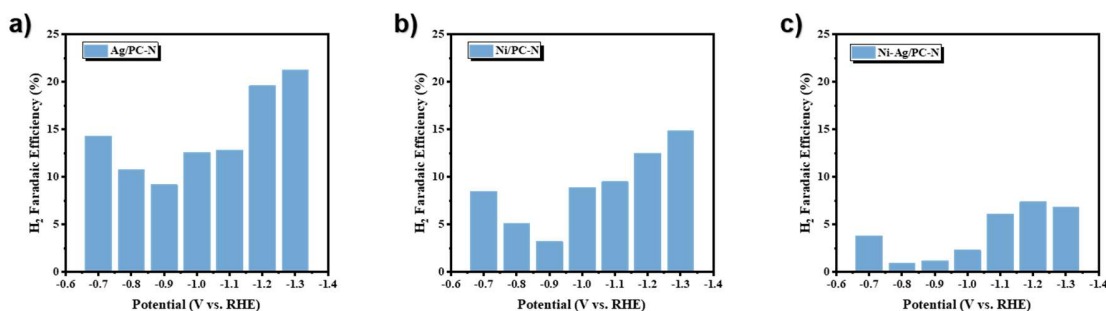


Figure 4.16: H₂ Faradaic efficiency of (a) Ag/PC-N, (b) Ni/PC-N and (c) Ni-Ag/PC-N during the CO₂RR process from -0.7 V to -1.3 V versus RHE.

Furthermore, **Figure 4.15c** demonstrates the dependence of the partial current density (j_{CO}) on the operating potential. At -0.8 V, the j_{CO} of the Ni-Ag/PC-N sample is 12.6 mA cm^{-2} , which is considerable higher than the j_{CO} values of Ni/PC-N (7.3 mA cm^{-2}), Ag/PC-N (4.2 mA cm^{-2}), Ni-Ag/PC (3.2 mA cm^{-2}), PC (2.0 mA cm^{-2}) and PC-N (1.7 mA cm^{-2}), with enhancement factors of 1.7, 3.0, 3.9, 6.3, and 7.4, respectively. This clearly demonstrates the superior performance of Ni-Ag/PC-N in terms of j_{CO} compared to other catalysts. This remarkable and continuous improvement in the j_{CO} of Ni-Ag/PC-N over Ni/PC-N and Ag/PC-N can be attributed to its excellent conductivity and high electron selectivity, resulting from the synergistic interactions in the heteronuclear Ni-Ag sites. These factors optimize electron transport and facilitates CO₂RR-to-CO [236].

Overall, the synthesized Ni-Ag/PC-N exhibits superior CO₂RR-to-CO performance compared to other reported high-performance dual-atom catalysts for CO₂RR-to-CO in H-cell, as shown in **Figure 4.15h** and **Table 4.5** [139, 161, 183, 262, 264-267, 284]. Moreover, Ni-Ag/PC-N exhibits good stability under 10 h operation at -0.8 V vs RHE (**Figure 4.17**).

Table 4.5: Comparison of CO₂RR-to-CO performance of Ni-Ag/PC-N, Ni/PC-N and Ag/PC-N electrocatalysts in this work with reported Ni- and Ag-based atomically dispersed electrocatalysts.

Catalyst	Electrolyte	FE _{CO} (%)	Potential (V)	CO Partial Current density (mA cm ⁻²)	Ref.
Ni-Ag/PC-N	0.1 M KHCO ₃	99.2	-0.8	12.6	This work
Ni/PC-N	0.1 M KHCO ₃	94.2	-0.9	9.8	This work
Ag/PC-N	0.1 M KHCO ₃	87.8	-0.9	5.7	This work
Ni-NG	0.1 M KHCO ₃	95	-0.73	11	[259]
Ni SAs/N-C	0.5 M KHCO ₃	71.9	-1.0	10.5	[263]
Ni SAs/NCNTs	0.5 M KHCO ₃	97	-0.9	41.5	[261]
Ni/Fe-N-C	0.5 M KHCO ₃	98	-0.7	7.4	[167]
H-Ni/NC	0.5 M KHCO ₃	97	-0.7	7.2	[262]
NiSA-N-PGC	0.1 M KHCO ₃	97.2	-0.76	26.2	[285]
h-Ni-N-C	0.1 M KHCO ₃	91.3	-0.75	15.1	[286]
NiN ₄ Cl-CINC	0.5 M KHCO ₃	98.7	-0.7	12.4	[287]
Ni-NCA-10	0.5 M KHCO ₃	99.7	-0.8	/	[258]
Ni/HMCS-3-800	0.5 M KHCO ₃	95	-1.0	10.5	[288]
Ni-N ₃ -V	0.5 M NaHCO ₃	96.1	-0.66	23.6	[260]
Fe ₁ -Ni ₁ -N-C	0.5 M KHCO ₃	96.2	-0.5	2.4	[254]
NiFe-DASC	0.5 M KHCO ₃	98	-0.7	7.4	[289]
Ag ₁ /MnO ₂	0.1 M KHCO ₃	95.7	-0.85	/	[290]
Ag-N ₃ -C	0.5 M KHCO ₃	95.2	-0.95	11.9	[267]
Ag ₂ -G	0.5 M KHCO ₃	93.4	-0.7	11.9	[266]

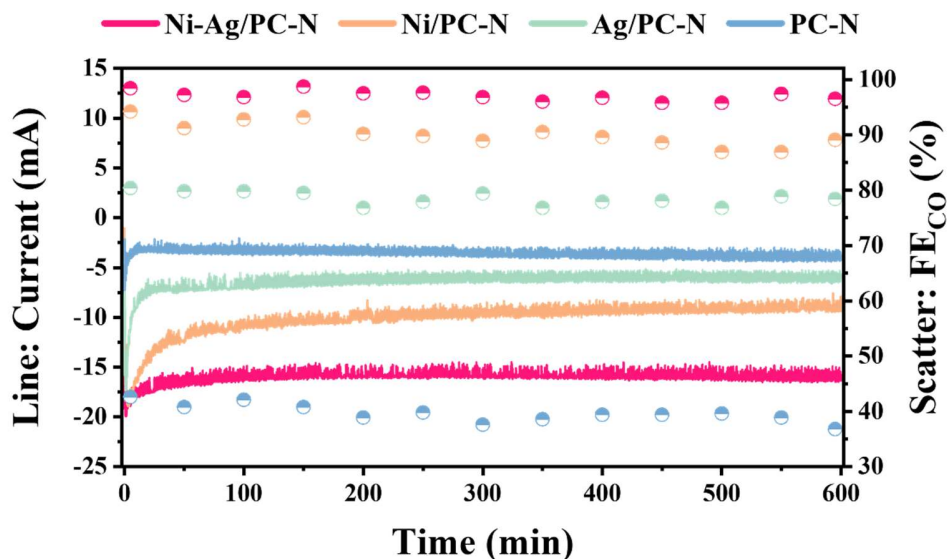
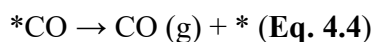
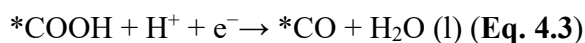
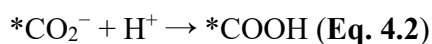
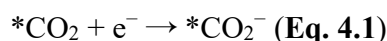


Figure 4.17: Long-term durability test of Ni-Ag/PC-N, Ni/PC-N, Ag/PC-N and PC-N at -0.8 V versus RHE for 10 h.

To unravel the underlying factors contributing to the exceptional catalytic activity of the Ni-Ag/PC-N catalyst, a comprehensive electrokinetic study was performed to elucidate the mechanism of CO₂ reduction on the heteronuclear Ni-Ag dual-atom sites. Building upon the previously reported electrochemical mechanism of CO₂ reduction to CO, four fundamental reaction steps can be proposed as shown in the following equations (* denotes the active site) [269]:



The rate-determining step (RDS) in the CO₂RR-to-CO process is heavily influenced by the electrode materials, such as the type of metal centre and the coordination

environment of the active sites. To determine the RDS of Ni-Ag/PC-N in the CO₂RR process, the corresponding Tafel slopes were fitted and analysed. Remarkably, the Tafel slope of Ni-Ag/PC-N is found to be 36 mV dec⁻¹, which is lower than that of Ni/PC-N (69 mV dec⁻¹), Ag/PC-N (86 mV dec⁻¹), Ni-Ag/PC-N (90 mV dec⁻¹), and PC (102 mV dec⁻¹), while the maximum value observed for PC-N is 103 mV dec⁻¹ (**Figure 4.15d**). This small Tafel slope of Ni-Ag/PC-N indicates its remarkable kinetic properties in the CO₂RR-to-CO process. Furthermore, the theoretically calculated Tafel slopes for CO₂RR are 118 mV dec⁻¹ (for the single electron transfer step, ET) and 59 mV dec⁻¹ (for the single proton transfer step, PT), respectively. Notably, the experimentally observed Tafel slope of Ni-Ag/PC-N closely aligns with the theoretical slope of 59 mV dec⁻¹. This suggests that the initial ET step (**Eq. 4.1**) does not serve as the RDS, while the subsequent PT step (**Eq. 4.2**) is a more plausible candidate for the RDS of the Ni-Ag/PC-N catalyst [167, 291].

To gain insights into the underlying factors contributing to the exceptional electrocatalytic performance, the electrochemically active surface area (ECSA) of the cathode catalyst was evaluated by quantifying the electrochemical double-layer capacitance (C_{dl}) (**Figure 4.15e** and **Figure A 3**). The C_{dl} values obtained follow the order of PC-N (0.9 mF cm⁻²) < PC (1.3 mF cm⁻²) < Ag/PC-N (1.4 mF cm⁻²) < Ni/PC-N (2.4 mF cm⁻²) < Ni-Ag/PC (2.6 mF cm⁻²) < Ni-Ag/PC-N (4.2 mF cm⁻²), which can be attributed to the higher metal density and active heteronuclear Ni/Ag coordination in Ni-Ag/PC-N. These findings further support the electrokinetic properties of Ni-Ag/PC-N that favour CO₂RR-to-CO process, which is consistent with the observations from the Tafel analysis.

Electrochemical impedance spectroscopy (EIS) was also conducted to examine the kinetic advantages of Ni-Ag/PC-N by analysing the catalyst's charge transfer resistance

(R_{ct}) obtained from semicircles in the low-frequency region. The R_{ct} value of Ni-Ag/PC-N is found to be 101.9 Ω , which is lower than that of Ag/PC-N (118.1 Ω), Ag-Ni/PC (125.0 Ω), Ni/PC-N (129.7 Ω), PC-N (138.7 Ω), and PC (162.7 Ω) (**Figure 4.15** and **Table 4.6**). Among these catalysts, Ni-Ag/PC-N exhibits the lowest R_{ct} value, indicating more efficient charge transfer and reaction kinetics, leading to a faster CO₂RR-to-CO process.

Table 4.6: Charge transfer resistance (R_{ct}) and solution resistance (R_s) values from EIS measurements.

Sample	R_{ct} (ohms)	R_s (ohms)
PC	162.7	33.8
PC-N	138.7	15.7
Ni/PC-N	129.7	16.3
Ag/PC-N	118.1	13.6
Ni-Ag/PC-N	101.9	13.6
Ni-Ag/PC	125.0	22.6

Additionally, the adsorption affinity of the intermediate $^*CO_2^-$ on the electrode surface was investigated by using OH^- species as a surrogate for $^*CO_2^-$ in the experiments [292, 293]. The adsorption of OH^- was carried out through oxidized LSV low-rate scan under N₂-saturated 0.1 M KOH electrolyte. The OH^- adsorption potentials follow the order of Ni-Ag/PC-N (−0.50 V) < Ni/PC-N (−0.38 V) < Ag/PC-N (−0.31 V) < Ag-Ni/PC (−0.28 V) < PC (−0.25 V) < PC-N (−0.14 V) (**Figure 4.15g**). The Ni-Ag/PC-N catalyst, with its abundant defects and special heteronuclear Ni-Ag coordination conformation, exhibits a more negative potential for OH^- adsorption, indicating the highest binding affinity for the intermediate $^*CO_2^-$ and promoting the formation of *COOH .

4.3.4 *In situ* spectroscopic analysis of CO₂RR over Ni-Ag/PC-N catalyst

In order to further validate the conclusions drawn from the Tafel slope and OH⁻ adsorption analysis, a time-dependent *in situ* FTIR spectrum was acquired to examine the details of the reaction intermediates over the heteronuclear Ni-Ag dual-atom sites, providing a comprehensive understanding of the dynamic behaviour of these intermediates throughout the CO₂RR-to-CO process and allowing for a more nuanced interpretation of the electronic interactions and catalytic mechanisms

Following a potentiostatic electrolysis at -1.0 V for a duration of 20 min, a gradual emergence of absorption peaks ranging from 1200 to 2000 cm⁻¹ is observed (**Figure 4.18a**). The IR bands at approximately 1400 and 1740 cm⁻¹, corresponding to symmetrical and asymmetrical stretching vibrations in carbonate groups (HCO₃⁻), are attributed to the dissolution of CO₂ in water [269]. It is important to note that a significant IR peak at 1547 cm⁻¹ is also identified, and its intensity increases remarkably over time. This absorption peak is believed to represent the carboxyl group of COOH* (**Figure 4.18b**), which serves as a crucial intermediate in the CO₂RR-to-CO (PT step, **Eq. 4.2**) [270, 285, 294]. This finding demonstrates that the Ni-Ag dual-atom sites effectively facilitate the activation of *CO₂⁻ to form the intermediate product COOH* and enhance the rate of RDS for CO₂RR.

In order to support the findings, potential dependent *in situ* surface-enhanced Raman spectra were applied to investigate the active sites and adsorbed intermediates on the Ni-Ag/PC-N catalyst. The applied potential was systematically decreased in increments of 100 mV from -0.05 to -1.85 V during *in situ* Raman spectroscopy test, and data were also recorded under open circuit potential (OCP) conditions.

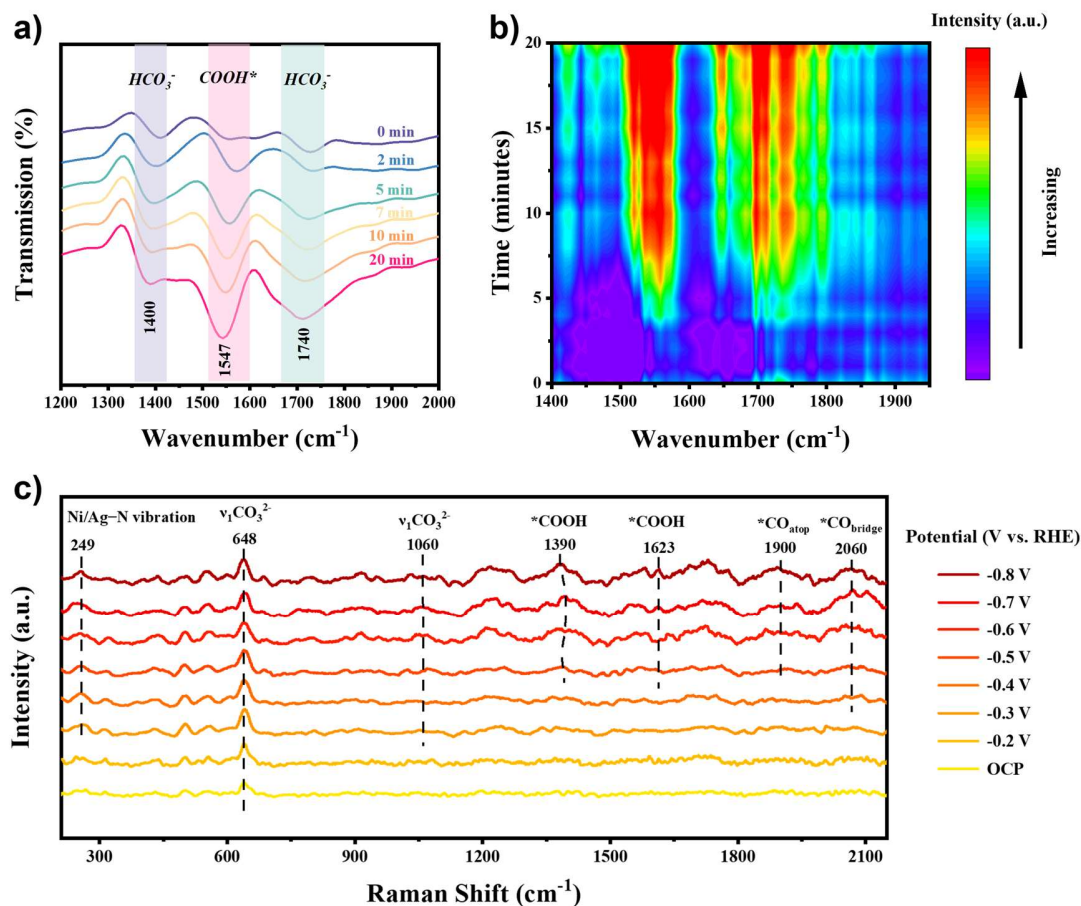


Figure 4.18: a) Time-dependent Electrochemical *in situ* FTIR spectra of the Ni-Ag/PC-N at the potential of -0.8 V vs RHE. All spectroscopic tests were conducted in CO₂-saturated 0.1 M KHCO₃; b) Corresponding 2D contour colour fill to the line plots; c) Potential-dependent *in situ* Raman spectra of the Ni-Ag/PC-N recorded after CV scan at OCP and the applied potential ranges from -0.2 to -1.2 V vs RHE with the potential interval of 0.1 V for 10 min.

As depicted in **Figure 4.18c**, a Raman peak at approximately 249 cm^{-1} is observed in the low wavenumber region, which could be assigned to the Ni/Ag-N stretching vibration peak [295]. Moreover, Raman bands at 648 cm^{-1} and 1060 cm^{-1} are observed, originating from the vibrational modes of CO₃²⁻ ($\nu_1\text{CO}_3^{2-}$) in the electrolyte solutions. Although HCO₃⁻ is the dominant carbonaceous species in the applied electrolyte, the presence of CO₃²⁻ as an adsorbed species could be explained by the phenomena of physisorption and chemisorption [274]. Apart from the $\nu_1\text{CO}_3^{2-}$ peak, Raman bands at 1900 cm^{-1} and 2060

cm⁻¹ are observed, which could be attributed separately to the ν CO of *CO on atop/bridge sites [273]. Notably, the Raman characteristic peaks at 1380 cm⁻¹ and 1623 cm⁻¹ are identified as the C-O stretching and C=O stretching of the reaction intermediate *COOH, respectively [272, 274]. This *in situ* Raman analyses further confirm the preferential nature of Ni-Ag/PC-N with heteronuclear dual-atom sites for the proton transfer step in the CO₂RR-to-CO process.

4.3.5 DFT calculations of CO₂RR on Ni-Ag/PC-N catalyst

To theoretically unveil the underlying factors contributing to the enhanced activity of neighbouring Ni-Ag sites in CO₂RR, DFT calculations were conducted based on the EXAFS fitting results. Specifically, the adsorption energy of intermediates on Ni (N₃-Ni*-Ag-N₃), Ag (N₃-Ni-Ag*-N₃) and Ni-Ag (N₃-Ni*-Ag*-N₃) coordination modes were simulated, using the N₃-Ni-Ag-N₃ coordination as a basis. The optimal model with the lowest free energy is determined to be N₃-Ni*-Ag-N₃, as shown in **Figure 4.19a**. The detailed analysis of the energy landscapes for these configurations provides insights into how atomic-level interactions influence reaction kinetics.

Additionally, the charge density differences of key intermediates (*COOH and *CO) over Ni-Ag/PC-N, Ni/PC-N and Ag/PC-N were calculated, as depicted in **Figure 4.19b** and **Figure 4.20**. The results provide evidence of significant electron interactions occurring among the dual-atom Ni-Ag pair, coordinated-N atoms, and the *CO/*COOH intermediates. This observation strongly suggests that the incorporation of Ni-Ag dual-atom pairs enhances the stabilization of *CO/*COOH adsorption and effectively reduces the energy barrier associated with the overall process.

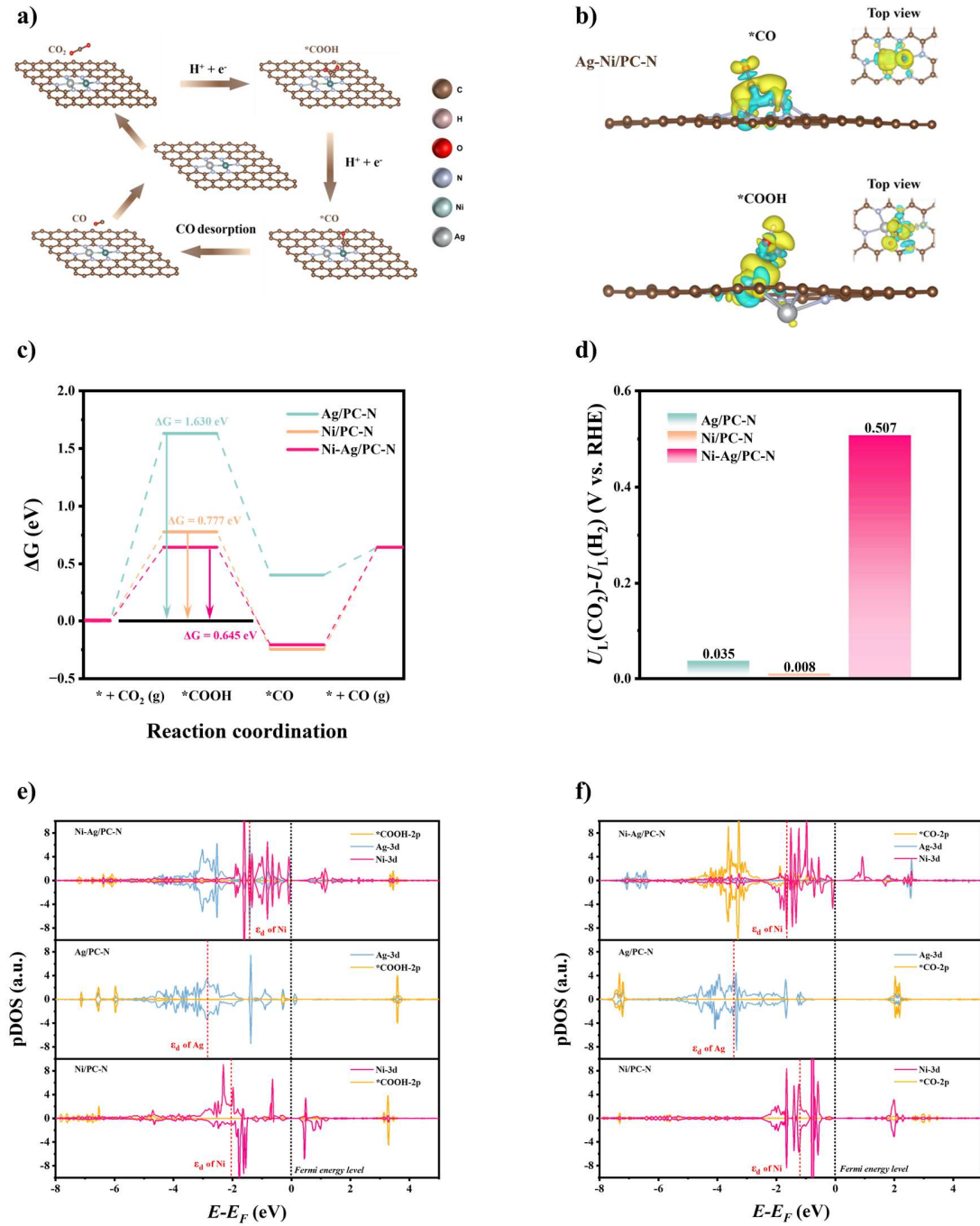


Figure 4.19: a) Schematic of the CO₂RR-to-CO mechanism of N₃-Ni*-Ag-N₃; b) Charge density difference of intermediates *CO and *COOH on the Ni-Ag/PC-N, Ag/PC-N and Ni/PC-N site, isosurface value is set to be 0.002 e/Å³, the yellow and cyan indicate the electron accumulation and electron depletion, respectively; c) Gibbs free energy diagram of CO₂RR-to-CO process, and d) Differences in theoretical limiting potential for CO₂RR and HER of Ag/PC-N, Ni/PC-N and Ni-Ag/PC-N; e and f) Partial densities of state for Ni-Ag/PC-N, Ni/PC-N and Ag/PC-N adsorbed different *CO/*COOH intermediates.

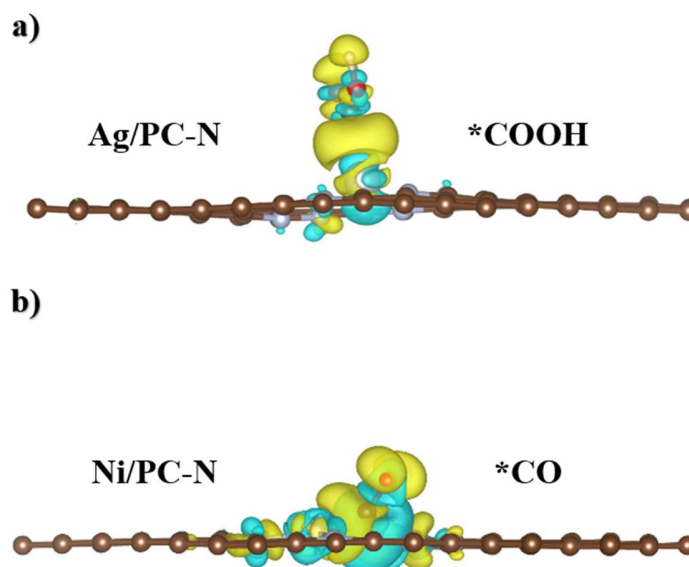


Figure 4.20: a) Charge density difference of *COOH intermediates on Ag/PC-N site and b) *CO intermediates on Ni/PC-N site (isosurface value is set to be $0.002 \text{ e}/\text{\AA}^3$, the yellow and cyan indicate the electron accumulation and electron depletion respectively).

Moreover, the free energy diagrams for CO₂RR yielding CO and the corresponding adsorption modes are revealed to evaluate the selectivity and reactivity in a specific manner. According to **Figure 4.19c**, the formation of *COOH species in the CO₂RR-to-CO steps is found to be an endothermic process with energy barriers of 0.64 eV, 0.78 eV, and 1.63 eV for N₃-Ni*-Ag-N₃, Ni-N₃, and Ag-N₃, separately. This is consistent with the Tafel results, which indicates that the *COOH formation step is the rate-determining step. The heteronuclear Ni-Ag dual-atom sites in Ni-Ag/PC-N decrease the energy barrier by 0.14 eV and 0.99 eV compared to Ni-N₃ and Ag-N₃, resulting in higher catalytic activity. Ni-Ag/PC-N exhibits the lowest adsorption energy for *COOH species. The affinity of CO species towards Ag/PC-N is notably the lowest, and it exhibits a decreasing trend from Ni-Ag/PC-N to Ni/PC-N, which aligns perfectly with the results derived from the difference in charge density (**Figure 4.19b**). The electron selectivity of the HER and CO₂RR, can be quantified by $U_L(\text{CO}_2) - U_L(\text{H}_2)$ values, whereas $U_L(\text{CO}_2)$ and $U_L(\text{H}_2)$ denote the theoretical

limiting potentials of CO₂RR and HER ($U_L = -\Delta G_0/e$), respectively (**Figure 4.19d** and **Figure 4.21**) [236, 296, 297]. The $U_L(\text{CO}_2) - U_L(\text{H}_2)$ values are highest for Ni-Ag/PC-N (0.507 V), followed by Ag/PC-N (0.035 V) and Ni/PC-N (0.008 V). Among the single-atom counterparts (i.e., Ni/PC-N and Ag/PC-N), the N₃-Ni-Ag-N₃ neighbouring site shows the most positive $U_L(\text{CO}_2) - U_L(\text{H}_2)$ value. These computational findings suggest that Ni-Ag/PC-N exhibits the best inhibition of HER and the highest selectivity towards CO₂RR.

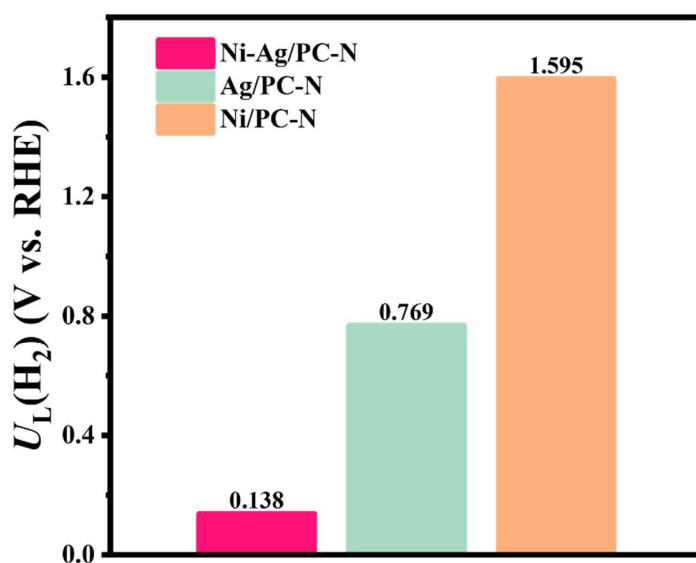


Figure 4.21: Theoretical limiting potential for HER of Ag/PC-N, Ni/PC-N and Ni-Ag/PC-N.

In order to gain a deeper understanding of the interactions between the reaction intermediates (*COOH/*CO) and the synergistic Ni-Ag/PC-N sites, the partial densities of state (pDOS) for the Ni-3d, Ag-3d, and C-2p orbitals among the Ni-Ag/PC-N, Ni/PC-N and Ag/PC-N were computed and analysed. The results depicted in **Figure 4.19e** and **f** reveal clear hybridization between the Ni-3d, Ag-3d, and C-2p orbitals (originating from *COOH and *CO) among the simulated models, signifying the presence of strong binding interactions within the coordination environment. Notably, in contrast to the mononuclear counterparts (Ni: -2.16 eV and Ag: -2.86 eV), the d-band centre of Ni in the hetero-

diatomic Ni-Ag/PC-N adsorbed *COOH (−1.41 eV) approaches the Fermi level ($E_f = 0$ eV) more closely. This can be attributed to the redistribution of charges induced in the Ni-Ag/PC-N model after the introduction of Ag species, resulting in the narrowing of the d-band gap of the Ni species in N₃-Ni*-Ag-N₃ and thus enhancing the electron mobility and accelerating the formation of *COOH [283]. However, the d-band centre of Ni in Ni-Ag/PC-N adsorbed *CO decreases from −1.20 eV to −1.59 eV compared to Ni/PC-N adsorbed *CO, indicating a weakened capability for electron transfer. This suggests a lower binding affinity of the *CO intermediate at the N₃-Ni*-Ag-N₃ site and a reduced resistance to CO molecule desorption, which is in close agreement with both the charge density difference and the free energy calculations [257, 287].

Based on the theoretical calculations, it has been determined that Ni/Ag dual-atom catalysts outperform their single-atom counterparts in CO₂RR-to-CO. The synergistic effects of the Ni-Ag dual-atom pairs have been explained in detail from a thermodynamic perspective. When compared to Ni-N₃, the introduction of Ag atoms eliminates the strong *CO affinity-induced poisoning effect on Ni atomic sites, as well as the limitations of the CO desorption step. Further, the inclusion of neighbouring Ni atoms significantly reduces the energy barrier for the formation of *COOH compared to Ag atomic sites.

4.4 Summary

To summarize, this work has successfully fabricated a Ni-Ag/PC-N electrocatalyst by the cascade-anchored pyrolysis method, which incorporates a layered porous and defective carbon matrix with heteronuclear Ni-Ag dual-atom sites. When tested in a 0.1 M KHCO₃ solution, the Ni-Ag/PC-N exhibits remarkable reactivity in CO production. It achieves a

high FE_{CO} of 99.2% at −0.8 V vs RHE and maintains a FE over 90% within a wider applied potential window of −0.7 to −1.3 V vs RHE. Furthermore, experimental evidence confirms that the synergistic Ni-Ag dual-atom sites in the Ni-Ag/PC-N catalyst promote the physical adsorption of CO₂ molecules and stabilize bicarbonate species *CO₂[−]. In-depth analyses using *in situ* FTIR and Raman reveal that *COOH radicals are key intermediates, further confirming that the conversion of *CO₂[−] to *COOH is the rate-determining step in the CO₂RR-to-CO process, aligning with the Tafel curve analysis. DFT calculations further support the notion that the construction of Ni-Ag dual-atom pairs addresses some intrinsic issues of Ni-/Ag-SACs, such as reducing the affinity of *CO to Ni atoms and lowering the adsorption energy barrier of *COOH to Ag atoms. This study establishes a general synthesis pathway for the symbiotic formation of heteronuclear dual-atom sites, which can greatly enhance the CO₂RR process. Furthermore, the combination of electrochemical experiments, *in situ* spectroscopy, and DFT calculations provide a comprehensive approach for understanding the synergistic effect within DACs and exploring the structure-function relationship between DACs and CO₂RR.

Chapter 5 La-doped CuO_x electrocatalyst for CO₂RR to C₁/C₂₊ products

*Parts of **Chapter 5** have been adapted with permission from the following publication:*

Z. Guo, H. Zhu, Z. Yan, L. Lei, D. Wang, Z. Xi, Y. Lian, J. Yu, K.L. Fow, H. Do, J.D. Hirst, T. Wu, M. Xu, Manipulating Adsorbed Hydrogen on Lanthanum-Modified CuO_x: Industrial-Current-Density CO₂ Electroreduction to C₂₊ products or CH₄, *Applied Catalysis B: Environment and Energy*, **2024**, 364, 124839.

In this chapter, a series of Cu/La bimetallic oxide electrocatalysts with controlled surface hydrogen adsorption, including OD-La_{0.10}-CuO_x and OD-La_{0.40}-CuO_x, were meticulously synthesized. These catalysts demonstrated excellent performance in CO₂RR, specifically in yielding C₂₊ products and CH₄. The electrochemical experimental results reveal that OD-La_{0.10}-CuO_x achieves a Faradaic efficiency exceeding 80% for C₂₊ products at a current density of 300 mA cm⁻². Furthermore, OD-La_{0.40}-CuO_x, with higher La doping, exhibits a Faradaic efficiency of 61.4% for CH₄ at a current density of 400 mA cm⁻². Confirmed by kinetic isotope experiments and *in situ* spectroscopy, the H₂O dissociation capacity on Cu/La catalysts varies with the degree of La doping, altering the intermediates formation pathway to the C₂₊ products or CH₄. According to density functional theory calculations, OD-La_{0.10}-CuO_x shows a moderate capacity for H₂O dissociation, which reduces the energy barrier for the conversion of *CHO to *OCCHO, thereby enhancing the production of C₂₊ products. In contrast, OD-La_{0.40}-CuO_x exhibits excellent H₂O dissociation capacity, supplying adequate adsorbed hydrogen to facilitate the hydrogenation of *CHO to *CH₂O, consequently promoting CH₄ formation. The generation of pathway-specific intermediates was successfully controlled by adjusting surface-adsorbed hydrogen, resulting in targeted production of C₂₊ products and CH₄, respectively. This study offers a valuable strategy for customizing products through the rational design and fabrication of copper electrocatalysts with varying doping levels.

5.1 Introduction

As reviewed in section 2.3.2, Despite extensive research on high-performance Cu-based electrocatalysts, the structure-function relationships in CO₂RR and the reaction pathways to various products at industrial current densities are not fully understood. A better understanding of correlations among various products would offer the prospect of increasing the conversion efficiency of desired CO₂RR products. In CO₂RR, multiple proton and electron transfer steps occur on the electrocatalyst surface, either sequentially or concurrently, leading to uncontrollable product distributions [298, 299].

Researchers have elucidated CO₂RR selectivity using theoretical and experimental approaches. For the C₁ product formation, Liu et al. demonstrated that the rate-determining step (RDS) in the CO₂RR-to-CO pathway is the coupling of *CO₂⁻ with H⁺ to form *COOH [295]. Xiong et al. revealed that the hydrogenation of *CO to *CHO is the RDS in the CO₂RR-to-CH₄ pathway, observing the *CHO intermediate using *in situ* FTIR [300]. Toward C₂₊ hydrocarbon formation, C-C coupling is widely recognized as a crucial step. Kim and collaborators observed the formation of *OCCO species through C-C coupling during the CO₂RR-to-C₂ process at a Cu electrode, using *in situ* ATR-SEIRAS [43, 301]. An increased local *CO concentration facilitates further protonation of *CO-*CO coupling, progressing to *CHO-*CO coupling [302]. These studies highlight that proton/*H activation and transfer are integral to various CO₂RR pathways, particularly for synthesizing desirable hydrocarbons such as CH₄, C₂H₄, and other C₂₊ products.

Typically, protons involved in CO₂RR are derived from sources such as H₂O, H₃O⁺ and HCO₃⁻ [303]. An isotope tracing study has demonstrated the direct role of H₂O in the electrochemical reduction of CO to ethanol [304]. Moreover, it is reported that accelerated

H₂O dissociation kinetics can lower the energy barrier for formate formation [305]. Therefore, customizing H₂O dissociation to modulate local *H donors emerges as a promising strategy to facilitate CO₂RR, enabling tailored distributions of C₁ and C₂₊ products. The introduction of single-atom [37, 306], oxygen vacancies [305], and rare-earth element doping, such as lanthanide [49], on catalyst surfaces has been reported to provide sites for H₂O dissociation. These sites expedite H₂O dissociation into *H, which subsequently participates in forming various hydrocarbons at CO₂ conversion sites [303, 304, 307]. Consequently, hydrocarbon production strongly depends on H₂O dissociation.

Among these strategies for modulating *H, heteroatom doping can alter the charge density around active sites and affect reaction intermediates, thereby improving the activity and selectivity of Cu-based catalysts for CO₂RR [50]. Compared to d-block metal elements, the unique physical and chemical properties of lanthanides stem from the special positioning of their 4f electrons and partially filled 5d orbitals. Specifically, lanthanum exhibits a high reduction potential (La³⁺/La⁰, -2.90 V vs RHE), remains stable during the CO₂RR process, and thus serves to modify the electronic structure of the Cu substrate [55]. For instance, La has been incorporated into constructs like La(OH)₃/Cu, Cu-based perovskite oxides, and Cu-based alloys for CO₂ electroreduction to various products [55, 56, 308].

While previous research has focused primarily on *H's effect on single product formation through CO₂RR, there is limited research on the branching pathways of CO₂RR to C₁ and C₂₊ products and their relationship with *H, particularly regarding *H transfer mechanisms in hydrogenation processes and competition with other intermediate formation processes such as dimerization. Although alkaline electrolytes commonly

employed in industrial-current-density CO₂ electroreduction hinder H₂O dissociation and *H transfer, thus effectively inhibiting HER, they also result in sluggish CO₂RR kinetics due to delayed *H activation and transfer [309, 310]. Therefore, managing adsorbed hydrogen production and its transfer kinetics, and simultaneously suppressing HER is crucial for the rational design of high-performance CO₂RR electrocatalysts.

In this study, a series of oxide-derived lanthanum-modified copper oxide (denoted as OD-La-CuO_x) catalysts with varied La doping are synthesized to investigate the effect of *H on CO₂RR product distribution at industrial current densities. The results show that hydrocarbon selectivity shifts from C₂₊ products (in OD-La_{0.10}-CuO_x) to CH₄ (in OD-La_{0.40}-CuO_x) as La doping increases. Kinetic isotope effect (KIE) experiments and *in situ* EIS were employed to elucidate the role of *H transfer in forming various CO₂RR products. *In situ* ATR-SEIRAS and DFT calculations reveal that La doping promotes H₂O adsorption and its dissociation to release *H. Additionally, the divergence between C₂₊ and CH₄ formation pathways lies in the subsequent conversion of *CHO. Specifically, during the CO₂RR-to-C₂₊ process, OD-La_{0.10}-CuO_x facilitates *CO protonation to *CHO and its further dimerization to *OCCHO, whereas OD-La_{0.40}-CuO_x promotes *CHO hydrogenation to *CH₂O, leading to CH₄ production.

5.2 Experimental

5.2.1 Synthesis of La-CuO_x catalyst

The La_{0.10}-CuO_x catalyst was synthesized using a facile alcohol-thermal approach. Initially, Cu(CH₃COO)₂·H₂O (3 mmol, 0.6 g) and La(NO₃)₃·6H₂O (0.3 mmol, 0.13 g) were dissolved in 50 mL ethanol through sonication for 30 minutes with the lanthanum to copper molar ratio of 0.1 to 1. The resultant blue mixture was transferred into a Teflon-lined

stainless-steel autoclave with a volume of 100 mL and heated at 150 °C for 20 hours. After allowing the system to cool to room temperature naturally, the precipitates were washed three times with ethanol and deionized water before being dried at 70 °C overnight.

5.2.2 Synthesis of control catalysts

Additionally, CuO_x control was synthesized under identical conditions without the inclusion of La(NO₃)₃·6H₂O. Besides, various La-modified CuO_x catalysts (La_{0.40}-CuO_x, La_{0.20}-CuO_x, La_{0.13}-CuO_x, and La_{0.06}-CuO_x) were prepared using a similar procedure, with adjustments in La-Cu ratios such that 1.2 mmol, 0.6 mmol, 0.4 mmol, and 0.2 mmol of La(NO₃)₃·6H₂O were added, respectively. The as-prepared catalysts were transformed into OD-La-CuO_x through electroreduction.

5.2.3 DFT calculation details

The CuO_x model was constructed using a 4-layer Cu₂O (111) surface, derived from the optimized and cleaved bulk Cu₂O. For OD-La_{0.10}-Cu, a Cu atom in the prepared Cu₂O (111) surface was substituted with a La atom. OD-La_{0.40}-Cu was based on a 3-layer La₂CuO₄ (113) surface, created by cleaving the optimized bulk La₂CuO₄ and placing a 2-layer Cu₂O structure on top. A vacuum space of 15 Å in the z-direction was employed to minimize the layer's interactions with its periodic images across all constructed models.

5.3 Results and discussion

5.3.1 Synthesis and characterization of La-CuO_x catalyst

The lanthanum-modified CuO_x nanoparticles, synthesized with various La-doping molar ratios, were used as pre-electrocatalysts. As depicted in **Figure 5.6a**, these catalysts were produced using a one-pot alcohol-thermal approach. The molar ratio of Cu to La was controlled by adjusting the concentration of the La precursor solution. Specifically, the La

content for La_{0.10}-CuO_x and La_{0.40}-CuO_x was measured at 9.9 wt.% and 25.6 wt.%, respectively, by ICP-MS (**Table 5.1**). This facile synthesis method involves the decomposition of Cu(CH₃COO)₂·H₂O and La(NO₃)₃·6H₂O into mixed-phase metal oxide catalysts in the presence of ethanol. Under alcohol-thermal conditions within a Teflon-lined stainless-steel autoclave, an esterification reaction between acetate and ethanol readily occurs. Previous research has confirmed the formation of ethyl acetate in reaction solvents through GC with a FID [311].

Table 5.1: ICP-MS results of the as-prepared La-modified CuO_x electrocatalysts.

Catalyst	La (wt. %)	Cu (wt. %)
La _{0.06} -CuO _x	6.88	72.5
La _{0.10} -CuO _x	9.9	69.2
La _{0.13} -CuO _x	17.4	55.4
La _{0.20} -CuO _x	20.1	42.7
La _{0.40} -CuO _x	25.6	44.8

TEM was employed to examine the structural morphology of the as-prepared La-modified CuO_x electrocatalysts. The CuO_x nanoparticles, synthesized without La(NO₃)₃·6H₂O, display regular particle sizes of under 10 nm (**Figure 5.1**). As shown in **Figure 5.6b** and **Figure 5.2**, low-level La doping (i.e., La_{0.10}-CuO_x) has a minimal impact on morphology, maintaining an average particle size of roughly 6 nm. However, with increased La doping (i.e., La_{0.40}-CuO_x), the original particle morphology is not preserved. **Figure 5.6c** and **Figure 5.3** show that ultra-small nanoparticles tend to agglomerate and increase in size.

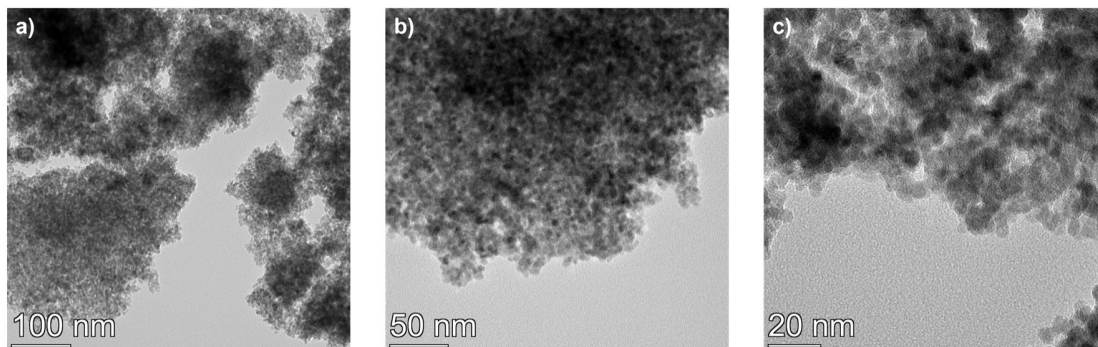


Figure 5.1: (a-c) TEM images of CuO_x nanoparticles at different magnifications.

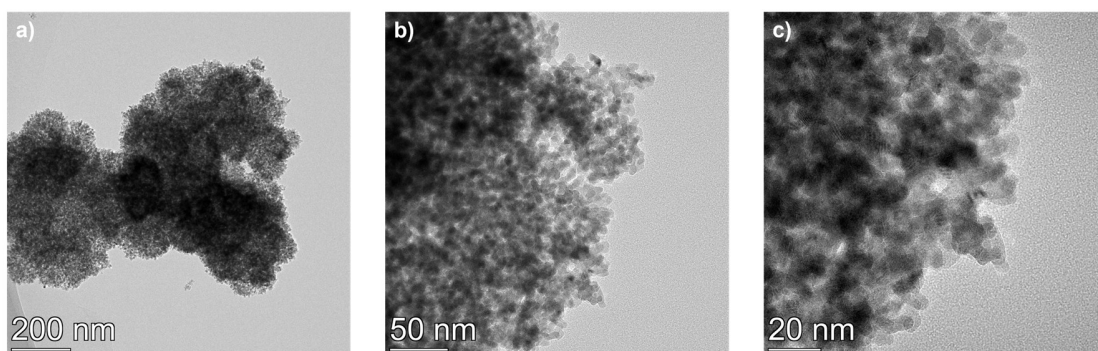


Figure 5.2: (a-c) TEM images of $\text{La}_{0.10}\text{-CuO}_x$ at different magnifications.

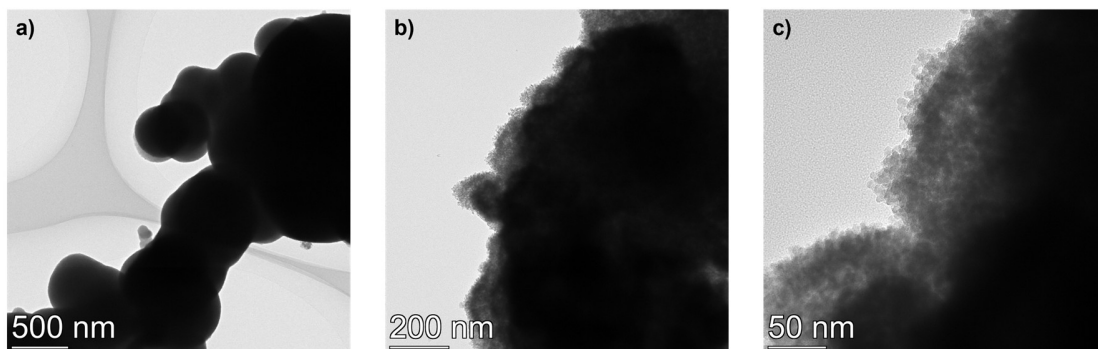


Figure 5.3: (a-c) TEM images of $\text{La}_{0.40}\text{-CuO}_x$ at different magnifications.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and corresponding EDS element maps reveal a uniform distribution of O, Cu, and La elements (**Figure 5.4** and **Figure 5.5**) and indicate the integration of La into the fabricated material.

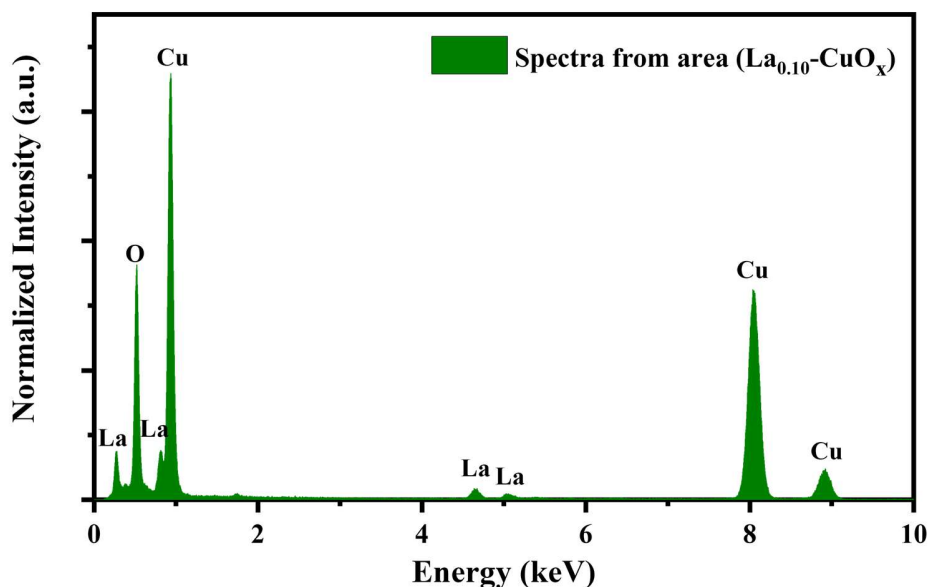


Figure 5.4: EDS of as-prepared La_{0.10}-CuO_x (corresponding to Figure 5.6b).

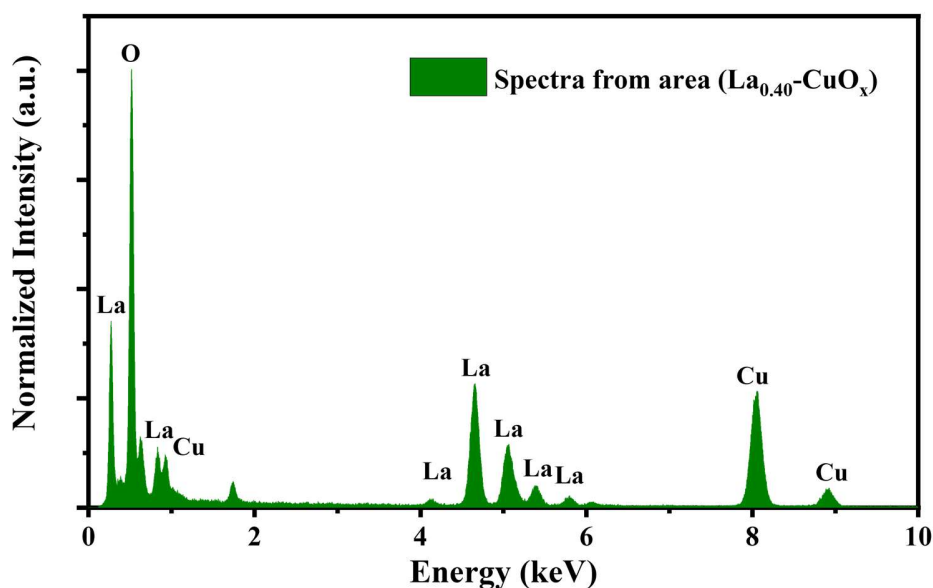


Figure 5.5: EDS of as-prepared La_{0.40}-CuO_x (corresponding to Figure 5.6c).

Additionally, HRTEM was applied to reveal the lattice fringe characteristics of the synthesized La-CuO_x catalysts. The HRTEM images of both La_{0.10}-CuO_x and La_{0.40}-CuO_x exhibit abundant grain boundaries, with lattice edges in multiple orientations (Figure 5.7 and Figure 5.8). The grain boundaries of La_{0.10}-CuO_x are highlighted by white dotted lines

in **Figure 5.7**, resulting from the incorporation of heteroatoms into the material via doping. This introduction disrupts the ordered lattice structure and crystal growth, leading to defect formation and high-density grain boundaries within the material [49].

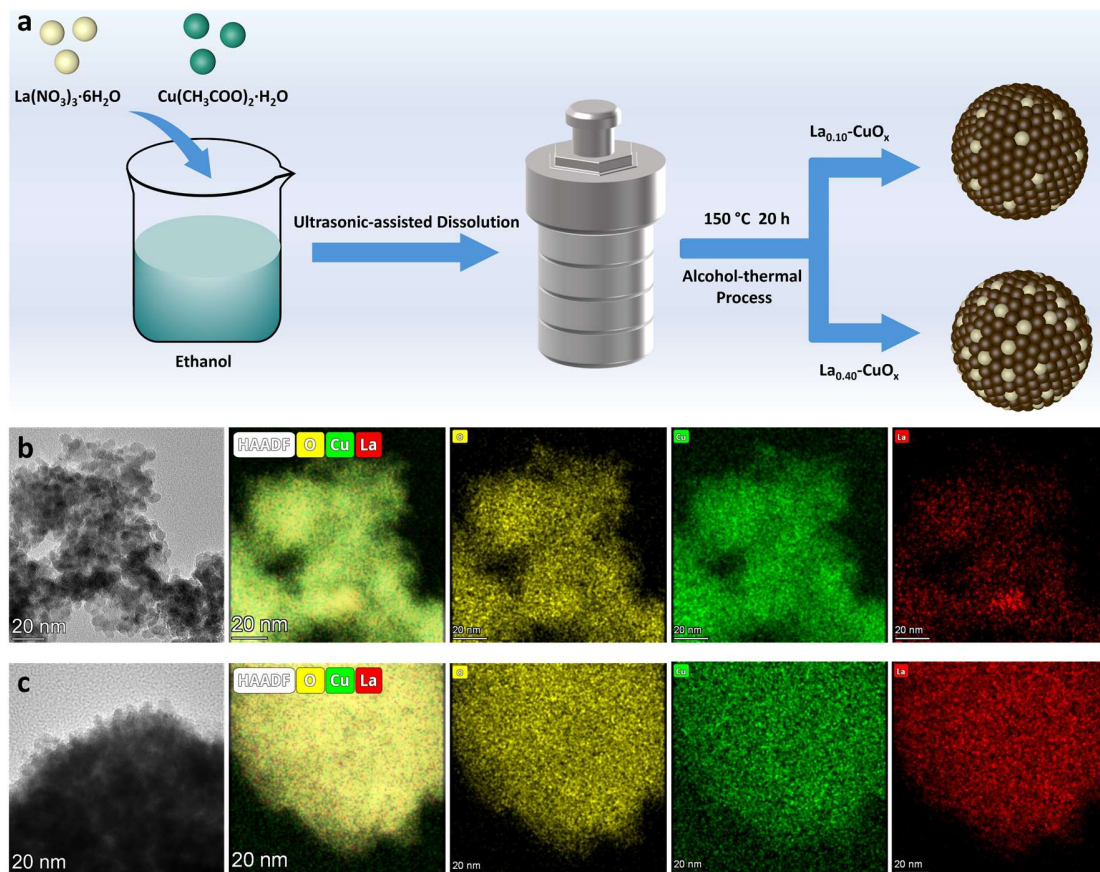


Figure 5.6: a) Schematic illustration of the synthetic procedures of CuO_x and La-CuO_x catalysts. TEM image, HAADF-STEM image, and corresponding EDS element maps of b) $\text{La}_{0.10}\text{-CuO}_x$ and c) $\text{La}_{0.40}\text{-CuO}_x$.

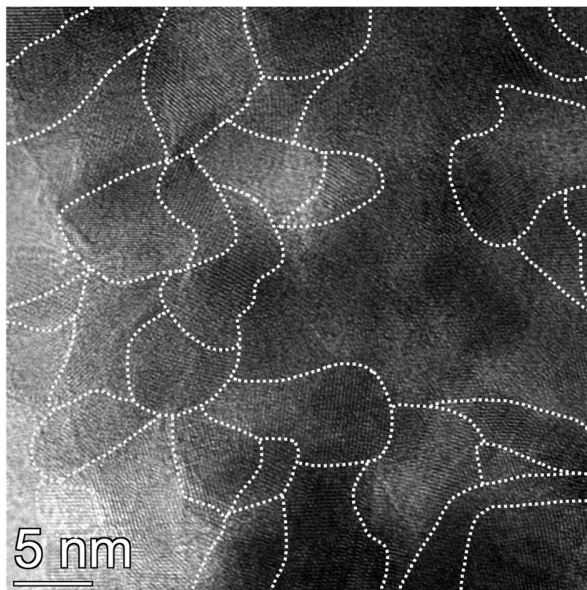


Figure 5.7: HRTEM image of as-prepared $\text{La}_{0.10}\text{-CuO}_x$. Different lattice orientation regions are delineated by white dotted lines.

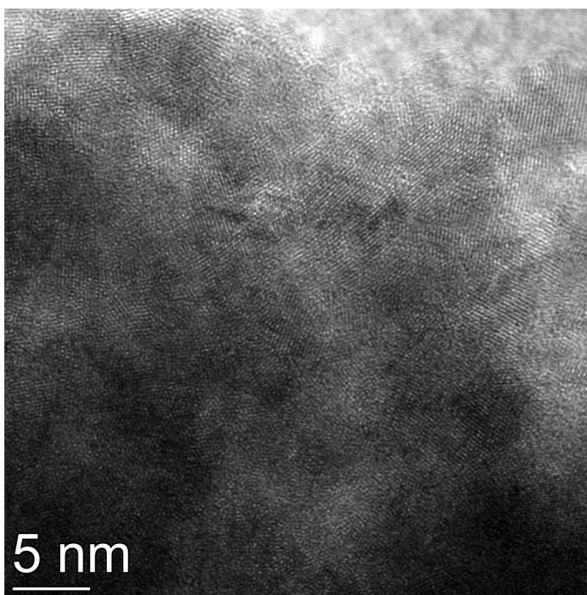


Figure 5.8: HRTEM image of as-prepared $\text{La}_{0.40}\text{-CuO}_x$.

To verify the phase composition of the synthesized La-CuO_x catalysts, PXRD analyses were performed on both the pure CuO_x and La-CuO_x catalysts (**Figure 5.14a**). For CuO_x without La doping, the diffraction peaks can be precisely indexed to the

monoclinic pure phase of CuO (JCPDS# 45-0937) with the most intense peaks at 35.6° for CuO (002) and 38.7° for CuO (111). When La is incorporated in small amounts, from La_{0.06}-CuO_x to La_{0.10}-CuO_x, the XRD patterns show a composition of CuO and Cu₂O (JCPDS# 05-0667). As La-doping increases, the diffraction peaks of CuO (002) and (111) weaken, while the peak for Cu₂O (111) becomes more pronounced. This behaviour is attributed to the ability of trivalent La to modify the CuO electronic structure, initiating possible redox reactions [49], such as the replacement of Cu²⁺-O²⁻-Cu²⁺ pairs with Cu⁺-O²⁻-La³⁺ pairs to maintain electroneutrality [312]. With significant La doping, particularly from La_{0.13}-CuO_x to La_{0.40}-CuO_x, additional crystalline phases are observed, attributed to La₂CuO₄ (as per JCPDS# 30-0487), with increasing peak intensity. Concurrently, the diffraction peaks of CuO and Cu₂O diminish, with some eventually disappearing.

Notably, the Cu₂O (111) and CuO($\bar{1}13$) facet peaks of La-CuO_x with higher La doping levels are slightly shifted to lower diffraction regions compared to La_{0.06}-CuO_x and undoped CuO_x, respectively (**Figure 5.9**). This shift is attributed to the doped La atoms, which have a larger atomic radius than Cu atoms [57, 313]. The Raman spectra of CuO_x show three peaks at 285, 336, and 619 cm⁻¹ (**Figure 5.10**), which correspond to the A_g, B_{g1} and B_{g2} vibration modes of CuO, respectively. The Raman peaks for La_{0.10}-CuO_x are shifted to higher wavenumbers, indicating changes in the electronic structure of CuO due to La doping. Moreover, a new Raman peak at 217 cm⁻¹ is assigned to the 2Γ₁₂⁻ phonon modes of the Cu₂O [57, 313].

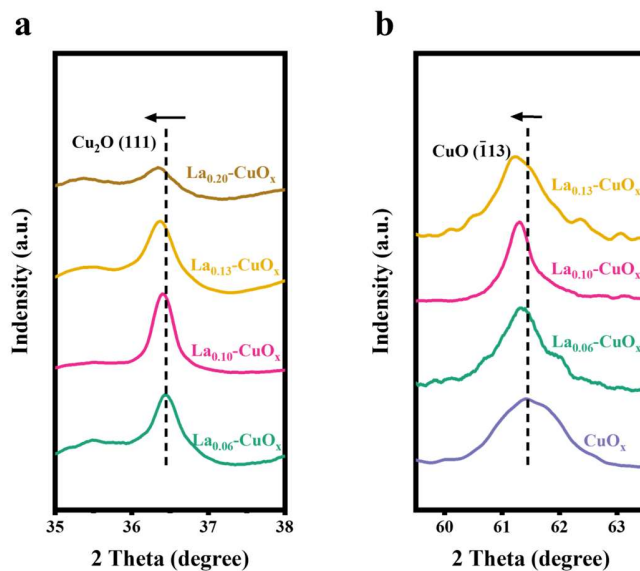


Figure 5.9: Magnified view of the XRD patterns in the region of Cu₂O (111) and CuO ($\bar{1}13$) facets.

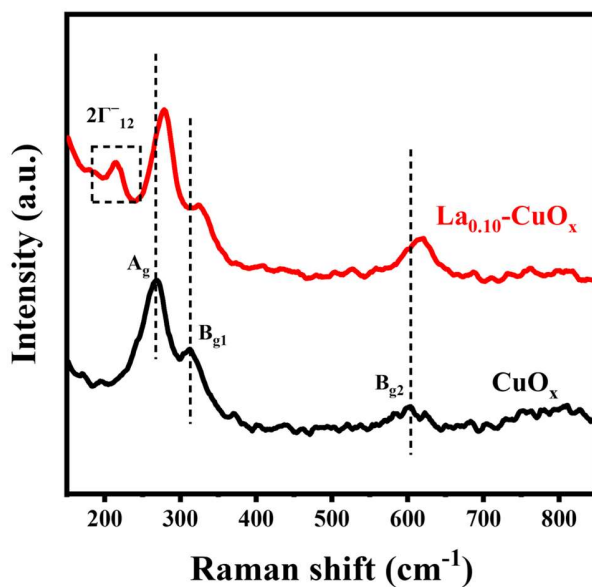


Figure 5.10: Raman spectra of La_{0.10}-CuO_x and CuO_x.

Following CO₂RR at a current density of 300 mA cm⁻² in 1 M KCl for 30 minutes, the OD-CuO_x only displays the characteristic peaks of the metallic Cu phase (**Figure 5.11a**). In contrast, the OD-La_{0.10}-CuO_x retains peaks corresponding to the Cu₂O phase,

dominated by the (111) facets, even after 60 minutes (**Figure 5.11b** and **Figure 5.14b**). This is likely due to the construction of unconventional 4f-2d-3d hybrid orbitals through La doping, which has been reported to effectively prevent lattice oxygen leaching, thereby maintaining the Cu₂O phase [39, 58, 314, 315]. The diffraction patterns of OD-La_{0.40}-CuO_x were also examined at various electrolysis duration in 1 M KOH at a current density of 400 mA cm⁻². The crystalline phases in OD-La_{0.40}-CuO_x, comprising La₂CuO₄ and Cu₂O, remain stable throughout electrolysis (**Figure 5.11c** and **Figure 5.14c**).

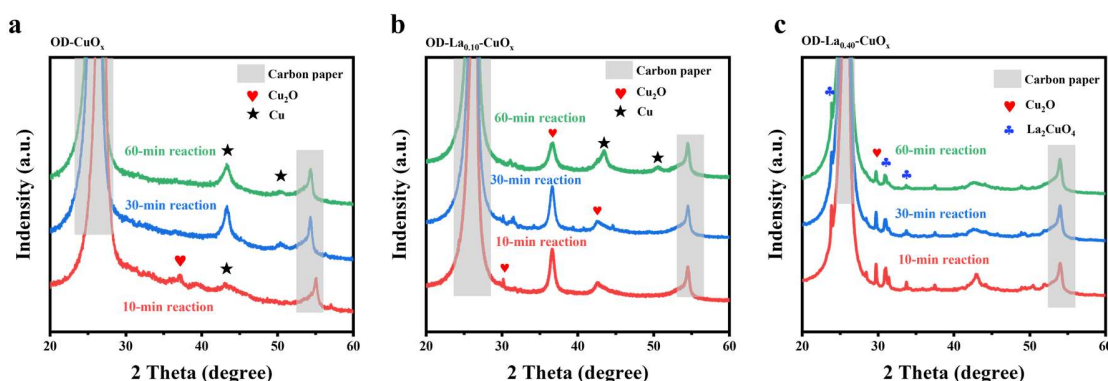


Figure 5.11: XRD patterns for (a) OD-CuO_x, (b) OD-La_{0.10}-CuO_x, and (c) OD-La_{0.40}-CuO_x electrode after varying CO₂RR times. Tests for OD-CuO_x and OD-La_{0.10}-CuO_x were conducted at 300 mA cm⁻² in 1 M KCl. OD-La_{0.40}-CuO_x was tested at 400 mA cm⁻² in 1 M KOH.

Additionally, *ex situ* Cu LMM Auger spectra of the reconstructed OD-CuO_x, OD-La_{0.10}-CuO_x, and OD-La_{0.40}-CuO_x were gathered under identical conditions as *ex situ* XRD tests to elucidate the Cu oxidation states. During CO₂RR, OD-CuO_x shows an increasing proportion of Cu⁰ species (918.4 eV) over 10-min increments, which fully occupies by 30 and 60 minutes (**Figure 5.12a**). Conversely, the Cu LMM spectra for OD-La_{0.10}-CuO_x indicate a stabilization of Cu⁺ (916.8 eV) during 60 minutes of CO₂ electrolysis (**Figure 5.12b**). Furthermore, the spectra for OD-La_{0.40}-CuO_x reveal a mixture of Cu⁺ (916.8 eV) and Cu²⁺ (917.8) species both before and after various electrolysis intervals (**Figure 5.12c**).

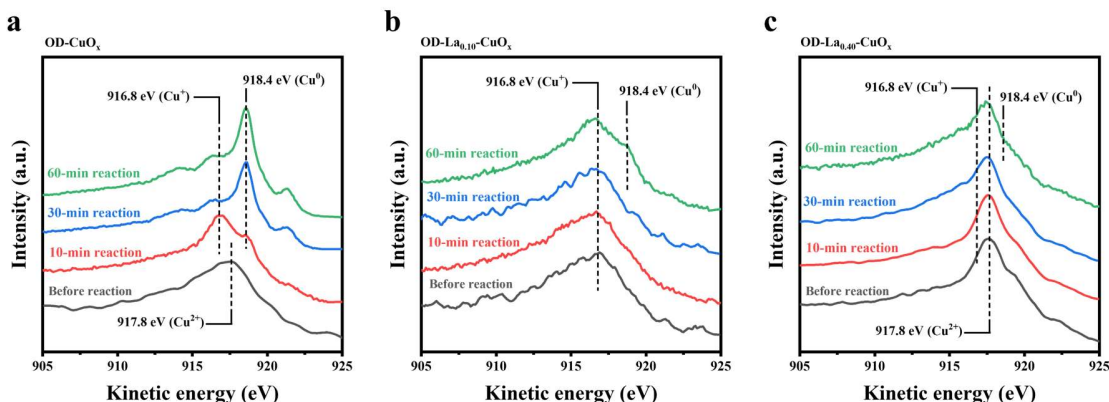


Figure 5.12: *Ex situ* XPS (Cu LMM) spectra for (a) OD-CuO_x, (b) OD-La_{0.10}-CuO_x, and (c) OD-La_{0.40}-CuO_x electrode, analysed before and after differing CO₂RR times. OD-CuO_x and OD-La_{0.10}-CuO_x tests were conducted at 300 mA cm⁻² in 1 M KCl; OD-La_{0.40}-CuO_x was tested at 400 mA cm⁻² in 1 M KOH.

Notably, *ex situ* XPS of La 3d spectra reveals that La³⁺ species remain unchanged in both OD-La_{0.10}-CuO_x and OD-La_{0.40}-CuO_x during 60 minutes of CO₂ electrolysis. As illustrated in **Figure 5.13**, peaks at 838.8 eV and 855.6 eV correspond to La³⁺ 3d_{5/2} and 3d_{3/2}, respectively. The spin-orbit splitting energy of 16.8 eV between the 3d_{5/2} and 3d_{3/2} states of La³⁺ is consistent with reported values for La₂O₃ [316].

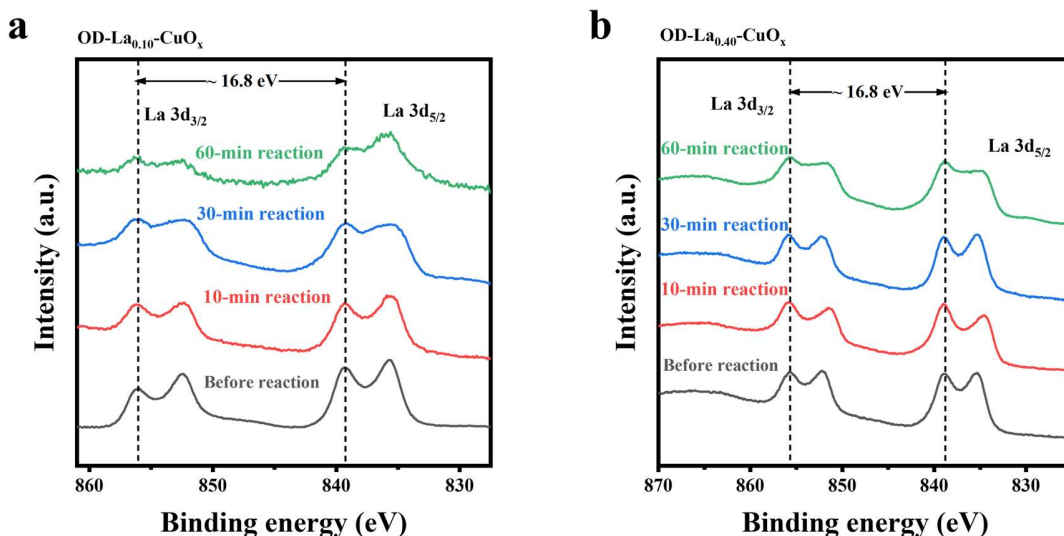


Figure 5.13: *Ex situ* XPS (La 3d) spectra of (a) OD-La_{0.10}-CuO_x and (b) OD-La_{0.40}-CuO_x electrode before and after various CO₂RR times. Tests for OD-La_{0.10}-CuO_x were performed at 300 mA cm⁻² in 1 M KCl, and OD-La_{0.40}-CuO_x at 400 mA cm⁻² in 1 M KOH.

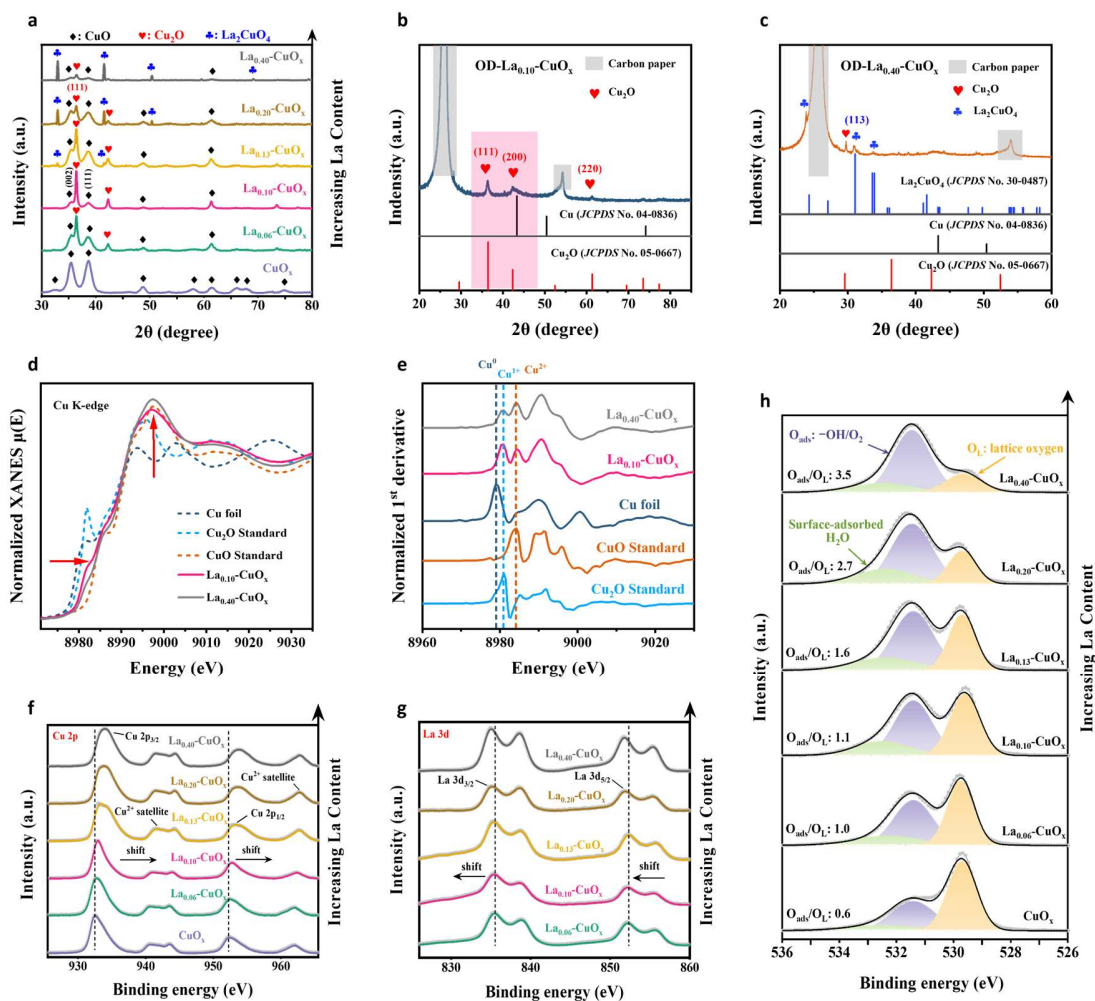


Figure 5.14: a) XRD patterns of CuO_x and various La-CuO_x catalysts prior to CO₂RR. The XRD patterns of b) OD-La_{0.10}-CuO_x and c) OD-La_{0.40}-CuO_x after CO₂RR at 300 mA cm⁻² for 30 minutes in 1 M KCl and 1 M KOH, respectively. d) Normalized intensity and e) First-order derivative of Cu K-edge X-ray absorption near edge structure (XANES spectra for La_{0.10}-CuO_x, La_{0.40}-CuO_x and other reference standards. High-resolution XPS spectra of f) Cu 2p, g) La 3d, and h) O 1s of CuO_x and the as-prepared La-CuO_x catalysts.

To further identify the Cu oxidation state and microstructure of localized Cu species, X-ray absorption spectroscopy (XAS) was conducted at the Cu K-edge for La_{0.10}-CuO_x, La_{0.40}-CuO_x and reference standards (Cu, Cu₂O and CuO). As shown in **Figure 5.14d**, the absorption edges of La_{0.10}-CuO_x and La_{0.40}-CuO_x in the normalized Cu K-edge XANES are positioned between those of the Cu₂O and CuO standards, indicating Cu valence states

between +1 and +2 for both samples. This finding aligns with XRD results, showing that La_{0.10}-CuO_x and La_{0.40}-CuO_x possess mixed phases of Cu₂O, CuO and La₂CuO₄. Furthermore, the white-line intensity of La_{0.40}-CuO_x surpasses that of the CuO standard and La_{0.10}-CuO_x, implying a higher oxidation state of Cu in La_{0.40}-Cu. The normalized first-order derivative of XANES for La_{0.10}-CuO_x and La_{0.40}-CuO_x display peaks overlapping with Cu₂O and CuO at approximately 8980 eV and 8984 eV, verifying the existence of Cu(I) and Cu(II) species in La_{0.10}-CuO_x and La_{0.40}-CuO_x (**Figure 5.14e**). In conjunction with XRD analysis, the Cu(II) species in La_{0.40}-CuO_x mainly derive from the La₂CuO₄ phase.

High-resolution XPS was employed to investigate electronic interactions between Cu and La and to determine the surface chemical states of elements in the as-prepared catalysts. With increased La doping, there is a marked reduction in peak intensity of Cu 2p, whereas that for La 3d rises. **Figure 5.14f** depicts the core-level XPS spectra of Cu 2p for CuO_x, La_{0.10}-CuO_x, and other La-CuO_x catalysts with different La doping levels. Notably, the Cu 2p_{3/2} and Cu 2p_{1/2} peaks in the La-CuO_x catalysts shift to higher binding energies with increased La doping compared to CuO_x peaks. This suggests charge transfer from Cu to La, attributed to the unique electronic structure of La's unfilled 4f orbitals [58]. Furthermore, strong Cu²⁺ satellite peaks, present in all samples, range between 940 eV and 945 eV, indicating either CuO or La₂CuO₄ phases, as supported by XRD analysis. Additionally, the peaks located between 917.8 eV and 916.8 eV in the Cu LMM spectra confirm the presence of Cu²⁺ and Cu⁺ species (**Figure 5.15**). This finding aligns with the XRD results (**Figure 5.14a**) discussed earlier. Similarly, the core-level XPS spectra of La 3d (**Figure 5.14g**) show significant shifts of La 3d_{3/2} and La 3d_{5/2} peaks to lower energy

with increased La content, suggesting electron transfer from Cu to La, which corroborates the findings from the Cu 2p XPS analysis and highlights favourable charge transfer within the La-CuO_x catalyst system.

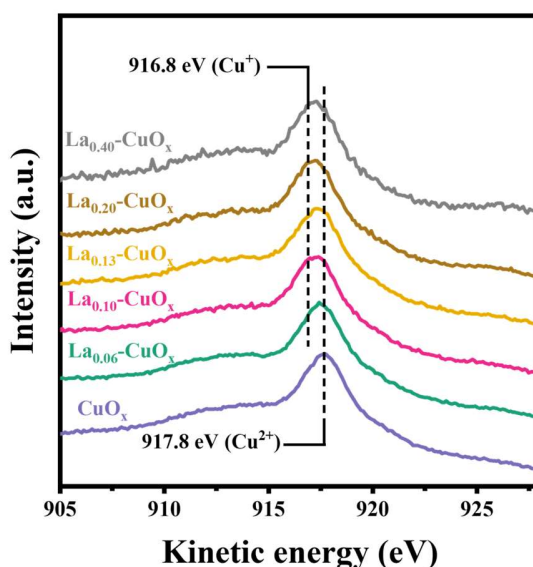


Figure 5.15: Cu LMM XPS spectra of CuO and La-CuO_x catalysts prior to CO₂RR.

To further explore the distribution of oxygen species in La-CuO_x catalysts, the O 1s spectra of the as-prepared La-CuO_x catalysts were examined via XPS. As shown in **Figure 5.14h**, the asymmetric O 1s peaks indicate the presence of different oxygen species, which deconvolute into three peaks at binding energies of 529.7, 531.5 and 532.7 eV, respectively. The peak at 529.7 eV corresponds to the lattice oxygen (O_L) within the Cu-O-Cu and Cu-O-La bonds [317, 318]. The peaks at 531.5 and 532.7 eV are attributed to surface-adsorbed hydroxyl or oxygen species (–OH/O₂, O_{ads}) and surface-adsorbed H₂O on the La-CuO_x matrix, respectively [319, 320]. Comparing the O_{ads} to O_L ratio reveals La doping markedly increases the proportion of surface-adsorbed –OH/O₂, elevating the ratio from 0.6 to 3.5. XPS results demonstrate that the La-CuO_x catalysts, fabricated through this one-pot thermal process, are rich in surface-adsorbed hydroxyl or oxygen species. Prior studies

indicate that surface oxygen-containing species play a role in stabilizing reaction intermediates for enhanced CO₂RR performance [321].

5.3.2 Electrochemical performance of CO₂RR on La-CuO_x catalyst

The electrocatalytic CO₂RR performance of oxide-derived CuO_x and La-CuO_x catalysts was evaluated in a custom liquid electrolyte flow cell under constant current densities in the range of 100 to 500 mA cm⁻² (**Figure A 4**). Unless otherwise specified, potentials were converted to the RHE scale using an 85% *iR* correction to minimize the variations between the actual and desired potential at high current densities. The catholyte consisted of 1 M KOH and 1 M KCl solutions to evaluate the electrocatalysts' performance at industrial current densities in both alkaline and neutral electrolytes, respectively. Prior to each on-line GC test, air-tightness checks, CV activation, and gas outlet flow rate tests were performed.

To assess the selectivity towards C₂H₄, Faradaic efficiencies (FEs) for the synthesized OD-CuO_x and La_{0.10}-CuO_x were evaluated in alkaline and neutral electrolytes across current densities of 100 to 500 mA cm⁻². As shown in **Figure 5.20a**, the CuO_x catalyst with its ultrasmall particle size exhibits a gradual increase in C₂H₄ selectivity with rising cathodic current density, achieving a maximum FE_{C₂H₄} of about 40%. In contrast, the OD-La_{0.10}-CuO_x shows enhanced FE_{C₂H₄} in both electrolyte types across the same current density range. It achieves up to 52% FE_{C₂H₄} in 1 M KCl at a current density of 300 mA cm⁻². The use of neutral electrolytes significantly mitigates challenges related to (bi)carbonate precipitation and GDE collapse, thus enabling stable electrolysis at high current densities [322, 323]. To investigate the impact of La doping on electron selectivity in CO₂RR-to-C₂H₄, chronopotentiometry tests were conducted on CuO_x and La-CuO_x

catalysts in both 1 M KOH and KCl solutions at a current density of 300 mA cm⁻². **Figure 5.20b** illustrates a notable increase in FE_{C₂H₄} with greater La content, peaking at OD-La_{0.10}-CuO_x. CO₂RR-to-C₂H₄ performance diminishes sharply with further La content increase, as observed in OD-La_{0.13}-CuO_x and beyond. Notably, for OD-La_{0.40}-CuO_x, FE_{C₂H₄} drops to 1.5% and 1.7% in 1 M KOH and 1 M KCl, respectively (**Figure 5.16** and **Figure 5.17**). This electron selectivity towards CH₄ can be attributed to the emergence of La₂CuO₄ phase, progressively replacing the initial mixed phase of OD-La_{0.10}-CuO_x (**Figure 5.14a**), aligning with the finding reported in a previous work [318].

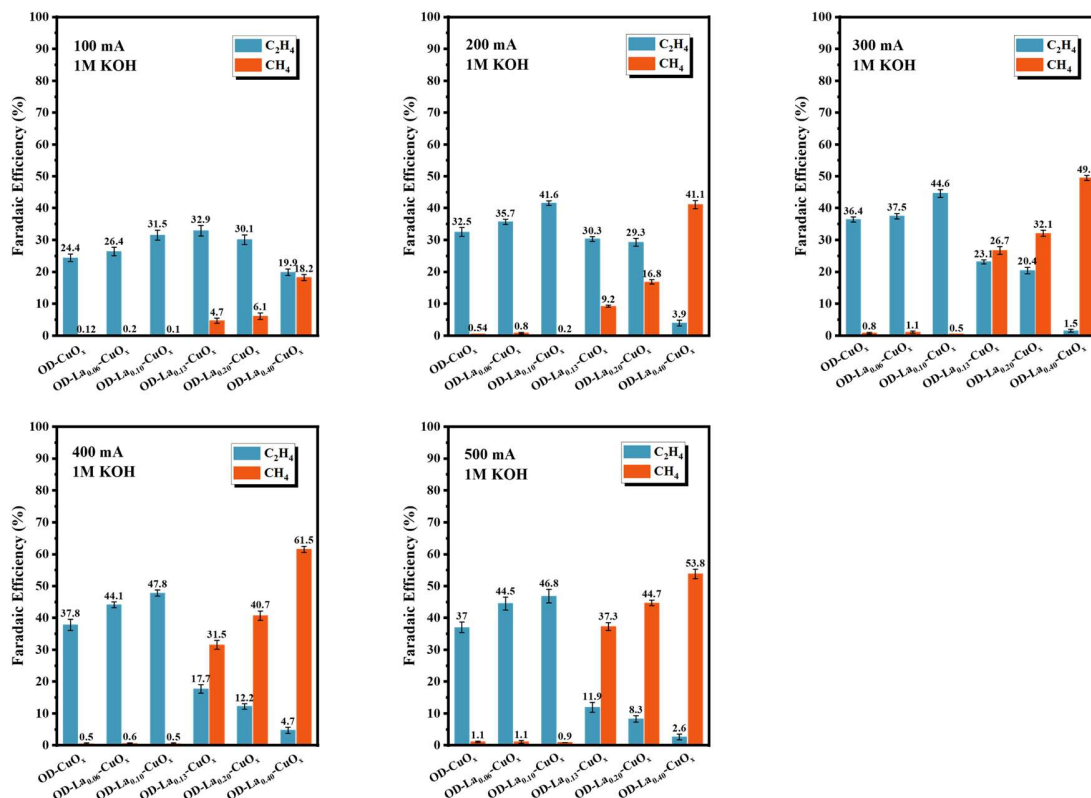


Figure 5.16: Faradaic efficiencies of C₂H₄ and CH₄ production over the as-prepared OD-CuO_x and OD-La-CuO_x catalysts (OD-La_{0.06}-CuO_x, OD-La_{0.10}-CuO_x, OD-La_{0.13}-CuO_x, OD-La_{0.20}-CuO_x, and OD-La_{0.40}-CuO_x) in 1 M KOH alkaline electrolyte (pH = 13.6) at current densities from 100 to 500 mA cm⁻².

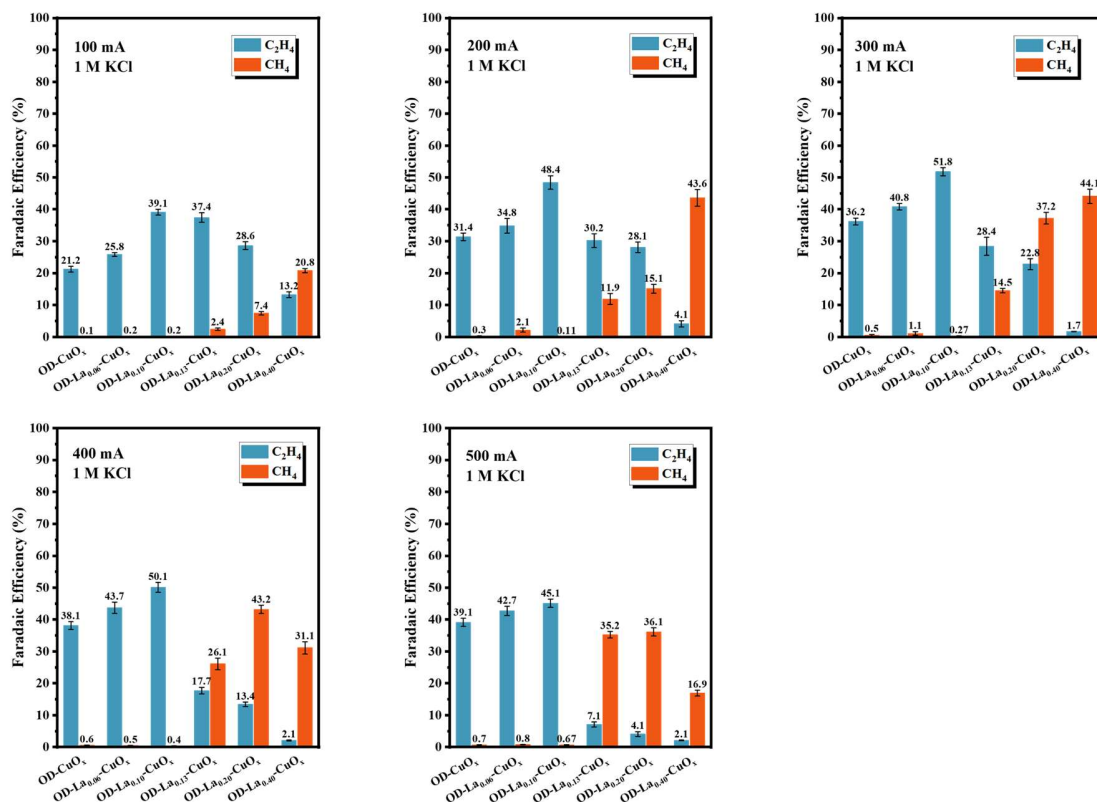


Figure 5.17: Faradaic efficiencies of C₂H₄ and CH₄ production over the as-prepared OD-CuO_x and OD-La-CuO_x catalysts (OD-La_{0.06}-CuO_x, OD-La_{0.10}-CuO_x, OD-La_{0.13}-CuO_x, OD-La_{0.20}-CuO_x, and OD-La_{0.40}-CuO_x) in 1 M KCl neutral electrolyte (pH = 6.4) at current densities from 100 to 500 mA cm⁻².

To gain insights into C₂+ product formation selectivity, the focus is placed on OD-La_{0.10}-CuO_x, which demonstrates the highest CO₂RR-to-C₂H₄ selectivity in 1 M KCl at 300 mA cm⁻². The FEs for various gas/liquid products over OD-La_{0.10}-CuO_x are compared in **Figure 5.18** to evaluate CO₂RR-to-C₂+ performance. Even at high current densities (300 mA cm⁻²), OD-La_{0.10}-CuO_x achieves an FE exceeding 80% for C₂+ products (**Figure 5.20c**) via CO₂ electroreduction, comprising 51.8% FE_{C₂H₄}, 21.5% FE_{C₂H₅OH}, and 7.1% FE_{n-propanol} (**Figure 5.18**). This impressive performance is attributed to the suppression of the competing HER. The FE of HER is limited to approximately 10% at current densities between 200 and 400 mA cm⁻² (**Figure 5.18**). Moreover, the rich grain boundaries in OD-La_{0.10}-CuO_x (**Figure 5.7**) are likely to enhance C-C coupling by improving *CO adsorption

and H₂O dissociation, thereby facilitating CO₂RR to C₂₊ products [56]. OD-La_{0.10}-CuO_x also demonstrates superior CO₂RR-to-C₂₊ performance in a neutral electrolyte, reaching C₂₊ partial current densities near 350 mA cm⁻² (**Figure 5.20c**).

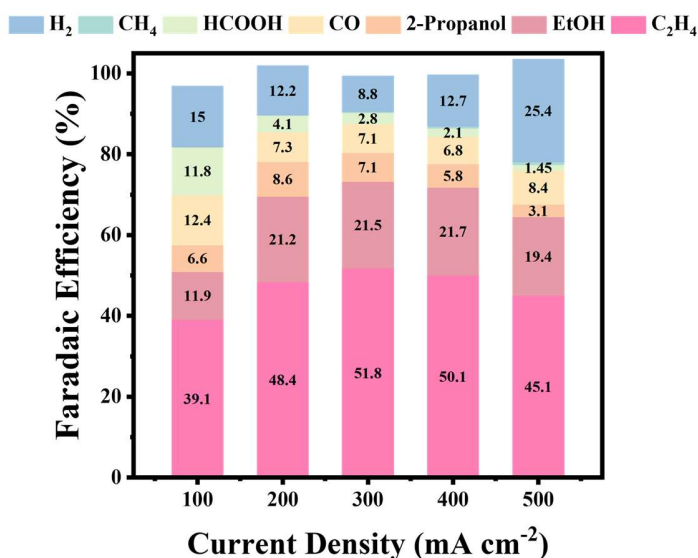


Figure 5.18: Faradaic efficiencies of gas and liquid products over OD-La_{0.10}-CuO_x in 1 M KCl at current densities from 100 to 500 mA cm⁻².

Beyond achieving excellent C₂₊ selectivity, the emergence of the La₂CuO₄ phase and its structure-function relationships with CO₂RR-to-CH₄ are of great interest. Consequently, online FE tests were conducted at 100-500 mA cm⁻² in both electrolytes to assess the effect of La₂CuO₄ phase on FE_{CH₄} (**Figure 5.16** and **Figure 5.17**). Notably, OD-La_{0.40}-CuO_x exhibits no less than 40% FE_{CH₄} at current densities of 200-500 mA cm⁻² in 1 M KOH (**Figure 5.20d**). However, undoped OD-CuO_x shows almost no FE_{CH₄}, achieving less than 1% in both alkaline and neutral electrolytes. FE_{CH₄} was further examined for CuO_x and La-CuO_x catalysts at 400 mA cm⁻² in 1 M KOH. As illustrated in **Figure 5.20e**, catalysts containing La₂CuO₄ phase (ranging from OD-La_{0.13}-CuO_x to OD-La_{0.40}-CuO_x) significantly promote CO₂ hydrogenation to CH₄, especially in alkaline environments. OD-

La_{0.40}-CuO_x achieves up to 61.5% FE_{CH₄} at 400 mA cm⁻² in 1 M KOH, with partial current densities reaching up to 270 mA cm⁻² (**Figure 5.20f**). This can be attributed to the increased La₂CuO₄ ratio and surface-adsorbed oxygen-containing species, which are considered to provide H₂O dissociation sites to enhance CO₂RR-to-CH₄ process [56, 324]. However, with further increase in La content, the highest FE_{CH₄} achieved by OD-La_{0.50}-CuO_x is below 40% in both 1 M KOH and 1 M KCl, accompanied by serious HER (**Table 5.2** and **Table 5.3**). Besides, comparing alkaline and neutral electrolytes, FE_{H₂} analysis for OD-La_{0.40}-CuO_x indicates that HER is boosted in 1 M KCl (**Figure 5.19**).

Table 5.2: Faradic efficiencies of gas products of OD-La_{0.50}-CuO_x at current densities from 100 to 500 mA cm⁻² in 1 M KOH.

Sample	Current density (mA cm ⁻²)	Faradaic efficiency (%)				
		H ₂	CO	CH ₄	C ₂ H ₄	C ₂ H ₆
OD-La _{0.50} -CuO _x	100	26.4	20.2	32.8	5.4	0
	200	27.1	18.4	38.7	3.2	0
	300	38.1	16.2	26.1	2.1	0
	400	54.5	9.9	19.1	0.4	0
	500	58.9	10.2	11.8	0	0

Table 5.3: Faradic efficiencies of gas products of OD-La_{0.50}-CuO_x at current densities from 100 to 500 mA cm⁻² in 1 M KCl.

Sample	Current density (mA cm ⁻²)	Faradaic efficiency (%)				
		H ₂	CO	CH ₄	C ₂ H ₄	C ₂ H ₆
OD-La _{0.50} -CuO _x	100	56.4	17.6	12.8	0	0
	200	67.2	8.0	8.7	0	0
	300	78.1	1.6	6.1	0	0
	400	84.5	1.8	4.1	0	0
	500	88.9	1.1	1.9	0	0

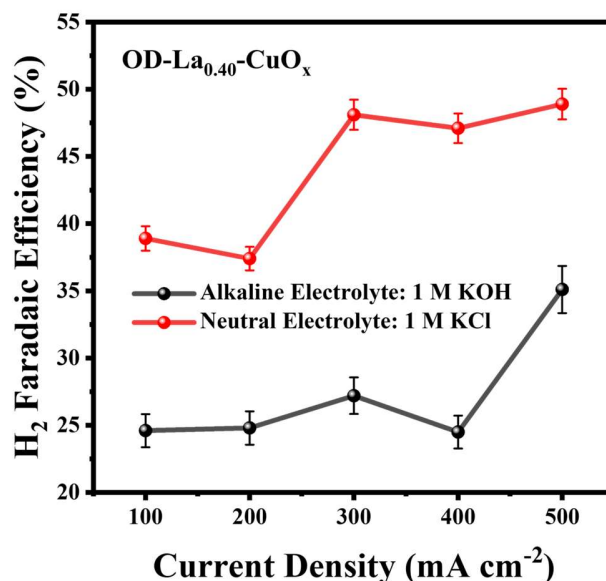


Figure 5.19: Faradaic efficiencies of H₂ production over OD-La_{0.40}-CuO_x in 1 M KCl and 1 M KOH at current densities ranging from 100 to 500 mA cm⁻².

In summary, the OD-La_{0.10}-CuO_x and OD-La_{0.40}-CuO_x catalysts demonstrate high electron selectivity for producing C₂H₄ and CH₄, respectively. As shown in **Figure 5.20g**, these electrocatalysts surpass the performance of most reported state-of-the-art Cu-based catalysts for CO₂RR-to-C₂₊ and CO₂RR-to-CH₄ in a gas-fed flow cell configuration, respectively. The original data supporting these findings are detailed in **Table 5.4** and **Table 5.5**. Energy efficiency and electrocatalyst stability remain challenges in the CO₂RR process [325]. Accordingly, the as-prepared electrocatalysts (OD-La_{0.10}-CuO_x and OD-La_{0.40}-CuO_x) were integrated into a gas-fed flow cell with 1 M KCl and 1 M KOH as electrolytes, and nickel foam as the anode, to evaluate their energy efficiency and stability. As shown in **Figure 5.20h** and **i**, at 300 and 400 mA cm⁻², the highest cathodic energy efficiencies for C₂H₄ and CH₄ of 23.0% and 28.2% are achieved on OD-La_{0.10}-CuO_x and OD-La_{0.40}-CuO_x, respectively, exceeding recent reports of 20.9% for C₂H₄ [326] and 20% for CH₄ [327]. Detailed current density, FE, cathodic energy efficiency, and applied

potential post-*iR* compensation for OD-CuO_x and OD-La_{0.10}-CuO_x in 1 M KCl and OD-CuO_x and OD-La_{0.40}-CuO_x in 1 M KOH are provided in **Table A 2** and **Table A 3**, respectively.

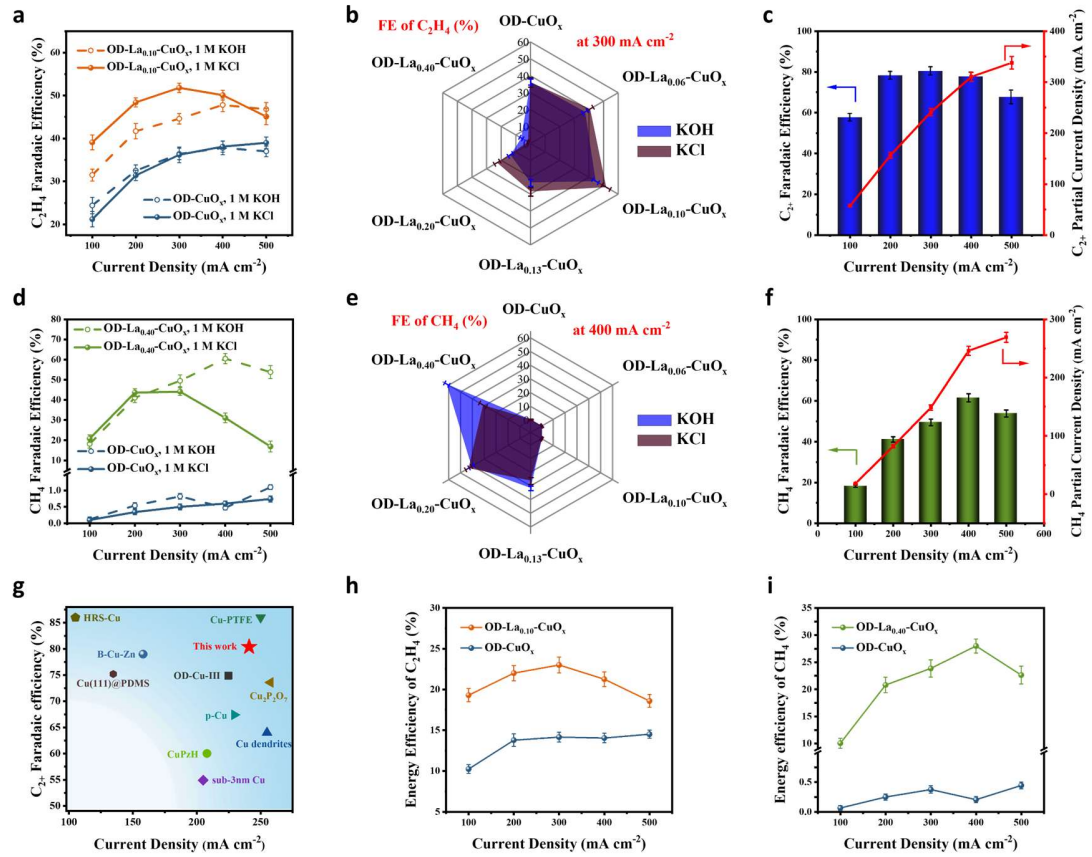


Figure 5.20: Performance on CO₂RR to C₂₊ products and CH₄ in a flow cell. a) FE of C₂H₄ on OD-La_{0.10}-CuO_x and OD-CuO_x in 1 M KOH and 1 M KCl at current densities from 100 to 500 mA cm⁻². b) FE of C₂H₄ on OD-CuO_x and OD-La-CuO_x catalysts at 300 mA cm⁻² in 1 M KOH and 1 M KCl; c) FE and partial current densities of C₂₊ products for OD-La_{0.10}-CuO_x in 1 M KCl at varying current densities; d) FE of CH₄ on OD-CuO_x and OD-La_{0.40}-CuO_x in 1 M KOH and 1 M KCl at current densities from 100 to 500 mA cm⁻²; e) FE of CH₄ on OD-CuO_x and various OD-La-CuO_x catalysts at 400 mA cm⁻² in 1 M KOH and 1 M KCl; f) FE and partial current densities of CH₄ for OD-La_{0.40}-CuO_x in 1 M KOH under different current densities. g) Comparison of the FE_{C₂₊} value of OD-La_{0.10}-CuO_x in this work with other reported high-performance Cu-based electrocatalysts [328-339]. h) Cathodic energy efficiency of C₂H₄ on OD-La_{0.10}-CuO_x and OD-CuO_x in 1 M KCl, and i) Cathodic energy efficiency of CH₄ on OD-La_{0.40}-CuO_x and OD-CuO_x in 1 M KOH, at current densities from 100 to 500 mA cm⁻².

Table 5.4: Comparison of the electrochemical performance for CO₂ reduction to C₂₊ products of this work as compared to the reported state-of-the-art Cu-based electrocatalysts.

Catalysts	Electrolyte	FE _{C2+} (%)	J _{C2+} (mA cm ⁻²)	Ref.
OD-La _{0.10} -CuO _x	1 M KCl	80.4	241	This work
OD-La _{0.10} -CuO _x	1 M KCl	77.6	310	This work
AEI-OD-Cu	1 M KOH	85.1	681	[247]
Cu-PTFE	1 M KOH	86	~250	[338]
HRS-Cu	2 M KOH	86.5	~105	[339]
Cu _{TPA}	3 M KOH	90.9	486	[340]
H-Cu ₂ O@C/N	1 M KOH	76	249	[341]
OD-Cu-III	1 M KHCO ₃	74.9	225	[335]
CuPzH	1 M KOH	60	208	[332]
Cu dendrites	1 M KOH	64	255	[334]
NGQ/Cu-nr	1 M KOH	74	208	[342]
MOF-augmented GDE	0.1 M KHCO ₃	70	175	[343]
B-doped Cu ₂ O	7.0 M KOH	77.8	233	[336]
Sub-3 nm Cu	1 M KOH	54.9	205	[329]
B-Cu-Zn	1 M KOH	79	158	[331]
M-Cu ₁ /Cu _{NP}	5 M KOH	75.4	289	[307]
Cu ₂ P ₂ O ₇	0.1 M KOH	73.6	258	[330]
<i>p</i> -Cu	1 M KCl	67.4	229	[337]
2F-Cu-BDC	1 M KOH	63	150	[344]
Cu(111)@PDMS	1 M KOH	75.2	135	[328]
Cu ₂ O(CO)	1 M KOH	77.4	387	[345]
CuO/Al ₂ CuO ₄	1 M KOH	70.1	421	[346]
Hex-2Cu-O	1 M KOH	55.4	155	[347]
Cu with PVP	0.5 M KOH	80	240	[348]
Cu ₅₀₀ Ag ₁₀₀₀	1 M KOH	50	160	[333]

Table 5.5: Comparison of the electrochemical performance for CO₂ reduction to CH₄ of this work as compared to the reported state-of-the-art Cu-based electrocatalysts.

Catalysts	Electrolyte	FE _{CH₄} (%)	J _{CH₄} (mA cm ⁻²)	Ref.
OD-La _{0.40} -CuO _x	1 M KOH	61.5	246	This work
CuPEDOT	1 M KOH	62.7±1.2	222	[349]
La ₅ Cu ₉₅	1 M KOH	64.5	193.5	[308]
Ir ₁ -Cu ₃ N/Cu ₂ O	1 M KOH	75	240	[350]
CoO/Cu/PTFE	1 M KHCO ₃	60	135	[351]
Cu-PzI	1 M KOH	52	149.5	[332]
Cu ₂ Te	1 M KOH	63	189	[352]
CuSiO _x	1 M KOH	60	170	[353]
Cu ²⁺ /Cu-Ce-O _x	1 M KOH	67.8	201	[233]
AA _n -COF-Cu	1 M KOH	77	128.1	[354]
7% Au-Cu	1 M KHCO ₃	56 ± 2	63	[355]
Cu-TDPP-NS	0.5 M PBS	70	183	[322]
Cu/CeO ₂ @C	1 M KOH	80.3	138.6	[356]
Cu/CeO ₂	1 M KOH	67	201	[357]
GSH-Cu/C	1 M KOH	61.7	153.7	[358]
Ca ₂ CuO ₃	1 M KOH	51.7	517	[359]
Sr ₂ CuO ₃	1 M KOH	50	300	[13]
Sr ₂ CuWO ₆	1 M KOH	73.1	292.4	[360]

Moreover, OD-La_{0.10}-CuO_x shows stable CO₂RR-to-C₂H₄ operation for 16 hours at 300 mA cm⁻² in 1 M KCl with a cation exchange membrane. As illustrated in **Figure 5.21**, there is only a slight decrease in FE_{C₂H₄} during the stability test, indicating excellent CO₂RR stability. The spent OD-La_{0.10}-CuO_x catalyst reaches its highest FE_{C₂H₄} at around 30 minutes and maintains 90% of the highest electron selectivity (FE_{C₂H₄} > 45%) in subsequent runs in a flow cell. OD-La_{0.40}-CuO_x sustains stable CO₂RR-to-CH₄ operation for 8 hours at 400 mA cm⁻² in 1 M KOH with an anion exchange membrane.

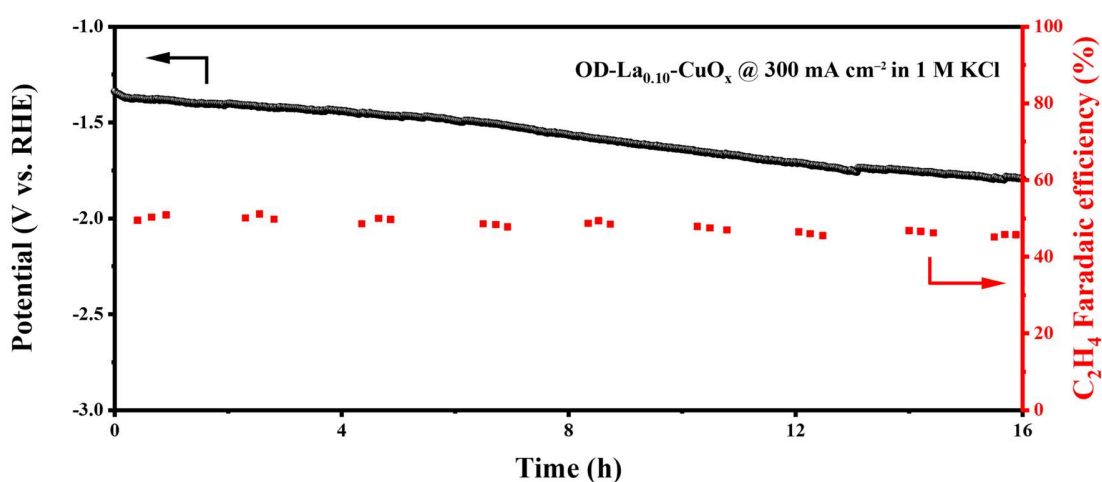


Figure 5.21: The electrochemical stability test for OD-La_{0.10}-CuO_x at a current density of 300 mA cm⁻² was carried out in 1 M KCl over 16 hours, with continuous electrolyte refreshment using peristaltic pumps.

As shown in **Figure 5.22**, despite the hydrophilic nature of OD-La_{0.40}-CuO_x causing slight fluctuations in the applied potential range, it achieves the highest FE_{CH₄} at around 30 minutes and maintains FE_{CH₄} over 50% during the first 6 hours. After 8 hours of catalyst stability testing, the GDE shows (bi)carbonate precipitation and flooding issues, leading to the blockage of the gas transfer channel in the flow cell, which reduces the electron selectivity for CH₄.

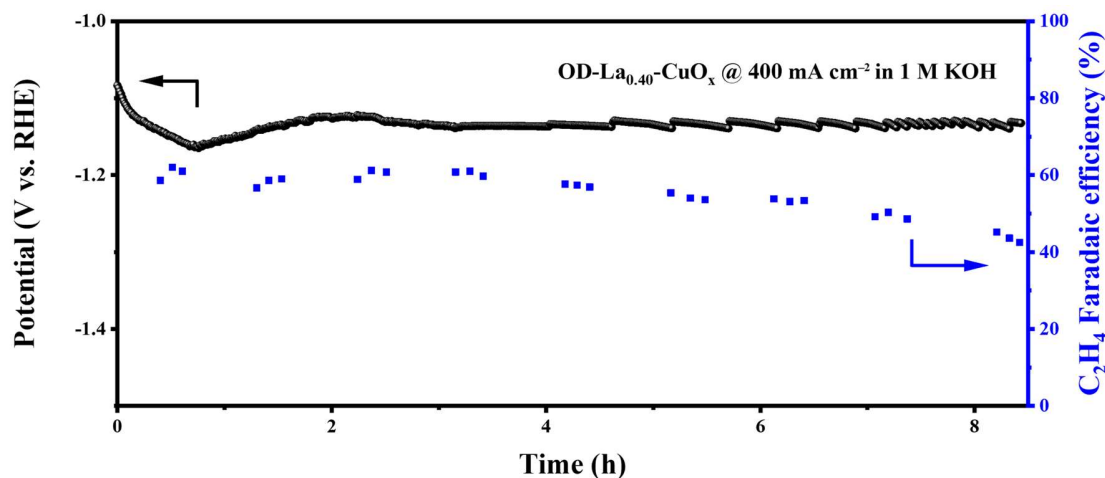


Figure 5.22: The electrochemical stability test for OD-La_{0.40}-CuO_x at a current density of 400 mA cm⁻² was carried out in 1 M KOH over 8 hours, with continuous electrolyte refreshment using peristaltic pumps.

5.3.3 Kinetic insights into CO₂RR on La-CuO_x catalyst

Electrocatalytic kinetic analysis is a well-established approach for investigating reaction mechanisms and determining the structure-function relationships of electrocatalysts. To elucidate the kinetics underlying the enhanced CO₂RR-to-C₂H₄/CH₄ performance of various OD-La-CuO_x catalysts, Tafel curves for the formation of C₂H₄ and CH₄ at different partial current densities were plotted. During the CO₂RR-to-C₂H₄ process, the Tafel slope for OD-La_{0.10}-CuO_x in 1 M KCl (144 mV dec⁻¹) is lower than that of undoped OD-CuO_x (152 mV dec⁻¹) and OD-La_{0.40}-CuO_x (173 mV dec⁻¹), the latter being enriched with La₂CuO₄ phases due to the increased La doping (**Figure 5.25a**). A similar trend was observed in 1 M KOH, indicating that OD-La_{0.10}-CuO_x has superior initial activity and kinetics for efficient C₂H₄ production (**Figure 5.23a**). Furthermore, kinetic analysis of the CO₂RR-to-CH₄ process reveals that the Tafel slope for OD-La_{0.40}-CuO_x in 1 M KOH is 85 mV dec⁻¹, lower than that of OD-CuO_x (88 mV dec⁻¹) and OD-La_{0.10}-CuO_x (117 mV dec⁻¹) (**Figure 5.25b**). OD-La_{0.40}-CuO_x also exhibits the lowest Tafel slope in 1

M KCl, indicating enhanced electrocatalytic activity, primarily due to accelerated electron transfer from the electrode to catalyst during CO₂ methanation (**Figure 5.23b**).

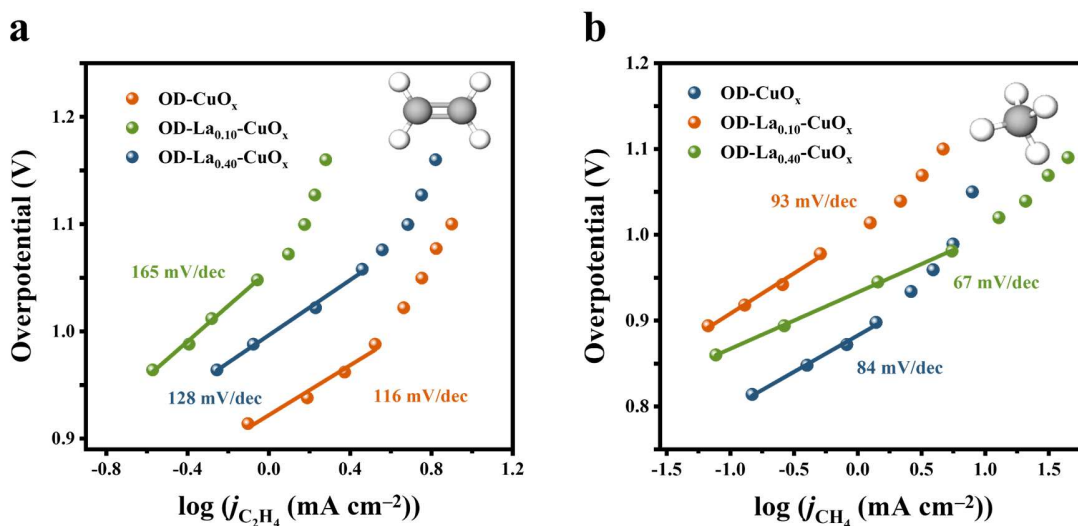


Figure 5.23: Tafel plots of the formation of (a) C₂H₄ in 1 M KOH and (b) CH₄ in 1 M KCl for OD-CuO_x, OD-La_{0.10}-CuO_x and OD-La_{0.40}-CuO_x.

Moreover, *in situ* EIS was employed to assess the catalytic kinetics and ion diffusion capabilities. **Figure 5.25c, d** and **Figure 5.24** show the frequency-dependent changes in the Bode phase plots for OD-La_{0.10}-CuO_x and OD-La_{0.40}-CuO_x under various applied potentials. Generally, the Bode plots show a shift of the phase angle (ϕ) towards higher frequency regions with increasing applied potential, along with a reduction in the peak value. This results in a decrease in Faradaic resistance and an increase in surface reaction rate, aligning with the electrocatalytic processes occurring on the surface [361, 362]. The Bode plot reveals a more substantial decline in phase angles for OD-La_{0.40}-CuO_x compared to OD-La_{0.10}-CuO_x in both 1 M KCl (**Figure 5.25c** and **Figure 5.24b**) and 1 M KOH (**Figure 5.25d** and **Figure 5.24a**) when subjected to potentials from -0.36 to -0.86 V. This suggests the surface of OD-La_{0.40}-CuO_x is more conducive to enhanced charge transfer and superior electronic conductivity [363].

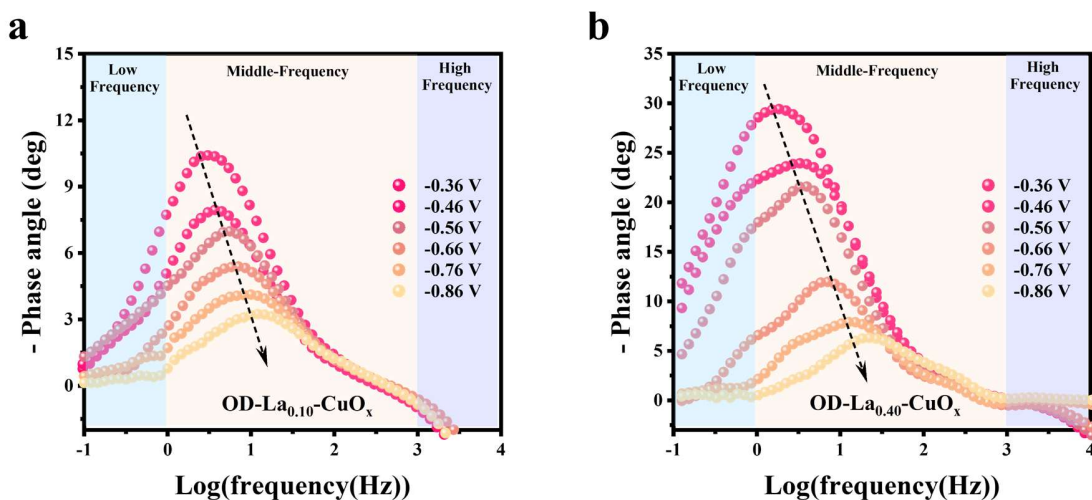


Figure 5.24: Bode phase plots of (a) OD-La_{0.10}-CuO_x in 1 M KOH and (b) OD-La_{0.40}-CuO_x in 1 M KCl at the equilibrium potential for CO₂ electrolysis.

In this work, KOH and KCl electrolytes were applied in the electrocatalytic CO₂RR processes, thus anticipating ^{*}H donation primarily from H₂O dissociation rather than HCO₃⁻ [303]. To understand the role of H₂O dissociation and ^{*}H transfer in the CO₂RR-to-C₂+ /CH₄ processes, the KIE of hydrogen/deuterium (H/D) on OD-CuO_x, OD-La_{0.140}-CuO_x, and OD-La_{0.40}-CuO_x is examined. The KIE value for H/D is determined by the ratio of the formation rates of the product before and after substituting H₂O with D₂O in the original electrolyte (**Eq. S5**). Generally, higher KIE values indicate more pronounced effects of H₂O dissociation and ^{*}H transfer in the rate-determining step (RDS). Typically, KIE values exceeding 1 indicate that H₂O activation and proton transfer are involved in the RDS [364]. A KIE value greater than 1.5 suggests that ^{*}H attraction significantly affects the reaction rate [365, 366].

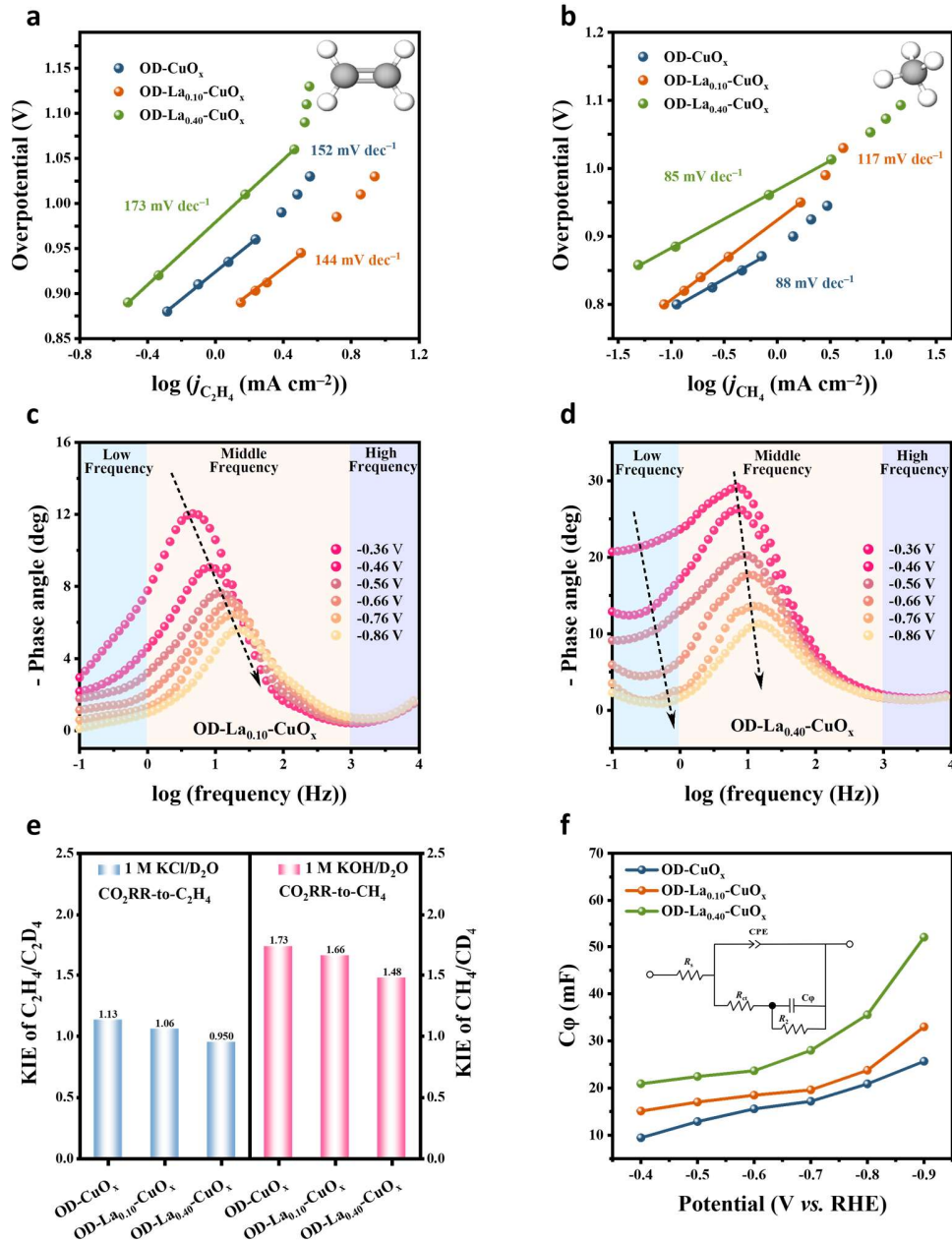


Figure 5.25: Tafel plots of the formation of a) C₂H₄ in 1 M KCl, and b) CH₄ in 1 M KOH for OD-CuO_x, OD-La_{0.10}-CuO_x, and OD-La_{0.40}-CuO_x. Bode phase plots of c) OD-La_{0.10}-CuO_x in 1 M KCl and d) OD-La_{0.40}-CuO_x in 1 M KOH at the equilibrium potential for CO₂ electrolysis. e) KIE values for CO₂RR-to-C₂H₄ on OD-CuO_x and OD-La_{0.10}-CuO_x measured at 300 mA cm⁻² in 1 M KCl (left) and KIE values for CO₂RR-to-CH₄ on OD-CuO_x and OD-La_{0.40}-CuO_x measured at 400 mA cm⁻² in 1 M KOH (right). f) Plots of calculated proton-adsorption pseudo-capacitance (Cφ) for OD-CuO_x, OD-La_{0.10}-CuO_x, and OD-La_{0.40}-CuO_x at different potentials in 1 M KOH, with inset showing the equivalent circuit for the single-adsorbate mechanism (R_s: solution resistance; R_{ct}: charge transfer resistance; R₂: hydrogen adsorption resistance; CPE: constant phase angle element).

To determine the KIE value of C₂H₄, D₂O was used instead of H₂O in the 1 M KCl electrolyte. As shown in **Figure 5.25e**, the KIE values of C₂H₄ for OD-CuO_x, OD-La_{0.10}-CuO_x, and OD-La_{0.40}-CuO_x are around 1, specifically 1.13, 1.06 and 0.950, respectively, suggesting there may be no *H-related RDS or multiple parallel *H-related RDSs in C₂H₄ formation mechanisms [364]. In addition, the KIE value of C₂H₄/C₂D₄ for OD-La_{0.40}-CuO_x is the lowest compared to OD-CuO_x and OD-La_{0.10}-CuO_x, confirming that the presence of La accelerates H₂O dissociation to provide *H for CO₂RR-to-C₂H₄. Similarly, by using D₂O instead of H₂O in 1 M KOH, the KIE values of CH₄ on OD-CuO_x, OD-La_{0.10}-CuO_x, and OD-La_{0.40}-CuO_x are 1.73, 1.66 and 1.48, respectively. This suggests that the CO₂RR-to-CH₄ kinetics on OD-La_{0.40}-CuO_x is constrained by *H transfer, as shown in **Figure 5.25e**.

Given the well-established effects of H₂O dissociation and protonation on the kinetics of CO₂RR-to-C₂₊/CH₄, the coverage of adsorbed *H on the catalyst surface is subsequently investigated using an equivalent circuit for a single-adsorbate mechanism (Armstrong's electric circuit) via *in situ* EIS measurements [367]. The proton-adsorption pseudo-capacitance (C_φ) in the second parallel component represents the *H coverage [81, 367, 368]. As illustrated in **Figure 5.25f** and **Figure 5.26**, C_φ for OD-La_{0.40}-CuO_x exceeds that of OD-La_{0.10}-CuO_x and OD-CuO_x across the same applied potential range (−0.4 to −0.9 V vs. RHE) in both 1 M KOH and 1 M KCl. This indicates that OD-La_{0.40}-CuO_x, with its high H₂O dissociation activity, can provide sufficient *H for the multistep protonation of CH₄ intermediates. Given that C_φ increases with rising La content, it is confirmed that doped-La favours proton delivery in CO₂RR, consistent with the results from the above KIE experiment.

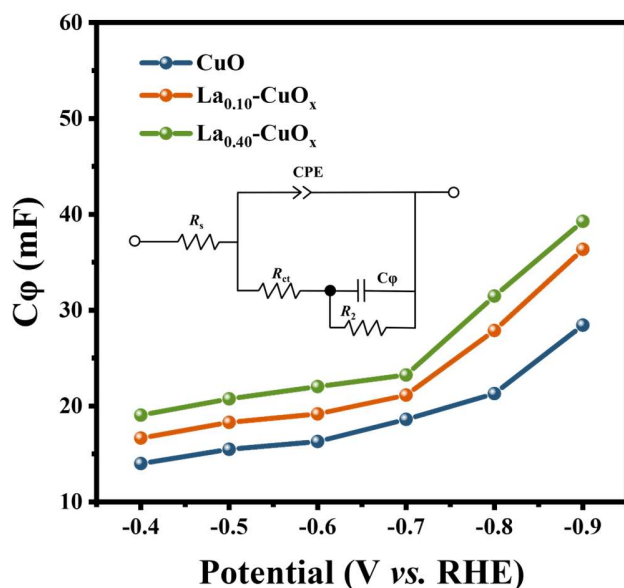


Figure 5.26: Plots of calculated proton-adsorption pseudo-capacitance (C_p) for OD-CuO_x, OD-La_{0.10}-CuO_x, and OD-La_{0.40}-CuO_x at different potentials in 1 M KCl, with inset showing the equivalent circuit for the single-adsorbate mechanism (R_s : solution resistance; R_{ct} : charge transfer resistance; R_2 : hydrogen adsorption resistance; CPE: constant phase angle element).

5.3.4 *In situ* ATR-SEIRAS observations of CO₂RR over La-CuO_x catalyst

To explore the mechanisms of dimerization and hydrogenation during CO₂RR on the as-prepared OD-La-CuO_x catalysts, time-resolved *in situ* ATR-SEIRAS was employed to monitor the formation of various intermediates on OD-CuO_x control, OD-La_{0.10}-CuO_x, and OD-La_{0.40}-CuO_x, focusing on the pathways leading to C₁ and C₂₊ products. **Figure 5.27a** illustrates the observed states of surface intermediates on undoped OD-CuO_x nanoparticles during a continuous 10-minute chronoamperometry test. The absorption peak at 1260 cm⁻¹, corresponding to the C=O stretching in the carboxylate radical (*COOH), intensifies with prolonged electrolysis [369]. The OD-CuO_x sample exhibits a distinct signal for the CO vibrational frequency (ν_{CO}) in *OCCOH at 1460 cm⁻¹, indicative of the intermediate in C₂₊ product formation [43]. Interestingly, a peak at 1556 cm⁻¹ indicates the presence of *OCCHO, a key intermediate in C₂H₄ formation along with *OCCOH [370]. The IR band

at 1640 cm⁻¹ is commonly associated with the bending mode of the H₂O molecule (H-O-H) [43]. These observations are consistent with the CO₂RR product distribution for the OD-CuO_x control.

Further analysis of the intermediate states was conducted using OD-La_{0.10}-CuO_x under identical conditions (**Figure 5.27b**). Continuous chronoamperometry reveals the same distinct absorption peaks near 1260 cm⁻¹ and 1642 cm⁻¹, originating from *COOH and *H₂O, respectively [43, 369]. Notably, a broad peak ranging from 1400 to 1470 cm⁻¹ is primarily composed of two peaks at 1410 cm⁻¹ and 1445 cm⁻¹, which correspond to the symmetric stretching of *COO⁻ and *C₂H₄, respectively [371, 372]. The observed *C₂H₄ reaction intermediates indicate the formation of C₂H₄ on OD-La_{0.10}-CuO_x. With continued electrolysis, a peak at 1500 cm⁻¹ appears, attributed to *OCCO [43]. Additionally, another time-dependent IR peak is detected at 1550 cm⁻¹, which is attributed to adsorbed *OCCHO [370]. By comparing the intensities of both *OCCO and *OCCHO peaks, it is found that *OCCHO dominates the C-C coupling process on OD-La_{0.10}-CuO_x. These results confirm that the surface of OD-La_{0.10}-CuO_x is predominantly covered with intermediates crucial for C₂₊ product formation, such as *C₂H₄, *OCCO, and *OCCHO. The increasing intensity of these peaks with ongoing electrolysis strongly corroborates the excellent performance for CO₂RR-to-C₂₊ discussed earlier.

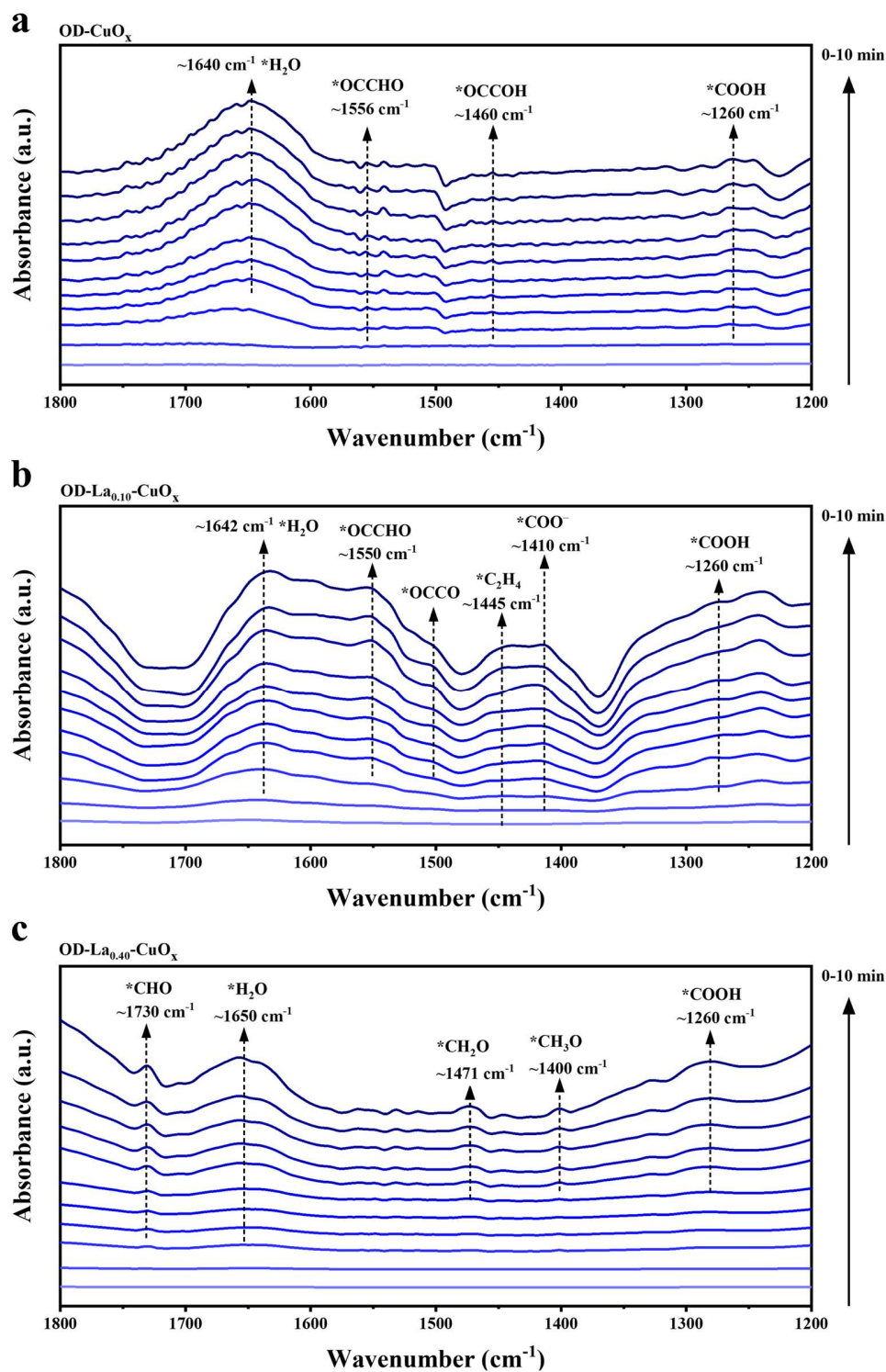


Figure 5.27: Time-dependent electrochemical *in situ* ATR-SEIRAS measurements of a) OD-CuO_x, b) OD-La_{0.10}-CuO_x, and c) OD-La_{0.40}-CuO_x at a potential of -0.8 V vs. RHE. All spectroscopic tests were conducted in a CO₂-saturated 1 M KCl solution over 10-min CO₂ electrolysis.

To further substantiate that varying La-Cu ratios influence product selectivity, *in situ* time-dependent ATR-SEIRAS tests were also performed on OD-La_{0.40}-CuO_x. A peak associate with *COOH is found at 1260 cm⁻¹ [369]. Interestingly, signals indicative of intermediates for C₂₊ formation (*OCCHO, *OCCO, and *OCCOH) are weakened or even absent (**Figure 5.27c**). Instead, a peak at 1730 cm⁻¹ arises from the C=O stretching of *CHO, a critical intermediate in the CO₂RR-to-CH₄ pathway [44]. Moreover, a distinct *CH₂O signal appears at 1471 cm⁻¹ from the protonation of *CHO [45]. Additionally, a peak corresponding to *CH₃O is detected at 1400 cm⁻¹, produced from further protonation of *CH₂O and serving as a crucial intermediate of electrochemical CO₂ methanation [45]. Throughout constant electrolysis, a prominent broad peak emerges in the IR range of 1600-1700 cm⁻¹, particularly around 1650 cm⁻¹, related to the H-O-H bending mode of H₂O molecules [43]. As mentioned above, this broad peak suggests the concurrent activation of H₂O on the La_{0.40}-Cu surface during CO₂RR.

Based on the intermediate information obtained from OD-La_{0.40}-CuO_x, it can be speculated that the adsorbed H₂O molecules continuously supply protons, enhancing the protonation of intermediates, promoting *CHO, *CH₂O, and *CH₃O formation, and optimizing CO₂RR kinetics [373]. In summary, the results of *in situ* ATR-SEIRAS depicted in **Figure 5.27c** demonstrate minimal amounts of intermediates for C₂₊ product formation on OD-La_{0.40}-CuO_x, but a substantial accumulation of intermediates related to CH₄, which is consistent with observations in product distribution of experiments.

5.3.5 DFT calculations of CO₂RR on La-CuO_x catalyst

To elucidate the reaction mechanisms and product correlations of La-CuO_x catalysts with varying levels of La doping in CO₂RR, DFT calculations at the functional/basis level

were performed. Based on the structural characteristics observed from the XRD patterns of the La-CuO_x catalysts post-reaction (**Figure 5.14b** and **c**), theoretical models of OD-CuO_x, OD-La_{0.10}-CuO_x, and OD-La_{0.40}-CuO_x were constructed (**Figure 5.28**).

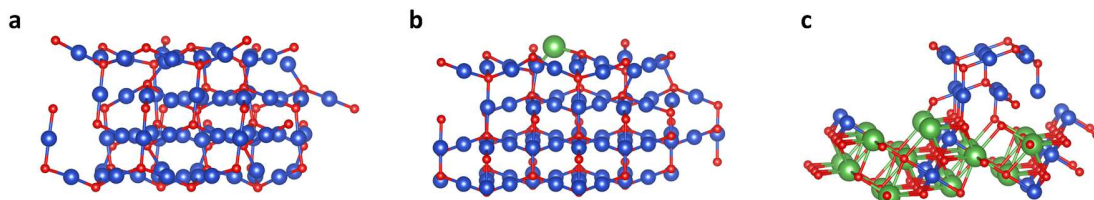


Figure 5.28: Schematic structures of (a) OD-CuO_x without La doping (Cu₂O (111)), (b) OD-La_{0.10}-CuO_x (La-doped Cu₂O (111)), (c) OD-La_{0.40}-CuO_x (La₂CuO₄ (113) / Cu₂O). The atoms in blue, green, red, brown and pale pink represent Cu, La, O, C and H, respectively.

Two primary reaction pathways for CO₂RR-to-CH₄ have been documented [348]: namely $*CO \rightarrow *CHO \rightarrow *CH_2O \rightarrow *CH_3O \rightarrow CH_4$ and $*CO \rightarrow *COH \rightarrow *C \rightarrow *CH \rightarrow *CH_2 \rightarrow *CH_3 \rightarrow CH_4$. To differentiate between these pathways, Gibbs free energy (ΔG) for $*CO \rightarrow *CHO$ and $*CO \rightarrow *COH$ transitions were calculated (**Figure A 5**). The results indicate that for all three electrocatalysts, the ΔG for $*CO \rightarrow *CHO$ is significantly lower than that for $*CO \rightarrow *COH$, effectively ruling out the latter pathway as viable for CH₄ formation. Additionally, OD-La_{0.10}-CuO_x displays the lowest ΔG for $*CO \rightarrow *CHO$ compared to OD-CuO_x and OD-La_{0.40}-CuO_x, indicating the improved $*CHO$ formation at moderate La doping levels. The subsequent analysis will prove why OD-La_{0.40}-CuO_x and OD-La_{0.10}-CuO_x exhibit enhanced selectivity towards CH₄ and C₂₊ products, respectively.

As illustrated in **Figure 5.32a**, the CH₄ formation pathway ($*CHO \rightarrow *CH_2O$) on OD-La_{0.40}-CuO_x is energetically more favourable ($\Delta G = -0.50$ eV) than on OD-CuO_x without La doping ($\Delta G = 0.83$ eV) and OD-La_{0.10}-CuO_x ($\Delta G = 1.48$ eV). This suggests that intermediates conducive to CH₄ formation are more readily generated on OD-La_{0.40}-CuO_x. Furthermore, when comparing the reaction energy barriers for the CO₂RR-to-C₂₊ process

among OD-La_{0.10}-CuO_x, OD-La_{0.40}-CuO_x, and OD-CuO_x (**Figure 5.32b**), it is evident that the energy barrier for the $^*\text{CHO} \rightarrow ^*\text{OCCHO}$ process on OD-La_{0.10}-CuO_x (1.10 eV) is lower than that of OD-CuO_x (1.35 eV) and OD-La_{0.40}-CuO_x (1.47 eV). This indicates that OD-La_{0.10}-CuO_x has optimal adsorption of $^*\text{OCCHO}$. Three widely accepted C-C couplings include CO-CO, CO-CHO and CO-COH [374]. **Figure A 5** suggests the CO-COH pathway is unlikely to occur due to a high energy barrier for $^*\text{CO}$ hydrogenation to $^*\text{COH}$. Additional comparisons of computed reaction energies between CO-CO and CO-CHO pathways (**Figure A 6**) indicate the $^*\text{OCCHO}$ formation pathway is spontaneous for both OD-CuO_x without La doping and OD-La_{0.10}-CuO_x (−1.46 eV and −1.82 eV), with substantially lower energy barriers than those for the $^*\text{OCCO}$ formation pathway (1.76 eV and −0.60 eV), underscoring the dominance of the $^*\text{CHO} \rightarrow ^*\text{OCCHO}$ pathway among the three C-C coupling routes. An examination of Gibbs free energy diagrams for CO₂RR-to-CH₄ and C₂₊ products reveals a close correlation between CO₂RR products on different OD-La-CuO_x catalysts and the divergence of $^*\text{CHO}$ and the formation of critical intermediates (i.e., $^*\text{CH}_2\text{O}$ and $^*\text{OCCHO}$), which agrees with *in situ* ATR-SEIRAS observations (**Figure 5.27**).

To understand the interactions between catalyst surfaces and key intermediates ($^*\text{OCCHO}/^*\text{CH}_2\text{O}$) involved in forming C₂₊ products and CH₄, an analysis of the projected density of states (PDOS) was conducted. The PDOS illustrated in **Figure 5.32c** and **d** reveal significant hybridization between the OD-La_{0.40}-CuO_x (3d) and $^*\text{CH}_2\text{O}$ (2p) orbitals, as well as between OD-La_{0.10}-CuO_x (3d) and $^*\text{OCCHO}$ (2p) orbitals, respectively. This implies robust binding interactions between the catalyst surfaces and these intermediates. Furthermore, the d-band centres (ϵ_d) of both OD-La_{0.40}-CuO_x and OD-La_{0.10}-CuO_x are

situated further from the Fermi energy level ($E_F = 0$ eV) and are more negative compared to the CuO_x without La doping. This observation indicates that *OCCHO and *CH₂O exhibit weaker binding affinities and hence less resistance to desorption on OD-La_{0.40}-CuO_x and OD-La_{0.10}-CuO_x, thereby lowering the reaction barriers for CO₂ electroreduction to C₂₊ product and CH₄.

Inspired by the results of KIE and *in situ* EIS, this work further explored how adsorbed hydrogen (*H) affects the *CHO divergence. The concentration of *H on La-CuO_x catalysts featuring different hybridized heterostructures was determined by calculating the free energy changes associated with water dissociation ($\Delta G(\text{H}_2\text{O})$) and hydrogen ad-desorption ($\Delta G(\text{H})$) on OD-CuO_x without La doping (**Figure 5.29**), OD-La_{0.10}-CuO_x (**Figure 5.30**) and OD-La_{0.40}-CuO_x (**Figure 5.31**). The $\Delta G(\text{H}_2\text{O})$ value of OD-La_{0.40}-CuO_x is 1.19 eV, which is lower than that of OD-La_{0.10}-CuO_x (1.72 eV) and OD-CuO_x without La doping (2.79 eV) (**Figure 5.32e**). This suggests that increased La doping enhances the thermodynamic favourability of H₂O dissociation in La-CuO_x catalysts, resulting in higher *H availability for the electrocatalytic process. In contrast, the absolute value of $\Delta G(\text{H})$ for OD-La_{0.40}-CuO_x, at 0.14 eV, is substantially lower than that of OD-CuO_x and OD-La_{0.10}-CuO_x (0.74 eV and 0.82 eV, respectively) (**Figure 5.32f**). This reveals the high activity of OD-La_{0.40}-CuO_x for HER, aligning with electrochemical test results (**Figure 5.19**).

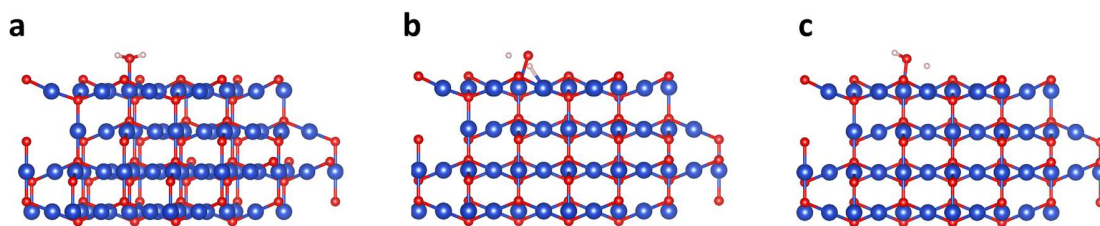


Figure 5.29: Geometries of the initial state (IS: $^*\text{H}_2\text{O}$), transition state (TS: HO--H), and final state (FS: $^*\text{OH} + \text{H}^*$) during water dissociation process on OD- CuO_x slab without La doping. The atoms in blue, red, brown and pale pink represent Cu, O, C and H, respectively.

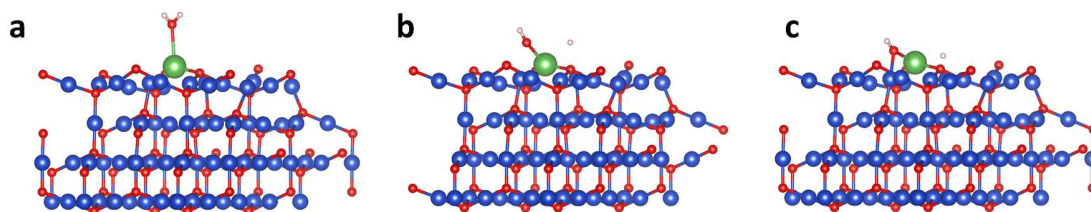


Figure 5.30: Geometries of the initial state (IS: $^*\text{H}_2\text{O}$), transition state (TS: HO--H), and final state (FS: $^*\text{OH} + \text{H}^*$) during water dissociation process on OD- $\text{La}_{0.10}\text{-CuO}_x$ slab. The atoms in blue, green, red, brown and pale pink represent Cu, La, O, C and H, respectively.

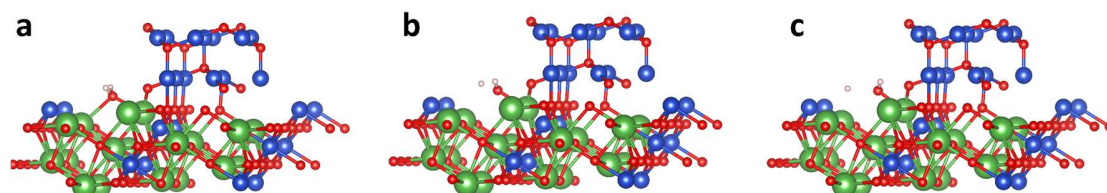


Figure 5.31: Geometries of the initial state (IS: $^*\text{H}_2\text{O}$), transition state (TS: HO--H), and final state (FS: $^*\text{OH} + \text{H}^*$) during water dissociation process on OD- $\text{La}_{0.40}\text{-CuO}_x$ slab. The atoms in blue, green, red, brown and pale pink represent Cu, La, O, C and H, respectively.

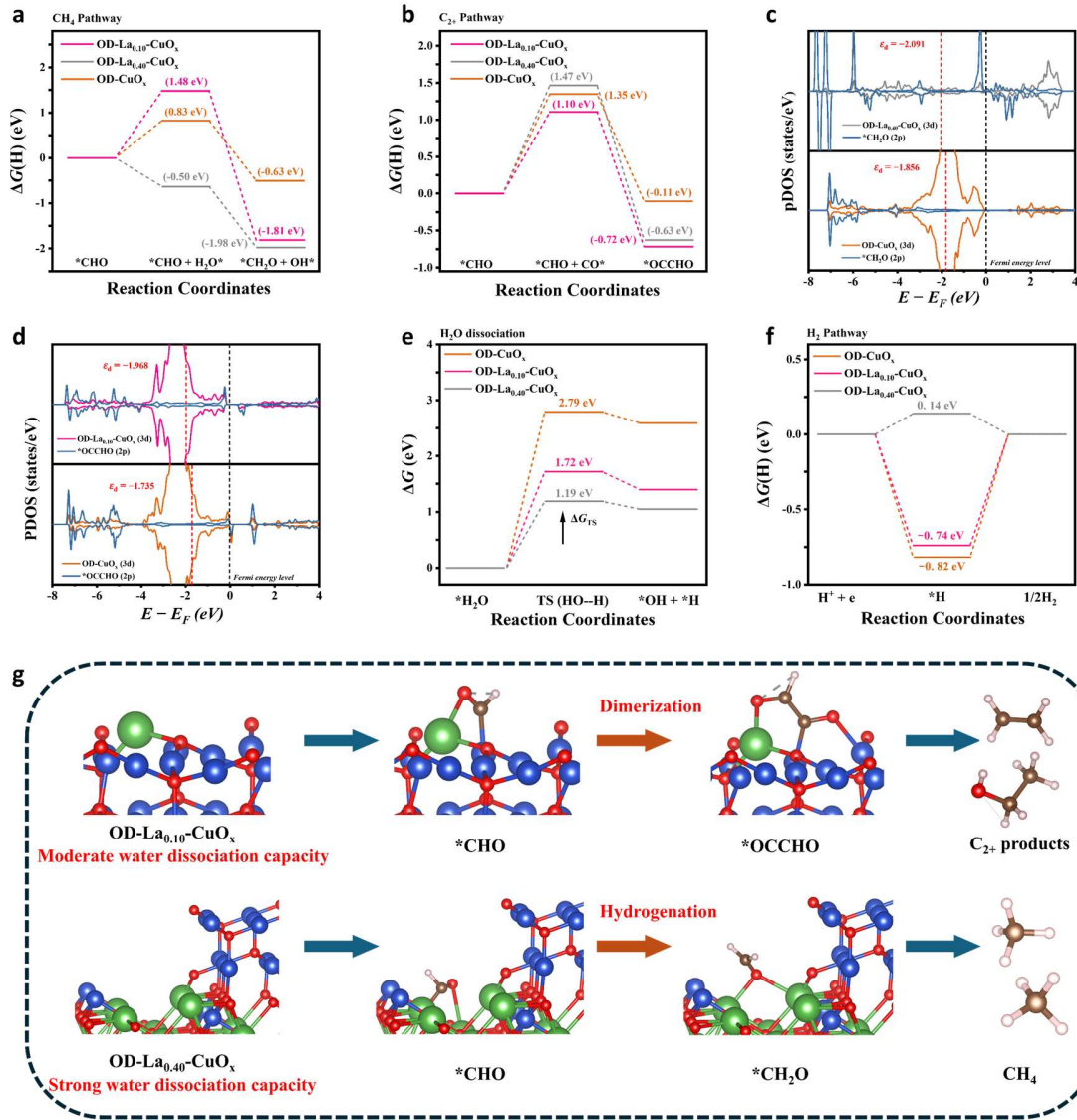


Figure 5.32: a) Gibbs free energy diagrams for the hydrogenation of *CHO to *CH₂O on OD-CuO_x surfaces without La doping and on OD-La_{0.40}-CuO_x; b) Gibbs free energy diagrams for the dimerization of *CHO to *OCCHO on OD-CuO_x surfaces without La doping and on OD-La_{0.10}-CuO_x; c&d) Projected density of states (PDOS) of d orbitals associated with *CH₂O and *OCCHO on OD-La_{0.40}-CuO_x and OD-La_{0.10}-CuO_x, respectively, with d-band centres (ϵ_d) indicated by red dashed lines. Adsorption energy diagram of (e) H₂O dissociation and (f) hydrogen ad-desorption for OD-CuO_x without La doping, OD-La_{0.40}-CuO_x and OD-La_{0.10}-CuO_x. (g) Proposed reaction mechanisms, illustrating CO₂ dimerization to C₂+ products on OD-La_{0.10}-CuO_x (top) and CO₂ hydrogenation to CH₄ on OD-La_{0.40}-CuO_x (bottom). Atoms are coloured as follows: Cu, blue; La, green; O, red; C, brown; and H, pale pink.

Therefore, based on insights from *in situ* spectroscopy and theoretical analyses, it can be concluded that OD-La_{0.10}-CuO_x and OD-La_{0.40}-CuO_x exhibit distinctive capacities for water dissociation, resulting in varied *H availability on their respective surfaces. As illustrated in **Figure 5.32g**, the presence of moderate *H on the OD-La_{0.10}-CuO_x surface and abundant *H on the OD-La_{0.40}-CuO_x surface lead to different *CHO conversion pathways, lowering energy barriers for both dimerization (*CHO → *OCCHO) and hydrogenation (*CHO → *CH₂O) processes, thereby achieving enhanced CO₂RR performance towards C₂₊ products and CH₄. These differences can be attributed to the varied dependence on proton transfer in the RDS for CO₂RR-to-C₂₊/CH₄. According to KIE results, the CO₂RR-to-C₂₊ process may lack a distinct proton-related RDS or involve multiple parallel proton-related RDSs, whereas the CO₂RR-to-CH₄ process is significantly influenced by proton transfer in its RDS. These findings are in line with observations from electrochemical performance tests and kinetic studies.

5.4 Summary

In summary, this work has developed a series of OD-La-CuO_x catalysts with tailored adsorbed hydrogen (*H) to achieve controlled industrial-current-density CO₂ conversion to C₂₊ products and CH₄. The OD-La_{0.10}-CuO_x catalyst exhibits outstanding performance of CO₂RR to C₂₊ products in 1 M KCl, reaching a FE of 80.4% for C₂₊ products at a current density of 300 mA cm⁻². Conversely, with increased La doping in OD-La_{0.40}-CuO_x, a maximum FE of 61.5% for CH₄ is achieved at 400 mA cm⁻² in 1 M KOH. Both experimental and kinetic studies reveal that increased La doping alters the phase composition of OD-La-CuO_x catalysts and correlates positively with higher concentrations

of *H, allowing for tuneable electron selectivity and kinetics of CO₂RR products. Notably, *in situ* ATR-SEIRAS and DFT studies demonstrate that the OD-La-CuO_x catalysts possess varying H₂O dissociation capacities, accounting for their variations in *H. Additionally, this modulation strategy can guide the reaction pathway toward either *CHO dimerization or hydrogenation, thereby lowering reaction barriers for producing target C₂₊ products and CH₄. OD-La_{0.10}-CuO_x, with its moderate H₂O dissociation capacity, favours the *CO → *CHO and *CHO → *OCCHO pathways, enhancing C-C coupling and leading to C₂₊ production. In contrast, OD-La_{0.40}-CuO_x, characterized by the lowest H₂O dissociation energy barrier, enhances proton transfer, promoting CO₂RR-to-CH₄ via the *CHO → *CH₂O pathway. The findings from this study provide a promising strategy for optimizing the selectivity of target CO₂RR products at industrial current densities.

Chapter 6 Eu(OH)₃-Cu electrocatalyst for CO₂RR to C₂H₄

In this chapter, a comprehensive study on Europium hydroxide modified oxide-derived CuO nanosheets (denoted as Eu(OH)₃-Cu NSs) is presented, which serve as an innovative electrocatalyst that significantly optimizes the local coverage of *CO intermediates and promotes C-C coupling process (*COCHO formation). This novel electrocatalytic system effectively facilitates the electroreduction of CO₂ to form valuable C₂₊ products with remarkable efficiency. The Eu(OH)₃-Cu electrocatalyst exhibits a pronounced enhancement in selectivity for C₂₊ products, achieving an impressive peak FE of 81.4% alongside a substantial partial current density of 326 mA cm⁻², in stark contrast to the performance exhibited by bare CuO nanosheets. Furthermore, in comparison to the CuO component, which experiences rapid cathodic corrosion, the Eu(OH)₃ component demonstrates remarkable durability and stability, maintaining its integrity at a current density of 400 mA cm⁻² within a flow cell system featuring the hybrid Eu(OH)₃-Cu configuration. Advanced *in situ* electrochemical impedance spectroscopy and infrared spectroscopy analyses reveal that the hybrid Eu(OH)₃-Cu system presents a lower onset potential and a pronounced accumulation of asymmetric *OCCHO intermediates, which are critical for enhancing reaction pathways leading to C₂₊ product formation. This engineering of the hydroxide-metal interface represents a valuable and highly promising strategy for advancing the selectivity and stability of catalytic systems designed for the electrochemical reduction of CO₂ to C₂₊ products.

6.1 Introduction

According to the introduction of section 2.1.3, among the various products, C₂₊ products with higher energy density and specific industrial value, such as ethylene (C₂H₄) and ethanol (C₂H₅OH), are of particular interest. Based on the existing research, copper (Cu)-based catalysts benefit from exhibiting moderate adsorption energies for the *CO intermediates, enabling them to effectively catalyse the electrochemical conversion of CO₂ into C₂₊ products, garnering significant interest in this field [31]. However, CO₂RR to C₂₊ products using Cu-based catalysts still faces significant challenges, including competition from HER, CO₂ activation, the formation of *CO, and the relatively high energy barriers for C–C coupling [374]. These obstacles hinder the application of Cu-based catalysts in the CO₂ electrolysis to produce target C₂₊ products with high activity and selectivity.

As presented in section 2.3.3, combining Cu with other rare earth elements (such as La [375], Ce [39], Gd [229], Sm [234], or Eu) has been demonstrated to modify the adsorption states of reactant species at the interface, thereby enhancing the selectivity for C₂₊ products. Generally, the enhanced performance of these bimetallic catalysts is attributed to synergistic effects. Cu-based catalysts modified with external components can achieve superior CO₂RR-to-C₂₊ performance compared to the original catalysts by altering the local reaction environment or optimizing the adsorption of key reaction intermediates. The unique physical and chemical properties of rare earth elements stem from the peculiar arrangement of their 4f electrons and the partially filled 5d orbitals [49].

Therefore, employing them as support for Cu-based catalysts is regarded as a potentially effective strategy for the development of high-performance electrocatalysts. For example, Yin et al. prepared Cu-modified CeO₂ composites (Cu_y/CeO₂) with different Cu

loadings for CO₂RR. Strong adsorption sites for CO₂ molecules exist at the interface between Cu and CeO₂, which serve to activate CO₂ molecules and subsequently facilitate the generation of *CO at the interface of adjacent Cu nanoparticles [41].

Moreover, the utilization of rare earth elements as co-catalysts allows for the manipulation of local electronic density in surrounding atoms through lanthanide contraction. This optimization of the electronic structure of the support significantly affects the adsorption capacity for each reaction intermediate, facilitating the achievement of controlled CO₂RR. Wang et al. enhanced the performance of CO₂RR to C₂H₄ by incorporating Sm³⁺ into a Cu₂O matrix. This enhancement is attributed to the formation of atypical 3d-2p-4f hybrid orbitals, which improve the adsorption of *CO intermediates and increase the coverage of *CO, thereby reducing the energy barrier for C-C coupling and accelerating the formation of C₂₊ products [57]. Additionally, the introduction of rare earth elements can create high-density grain boundaries that serve as active sites, which is stable during the catalytic process. For instance, Huang's group prepared a La₂CuO₄ nano bamboo (NB) catalyst with abundant twinning boundaries (TBs), which exhibited a high FE of 60% for C₂H₄ production [56]. Overall, the modification of Cu-based catalysts' surface with rare earth elements can enhance the CO₂RR-to-C₂₊ performance. However, the complex mechanism behind this enhancement requires further investigation through *in situ* spectroscopy and theoretical calculations.

Herein, a series of Eu(OH)₃-Cu hybrid catalysts with different molar ratios of Eu to Cu have been successfully prepared by surfactant-assisted coprecipitation strategy in the aqueous solution, followed by the *in situ* electrochemical reconstruction. The composition-activity relationship and reaction mechanism of Eu(OH)₃-Cu catalysts for CO₂RR-to-C₂₊

products are systematically investigated. The as-prepared Eu(OH)₃-Cu catalyst with an optimal Eu doping amount (5%) achieves a maximum electron selectivity (FE = 81.4%) and cathodic energy efficiency of 37.3% toward multi-carbon products at the current density of 400 mA cm⁻² in 1 M KOH using gas-fed flow cell. *In situ* FT-IR spectroscopy probed *CHO and *OCCHO as the key intermediates for CO₂RR-to-C₂+ products. Moreover, DFT study reveal that Eu(OH)₃-Cu can inhibit CO desorption, stabilize *CO and depress HER, all of which are beneficial for forming asymmetric *OCCHO to ultimately generate multicarbon products.

6.2 Experimental

6.2.1 Synthesis of CuO catalyst

The pristine CuO nanosheets (NSs) followed the reported procedure with modification [376]. In the synthetic process, 4.4 g hexadecyl trimethyl ammonium bromide (CTAB) and 24 g NaOH were dissolved in 180 mL deionized (DI) water through thermostat water bath with the temperature of 65°C to get solution **1**. In a separate beaker, 0.68 g Cu(NO₃)₂·3H₂O (14 mM) was dissolved in 20 mL DI water under room temperature to get solution **2**. Once dissolved, the solution **2** was quickly injected into solution **1** and the mixed solution was held at a constant temperature of 65°C and under magnetic stirring. After 2 hours, the flask was taken out from the thermostat water bath and cooled down to room temperature. The final solution was filtered by centrifuge at 7000 rpm for 5 minutes and washed with DI water and ethanol for several times. The black precipitate was collected and dried at 60 °C overnight to obtain the CuO NSs without further treatment.

6.2.2 Synthesis of Eu(OH)₃-Cu catalyst

The Eu(OH)₃-Cu NSs were fabricated by a similar method to that mentioned above. After obtaining the solution **1**, 0.68 g Cu(NO₃)₂·3H₂O (14 mM) and 0.042 g, 0.063 g, 0.125 g and 0.25 g Eu(NO₃)₃·6H₂O (0.46 mM, 0.7 mM, 1.4 mM and 2.8 mM) were mixed and dissolved in 20 mL DI water to obtain solution **2** under identical conditions. Due to the different Eu doping ratio, these as-prepared catalysts were donated as Eu(OH)₃-Cu-3%, Eu(OH)₃-Cu-5%, Eu(OH)₃-Cu-10% and Eu(OH)₃-Cu-20%. The optimum Eu(NO₃)₃·6H₂O addition was confirmed as 0.7 mM (with the Cu-Eu doping ratio of 20:1) in the following CO₂ electroreduction performance tests. Thus, unless otherwise stated, the Eu(OH)₃-Cu refers to Eu(OH)₃-Cu-5%.

6.2.3 DFT calculation details

Apart from the DFT calculation details discussed in section 3.4, for undoped face-centred cubic Cu, the model was constructed on the Cu(200) surface using a 3-layer Cu surface, derived from the optimized and cleaved bulk Cu. For Eu(OH)₃-Cu, the corresponding model was performed on a 3-layer Cu(200) surface and placing a 2-layer Eu(OH)₃ structure on top. A vacuum space of 15 Å in the z-direction was employed to minimize the layer's interactions with its periodic images across all constructed models.

6.3 Results and discussion

6.3.1 Synthesis and characterizations of Eu(OH)₃-Cu catalyst

As illustrated in the **Figure 6.1a**, cetyltrimethylammonium bromide (CTAB) was used as the cationic surfactant, copper nitrate trihydrate (Cu(NO₃)₂·3H₂O) and europium nitrate hexahydrate (Eu(NO₃)₃·6H₂O) as metal sources, and the Cu/Eu atom doping ratio

was 20:1 (designed Eu metal atom doping amount of 5%). Eu(OH)₃-modified CuO was prepared by coprecipitation under the strong alkaline conditions created by sodium hydroxide (NaOH), and then *in situ* electrochemical reconstruction was carried out under CO₂ electroreduction conditions. During the coprecipitation of the catalyst, the Cu²⁺ and Eu³⁺ ions combine with OH⁻ to form a homogeneous mixture of Cu(OH)₂ and Eu(OH)₃. In the subsequent heating process, Cu(OH)₂ gradually dehydrates and decomposes into CuO [376]. Meanwhile, due to the high decomposition temperature of Eu(OH)₃ [377], it remains stable and deposits on the surface of CuO, forming the Eu(OH)₃-Cu hybrid structure (denoted as Eu(OH)₃-Cu).

More control samples of the Eu(OH)₃-Cu hybrid catalyst with different Eu additions ratio (such as 3 at.%, 10 at.% and 20 at.%) and Eu(OH)₃ were prepared following the same method. Additionally, ICP-MS results indicate that the mass percentages of Eu and Cu in Eu(OH)₃-Cu-5% are 70.45 wt.% and 9.15 wt.%, respectively (**Table 6.1**).

Table 6.1: ICP-MS analysis results of the as-prepared Eu(OH)₃-Cu hybrid electrocatalysts.

Catalyst	Cu (wt. %)	Eu (wt. %)
Eu(OH) ₃ -Cu-20%	57.20 %	28.03%
Eu(OH) ₃ -Cu-10%	65.27 %	15.82 %
Eu(OH) ₃ -Cu-5%	70.45 %	9.15 %
Eu(OH) ₃ -Cu-3%	73.13 %	6.06 %
CuO	80.20 %	0 %

Field emission SEM images show that Eu(OH)₃-Cu has a typical two-dimensional sheet structure (**Figure 6.1b**). According to previous reports, two-dimensional (2D) nanomaterials can provide more surface-active sites during electrocatalytic processes to

achieve better catalytic stability and activity. Minor doping with Eu(OH)₃-Cu-5% retains more well-preserved 2D sheet structures. However, with further increases in Eu doping, broken and smaller sheet structures are observed in the SEM images of Eu(OH)₃-Cu-10% and 20% (**Figure 6.2**).

The microstructure and chemical composition of Eu(OH)₃-Cu were further analysed TEM combined with EDS. The results observed in the TEM images are consistent with the SEM images, confirming the 2D nanosheet structure of Eu(OH)₃-Cu (**Figure 6.1c** and **Figure 6.3**). The crystal structure of Eu(OH)₃-Cu was subsequently studied by HRTEM. As illustrated in the **Figure 6.1d**, the well-defined lattice fringes with distances of 0.232 and 0.301 nm correspond to CuO (111) (PDF#72-0629) and Eu(OH)₃ (101) (PDF#17-0781) [376, 378]. Analysis of the EDS elemental mapping revealed that the Cu, Eu and O elements are uniformly distributed in the Eu(OH)₃-Cu (**Figure 6.1e**), which demonstrates tight contact between Eu(OH)₃ and CuO to form a two-phase hybrid structure.

To verify the phase composition of the synthesized Eu(OH)₃-Cu hybrid catalyst, PXRD analysis was performed on a series of Eu(OH)₃-Cu samples and an undoped CuO catalyst. As shown in **Figure 6.1f**, the diffraction peaks of the Eu(OH)₃-Cu samples with different Eu addition levels match well with those of the standard Eu(OH)₃ (PDF#17-0781) and CuO (PDF#72-0629), providing further evidence of the successful synthesis of two-phase hybrid structure composed of Eu(OH)₃ and CuO. For CuO without Eu doping, the peaks can be precisely assigned to the monoclinic pure phase of CuO (JCPDS # 45-0937), where the strongest peaks of CuO (002) and CuO (111) are located at 35.6° and 38.7°, respectively. With the addition of Eu, diffraction peaks attributable to the hexagonal phase

of Eu(OH)₃ (PDF#17-0781) appear, including peaks at 28.0°, 29.3° and 50.3° corresponding to (110), (101) and (211) of Eu(OH)₃.

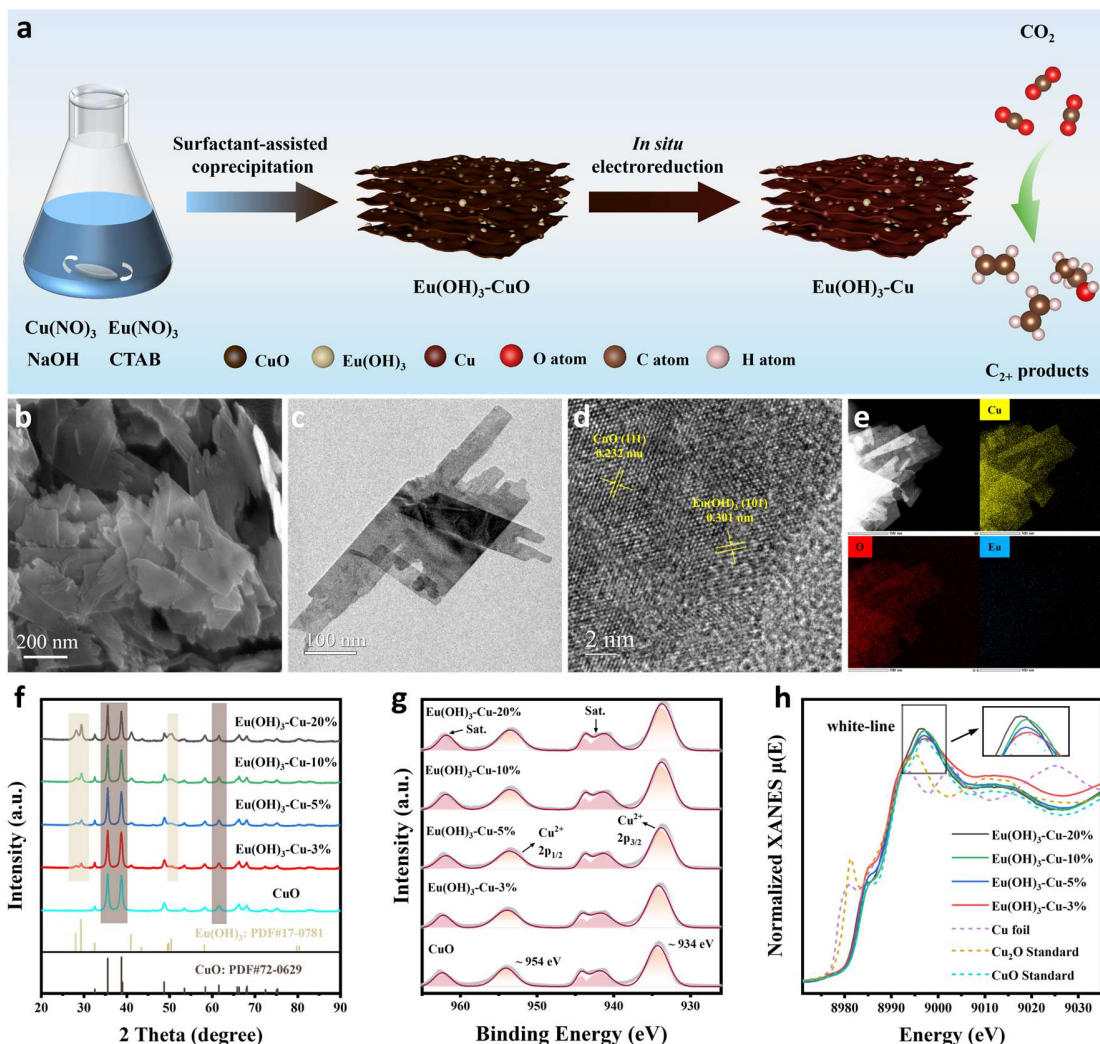


Figure 6.1: Morphology and structural characterization. (a) Schematic illustration for fabrication of Eu(OH)₃-Cu. (b) SEM, (c) TEM, (d) HETEM images and (e) EDS mappings of Eu(OH)₃-Cu-5% (yellow, red and blue represent Cu, O and Eu elements, respectively). (f) XRD patterns, (g) Cu 2p XPS spectra and (h) Cu K-edge XANES spectra of as-prepared CuO and Eu(OH)₃-Cu with different doping ratio of Eu to Cu (from 3% to 20%).

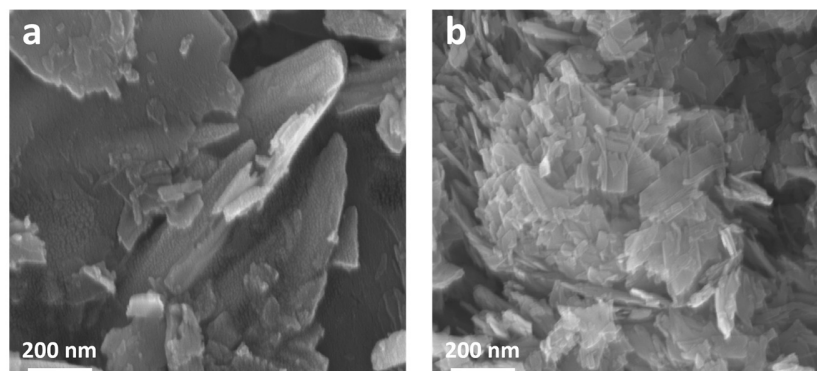


Figure 6.2: SEM images of (a) Eu(OH)₃-Cu-10% and (b) Eu(OH)₃-Cu-20%

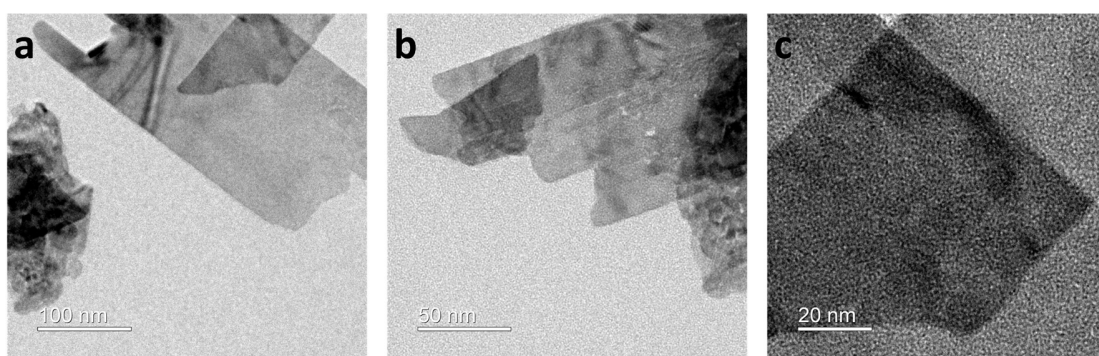


Figure 6.3: (a-c) TEM images of Eu(OH)₃-Cu-5% at different magnifications.

To gain a comprehensive understanding of the surface components and electronic properties of the Eu(OH)₃-Cu sample, XPS analysis was also performed. In the high-resolution Cu 2p spectrum (**Figure 6.1g**), the two peaks with binding energies at 934.5 and 954.2 eV can be attributed to the characteristic spin-orbit splitting of Cu²⁺ 2p_{3/2} and Cu²⁺ 2p_{1/2}, respectively. In addition, the peaks at 944.1 and 962.4 eV are satellite peaks of Cu²⁺ [56]. From the obtained Cu Auger LMM spectrum, a characteristic peak of Cu²⁺ can be observed at a kinetic energy of 917.8 eV, indicating that Cu²⁺ is the main valence state of the as-prepared Eu(OH)₃-Cu materials, which is consistent with the above HRTEM and XRD results [39]. Moreover, the characteristic peak corresponding to the Eu³⁺ 3d_{5/2} (~1135 eV) was found in the high-resolution Eu 3d spectrum of the Eu(OH)₃-Cu sample with different Eu doping levels [379]. Interestingly, with an increase in the Eu doping amount

(from 3 at% to 20 at%), the Eu³⁺ 3d_{5/2} peak shifts to the lower energy side (**Figure 6.4**). This gradual increase in shift indicates that Eu is gaining electrons from Cu, further supporting the existence of a strongly coupled hybrid interface in Eu(OH)₃-Cu. This shift was not observed in the Cu 2p spectrum because the high content of the component CuO in Eu(OH)₃-Cu resulted in the Cu 2p peaks remaining unaffected.

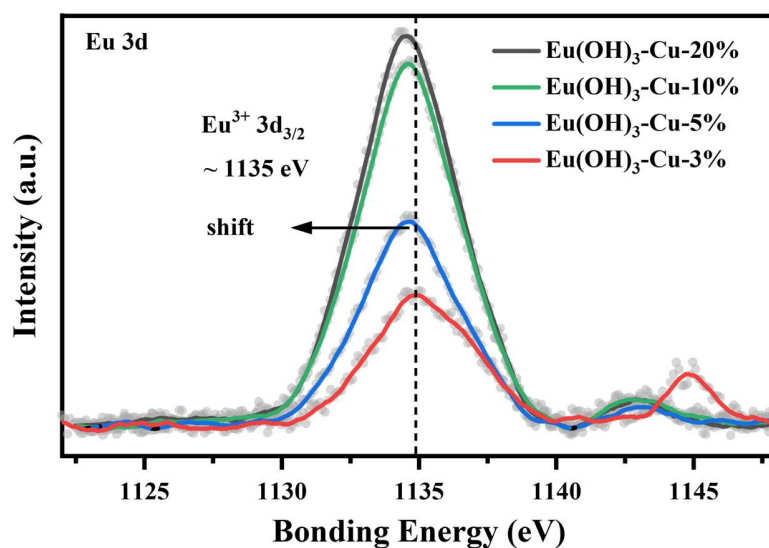


Figure 6.4: Eu 3d XPS spectra of Eu(OH)₃-Cu with different doping ratio of Eu to Cu.

To further confirm the valence state and local microstructure of the Cu species, XANES and EXAFS analyses were performed on the Cu K edges of Eu(OH)₃-Cu and standards (Cu, Cu₂O and CuO). The absorption edge of Eu(OH)₃-Cu is shown to be the same as that of the CuO standard sample, indicating that the valence state of Cu species in Eu(OH)₃-Cu is +2. In addition, with increasing Eu content, the white line peak intensity of Eu(OH)₃-Cu gradually increases, higher than that of the CuO standard sample (**Figure 6.1h**). These results indicate that the introduction of Eu will increase the total charge of Cu in Eu(OH)₃-Cu, which will promote the electron transfer from Cu to Eu. This conclusion is consistent with the above XPS analysis results.

6.3.2 Electrochemical performance of CO₂RR on Eu(OH)₃-Cu catalyst

The electrocatalytic CO₂RR performance of as-prepared CuO NS and Eu(OH)₃-Cu NS was evaluated by applying a constant current density in a custom-made electrochemical flow cell (**Figure A 4**). Unless otherwise stated, potentials are converted to the RHE scale using an 85% iR correction. For the evaluation of the performance of the electrocatalyst in an alkaline electrolyte, 1 M KOH was used as the electrolyte. Before each online gas chromatograph test, airtightness checks, LSV and CV activation and gas outlet flow rate tests were performed. In this section, except where otherwise noted, Eu(OH)₃-Cu refers to Eu(OH)₃-Cu-5% (a Cu-Eu doping ratio of 20:1). This ratio has been determined to be the optimal amount of Eu doping, as discussed below.

To verify the electrochemical activity of as-prepared catalysts, LSV curves of CuO and Eu(OH)₃-Cu electrodes were measured under Ar and CO₂ feed conditions (**Figure 6.5a**). Obviously, under both Ar and CO₂ feed conditions, Eu(OH)₃-Cu has a higher current density than CuO under the same applied potential. This enhancement is due to the strongly coupled hybridization in Eu(OH)₃-Cu. Moreover, Eu(OH)₃-Cu has a lower initial potential and higher electrochemical activity in a CO₂-saturated electrolyte than in an Ar-saturated electrolyte, indicating notably higher CO₂RR activity. The chronoamperometry (CP) method is applied to evaluate the performance of as-prepared catalysts. The test is carried out at a range of current densities between 100 and 500 mA cm⁻². The catalytic product distribution shows that the 2D CuO NS prepared by surfactant-assisted method exhibits remarkable ability to inhibit competing reactions of hydrogen evolution, suppressing the FE of H₂ below 20% at the tested current density (**Figure 6.5b**). At the current density of 400 mA cm⁻², the CuO NS exhibits a total FE_{C₂+} of 72.2%, of which FE_{C₂H₄} is 44.9%.

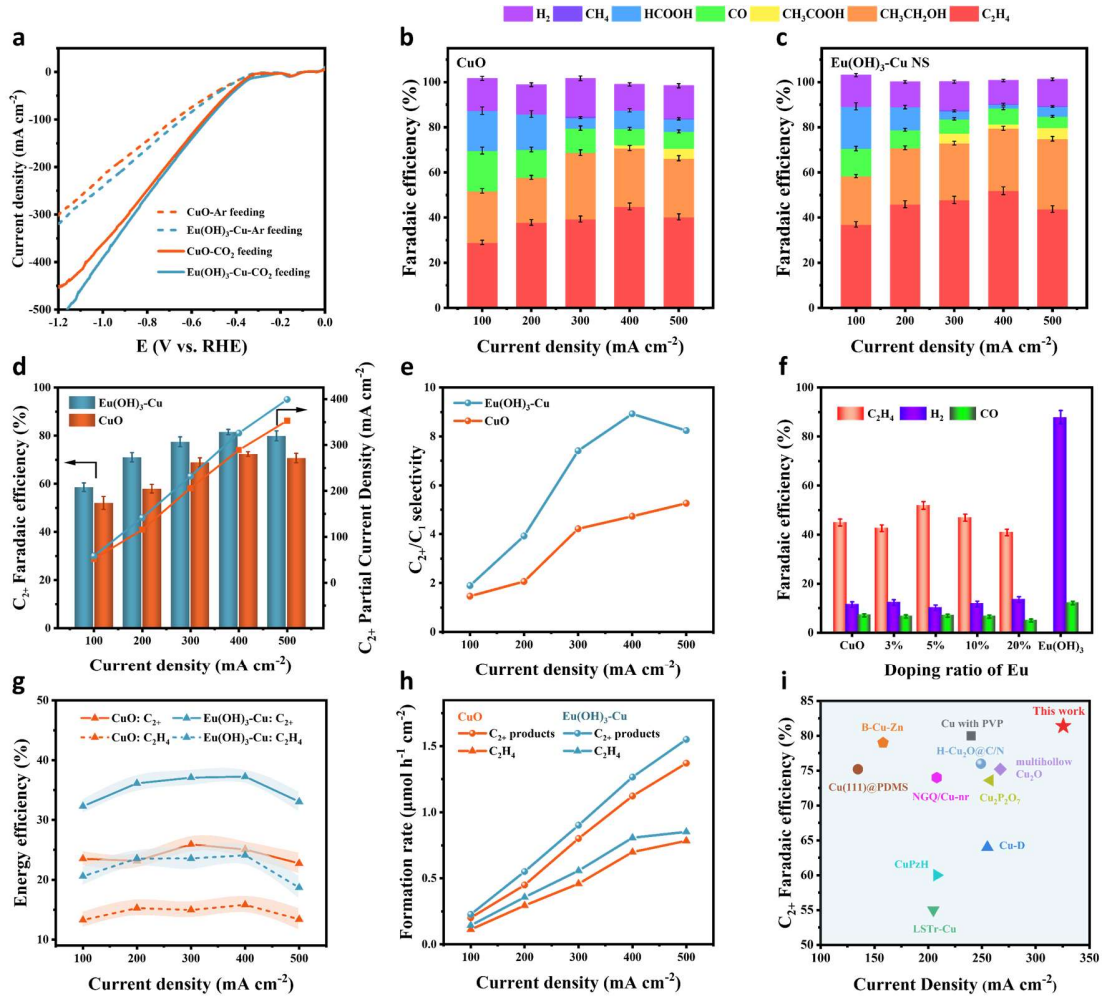


Figure 6.5: Electrochemical CO₂RR performance. (a) LSV curves of CuO and Eu(OH)₃-Cu in Ar and CO₂ feeding. FE values of CO₂RR products at the current density range of 100-500 mA cm⁻² on (b) CuO and (c) Eu(OH)₃-Cu in 1 M KOH. (d) FE and partial current densities of C₂⁺ products and (e) Ratio of C₂⁺ to C₁ products on CuO and Eu(OH)₃-Cu. (f) FE of C₂H₄, H₂ and CO on Eu(OH)₃ modified Cu with different Cu-Eu ratio at 400 mA cm⁻². (g) Energy efficiency and (h) formation rate of C₂⁺ products and C₂H₄ on CuO and Eu(OH)₃-Cu in 1 M KOH by flow cell. (i) FE_{C₂⁺} value and C₂⁺ partial current density of Eu(OH)₃-Cu in this work and other reported high-performance Cu-based electrocatalysts for CO₂RR-to-C₂⁺ products [322, 328-332, 334, 337, 343, 349].

Moreover, the Eu(OH)₃-Cu hybrid material constructed by Eu doping shows significant changes in the FE of H₂, C₁ products, and C₂⁺ products. The introduction of Eu(OH)₃ further suppresses HER, and the FE_{H₂} of Eu(OH)₃-Cu is lower than that of CuO and remains at around 10% in the current density range of 100-500 mA cm⁻². In addition,

the FE_{C1} of Eu(OH)₃-Cu is lower than that of CuO. For example, at a current density of 400 mA cm⁻², the FE_{CO} and FE_{HCOOH} are only 5.0% and 4.3%, respectively. Apart from that, as depicted in the figure, Eu(OH)₃-Cu has a higher electron selectivity for C₂₊ products. It achieves the highest FE_{C2+} of 81.4% at a current density of 400 mA cm⁻², which is an increase of about 9.2% compared to FE_{C2+} of CuO (**Figure 6.5c**).

With the increase of current density (from 100 to 400 mA cm⁻²), C₂₊ products selectivity of both prepared electrocatalysts increased, while C₁ products selectivity decreased, indicating that C-C coupling occurs at a larger overpotential and generates multicarbon products. As shown in **Figure 6.5d**, within the total current density range of 100-500 mA cm⁻², Eu(OH)₃-Cu exhibits the high partial current density of the C₂₊ product (326 mA cm⁻²) with a high FE_{C2+} over 80%, which is higher than that of CuO (289 mA cm⁻²). To investigate the efficiency of C-C coupling in CO₂RR, the ratio of the electronic selectivity of C₂₊ and C₁ products on CuO and Eu(OH)₃-Cu was calculated. **Figure 6.5e** indicates that Eu(OH)₃-Cu has a high C₂₊/C₁ selectivity ratio of 8.9 at a current density of 400 mA cm⁻², which is much higher than that of CuO (4.7). The above results demonstrate that the construction of Eu(OH)₃-Cu hybrid structure through Eu doping improves the activity and selectivity of CO₂RR-to-C₂₊ products.

Table 6.2: The electrochemical CO₂RR-to-C₂⁺ performance comparison of Eu(OH)₃-Cu-5% in this work with the reported state-of-the-art electrocatalysts in flow cell.

Catalysts	Electrolyte	FE _{C2+} (%)	J _{C2+} (mA cm ⁻²)	Ref.
Eu(OH) ₃ -Cu	1 M KOH	81.4	325.6	This work
AEI-OD-Cu	1 M KOH	85.1	681	[247]
Cu-PTFE	1 M KOH	86	~250	[338]
HRS-Cu	2 M KOH	86.5	~105	[339]
Cu _{TPA}	3 M KOH	90.9	486	[340]
Cu with PVP	0.5 M KOH	80	240	[348]
M-Cu ₁ /CuNP	5 M KOH	75.4	267	[307]
Cu-D	1 M KOH	64	255	[334]
H-Cu ₂ O@C/N	1 M KOH	76	249	[341]
LSTr-Cu	1 M KOH	55	204.8	[329]
Multi-hollow Cu ₂ O	2 M KOH	75.2	267	[380]
Cu ₂ P ₂ O ₇	0.1 M KOH	73.6	257.6	[330]
Cu(111)@PDMS	1 M KOH	75.2	134.6	[328]
CuPzH	1 M KOH	60	208	[332]
B-doped Cu ₂ O	7.0 M KOH	77.8	233	[336]
Cu ₂ O(CO)	1 M KOH	77.4	387	[345]
NGQ/Cu-nr	1 M KOH	74	208	[342]
CuO/Al ₂ CuO ₄	1 M KOH	70.1	421	[346]
2F-Cu-BDC	1 M KOH	63	150	[344]
B-Cu-Zn	1 M KOH	79	158	[331]
Hex-2Cu-O	1 M KOH	66.2	182	[347]
Cu ₅₀₀ Ag ₁₀₀₀	1 M KOH	50	160	[333]

The effects of Eu doping on CO₂RR performance were investigated by testing CuO, Eu(OH)₃-Cu and Eu(OH)₃ catalysts prepared with different Eu atom doping ratios (0 at.%, 3 at.%, 5%, 10 at.%, 20 at.% and 100 at.%). **Figure 6.5f** presents the values of FE_{C₂H₄}, FE_{H₂} and FE_{CO} of Eu(OH)₃-Cu with different Eu doping ratios at a current density of 400 mA cm⁻². A volcano-type relationship between FE_{C₂H₄} and Eu doping content can be observed. The maximum value of the FE_{C₂H₄} (~52%) is achieved when the Eu doping amount is 5%. Furthermore, with the addition of an appropriate amount of Eu, the catalyst's ability to inhibit hydrogen evolution is not significantly affected. A sharp increase in H₂ production and the disappearance of C₂H₄ production were found on Eu(OH)₃ without CuO presence. This confirms that the proper introduction of Eu to form the Eu(OH)₃ hybrid structure can improve the selectivity of C₂+ products, especially C₂H₄.

Thereafter, the cathodic energy efficiency and the formation rate of CuO and Eu(OH)₃-Cu based on the measured overpotential, and FE of each product are determined (**Figure 6.5g**). Obviously, the energy efficiency and rate of C₂+ products and C₂H₄ formation on Eu(OH)₃-Cu are higher than those on CuO. Within the current density range of 100-500 mA cm⁻², Eu(OH)₃-Cu has the highest energy efficiency for C₂+ product and C₂H₄ formation at the current density of 400 mA cm⁻², which is 37.3% and 24.1%, respectively (**Table A 4** and **Table A 5**). Moreover, the calculated results show that at the current density of 500 mA cm⁻², the formation rates of C₂+ products and C₂H₄ on Eu(OH)₃-Cu are 1.55 mmol h⁻¹ cm⁻² and 0.85 mmol h⁻¹ cm⁻², which is higher than that of undoped CuO (1.37 mmol h⁻¹ cm⁻² and 0.78 mmol h⁻¹ cm⁻²) and comparable to the most advanced electrodes (**Figure 6.5h**).

For the prepared CuO and hybrid Eu(OH)₃-Cu catalysts with different Eu doping levels, Tafel curves for CO₂RR-to-C₂H₄ at different partial current densities are further plotted to elucidate the kinetics. Tafel analysis indicates that the slopes turn lower in the presence of moderate amounts of Eu, with Eu(OH)₃-Cu-5% being the lowest and lower than undoped CuO and other Eu(OH)₃-Cu with different doping amounts. The lowest Tafel slopes suggest that Eu(OH)₃-Cu-5% has optimal kinetics in C₂H₄ formation (**Figure 6.6a**). Further, the Tafel slope of Eu(OH)₃-Cu-5% is close to the theoretical value of 118 mV/dec, suggesting that single-electron transfer may be involved in the rate-determining step [37]. Additionally, the monitored CO temperature-programmed desorption (CO-TPD) traces probe the desorption intensity of CO adsorbed on the surface of the prepared catalysts. As shown in **Figure 6.6b**, a distinct CO desorption peak appeared near 250 °C for both Eu(OH)₃-Cu and CuO. Moreover, the desorption peaks of Eu(OH)₃-Cu are at higher temperatures compared to CuO, suggesting that the presence of the Eu(OH)₃ component can enhance the adsorption affinity for *CO and *CO-related intermediates [381, 382].

To further investigate the effect of *CO adsorption energy on the C-C coupling kinetics, the CO generation and dimerization rates of CuO and Eu(OH)₃-Cu are analysed and compared. The CO generation rate is the summation of the normalized generation rates of CO, CH₄ and C₂₊ products [381]. Compared to CuO, Eu(OH)₃-Cu exhibited higher CO generation rates and provided more CO from the current density range of 200-500 mA cm⁻², suggesting that the construction of hybrid interfaces is more favourable to improve the CO formation (**Figure 6.6c**). Additionally, the CO dimerization rate is derived from the normalized generation rate of each C₂₊ product. Specifically, the CO dimerization rate of Eu(OH)₃-Cu is significantly higher than that of CuO in the applied current density

interval of 100-500 mA cm⁻² (**Figure 6.6d**). This suggests that the doping of Eu enhances the formation efficiency of C₂₊ intermediates, such as *COCO, *COCHO and *COCO₂H, which further contributes to the electron selectivity in the production of C₂₊ products [383]. Overall, the kinetics of *CO formation is optimized by the stronger adsorption of *CO on Eu(OH)₃-Cu with hydroxide-metal interfacial sites as compared to undoped CuO. This enhancement contributes to the increase in the surface coverage of *CO, which in turn improves the reaction efficiency of C-C coupling to produce C₂₊ products, especially C₂H₄. Furthermore, Eu(OH)₃-Cu hybrid structure exhibits excellent electron selectivity and stability towards the formation of C₂H₄ and C₂₊ products. As shown in **Figure 6.5I** and **Table 6.2**, Eu(OH)₃-Cu outperforms most of the state-of-the-art Cu-based catalysts reported for electrochemical CO₂RR-to-C₂₊ in an alkaline gas-fed flow cell.

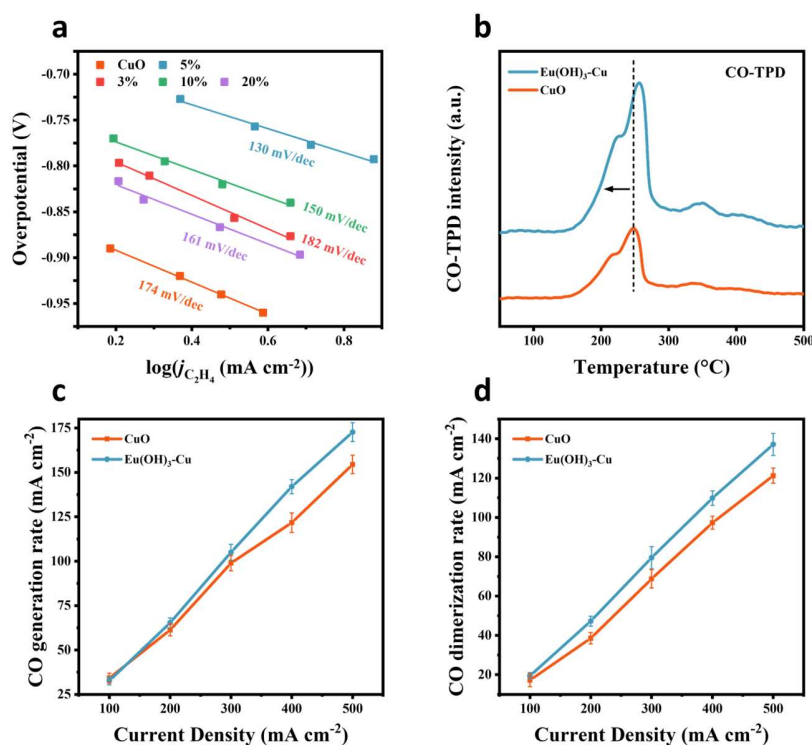


Figure 6.6: (a) Tafel plots of the C₂H₄ formation of CuO and Eu(OH)₃-Cu. (b) CO-TPD patterns of CuO and Eu(OH)₃-Cu. (c) CO generation and (d) CO dimerization rate between CuO and Eu(OH)₃-Cu at different current densities.

6.3.3 Compositional characterization before and after CO₂RR

When the electrocatalysts were activated by LSV within a wide potential range, it is found that CuO and Eu(OH)₃-Cu show a significant irreversible reduction peak between 0 and -0.6V when the current is first applied, which can be attributed to the reduction of Cu²⁺ to Cu⁺/Cu⁰ (错误!未找到引用源。).

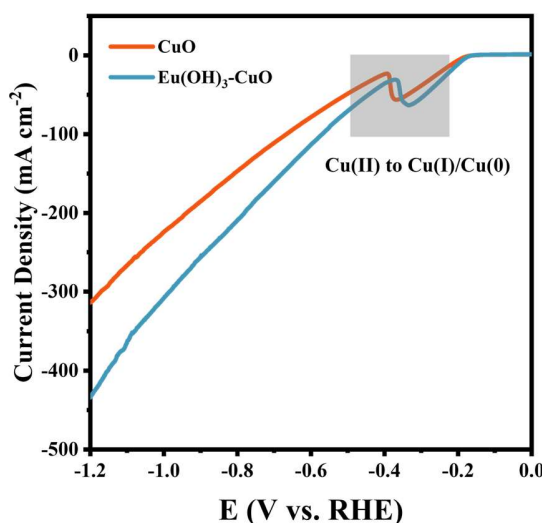


Figure 6.7: LSV of CuO and Eu(OH)₃-Cu in 1 M KOH by flow cell with iR-corrected

To obtain a deeper understanding of the observed changes in the phase and surface information of the electrode material under CO₂RR conditions, different material characterisation techniques are performed on the electrocatalyst before and after the electrochemical reaction. In this section, Eu(OH)₃-Cu refers to Eu(OH)₃-Cu-5%. Firstly, XRD patterns of the CuO and Eu(OH)₃-Cu samples loaded on carbon paper before and after CO₂ electrolysis were obtained. After conducting CO₂ electrolysis for 30 minutes in 1 M KOH at the current density of 400 mA cm⁻², the XRD pattern of CuO only retains the characteristic peaks of the metal Cu phase, indicating that the Cu²⁺ species were reduced to Cu⁰ species during the CO₂RR process (**Figure 6.8a**). Meanwhile, under the same electrochemical conditions, although the CuO phase in the Eu(OH)₃-Cu is also reduced to

the metal Cu phase, the Eu(OH)₃ phase remains stable during the CO₂RR process (**Figure 6.8b**). Subsequently, *in situ* hydroxide electrosorption (OH_{ads}) experiments were performed to probe the surface structure of CuO and Eu(OH)₃-Cu, as different facets of Cu exhibit distinct OH_{ads} peak at specific potentials. The OH_{ads} experiment avoids possible oxidation of the sample during exposure to air by *in situ* switching the gas feed, thus accurately capturing the change in the valence state of Cu in electrocatalysis under CO₂RR conditions. As indicated in the figure, the voltammogram of CuO and Eu(OH)₃-Cu shows a series of reversible peaks in the potential range of 0.30-0.50 V. These signal peaks can be attributed to the characteristics of low-index facets of the face-centred cubic (fcc) Cu, including (100): ~0.36 V, (110): ~0.43 V, and (111): ~0.45 V (**Figure 6.8c**) [384].

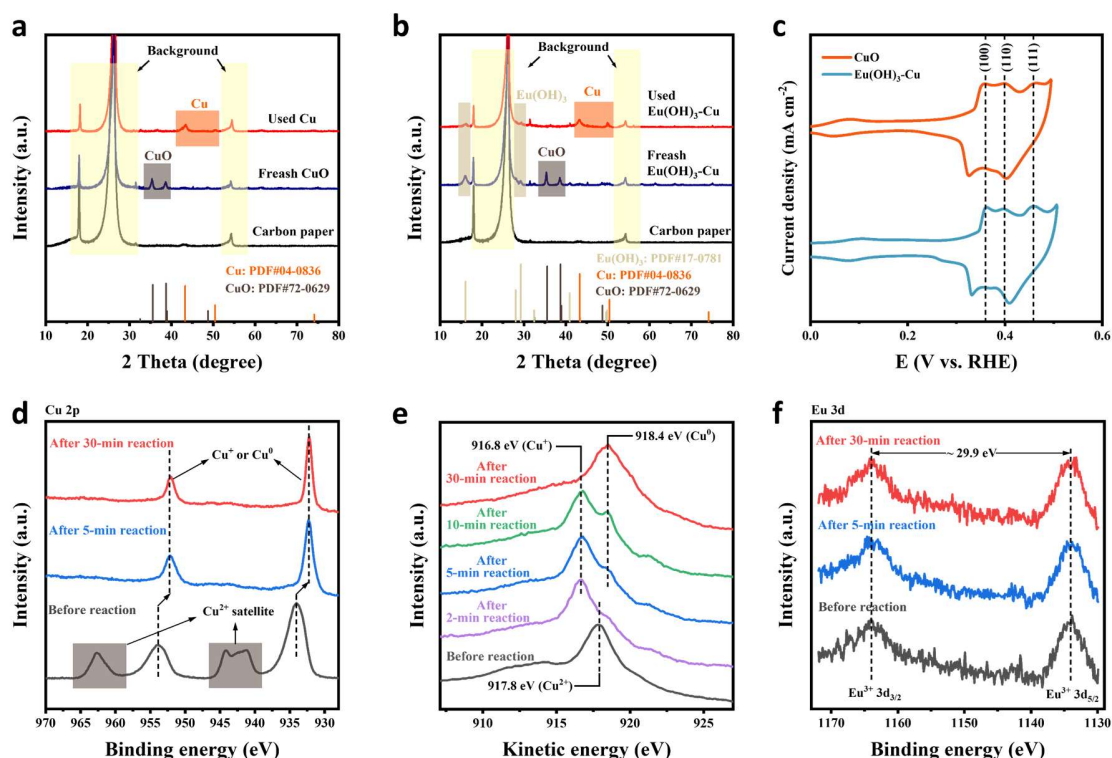


Figure 6.8: *Ex situ* characterizations of reconstructed electrocatalysts. (a) XRD patterns and carbon paper, fresh and used (a) CuO and (b) Eu(OH)₃-Cu. (c) Voltammograms of OH_{ads} peaks collected in an Ar-purged 1 M KOH batch cell. *Ex situ* (d) Cu 2p, (e) Cu LMM and (f) Eu 3d XPS spectra of Eu(OH)₃-Cu, analysed before and after differing CO₂RR times.

Furthermore, XPS studies of the reconstructed Eu(OH)₃-Cu hybrid material before and after different electrolysis times were carried out. Compared with the Eu(OH)₃-Cu before the CO₂RR, the Cu 2p spectrum of the reconstructed Eu(OH)₃-Cu after only 2-min electroreduction treatment cannot observe the Cu²⁺ satellite peak at 944.1 eV, indicating that there is no CuO. In addition, as the electrochemical reduction reaction time increases, the Cu 2p_{3/2} and Cu 2p_{1/2} peaks of Eu(OH)₃-Cu shift to a lower energy side, indicating that electrons are received by the catalyst surface. The shifted Cu 2p_{3/2} and Cu 2p_{1/2} peaks are located at 952.5 eV and 932.6 eV, which can be assigned to Cu⁺ / Cu⁰ (**Figure 6.8d**) [39]. To distinguish the ratio of Cu⁺ and Cu⁰ species, Cu LMM Auger spectra were collected before and after the reaction at 2, 5, 10 and 30 minutes to provide information on the Cu oxidation state. There are three main peaks in this series of Cu LMM Auger spectra, including Cu⁺ peak with a kinetic energy of 916.7 eV, Cu²⁺ peak with a kinetic energy of 917.8 eV, and Cu⁰ peak with a kinetic energy of 918.4 eV. In the early stages of the reaction (2-10 minutes), Cu⁺ and Cu⁰ species coexist on the surfaces of the two catalysts, and the proportion of Cu⁰ species gradually increases as the reaction proceeds. After the surface reconstruction through 10-minute electrolysis, only the Cu⁰ species of Eu(OH)₃-Cu remain, which is consistent with the XRD and OH_{ads} results (**Figure 6.8e**).

Interestingly, the comparison of Eu 3d region before and after the reaction showed that there was no significant shift in the Eu³⁺ 3d peaks during the 30-minute CO₂ electrolysis process. As shown in the figure, the two main peaks at 1134.5 eV and 1164.4 eV can be assigned to Eu³⁺ 3d_{5/2} and 3d_{3/2}, respectively. Besides, the spin-orbit splitting energy (= 29.9 eV) between the 3d_{5/2} and 3d_{3/2} states of Eu³⁺ is consistent with the reported

splitting energy in Eu₂O₃ (**Figure 6.8f**) [385]. These Eu 3d spectra show that the Eu³⁺ in Eu(OH)₃ maintains excellent electrochemical stability during the CO₂RR process.

6.3.4 *In situ* spectroscopic analysis of CO₂RR over Eu(OH)₃-Cu catalyst

The difference in interfacial electrochemical kinetics between CuO and Eu(OH)₃-Cu during electrocatalysis was investigated by *in situ* EIS. As illustrated in **Figure 6.9a** and **b**, the Bode phase plots of CuO and Eu(OH)₃-Cu were obtained as frequency-dependent for a potential range from −0.16 V to −0.96 V. For *in situ* EIS testing in CO₂ electrolysis, with the applied potential moving more negatively, the peak of the phase angle (φ) in the Bode plot gradually shifts to higher-frequency region, along with a decrease in the peak intensity. For CuO, the phase angle changes gradually when the applied potential is between −0.16 V and −0.46 V. When the potential is more negative than −0.46 V, the phase angle decreases rapidly, suggesting that the faradaic resistance decreases and the surface reaction rate increases, indicating that electrocatalytic reduction begins. Meanwhile, a similar trend is observed in the Bode phase plot of Eu(OH)₃-Cu. However, compared with CuO (−0.56 V), the inflection point of the phase angle change of Eu(OH)₃-Cu shifts to an applied potential of approximately −0.46 V, indicating an advance in the electroreduction behaviour [386]. This finding confirms that Eu(OH)₃-Cu has a lower onset potential.

To explore the mechanism of Eu(OH)₃-Cu in improving the selectivity of C₂₊ products during CO₂RR, *in situ* FTIR was performed by three-electrode electrochemical cell. Specifically, time-dependent *in situ* FTIR was performed on undoped CuO and Eu(OH)₃-Cu at −1 V vs RHE. The state of different reaction intermediates on the surfaces of the two catalysts was detected, especially those of C-C coupling. As shown in **Figure 6.9c**, for CuO NS, only four major intermediate species are observed. First, the broad and strong IR

bands at 1640 and 1380 cm⁻¹ are attributed to the H-O-H bending mode of adsorbed H₂O and bidentate carbonate (b-CO₃²⁻) [387, 388]. These are formed by the adsorption of CO₂ and H₂O on the electrode surface. With increasing electrolysis time, a characteristic IR peak attributable to *COOH was detected at 1260 cm⁻¹ [369]. The COOH* species is a typical reaction intermediate in the CO₂ reduction to hydrocarbons. Generally, during the CO₂RR process, CO₂ molecules are first activated to form *COOH, which is then further converted to *CO. The resulting *CO can either desorb or combine with other intermediate species to form different products. In addition, the IR band at 1560 cm⁻¹ can prove the existence of *OCCHO species, which is a key intermediate in C₂₊ product formation. [370].

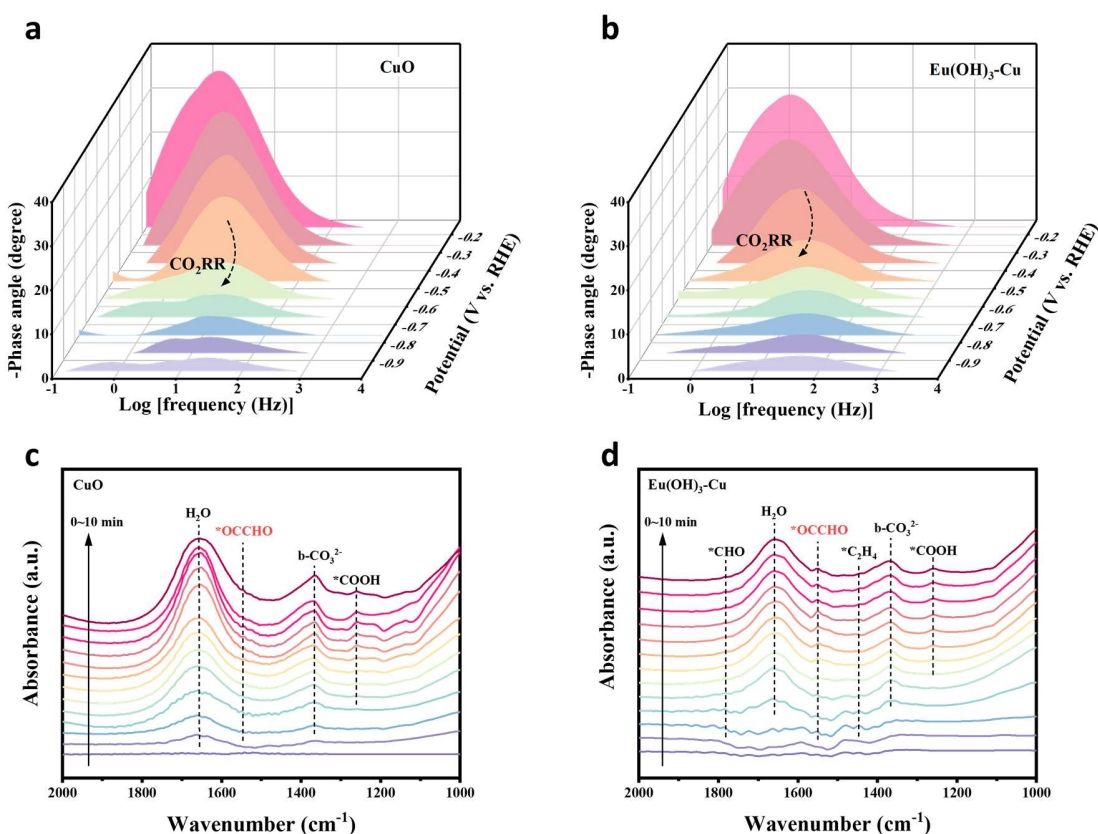


Figure 6.9: Operando EIS plots from -0.16 to -0.96 V vs. RHE (without iR compensation) of (a) CuO and (b) Eu(OH)₃-Cu with a frequency range from 0.1 Hz to 10 kHz. Time-dependent electrochemical *in situ* FTIR measurements of (c) CuO and (d) Eu(OH)₃-Cu at a potential of -1 V vs. RHE. All spectroscopic tests were conducted in a CO₂-saturated 1 M KHCO₃ solution over 10-min CO₂ electrolysis.

Compared with undoped CuO, the type and intensity of the bands in the *in situ* FTIR of the Eu(OH)₃-Cu hybrid material have changed. Similarly, the adsorption of CO₂ and H₂O caused the appearance of IR bands attributable to H₂O and b-CO₃²⁻ on the surface of Eu(OH)₃-Cu. Moreover, compared with CuO (**Figure 6.9d**), the relative intensity of the characteristic peak of the *OCCHO intermediate at 1560 cm⁻¹ is significantly enhanced. This indicates that the construction of the Eu(OH)₃-Cu hybrid structure facilitates the *OCCHO intermediate on the catalyst surface and enhances the efficiency of C-C coupling [370]. This conclusion is in line with the above experimental results that Eu(OH)₃-Cu has higher C₂₊ product selectivity. The *OCCHO species is reported to be a reaction intermediate formed by the asymmetric coupling of *CO and *CHO species. Given that peaks of the *COOH and *CHO intermediates are observed at 1260 cm⁻¹ and 1780 cm⁻¹, it is speculated that part of the reaction mechanism of CO₂ reduction to C₂₊ products can be expressed as follows: CO₂ → *COOH → *CO → *CO + *CHO → *COCHO [44, 369]. Subsequently, a weak peak at 1446 cm⁻¹ that can be attributed to *C₂H₄ are also observed, which indicates the formation of C₂H₄ [372]. This characteristic peak, which is not detected in above *in situ* FTIR on undoped CuO, demonstrates that the introduction of the Eu(OH)₃ component is beneficial to the CO₂RR-to-C₂H₄ process.

6.3.5 DFT calculations of CO₂RR on Eu(OH)₃-Cu catalyst

To further confirm the above conclusion, DFT calculations are conducted to comprehensively understand the reaction mechanisms and structure-function relationships of the Eu(OH)₃-Cu in the CO₂RR-to-C₂₊ product process. Although the Cu (100) and Cu (111) facets are observed in *ex situ* XRD patterns, based on previous experimental and theoretical studies, the Cu (100) facet is more favourable for the generation of C₂₊ products,

as it has a lower C-C coupling energy barrier compared to the Cu (111) facet [217]. Therefore, by combining the structural features obtained from *ex situ* XPS and XRD, simplified models of the Cu (100) and Eu(OH)₃/Cu (100) are constructed to represent the undoped Cu and Eu(OH)₃-Cu, respectively (**Figure 6.10**).

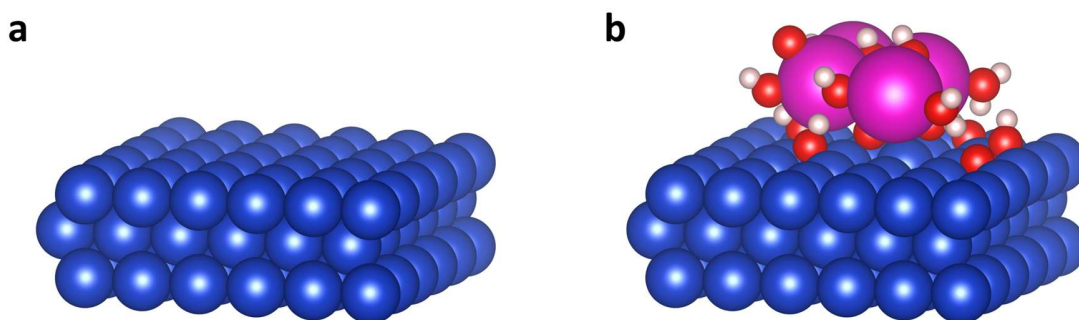


Figure 6.10: Schematic structures of (a) Cu (111) and (b) Eu(OH)₃-Cu (Eu(OH)₃ cluster/Cu (100)). The atoms in blue, pink, white, and red represent Cu, Eu, H and O, respectively.

Firstly, the HER performance of the Cu and Eu(OH)₃-Cu catalysts was evaluated. By comparing the hydrogen adsorption-desorption free energies, it is found that the absolute value of $\Delta G(H)$ for Eu(OH)₃-Cu (0.24 eV) is higher than that of the undoped Cu (0.10 eV) (**Figure 6.11a**). This indicates that the Eu(OH)₃-Cu catalyst suppresses HER activity and reduces the selectivity for H₂ production, which is consistent with the electrochemical testing results. Moreover, the discussion on the adsorption of the *CO intermediate are extended by calculating the adsorption energy of *CO on Cu and Eu(OH)₃-Cu (**Figure 6.11b**). The results indicated that the *CO intermediate is more strongly adsorbed on Eu(OH)₃-Cu than on Cu, which is consistent with the analysis from CO-TPD and the calculated CO generation rates. The higher adsorption energy of *CO on the Eu(OH)₃-Cu makes *CO more difficult to desorb, thereby reducing the electron selectivity for C₁ products, such as CO. Additionally, the increased adsorption energy of *CO enhances the

probability of protonation and C-C coupling, facilitating the formation of various hydrocarbons, such as C₂H₄.

Further, the factors contributing to the enhanced selectivity of CO₂RR-to-C₂₊ products on Eu(OH)₃-Cu and the specific C-C coupling pathways are investigated. To obtain a more rigorous mechanism of C₂₊ product generation, the reaction energy barriers of the four most widely accepted C-C coupling pathways (*CO-*CO, *CO-*CHO, *CO-*COH, and *CHO-*CHO) are compared. The formation of C₂₊ products via the *CO-*COH pathway is difficult since the energy barrier for the hydrogenation of *CO to form *COH (0.84 eV) is much higher than that for the formation of *CHO (0.36 eV) (**Figure 6.11c** and **Figure 6.12**). For the symmetric *CO-*CO and *CHO-*CHO coupling pathways, Eu(OH)₃-Cu exhibits high free energy barriers of 1.68 eV (*CO+*CO to form *OCCO) from **Figure 6.11d** and 0.81 eV (*CO to form *CHO+*CHO) from **Figure 6.11e**, respectively. Interestingly, as shown in **Figure 6.11f**, for asymmetric *CO-*CHO coupling pathway, Cu and Eu(OH)₃-Cu exhibit relatively low energy barriers of 0.14 eV and 0.12 eV, respectively (**Figure 6.13** and **Figure 6.14**).

In short, based on the comparison of four C-C coupling pathway calculations, the asymmetric *OCCHO coupling path predominates the CO₂RR-to-C₂₊ product process. This conclusion aligns with the previously mentioned *in situ* FTIR observations and corresponding interpretations. Additionally, by comparing the free energy diagrams of the *OCCHO coupling pathway for undoped Cu and Eu(OH)₃-Cu, it is evident that the doping of Eu can lower the C-C coupling energy barrier and stabilize the key intermediate *OCCHO, which facilitates the formation of C₂₊ products. This is consistent with the product distribution from the electrocatalytic performance tests.

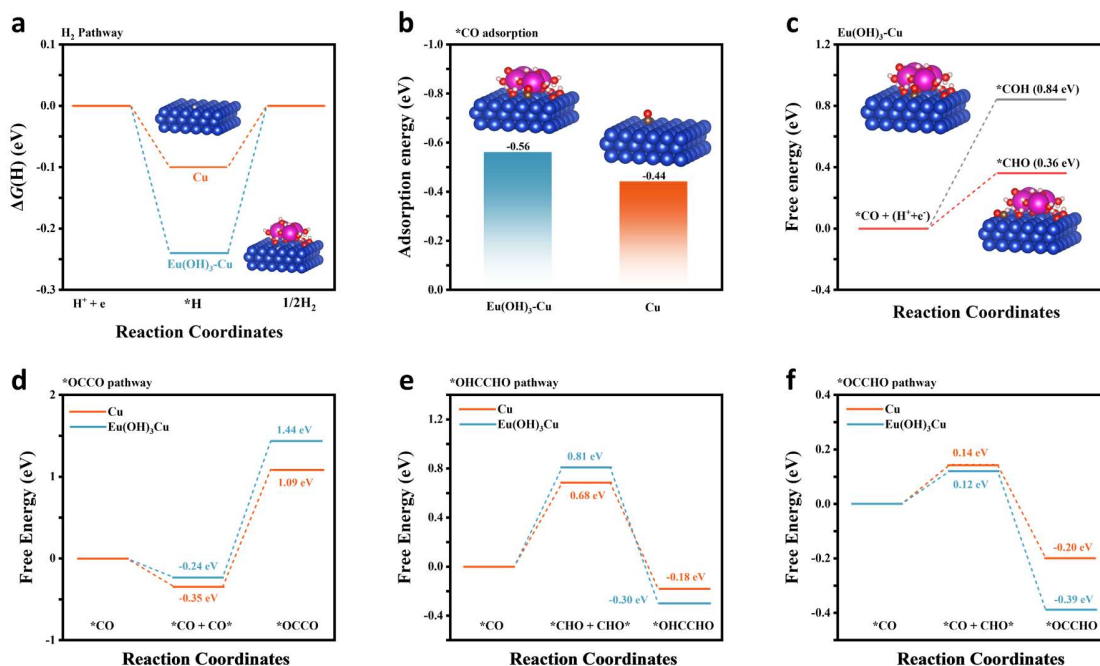


Figure 6.11: (a) Gibbs free energy diagram of hydrogen ad-desorption and (b) the adsorption energy of *CO on CuO and Eu(OH)₃-Cu. (c) Gibbs free energy diagram for the hydrogenation of *CO to *CHO or *COH on Eu(OH)₃-Cu. Insets illustrate the geometries of the corresponding intermediates (*H , *CO , *COH and *CHO) on CuO and Eu(OH)₃-Cu. The atoms in blue, pink, brown, white, and red represent Cu, Eu, C, H and O, respectively. Gibbs free energy diagram for C-C coupling reactions: (d) two *CO forming *OCO , (e) two *CHO forming *OHCCHO and (f) *CO and *CHO forming *OCCHO on undoped CuO and Eu(OH)₃-Cu.

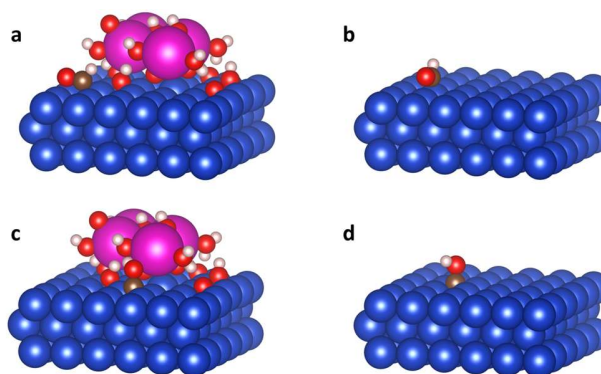


Figure 6.12: The geometries of the corresponding *CHO intermediates on (a) Eu(OH)₃-Cu and (b) Cu, and *COH intermediates on (c) Eu(OH)₃-Cu and (d) Cu. The atoms in blue, pink, brown, white, and red represent Cu, Eu, C, H and O, respectively.

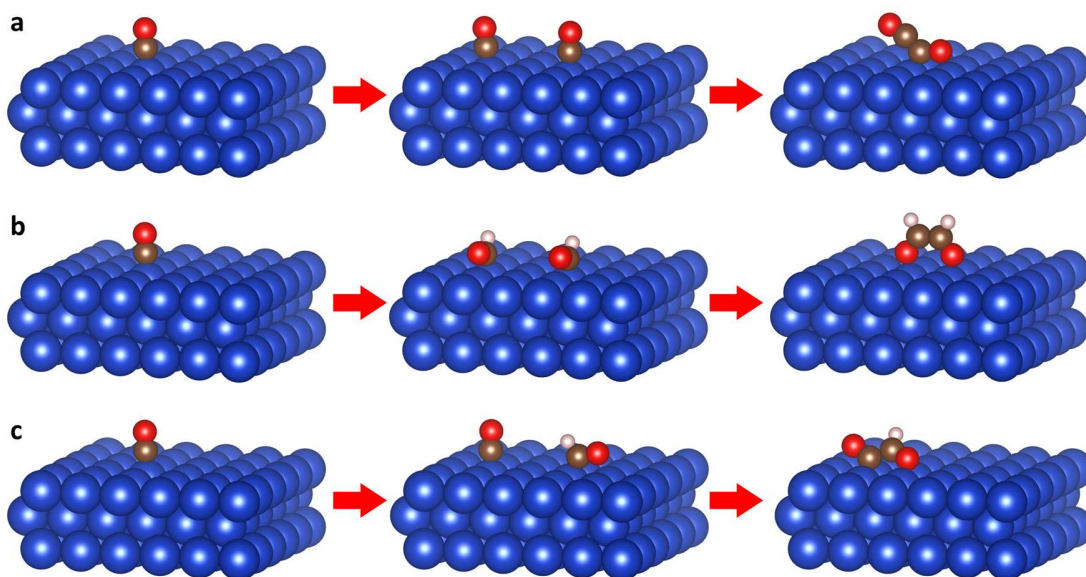


Figure 6.13: The geometries of the corresponding (a) $\ast\text{CO}-\ast\text{CO}$, (b) $\ast\text{CHO}-\ast\text{CHO}$ and (c) $\ast\text{CO}-\ast\text{CHO}$ coupling pathways on Cu without Eu doping. The atoms in blue, brown, white, and red represent Cu, C, H and O, respectively.

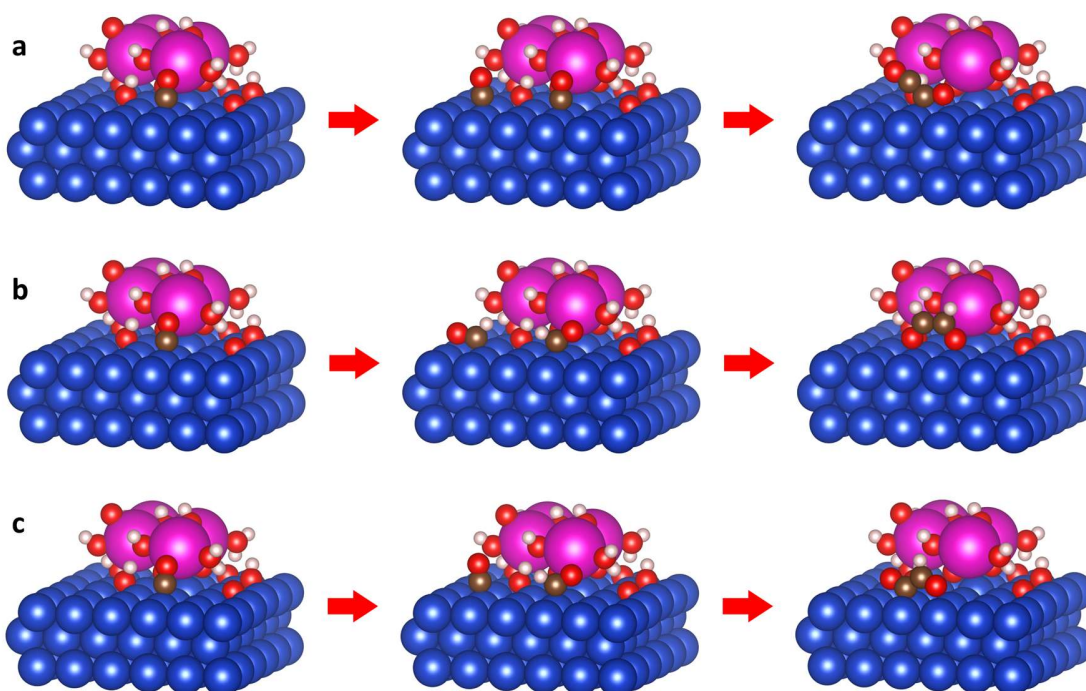


Figure 6.14: The geometries of the corresponding (a) $\ast\text{CO}-\ast\text{CO}$, (b) $\ast\text{CHO}-\ast\text{CHO}$ and (c) $\ast\text{CO}-\ast\text{CHO}$ coupling pathways on $\text{Eu}(\text{OH})_3\text{-Cu}$. The atoms in blue, pink, brown, white, and red represent Cu, Eu, C, H and O, respectively.

6.4 Summary

In summary, this work has explored an innovative application of Europium hydroxide modified oxide-derived CuO (Eu(OH)₃-Cu) nanosheet with hybrid hydroxide-metal interface for CO₂ electroreduction into valuable C₂₊ products with industrial-current-density. The Eu(OH)₃-Cu-5% catalyst demonstrates the peak FE of 81.4% at partial current density of 326 mA cm⁻², outperforming undoped CuO nanosheets. Additionally, while CuO component suffers from rapid cathodic corrosion and can be reduced to Cu(0) after CO₂RR, the Eu(OH)₃ component exhibits remarkable durability, maintaining the phase stability at a current density of 400 mA cm⁻² in 1 M KOH by flow cell. Moreover, this modified catalyst significantly enhances *CO generation and dimerization rates, leading to the stable adsorption of *CO intermediates and efficient formation of C₂₊ products. *In situ* EIS and FTIR analyses indicate that this hybrid catalyst has a lower onset potential for CO₂RR and facilitates the accumulation of *OCCHO intermediates, crucial for enhancing C₂₊ product formation. Notably, DFT studies demonstrate that the Eu(OH)₃-Cu catalyst, characterized by enhanced local coverage of *CO, favours the protonation of *CO to *CHO and *CO-*CHO asymmetric coupling pathway to *OCCHO, leading to highly selective C₂₊ product formation. The findings of this study indicate that engineering the hydroxide-metal interface is a significant advancement in electrocatalysis. This novel approach not only enhances the selectivity and stability of electrocatalysts for CO₂ electroreduction to C₂₊ products but also substantially improves the operational stability of the catalytic system at industrial current densities.

Chapter 7 Conclusions and Future Work

This chapter presents a thorough summary of the entire thesis, emphasizing the key findings and outlook. In Section 7.1, the combination of experimental and computational results illustrates the successful construction of advanced electrocatalysts for electrochemical CO₂RR to value-added products from C₁ to C₂₊ products. Moreover, a comprehensive and detailed investigation of structure-function relationships and reaction mechanisms has been conducted. The findings and contributions presented offer valuable insights into the future design and evaluation of high-performance electrocatalysts for CO₂RR. Additionally, in Section 7.2, the limitations of current studies are addressed, along with recommendations for future electrochemical CO₂RR research directions. Through these suggestions, this project aims to steer subsequent research efforts, ultimately advancing sustainable technologies to combat climate change and energy crisis.

7.1 Conclusions

This thesis focused on applying different design strategies to construct highly active and selective transition metal electrocatalysts for CO₂RR to various products, such as CO, CH₄ and C₂H₄. Detailed reaction mechanisms of CO₂RR-to-products, including specific reaction pathways and carbon-containing intermediate state are investigated. Furthermore, the above work successfully established and analysed the relationship between different reaction intermediates (*COOH, *H, and *CO) and the electrocatalytic product distribution in this thesis. In **Chapter 4**, synergistic engineering of heteronuclear Ni-Ag dual-atom catalysts for high-efficiency CO₂ electroreduction with nearly 100% CO selectivity is achieved. Next, in **Chapter 5**, adsorbed hydrogen on lanthanum-modified CuO_x is

manipulated for CO₂ electroreduction to C₂₊ products or CH₄ at total industrial-current-density over 300 mA cm⁻² with the FE of 80.4% and 61.4% respectively. Moreover, based on previous studies, the performance of CO₂ electroreduction to C₂₊ products is further improved with higher electron selectivity of 81.4% alongside a substantial partial current density of 326 mA cm⁻² on the synthesized Eu(OH)₃-Cu nanosheet catalysts via tuning of *CO affinity in **Chapter 6**. The detailed conclusions for each chapter are elaborated below.

(1) Heteronuclear dual-atom catalysts of Ni and Ag supported on a nitrogen-rich porous carbon matrix (Ni-Ag/PC-N), with a confirmed configuration of N₃-Ni-Ag-N₃, were synthesized for efficient CO₂RR-to-CO. The Ni-Ag/PC-N catalyst showed a high CO Faradaic efficiency exceeding 90% across a potential range of -0.7 to -1.3 V, peaking at 99.2% at -0.8 V vs. RHE. Tafel analysis indicated that the formation of *COOH intermediates is the rate-determining step, highlighting the catalyst's superior electrokinetic performance. *In situ* infrared and Raman spectroscopies revealed enhanced formation of *COOH and improved mass transfer. DFT calculations underscored the electrocatalyst's outstanding activity and the synergistic effects arising from the interaction of dual atoms. The neighbouring Ni atom lowers the energy barrier for *COOH formation, aiding *CO desorption, while the adjacent Ag atom alleviates *CO poisoning by diminishing its strong adsorption to Ni sites.

(2) Lanthanum-modified CuO_x bimetallic catalysts with tailored surface hydrogen adsorption, including La_{0.10}-CuO_x and La_{0.40}-CuO_x, were systematically synthesized for controllable CO₂RR-to-CH₄/C₂₊ products. The OD-La_{0.10}-CuO_x demonstrated a Faradaic efficiency exceeding 80% for C₂₊ products at a current density of 300 mA cm⁻², while OD-La_{0.40}-CuO_x, featuring higher La doping, achieved 61.4% Faradaic efficiency for CH₄ at

400 mA cm⁻². Kinetic isotope experiments and *in situ* spectroscopy confirmed that H₂O dissociation capacity on the Cu/La catalysts varied with La doping, influencing the pathways for producing C₂₊ products or CH₄. DFT calculations indicated that OD-La_{0.10}-CuO_x has a moderate H₂O dissociation capacity, reducing the energy barrier for *OCCHO formation, which enhances C₂₊ product yields. Conversely, OD-La_{0.40}-CuO_x showed high H₂O dissociation capacity, providing sufficient *H for *CHO hydrogenation to *CH₂O, thus favouring CH₄ production. This study demonstrates a strategic approach to tailor CO₂RR pathways and products by manipulating surface-adsorbed hydrogen through varied doping levels in copper electrocatalysts.

(3) Eu(OH)₃-modified oxide-derived CuO nanosheets, denoted as Eu(OH)₃-Cu, were investigated as an advanced electrocatalyst for CO₂RR-to-C₂₊ products through enhanced local *CO coverage and improved *COCHO formation. The Eu(OH)₃-Cu catalyst significantly improves the selectivity for multi-carbon products, achieving the Faradaic efficiency of 81.4% and the partial current density of 326 mA cm⁻² in 1 M KOH, outperforming undoped CuO nanosheets. While the CuO component is prone to rapid cathodic corrosion, the Eu(OH)₃ component exhibits exceptional durability and stability, maintaining its performance at a current density of 400 mA cm⁻² in a flow cell. DFT calculation and *in situ* electrochemical impedance and infrared spectroscopy indicate that this hybrid system features a lower onset potential and increased accumulation of asymmetric *OCCHO intermediates, crucial for facilitating C₂₊ product formation. This interface engineering approach holds significant promises for enhancing the selectivity and stability of catalytic systems aimed at CO₂ electroreduction to C₂₊ products.

7.2 Future work

Despite great advancements that have been achieved for effective CO₂RR to value-added products in this thesis, there are still significant challenges to be overcome to move this clean technology from the lab to fab, which are listed as the following.

(1) Real-time visualization of CO₂ electrolysis by *in situ* TEM

In CO₂RR, the cathodic catalysts typically undergo reconstruction due to applied potentials [389-399]. Elucidating these structural changes is essential for comprehending CO₂RR mechanisms, as they correlate with catalyst activation/deactivation [397] and structure-function relationships [395]. However, conventional *in situ* characterizations are limited in providing intuitive and precise information regarding alterations in catalyst morphology, components, valence states, and phase structure during CO₂ electrolysis. To address these limitations, *in situ* TEM techniques have been developed.

In situ liquid cell TEM (LC-TEM) systems leverage microelectromechanical system (MEMS) micromachining to fabricate a nano-laboratory within the sample stage, enabling time-resolved observations in liquid or gaseous environments incorporating heating and/or biasing the sample. For CO₂RR studies, potentials are applied through MEMS chips to simulate authentic CO₂ electrolysis conditions. When integrated with various state-of-the-art analytical techniques, such as electron energy loss spectroscopy (EELS) [400], SAED [401], and EDS [402], these advanced *in situ* or operando LC-TEM or liquid cell scanning TEM methodologies provide valuable insights into dynamic structural evolution, structure-function relationships and activation/deactivation mechanisms in CO₂RR through direct visualization of the electrocatalytic processes.

(2) Upgrade electrolysis system by coupling alternative anode reactions

Currently, most research on CO₂RR emphasizes the cathodic part, while relatively little attention has been paid to the anodic part. The traditional CO₂RR processes are typically coupled with oxygen evolution reactions (OER) at the anode, which have high theoretical onset potential (1.23 V), and low energy utilization efficiency compared to the cathodic reaction [403]. To reduce overall energy consumption, it is essential to investigate alternative anodic oxidation reactions with lower energy requirements. When conducting this upgrade electrolysis research, various factors under different reaction conditions must be considered. Among these, the selection of anodic catalyst designs are critical directions. Optimizing these variables will not only reduce energy input but also enhance the overall product value of CO₂RR [404]. Thus, a thorough exploration of how to maximize reaction efficiency and product value through appropriate anode materials and conditions will provide important theoretical insights and practical guidance for advancing CO₂RR.

For upgrade electrolysis system design by coupling alternative anode reactions, the anodic reaction should be analysed from the perspectives of energy conservation and economic efficiency. For example, electro-oxidation reactions for wastewater treatment and fine chemical synthesis may serve as alternatives to the anodic OER, including the urea oxidation reaction [405], hydrazine oxidation reaction [406] and methane oxidation reaction [407]. Moreover, with the continuous progress of organic electro-oxidation reactions, more research is focusing on the coupling of important organic molecule oxidation reactions, such as benzyl alcohol [408], 5-hydroxymethylfurfural [409] and 3-hydroxy decanoic acid [410], which can produce higher value-added organic chemicals compared to OER.

(3) Mitigation of carbonate issues by applying acidic electrolyte

Previous studies on CO₂RR have demonstrated high current density and Faradaic efficiency in alkaline and neutral electrolytes using flow cells [37, 42]. These impressive performances are largely attributed to the suppression of HER. However, in traditional alkaline or neutral electrolytes, CO₂RR suffers from severe carbon loss, resulting in the single-pass carbon conversion efficiency (SPCE) of less than 50% for CO₂. Specifically, alkaline electrolytes can absorb CO₂, leading to the low SPCE of CO₂. The formation of KHCO₃ crystals in the GDE near the flow channel can result in flooding of the GDE and a permanent loss of hydrophobicity, posing significant challenges to long-term stability [411]. Additionally, neutral electrolytes can result in higher ohmic and anodic energy losses compared to acidic conditions, leading to approximately 14% greater total energy consumption [412].

The reliance on alkaline and neutral electrolytes is not a sustainable long-term solution for the future commercial application of CO₂RR. Acidic CO₂RR process can theoretically address CO₂ loss and carbonate issues. For example, the Sargent group demonstrated a high carbon efficiency of 77% at a pH of 0.8, utilizing 1 M H₃PO₄ and 3 M KCl, which significantly surpasses the benchmark carbon utilization efficiency observed in neutral and alkaline solutions [413]. However, the activity of current acidic CO₂RR catalysts remains relatively low, primarily due to the competition of HER. While high Faradaic efficiency can be attained for C₁ products such as CO and HCOOH, the selectivity for high value-added C₂₊ products remains unsatisfactory. The challenges associated with acidic CO₂RR can be categorized into several key areas: degradation of electrode, low FE of target products, unclear acidic CO₂RR mechanism, and high full-cell voltage [414].

(4) Direct electroreduction of CO₂-loaded capture agents

Integration of electrochemical CO₂ capture and conversion by direct electrolysis of CO₂ capturing solution are increasingly demonstrating their advantages. Compared to traditional independent methods, this innovative approach offers clear benefits by eliminating the need for costly recovery and compression steps associated with the capture medium [415, 416]. Many amine-based CO₂ capture technologies, which involve the absorption of CO₂ using an amine capturing solution, are already being applied in industrial settings [417]. For instance, CO₂ can be captured through nucleophilic reactions with diamines, alkylamines, and their derivatives to form the corresponding carbamates [418].

Sullivan et al. have summarized the various system types for coupling electrochemical capture and conversion. Type-I (Independent): In this configuration, CO₂ capture, and conversion processes operate independently. The captured CO₂ is stored and utilized separately, allowing for flexibility in approach. However, this type requires complete separation of two processes due to incompatible operating temperatures. Type-II (Subsequent): This configuration involves local coupling of the capture and conversion processes. CO₂ is still the reactant for conversion, but there is a need to match the flux between the capture and conversion processes to optimize performance. Various technologies, such as electrochemically mediated amine regeneration and redox active carriers, can be employed in this setup. Type-III (Fully Integrated): This approach integrates CO₂ capture and conversion processes, allowing for the direct electroreduction of CO₂-loaded capture agents. By bypassing the traditional steps of CO₂ release and capturing media regeneration, Type-III configurations can potentially enhance energy efficiency and lower the overall costs of reduced products [418].

Appendix

Supporting Figures

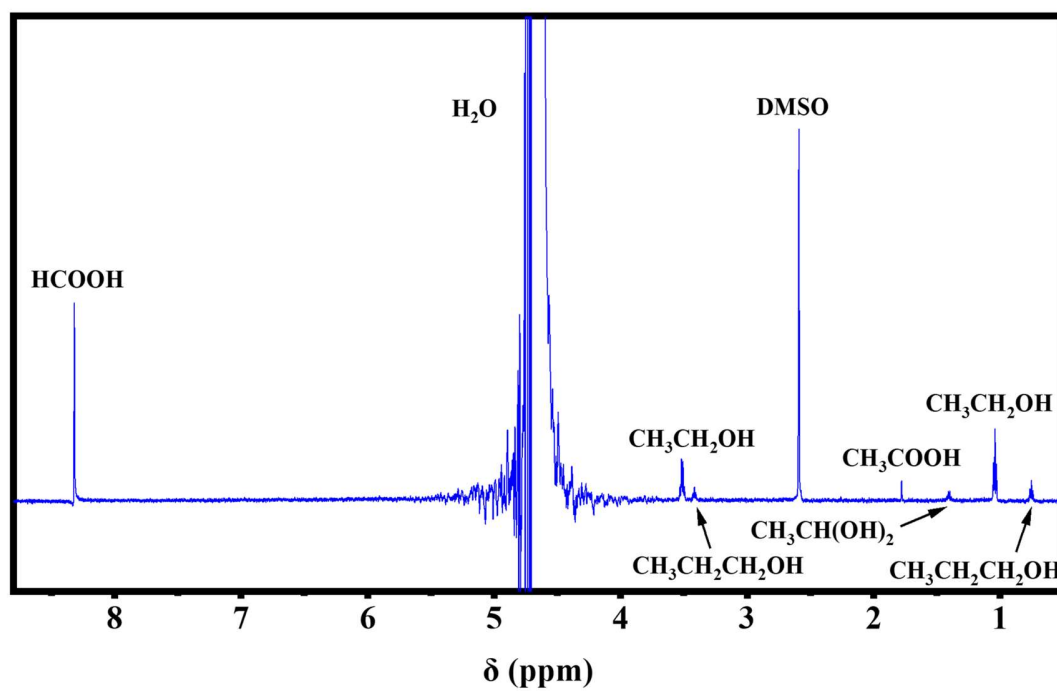


Figure A 1: Representative ^1H NMR spectrum of the standard solution containing the liquid product mixture.

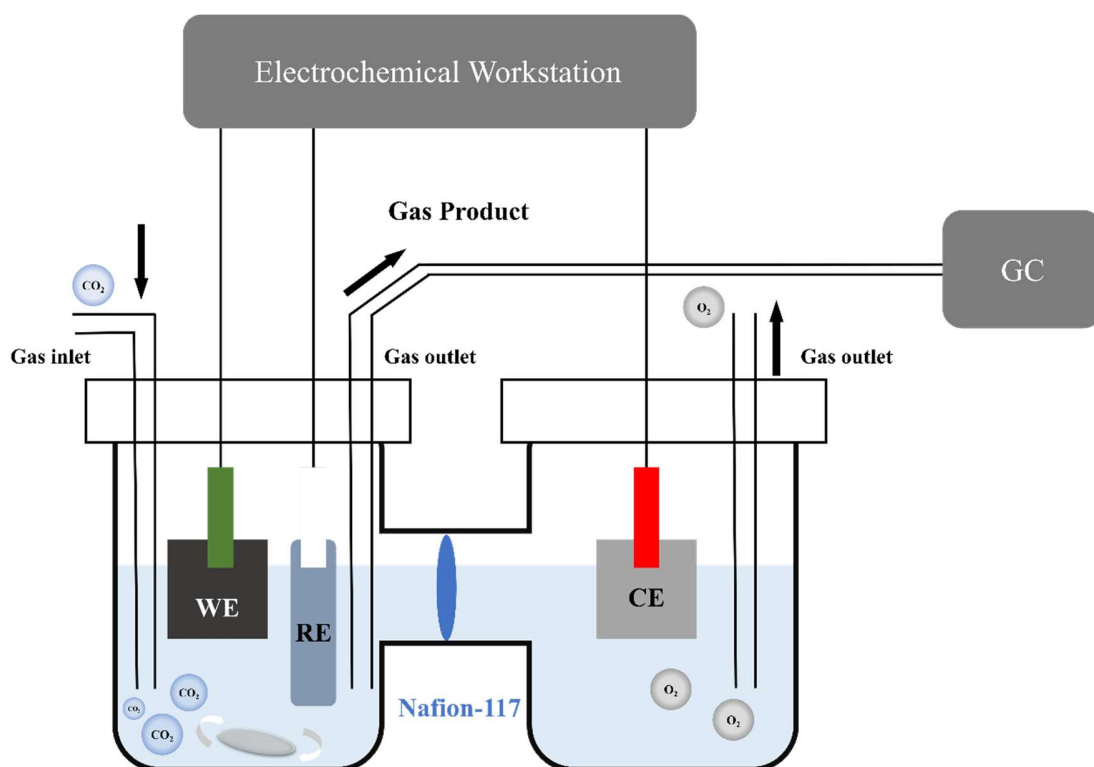


Figure A 2: A schematic representation of the gastight H-type electrolytic cell used for CO₂RR test.

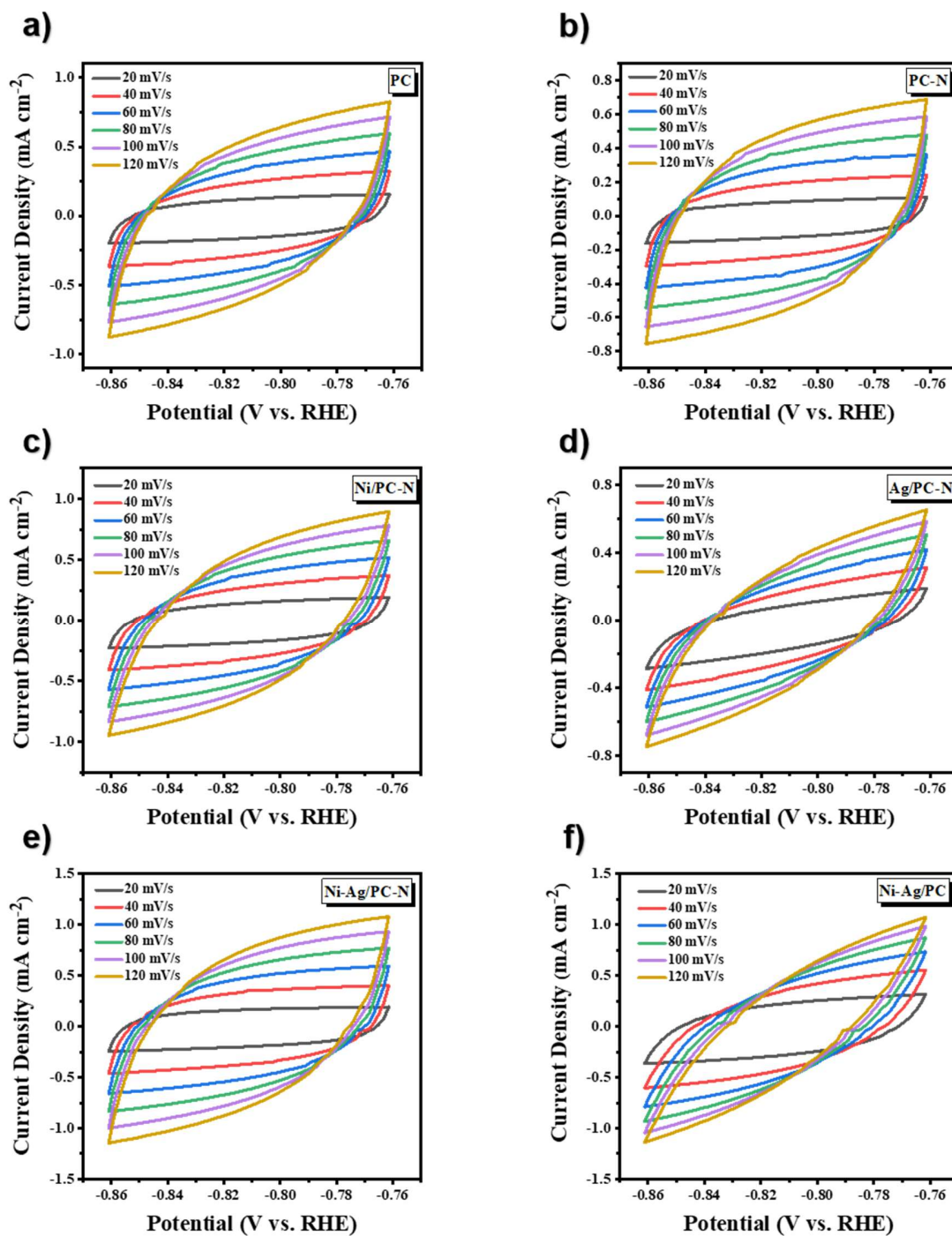


Figure A 3: Cyclic voltammograms recorded at (a) PC, (b) PC-N, (c) Ni/PC-N, (d) Ag/PC-N, (e) Ni-Ag/PC-N and (f) Ni-Ag/PC electrodes between -0.86 ~ -0.76 V vs RHE at different scan rates of 20 ~ 120 mV s^{-1} .

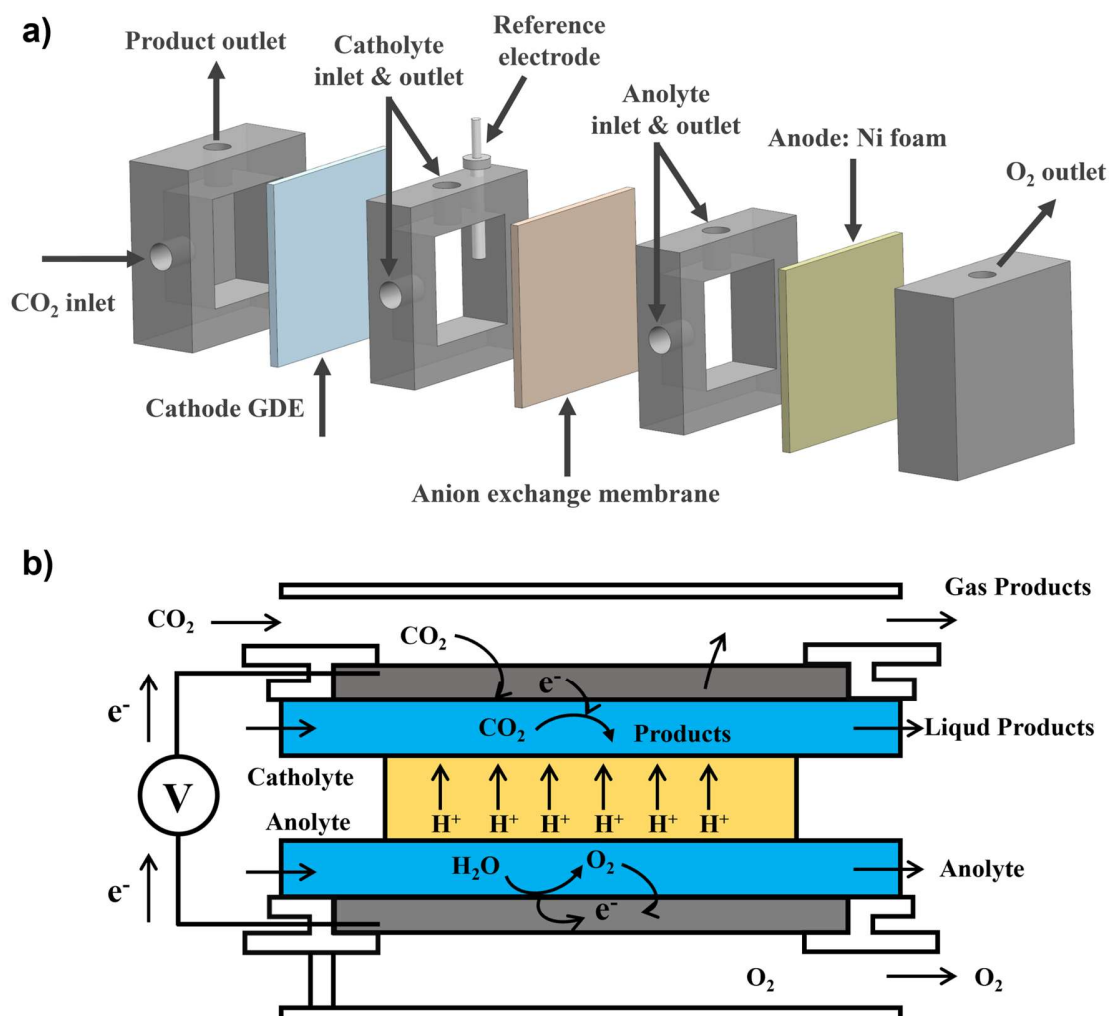


Figure A 4: The electrochemical gas-fed flow cell utilized for CO₂RR testing in this study: (a) exploded view; (b) cross-sectional diagram.

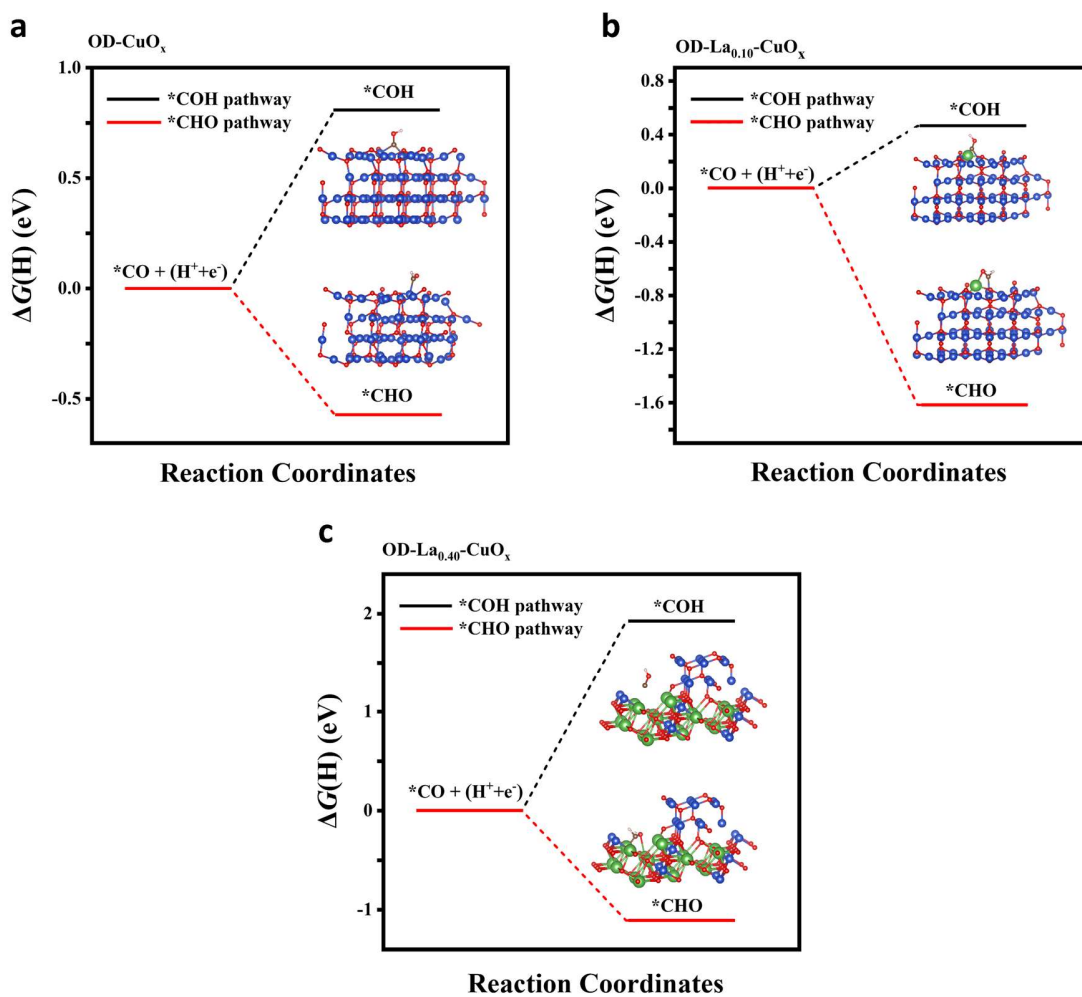


Figure A 5: Gibbs free energy diagram for the hydrogenation of *CO to *CHO or *COH on (a) OD-CuO_x without La doping, (b) OD-La_{0.10}-CuO_x, and (c) OD-La_{0.40}-CuO_x. Insets illustrate the geometries of the corresponding intermediates (*COH and *CHO) on OD-CuO_x without La doping, OD-La_{0.10}-CuO_x, and OD-La_{0.40}-CuO_x. The atoms in blue, green, red, brown and pale pink represent Cu, La, O, C and H, respectively.

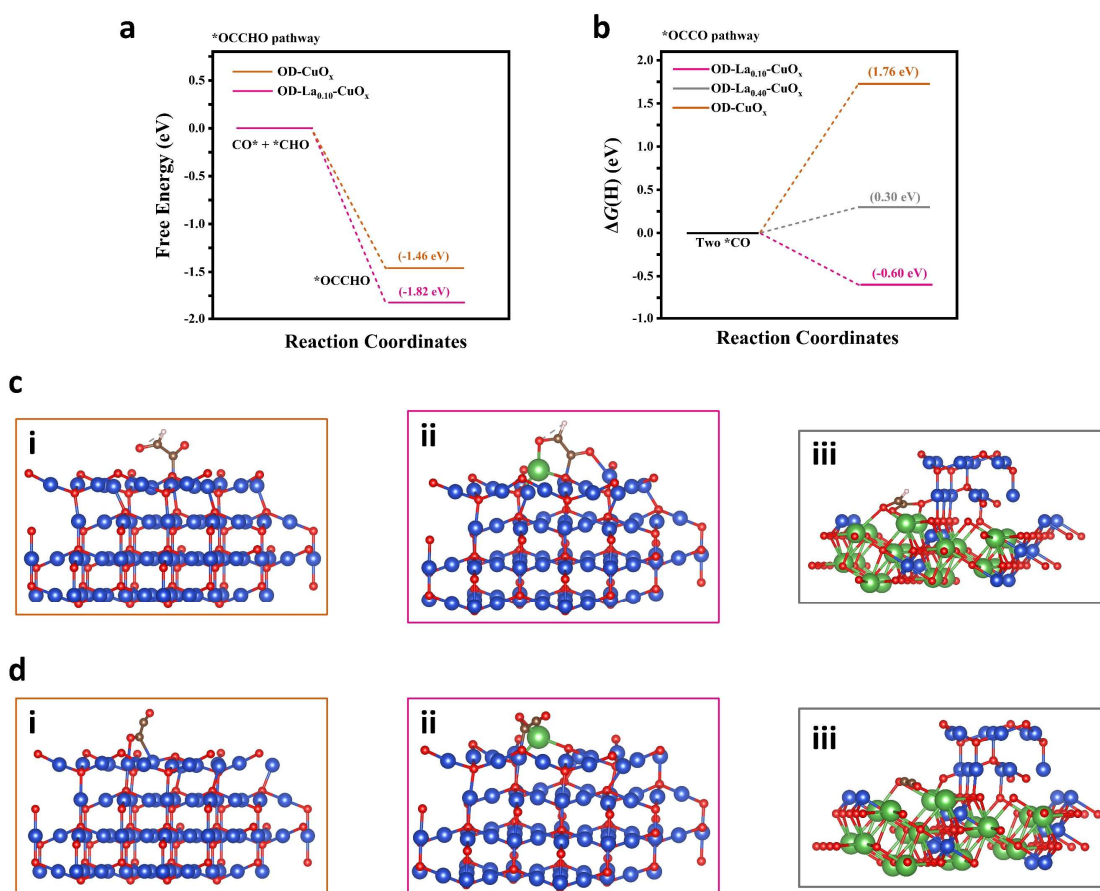


Figure A 6: Gibbs free energy diagram for C-C coupling reactions: (a) $^*\text{CO}$ and $^*\text{CHO}$ forming $^*\text{OCCHO}$, and (b) two $^*\text{CO}$ forming $^*\text{OCCO}$, on OD-CuO_x without La doping and OD-La-CuO_x. The geometries of the corresponding (c) $^*\text{OCCHO}$ and (d) $^*\text{OCCO}$ intermediates on i: OD-CuO_x, ii: OD-La_{0.10}-CuO_x, and iii: OD-La_{0.40}-CuO_x. The atoms in blue, green, red, brown and pale pink represent Cu, La, O, C and H, respectively.

Supporting Tables

Table A 1: Electrochemical CO₂ reduction reactions toward various products with corresponding thermodynamic equilibrium potentials in an aqueous electrolyte at pH 7, 1 atmosphere of pressure, and 25 °C, referenced to RHE.

Half electrochemical reactions	Number of electrons transferred	Standard potential (V vs. RHE)	Product type
C₁ compounds			
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO(g)} + \text{H}_2\text{O}$	2	−0.11	Carbon monoxide
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH(aq)}$	2	−0.12	Formic acid
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH(aq)} + \text{H}_2\text{O}$	6	0.03	Methanol
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4\text{(g)} + 2\text{H}_2\text{O}$	8	0.17	Methane
C₂₊ compounds			
$2\text{CO}_2 + 10\text{H}^+ + 10\text{e}^- \rightarrow \text{CH}_3\text{CHO(aq)} + 3\text{H}_2\text{O}$	10	0.06	Acetaldehyde
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4\text{(aq)} + 4\text{H}_2\text{O}$	12	0.08	Ethylene
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH(aq)} + 3\text{H}_2\text{O}$	12	0.09	Ethanol
$2\text{CO}_2 + 14\text{H}^+ + 14\text{e}^- \rightarrow \text{C}_2\text{H}_6\text{(aq)} + 4\text{H}_2\text{O}$	14	0.14	Ethane
$2\text{CO}_2 + 16\text{H}^+ + 16\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{CHO(aq)} + 5\text{H}_2\text{O}$	16	0.09	Propionaldehyde
$3\text{CO}_2 + 18\text{H}^+ + 18\text{e}^- \rightarrow \text{C}_3\text{H}_7\text{OH(aq)} + 5\text{H}_2\text{O}$	18	0.10	Propanol

Table A 2: Cathodic energy efficiencies and applied potentials of OD-CuO_x and OD-La_{0.10}-CuO_x at current densities from 100 to 500 mA cm⁻² in 1 M KCl after *iR* compensation.

Sample	Current density (mA cm ⁻²)	Potential after <i>iR</i> compensation (V vs. RHE)	Faradaic efficiency (%)	Cathodic energy efficiency (%)
OD-CuO _x	100	-1.15	21.2	10.2
	200	-1.39	31.4	13.8
	300	-1.71	36.2	14.2
	400	-1.89	38.1	14.0
	500	-2.05	39.0	14.5
OD-La _{0.10} -CuO _x	100	-1.1	39.1	19.3
	200	-1.3	48.4	22.1
	300	-1.37	51.8	23.1
	400	-1.45	50.1	21.3
	500	-1.56	45.1	18.6

Table A 3: Cathodic energy efficiencies and applied potentials of OD-CuO_x and OD-La_{0.40}-CuO_x at current densities from 100 to 500 mA cm⁻² in 1 M KOH after *iR* compensation.

Sample	Current density (mA cm ⁻²)	Potential after <i>iR</i> compensation (V vs. RHE)	Faradaic efficiency (%)	Cathodic energy efficiency (%)
OD-CuO _x	100	-0.72	0.12	0.07
	200	-1.06	0.54	0.25
	300	-1.08	0.82	0.38
	400	-1.18	0.47	0.21
	500	-1.39	1.1	0.45
OD-La _{0.40} -CuO _x	100	-0.67	18.2	10.2
	200	-0.85	41.1	20.9
	300	-0.96	49.5	24.0
	400	-1.08	61.5	28.2
	500	-1.29	53.8	22.6

Table A 4: Cathodic energy efficiencies and applied potentials of CuO and Eu(OH)₃-Cu for CO₂RR-to-C₂H₄ at current densities from 100 to 500 mA cm⁻² in 1 M KOH after *iR* compensation.

Sample	Current density (mA cm ⁻²)	Potential after <i>iR</i> compensation (V vs. RHE)	Faradaic efficiency (%)	Cathodic energy efficiency (%)
CuO	100	-1.33	29.0	13.3
	200	-1.67	37.9	15.3
	300	-1.85	39.4	15.0
	400	-2.1	44.9	15.8
	500	-2.3	40.3	13.4
Eu(OH) ₃ -Cu	100	-0.87	37.0	20.6
	200	-1.05	45.9	23.5
	300	-1.15	47.8	23.6
	400	-1.29	52.0	24.1
	500	-1.51	43.8	18.7

Table A 5: Cathodic energy efficiencies and applied potentials of CuO and Eu(OH)₃-Cu for CO₂RR-to-C₂₊ products at current densities from 100 to 500 mA cm⁻² in 1 M KOH after *iR* compensation.

Sample	Current density (mA cm ⁻²)	Potential after <i>iR</i> compensation (V vs. RHE)	Faradaic efficiency (%)	Cathodic energy efficiency (%)
CuO	100	-1.33	51.8	23.5
	200	-1.67	57.8	23.2
	300	-1.85	68.7	25.9
	400	-2.1	72.2	25.1
	500	-2.3	70.6	22.7
Eu(OH) ₃ -Cu	100	-0.87	58.4	32.3
	200	-1.05	70.9	36.1
	300	-1.15	77.3	37.1
	400	-1.29	81.5	37.3
	500	-1.51	80.0	33.1

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