Selectivity enhancement on heterogeneous electrocatalytic CO₂ reduction : from modification of metallic electrodes to heterogenization of monofunctional molecular catalysts

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2019

Peng, Y. (2019). Selectivity enhancement on heterogeneous electrocatalytic CO₂ reduction: from modification of metallic electrodes to heterogenization of monofunctional molecular catalysts. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/136767>

<https://doi.org/10.32657/10356/136767>

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**SELECTIVITY ENHANCEMENT ON
HETEROGENEOUS ELECTROCATALYTIC CO₂
REDUCTION: FROM MODIFICATION OF METALLIC
ELECTRODES TO HETEROGENIZATION OF
MONOFUNCTIONAL MOLECULAR CATALYSTS**

PENG YUECHENG

**SCHOOL OF CHEMICAL AND BIOMEDICAL
ENGINEERING**

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PENG YUECHENG

SCHOOL OF CHEMICAL AND BIOMEDICAL
ENGINEERING

A thesis submitted to the Nanyang Technological University in partial
fulfilment of the requirement for the degree of Doctor of Philosophy

2019

Statement of Originality

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Peng Yuecheng

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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from 1 paper(s) published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 3 included a work which has been published in ACS Applied Materials & Interfaces. Reproduced by permission of American Chemical Society, Copyright 2017. Peng, Y.; Wu, T.; Sun, L.; Nsanzimana, J. M.; Fisher, A. C.; Wang, X., Selective electrochemical reduction of CO₂ to ethylene on nanopores-modified copper electrodes in aqueous solution. ACS applied materials & interfaces 2017, 9 (38), 32782-32789.

The contributions of the co-authors are as follows:

- Prof. Wang provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.
- I co-designed the study with Prof. Wang. I have done all the synthesis, characterization and analysis work of nanoporous copper foils at School of Chemical and Biomedical Engineering.
- Dr. Wu, Dr. Sun and Mr. Nsanzimana helped me to revise the manuscript.
- Prof. Fisher and Prof. Wang provided financial support.

08/23/2019

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Acknowledgement

First of all, I would like to convey my sincere thanks to my supervisor Professor Wang Xin, who provide the valuable opportunity for me to study and carry out the research during my PhD period in this honored university. Besides, his patient guidance and illuminating ideas always inspire me to overcome the impedence all along my four-year PhD career.

I would also like to express my sincere thanks to Dr. Sun Libo, for his great advices to improve both my laboratory and academic writing skills. I am also very grateful with his help on the theoretical computation contents. I would also give my thanks to the current post-docs of our group, Dr. Wang Jiong, Dr. Huang Zhenfeng and Dr. Dou Shuo. They have provided plenty of enlightening suggestions with experimental techniques for me. My appreciation also goes to Dr. Wu Shuyang, who helped me a lot on electron microscopy. I would like to thank Dr. Pan Meilan for her kind help on liquid chromatography. Moreover, I must give my gratitude to Mr. Yu Zhongzheng, who helped me a lot on reviewing this thesis. All your help is indispensable for my research and accomplishment of this thesis work.

I would like to thank my other laboratory colleagues including former members of our group for these four years, they are Mr. Jean Marie Vianney Nsanzimana, Mr Vikas Reddu, Dr. Li Xiaogang, Dr. Lu Yizhong, Dr. Zhang Wenyu, Dr. Yan Ya, Dr. Xia Baoyu, Miss Larissa Thia, for their selfless help. Also thank to all of my friends in Singapore and China for their help and encouragement, my apologies for that I could not list them all, but all of them are extremely important during my PhD period.

I would like to thank all the technical and administrative executives in SCBE, for their supporting and assistance in all aspects both on my laboratory work daily affair.

I would like to express my greatest gratitude to my parents along with all other family members. Without their caring and encouragement from my childhood I could not determine to start this PhD career. Last but not the least, thanks to my beloved girlfriend Miss Zhu Lei. I will always remember that we have supported each other for all these days, and of course we will keep it up.

Besides, acknowledgement is also given to the financial support from the academic research fund AcRF tier 2 (M4020246, ARC10/15), Ministry of Education, Singapore. Also, thanks to Nanyang Technological University, Campus for Research Excellence and Technological Enterprise (CREATE) and all other institutions who offered the opportunity and support on my project as well as this comfortable research environment.

Abstract

The work included in the thesis was aimed to improve the selectivity regarding the product distribution for CO₂ electrocatalytic reduction performed on heterogeneous catalysts. Strategies for this purpose can be diverse. In the thesis, two directions were applied. On the one hand, surface morphology modifications can be done on metal electrode to regulate the active sites to raise the selectivity for certain product. On the other hand, creating monofunctional active sites originated from molecular catalysts has also been proven to be effective.

First, a nanoporous structure was obtained on polycrystalline copper electrode through an alloy-dealloy process. Such modified copper electrode can selectively catalyze the production of C₂H₄ over CH₄, compared to nonmodified copper electrode. Moreover, the Faradaic efficiency for ethylene can reach up to 35%. Probable explanation for the selectivity enhancement could be the exposure more crystalline orientation that favor ethylene production.

Second, bipyridine carbonyl rhenium (I) complex are known to be active for electrocatalyzing CO₂ reduction to CO. By grafting π -electron enriched groups like pyrene onto a molecule, a more stable heterogeneous attachment can be achieved on graphene support, realizing a catalytic CO₂-to-CO conversion at 92% of efficiency on aprotic solvents.

Third, an iron porphyrin complex with -NH₂ pendant groups on the porphyrin ligand as a type of intramolecular H-bond donor presented superior selectivity and production rate towards CO₂ reduction to CO after immobilized onto graphene as a heterogeneous catalyst in aqueous solution, with the faradaic efficiency of 99% for CO production. Electrochemical and theoretical studies revealed the reduced CO₂

intermediate was stabilized by H-bond on Fe(0) site, accounting for better performance compared with analogues which lacked the intramolecular H-bond donor feature.

In sum, morphological modification of catalysts with diverse active sites for CO₂ electroreduction can benefit the selectivity towards certain product. By the way, construction composites with monofunctional active units while performing some molecular tuning can also boost the generation to specific product from CO₂ electrocatalytic reduction.

Keywords: CO₂ electroreduction, selectivity, copper electrode, modification, nanoporous, active sites, molecular catalyst, heterogenization, π - π stacking, intramolecular H-bond donor

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List of Abbreviations

ACN	Acetonitrile
bpy	bipyridine
CN	Coordination number
CNT	Carbon nanotube
COF(s)	covalent organic framework(s)
CPE	Controlled Potential Electrolysis
CTAB	Hexadecyltrimethylammonium bromide
DMF	dimethylformamide
DMSO	Dimethyl sulfoxide
EA	Elemental analysis
ECSA	electrochemically active surface area
EDX	energy dispersive X-ray spectroscopy
FE	Faradaic efficiency
FESEM	Field emission scanning electron microscopy
FID	flame ionization detector
FTIR	Fourier-transform infrared spectroscopy
GC	Gas Chromatography
GDE	Gas diffusion electrode
GO	graphene oxide
GQD	graphene quantum dots
HER	hydrogen evolution reaction
HOMO	Highest Occupied Molecular Orbital
ICP	Inductively Coupled Plasma
IR-SEC	Infrared Spectroelectrochemistry
LSV	linear sweep voltammetry
LUMO	Lowest Unoccupied Molecular Orbital
MOF(s)	Metal Organic Framework
NGQD	nitrogen doped graphene quantum dots
NMR	Nuclear magnetic resonance
NP(s)	nanoparticle(s)
NRGO	Nitrogen doped reduced graphene oxide
oTAP	5,10,15,20-(tetra-2-aminophenyl)porphyrin
PEM	Proton exchange membrane
RHE	Reversible Hydrogen Electrode
SAC	Single atom catalyst
SEC	Spectroelectrochemistry
SHE	Standard Hydrogen Electrode
TAP	5,10,15,20-(tetra-4-aminophenyl)porphyrin
TBAB	Tetrabutylammonium tetrafluoroborate
TCD	thermal conductivity detector

TOF
TON
TPP
XPS
XRD

Turnover frequencies
Turnover numbers
tetraphenyl porphyrin
X-ray photoelectron spectroscopy
X-ray diffraction

Chapter 1. Introduction and Scope of Thesis

1.1 Introduction

Energy and environment concerns have kept troubling mankind for many decades. The imminent depletion of reserves of the fossil fuels will lead to a series of economic, social, even political problems. Despite our human beings are aware of the importance of the energy transformation to clean energy, our technologies are awaiting the next evolution for efficiently utilization of clean energy like solar energy, wind power, hydro energy and so on. During this transition period, one severe problem could retain for quite long, which is the carbon dioxide (CO₂) level in atmosphere. The increase can bring about unforeseeable and uncontrollable problems for the world environment and climate. One of the problems is the ocean acidification. The oceans can take up more than 2×10^9 tons of anthropogenic CO₂ per year.¹ With the increase of CO₂ uptake in ocean, the balance of photosynthesis and acidification in ocean can be destroyed. On the other hand, accompanied with the increasing consumption of fossil fuels since the industrial evolution began 150 years ago, CO₂ has contributed to more than 50% effect among various of greenhouse gases (CH₄, CCl₂F₂, N₂O).² As CO₂ is the ultimate product of burning fossil fuels, reuse of atmospheric CO₂ can be an alternative way to step up solving the energy along with the environmental problem.³

Recently, techniques for CO₂ capture and fixation have become increasingly mature which is capable in practice. Novel types of porous polymers, such as hypercrosslinked aromatic heterocycle, constructed by Luo et al., exhibited high CO₂ adsorption capacity and selectivity with CO₂/N₂ selectivity of 117 at 273K.⁴ However,

among all the components of air, CO₂ only consists about 0.034% by volume.² Because of this low partial pressure, capturing trace amount of CO₂ from atmosphere can be much more difficult than capturing CO₂ from large emitting point sources. Investigations and analysis have shown that it is an extremely energy-consuming and expensive approach to enrich CO₂ directly from air. Meanwhile, it could only make sense that such capture process is powered by CO₂-neutral power sources, which raises the technical barrier for most cases.⁵

Another alternative approach is to chemically convert CO₂ into useful chemicals before emitted out. As the carbon in CO₂ is at its maximum oxidation state, the reduction of CO₂ can be the only direction for CO₂ conversion. The reduction of CO₂ has already been initialized and expected to be an ultimate solution to create chemical feedstocks while control CO₂ emission simultaneously.⁶ Fortunately, some of technologies like CO₂ derived Fischer-Tropsch synthesis (*i.e.* carbon monoxide hydrogenation) and CO₂ hydrogenation have been already come into service for producing fine chemicals from C₁ to C₅₊ products while avoiding usage of fossil resources.⁷⁻⁸ As the CO₂ presented both kinetic and thermodynamic stability in ambient conditions, there could be a significant barrier to overcome the reduction reaction can take place. With regarding to typical Fischer-Tropsch and CO₂ hydrogenation process, even with the existence of robust catalysts, the system temperature must be raised to a very high level (more than 600K) to maintain the reaction,⁹ which can be inevitably energy-consuming.

Other than traditional thermal catalysis, alternative prescriptions for CO₂ reduction has been under elaborate investigation, including mimicking biological conversion,³ photochemical reduction¹⁰ and electrochemical reduction.¹¹ In view of

artificial biological CO₂ fixations, the selection of enzymes and the understanding of the structure-controlled effects of these dynamic processes still need further investigation.³ Moreover, the optimal working conditions and large amount of enzymes could not be readily accessible for application in large scale.¹² Photocatalytic reduction is considered as one of promising approaches to utilize CO₂ from clean energy like solar energy. However, ambient lighting might not be able to trigger the reaction properly. Usually a 300W Xe arc lamp should be equipped, including a proper cooling system.¹³ In addition, the limitation on the diversity of catalysts (mostly TiO₂¹⁴⁻¹⁵ and C₃N₄¹⁶⁻¹⁷ based systems) can bring about challenges for further applications. On the other hand, the consistent and stable production during catalysis can be always a problem. Herein, for electrocatalytic reduction of CO₂, the accessible reactor with low power consumption, diverse choice of catalysts and continuous production rate during electrolysis with high efficiency and selectivity can be the bonus to be a promising method on conducting CO₂ reduction reaction (CO₂RR).

First, the choices for catalyst materials are rather flexible. Metallic, nonmetallic, molecules, composites and nanostructured materials can exhibit robust performance under proper conditions.¹⁸⁻¹⁹ The product from electrochemical reduction of CO₂ can vary with types of catalysts applied. For example, metallic copper materials are unique with the ability to catalyze CO₂ into hydrocarbons.²⁰ Second, electrocatalysts can significantly lower the energy barrier of CO₂ reduction,²¹ making it possible to run the catalysis process at low power consumption level in ambient settings. However, there are still challenges for researchers to cope with. For instance, the hydrocarbon yield based on copper catalyst could not present expected

efficiency and selectivity. Since protons are essential for CO₂ reduction to hydrocarbons and the potential for hydrogen evolution is close to these reactions, hydrogen will come as the side product, lowering the efficiency for targeted products.²² Moreover, deactivation of cathode catalysts driven by deposition of impurities or intermediates could be a problem too.

To cope with the existing problems on electrochemical reduction of CO₂, fundamental and mechanistic research should first be investigated regarding all dimensions of the process throughout chemical, thermodynamic and kinetic aspects, establishing a blueprint for catalyst selection, modification and construction.²³ Besides, more advanced methods can also be involved to help understand the details of the interactions between catalysts and CO₂ along with relevant intermediates, like *in-situ* spectroscopy or theoretical computational studies.²⁴⁻²⁵ To industrialize such electrochemical process, efforts also have been made for high-current and high-pressure electrolysis for larger amount of products by means of gas diffusion electrode (GDE)²⁶⁻²⁸, three-phase electrodes²⁹⁻³⁰ and solid polymer electrolyte³¹⁻³³, which can be regarded as the very first step for dealing with the global CO₂ issue.

1.2 Scope of the thesis

The works included in the thesis are based on heterogeneous electrocatalysts for CO₂ reduction to various chemical feedstocks, comprising developing new strategies to regulate the selectivity of hydrocarbons on copper-based electrocatalysts, heterogenization of monofunctional molecular catalysts for improvement of catalytic performance.

Chapter 1 provides a briefing on the background of how CO₂ affect the global environment, the importance and approaches of CO₂ exploitation and efforts that researches has been made to develop CO₂ electrocatalysis.

Chapter 2 gives detailed review on fundamental chemistry, general approaches for probing mechanistic insights and recent advances in the application diverse catalyst materials.

In Chapter 3, a nanostructured copper surface morphology was obtained by alloy-dealloy process, presenting a bias on catalyzing producing ethylene against methane, where the exposed high-indexed facets might account for the selectivity for ethylene.

In Chapter 4, a strategy of grafting π -electron enriched groups like pyrene onto a molecular bipyridine carbonyl rhenium (I) complex was developed to allow a more stable heterogeneous attachment on graphene support, rendering a more robust current density during CO₂-to-CO catalysis process.

In Chapter 5, an iron porphyrin complex with intramolecular H-bond donor presented superior selectivity and production rate towards CO₂ reduction to CO after immobilized onto graphene as a heterogeneous catalyst. Electrochemical and theoretical studies revealed the reduced CO₂ intermediate was stabilized by H-bond, accounting for better performance compared with analogues which lacked this H-bond feature.

Chapter 6 summarizes and concluded what have been done through abovementioned works. The prospect of future work is also included at last.

Chapter 2. Literature Review

2.1 Fundamentals of CO₂ electroreduction

CO₂ electroreduction to elemental fuels and/or other profitable chemical resources can be particularly meaningful if the consumed electric energy is powered from renewable energy sources. Only in this way, those converted CO₂ can re-enter the global carbon cycle,³⁴ meanwhile, no newly generated CO₂ would be re-emitted into atmosphere during such CO₂ reduction process. The increasing amount of CO₂ emission can thus be controlled. It is well-known that CO₂ can be quite stable under ambient conditions thermodynamically, barely participating into redox reactions. However, CO₂ reduction can be realized under relatively mild conditions through electrochemical way, compared to traditional thermal reductions like Fischer-Tropsch catalysis.³⁵ Before putting CO₂ reduction into practice, fundamental studies on thermodynamics and kinetics of CO₂ reduction reactions can be the prerequisites for subsequent optimization of efficiency and selectivity regarding producing specific reduced products from CO₂. In terms of this, it is essential to discuss the fundamental theory of CO₂ electroreduction in the first place.

2.1.1 Chemistry of CO₂ reduction

The electroreduction of CO₂ can be performed via from one- to eight-electron reduction pathways (especially at two-, four-, six-, or eight-electron transfer per reaction). With respect to the products generated, carbon monoxide (CO)³⁶ and formate species (HCOOH/HCOO⁻)³⁷ are the most frequently achieved as the amount of the electrons transferred per reaction is only two. On the other hand, only single

active site can be necessary for such reactions to proceed. Other products such as formaldehyde (CH_2O),³⁸ methanol (CH_3OH),³⁹ oxalic acid or oxalate ($\text{C}_2\text{O}_4\text{H}_2/\text{C}_2\text{O}_4^{2-}$)⁴⁰ and ethanol ($\text{C}_2\text{H}_5\text{OH}$)⁴¹ are seldom reported as the reduction from CO_2 to these products needs multiple charge transfer coupled with protonation processes, quite demanding for most catalysts. For particular products like methane (CH_4)⁴²⁻⁴³ or ethylene (C_2H_4),⁴³⁻⁴⁴ can be found in specific electrocatalysts like metallic copper. A collection of possible CO_2 electroreduction pathways along with the corresponding standard redox potentials E^0 for aqueous solution is listed in Table 2.1.

Table 2.1 Selected electroreduction pathways for CO_2 in aqueous solution, pH=7.0, 25°C, 1 atm.⁴⁵

Possible pathways of CO_2 Electroreduction	E^0/V vs. SHE
$\text{CO}_2 + \text{e}^- \rightarrow \text{CO}_2^{\cdot-}$	-1.90
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.53
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-0.61
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.51
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.38
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-0.24
$2\text{CO}_2 + 12\text{H}^+ + 8\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	-0.34
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	-0.42

The very first step in the reduction of CO_2 requires an activation to decrease of the C=O bond orders. Once activated, the C-O bond will be elongated, and the O-C-O configuration will not be 180° anymore, revealing a bent configuration of CO_2 molecule. Bent CO_2 interacts with electrophiles and nucleophiles, for general catalysis, electrophiles and nucleophiles are often observed to be metal active centers

and protons, respectively. Such activation is very energy consuming, which is reflected in the very negative potential at -1.9V vs SHE (see Table 2.1). Correspondingly, in its activated status, CO₂ is susceptible to participate into two-electron transfer rather than merely one-electron transfer.⁴⁶ However, the coupled multi-electron and multi-proton reactions occur at relatively modest potentials (Table 2.1, row 2-6). As they involve protons, such reactions are more favorable if proton source is available. In this session, we will further discuss possible reduction pathways of CO₂ reduction separately.

(1) Reduction of CO₂ to CO and HCOOH/HCOO⁻

One of the key steps in catalytic CO₂ reduction involves the binding of CO₂ to a vacant catalytic active coordination site at the metal center within a reduced catalyst. Carbon dioxide will approach to metal coordination site on the catalyst and bonded through the electrophilic carbon atom, shown as equation 2.1 and 2.2 (M: metal center; L: ligands of the complex):⁴⁷

The rate constants of the equilibria (equation 2.1, 2.2) can give an overall possibility of the generation of a target product (*e.g.* CO). However, kinetic parameters for CO₂ binding are required to be neither too small nor too large, giving a sufficient driving force for processing the catalysis while avoiding forming a highly stable ML(CO₂)⁺ adduct. After the first charge transfer, the reduced catalyst species are supposed to bind with CO₂ (or H⁺). If a ML(H)²⁺ is formed (equation 2.3),

CO₂ may insert into the M–H bond to give the formate adduct, *i.e.* M–OCHO (equation 2.4). The CO, formate (HCOO[−]), and H₂ yields will be determined based on those binding equilibria and the reaction rates of these competing reactions.

Figure 2.1 shows a typical mechanism of the CO₂-to-CO reaction cycle catalyzed by a monofunctional Pd complex. The CO₂-to-CO conversion usually includes two charge transfer steps and two protonation process. While the C–O cleavage takes place after the second protonation, accompanied by a dehydration process.³

Figure 2.1 Proposed mechanism for the reduction of CO₂ to CO mediated by [Pd(triphosphine)(solvent)]²⁺ complexes. Reprinted from Ref.³, with permission of American Chemical Society, Copyright 2013.

Figure 2.2 interpreted the universal mechanisms of metal cyclam complexes catalyzing CO₂ reduction (HER as well) to CO or formate species. By controlling the ambient pH, the metal center of these cyclam-like complexes can either combine CO₂ or protons. Based on the protonated ML(H)²⁺ species, CO₂ can be inserted in between the M-H bond, binding metal center with oxygen atom rather than carbon.⁴⁸

Figure 2.2 Proposed mechanisms of CO₂ and water reductions catalyzed by M (Co or Ni) 'cyclam-like' complexes; HER (blue), HCO₂⁻ production (red), CO generation (brown), and assumed intermediates (green dashed frame). Reprinted from Ref.⁴⁸, with permission of American Chemical Society, Copyright 2009.

Some catalysts are capable to reduce CO₂ further beyond CO/HCOO⁻. Therefore, it is necessary to involve this aspect into the discussion.

(2) Reduction to products beyond CO/formates

To begin with, the first reaction mechanisms for advanced products is methanol synthesis on a copper catalyzed process.⁴⁹ There are several types of proposed mechanisms.⁵⁰ In this session, the “formate mechanism”, including an adsorbed HCOO⁻ intermediate, will help us understand the pathways leading to formation of methanol through several steps of charge transfer coupled with carbon- and oxygen-based hydrogenation, as well as C-O cleavage steps.

Figure 2.3 Three possible pathways for the catalytic hydrogenation of CO₂ to methanol born on copper surface. Reprinted with permission from Ref. ⁴⁹, Copyright 2013 Elsevier. The prefixes cis/ c, trans/t, refer to the conformation of the partially hydrogenated species,

and mono- and bi- refer to the number of copper centers attached to the substrates, 1 and 2, respectively.

As interpreted in the rightmost branch in Figure 2.3, combined with the abovementioned pathways leading to HCOO^- formation, the formate mechanism here started with a formate intermediate chemisorbed on single site of Cu atom. Actually, such intermediate can be detected by *in situ* FTIR spectroscopy, identifying the shift of carbonyl species.⁵¹ To continue to produce methanol via the formate pathway, another protonation would occur to the carbon atom of the chemisorbed formate intermediate to generate adsorbed dioxomethylene intermediate (Cu-OOCH_2). This step has been considered as the rate-limiting step as a high energy barrier is assumed to be required.⁵²⁻⁵³ Formate species as side products were detectable when performing the reaction for methanol. Dioxomethylene intermediates can be further protonated to render a formaldehyde intermediate accompanied with a removal step of H_2O . However, a controversy against this theory was raised assuming that the adsorbed formaldehyde can be regarded as an important intermediate which remains undetected during the whole process, though.⁵⁰ To carry on, methanol would start to be available after another hydrogenation step on proposed formaldehyde intermediate that leads to methoxy species before the final step of Cu-O cleavage, followed by the eventual protonation of the untethered $-\text{OCH}_3$ species.

(3) C-C bond formation during reduction of CO_2

Among all the products subjected to CO_2 electroreduction, the presence of C_2 , even C_3 products during the reduction process on Cu surface has drawn a great level attention. Ethylene,⁵⁴ ethanol, ethylene glycol⁵⁵ and so on have been gradually

discovered with a comparable Faradaic efficiency (FE) ($\geq 1\%$). Typical on metallic copper surface, the C-C coupling still can be originated of the adsorbed $\ast\text{CO}$ intermediates.⁵⁶ The dimerization of CO was first assumed to be the rate-determining step in C_2 formation, followed by either the formation of an enediol-like intermediate ($\text{HO-C}=\text{C-OH}$) or an oxalometallacycle coupled with protonation. However, a study from *Nørskov* unveiled that kinetic barriers to C-C coupling can be much lower from hydrogenated $\ast\text{CO}$ intermediates rather than from $\ast\text{CO}$ coupling directly. The complexity of the electrochemical environment near the copper surface can vary the chemical potential of hydrogen (including protons), allowing a variation of levels of hydrogenation of the adsorbed intermediates, as well as different activation barriers of C-C coupling. Ultimately, the final product could be varied in terms of diverse pathways.⁵⁷

Figure 2.4 has depicted proposed mechanism for CH_4 production as well as other products like C_2H_4 and ethanol depending on C-C coupling.⁵⁴ The rate determining step of CH_4 formation is the second electron transfer to a supposed intermediate $\ast\text{COH}$ species. It is reported that there exists a step of CO splitting on Cu electrodes with $\ast\text{C}$ species generating from the $\ast\text{CO}$.⁵⁸ The $\ast\text{C}$ species are susceptible to be protonated into $\ast\text{CH}_2$. The $\ast\text{CH}_2$ will either dimerize into C_2H_4 or form a $\text{CH}_2\text{CO}\ast$ with an insertion of another CO molecule, which will readily be protonated into aldehydes and alcohols.

Figure 2.4 Molecular reaction pathway diagram of CO reduction to advanced products. H_2^+ represents H_2^+ or a combined $\text{H}(\text{ads}) + \text{H}^+$. The $\rightarrow$ with a $\wedge$ across it represents a rate-determining step. Reprinted with permission from Ref. ⁵⁴, Copyright (1997) American Chemical Society.

The above brief discussion of the CO_2 reduction chemistry is the foundation of performing CO_2 electroreduction. A blueprint of product types corresponding with the possibilities can be established on the basis of thermodynamics and kinetics of CO_2 chemistry, which will provide us the significance of performing the CO_2 electroreduction.

2.1.2 Practical methods for engineering CO_2 electroreduction

(1) Electrolyzer for performing CO_2 electroreduction

Proton exchange membrane (PEM) electrolyzer system is widely used in CO₂ electrocatalysis in aqueous phase. The membrane fixed in between is usually Nafion®, which is functioned to conduct protons from anode pool to cathode pool. Water in the anodic chamber will adsorbed onto the electrode, oxidized into oxygen and freeing the protons into the membrane to travel to the cathode, where those protons will be transported onto the catalyst sites, recombining with electrons to form H₂ or with the intermediate from CO₂ reduction to form carbon species.

Figure 2.5 A typical depiction of a PEM based CO₂ electrolyzer. Reprinted from Ref. ⁵⁹, with permission from Elsevier, Copyright 2016.

As the CO₂ reduction is generally a thermodynamic uphill reaction, regarding the first electron transfer to form CO₂^{•-}, an external voltage should be applied to drive the reaction overcome the activation barrier. However, in aqueous based CO₂ reduction, HER and other proton-involved CO₂ reduction process can be relatively favorable within a large range of voltage (from -0.2 to -0.6V vs SHE, listed in Table 2.1). Side reactions of HER and various products from CO₂, may compete with each other in the cathode side, making it difficult for us to obtain what we expected.

Therefore, for performing CO₂ electrolysis, the choice of the applied potential is of great importance. At different bias, even the same cathode will produce various of products. A broad-spectrum investigation for CO₂ regarding a specific potential range is often recommended.

(2) Choice of the electrolyte

Aqueous as well as nonaqueous electrolytes have been widely applied to investigate CO₂ reduction. For aqueous solutions, 0.1 - 0.5 M KHCO₃ (or NaHCO₃) is the most commonly used electrolyte with pH near 7 after saturation by CO₂.³ The bicarbonate here can also act like a buffer system to maintain the system pH value.⁶⁰ Bicarbonates are economic, accessible and environmental friendly, making it become the most popular electrolyte used for CO₂ reduction.⁵⁹

Peter Strasser *et al.* addressed that the variation of the concentration of the bicarbonate electrolyte could tune the activity and selectivity of copper electrode during the CO₂ electrolysis.⁶¹ Demonstrated on Figure 2.6, electrolytes with high buffer capacity, *i.e.* high concentration of KHCO₃ solution, favored proton-assisted processes, coupled with charge transfer, yielding higher ratio of CH₄. With respect to diluted KHCO₃ electrolyte with low buffer capacity, these two products were not as favorable as performed in high concentration of KHCO₃. The product ratio of C₂H₄, however, favored in electrolytes with low buffer capacities. As the formation of ethylene was relatively sensitive to high local pH, since the effect of local pH near catalysis sites can become more pronounced under low buffer capacity with high current densities, the production rate of ethylene can be enhanced under this circumstances, which was also evidential for the idea that coupled proton and electron transfer was NOT a rate determining step regarding C₂H₄ generation.⁶²⁻⁶³

Figure 2.6 FEs of products of a) H_2 , b) CO, c) CH_4 and d) C_2H_4 versus applied bias on copper electrode in CO_2 bubbled 0.05M (blue), 0.1M (red) and 0.2M (black) $KHCO_3$ aqueous solution. Reprinted with Ref. ⁶¹, with permission from Elsevier, Copyright 2016.

Other aqueous electrolytes were also investigated. For instance, KOH was believed as a superior candidate for perform CO_2 reduction as the high concentration of OH^- anion can reduce the overpotential of oxygen evolution on anode.⁶⁴ Moreover, high pH value can boost those reactions favoring high local pH, such as C_2H_4 formation.⁶⁵

Nonaqueous electrolytes, usually containing aprotic polar solvents and quaternary ammonium salt as conducting medium. N,N-dimethylformamide (DMF) and acetonitrile (ACN) can cover the most choices of the solvents while tetrabutylammonium tetrafluoroborates, hexafluorophosphates or perchlorates are candidates of the supporting conductive media. Such electrolytes are usually utilized as the medium for investigating molecular catalysts homogeneously.⁶⁶⁻⁶⁷ On the other

hand, the solubility of CO₂ in such organic solvents is higher than that in water,⁶⁸ thus, the standard potential of CO₂ conversion to specific product could vary in different solvents.⁶⁹⁻⁷⁰ Such aprotic solvents are suitable for electrochemically probing the influence on the catalysis resulting from the presence or absence of protons,⁷¹⁻⁷² which can be significant towards mechanism studies.

2.1.3 Comparisons between heterogeneous and homogeneous CO₂ electroreduction

(1) Heterogeneous CO₂ electrocatalysis

In some cases, plenty of materials are capable to bond with the substrate (CO₂ here) through chemisorption prior to electron transfer, among which the activation energy barrier may be lowered as well as further reduction can be proceeded, interpreted by the top chart of Figure 2.7. Such materials are suitable for heterogeneous electrolysis. Due to insolubility to any type of solvents, some material can only serve as heterogeneous electrocatalysts for CO₂ reduction. Such materials can be categorized into metals with relevant alloys, transition metal oxides or chalcogenides, and metal organic frameworks (MOFs).¹⁸

The factors that can affect the reactivity and selectivity of products when performing CO₂ electrolysis on heterogeneous catalysts can be diverse. In essence, the binding energy between the intermediates and the catalyst will determine the product distribution.⁷³ However, additional variables, such as solvent, temperature, partial pressure of CO₂, the electrolyte and surface morphology of catalyst, can also impose influence on the product spectrum.¹⁹

Figure 2.7 General scheme of heterogeneous (top) and homogeneous (bottom) process of CO₂ electroreduction. C_{ox} and C_{red} are referred to catalyst in oxidized and reduced state, respectively. Reprinted with Ref. ¹⁹, with permission from American Chemical Society, Copyright 2018.

(2) Homogeneous CO₂ electrocatalysis

With regard to electrocatalysis of CO₂ reduction in homogeneous manner, molecular compounds which can dissolve in applied solvent/electrolyte are targeted as the object for relevant research. The charge transfer, with or without assistance by other agents like protons, was conducted homogeneously in solution, rather than a direct interact occurred on the surface of electrode material presented by heterogeneous process. Therefore, the catalysis can be dependent on the capability of the molecular compound itself. By the way, the transport process of the catalyst through the diffusion layer to electrode surface could be controlled by the potential applied, corresponding to the catalysis current.⁷⁴ In a word, in homogeneous catalysis, both the electron transfer from the electrode to the catalyst and the interaction

between catalyst and CO₂ must reconcile each other to reach a commonly favorable kinetics.¹⁹

In most cases regarding homogeneous catalysis, transition metal complex (usually a reduced ion under electrocatalytic condition) can serve as a monofunctional active site. During the catalysis, a qualified homogeneous catalyst must be activated before the thermodynamic potential of specific CO₂ reduction reaction, meanwhile the charge transfer to CO₂ along with a series followed-up processes, such as protonation, the cleavage of C-O bond and product desorption, should maintain in a fast rate to fulfill a turnover as soon as possible, revealing considerable catalytic current.¹⁹

Therefore, to regulate the reactivity and selectivity towards certain homogeneous catalysis process, only a suitable transition metal center coupled with the choice of optimized ligand configuration should be taken into account, as long as the choice for solvent and the inert electrode is fixed.⁷⁵⁻⁷⁷ Since the universal and homogeneous electron availability and the charge transfer coupled with other reaction are processed in homogeneous manner in the electrolyte, we don't have to involve those factors into the tuning of catalytic performance.

(3) Summary

It is unreasonable and unscientific to judge whether heterogeneous or homogeneous catalysis superior or more promising to another as they both can serve well in terms of different situations. For heterogeneous catalysis of CO₂ reduction, the accessible product separation, convenient post-processing and flexibility to fit into special electrode conformation like gas diffusion electrode (GDE),⁷⁸ making it inevitable to achieve high current densities and generation of advanced products like

hydrocarbons. However, due to various types of active sites and other variables, high selectivity for specific product may become difficult to achieve.

While in homogeneous catalysis based on transition metal complexes, the structure-performance relationships can be much more accessible to investigate to achieve optimal catalyst configurations. The electrode poisoning can be a great concern for the deactivation of heterogeneous electrocatalysts.⁷⁹ However, slow degradation of homogeneous molecular catalyst can also lead to unexpected side reactions or products,⁸⁰ which can also damage the catalytic performance. Therefore, in both cases, solid improvements must be conducted to push CO₂ electroreduction forward into broader applications.

2.2 Mechanistic study techniques for CO₂ electroreduction

In principle, the catalytic CO₂ electroreduction process can usually be divided into 3 steps: electron transfer from electrode to the catalyst or an active intermediate, interaction between the active species of the catalyst and CO₂ (either via bonding the metal site with CO₂ or via non-bond electron transfer from metal to CO₂), and protonation or other followed-up process of catalytic intermediates. Plenty of techniques can be transfused into probing such processes not just via traditional electrochemical and spectroscopic approaches, but also some state-of-art techniques like theoretical computations on the basis of density functional theory (DFT).

2.2.1 Electrochemical techniques

Cyclic Voltammetry (CV) is particularly help for to detect the electrochemical response redox reaction behavior, the rate of electron transfer from the electrode to the catalyst, and even chemical kinetics in some cases.^{19, 81}

First, when the catalytic system is absent of CO₂, CV can be conducted regarding an appropriate range of potentials to determine specific potentials where the redox reactions of the catalyst can occur. Moreover, the catalytic activity after applying the substrates (in this case, CO₂) can be evaluated via comparing the peak currents with that obtained from inert condition at the potential where the catalytic reaction occurs. If the peak current increased under catalytic condition, we can conclude that the CO₂ reduction can be catalyzed with the help of a reduced form of catalyst at specific potential, which can be denoted as E_{cat}^0 . Such reduced catalyst species can be defined according to the corresponding redox peak at the same potential under inert conditions. The peak current which is determined under inert condition can be denoted as i_p while catalytic current is denoted as i_{cat} in this case. Figure 2.8 gives a universal example for a series of typical CV curves on the investigation of a catalytic process.

Figure 2.8 Simplified systematic illustration of cyclic voltammetric analysis of an electrocatalytic CO₂ process. (1) Voltammetry curve of the catalyst under argon gas atmosphere (black). (2) Under CO₂ atmosphere (may contain other essential additives like proton sources). (3) Blank electrolyte with catalyst added, Ar atmosphere. (4) Blank electrolyte, CO₂ atmosphere. Notes: η_{cat} , overpotential; $E^0(CO_2/P)$, thermodynamic potential of CO₂ reduction to specific product; E_{onset} : direct CO₂ reduction at any electrode (noncatalytic process). Reprinted with Ref. ¹⁹, with permission from American Chemical Society, Copyright 2018.

At E_{cat}^0 , under catalytic condition, a significant current gain can be discovered, with a specific i_{cat} and i_p can be identified at the same potential. The driving force, *i.e.* the overpotential η_{cat} of such catalytic reduction from CO₂ to product P, can be obtained by comparing E_{cat}^0 with the standard thermodynamic potential $E^0(CO_2/P)$. For clearance, the blank scan regarding both inert and catalytic conditions should also be included. As can be seen from curve 1 and 2, the reversible redox presented in curve 1 can transfer to irreversible curve 2. No oxidation wave is presented as all the reduced catalyst will participate in the catalytic process and will be reoxidized after

a catalytic turn over.⁸² Another essential parameter which can also be determined through such CV analysis is apparent rate constant (k_{app}), which represents the overall reaction rate of the homogeneously catalyzed reaction. TOF_{max} is often applied as a synonym of k_{app} here. TOF (Turnover frequency) is widely used to quantify the numbers of the active catalysts participated in the reaction per unit time. The consideration of the quantification only relies on those catalysts located in the reaction-diffusion layer instead of the total amount dissolved in the system.

The TOF-overpotential relationship in a specific reduction from CO_2 to product P can be expressed as equation 2.6,⁸³ where $E_{cat/2}$ is catalytic half-wave potential. Prior to the discussion on the TOF in homogeneous catalysis, the k_{app} or TOF_{max} can be derived from equation 2.5.⁸² Here, z is the number of the electron transferred per reaction from CO_2 to product. F is Faradaic constant. v is the scan rate of the CV test. R = universal gas constant, T = temperature. As there is only one variable η in equation 2.6, the plot of TOF vs η can be readily obtained since $E_{CO_2/P}^0$ and $E_{cat/2}$ are constants for specific catalyst in specific reduction reaction. Figure 2.9 depicted the relationship between the overpotential and TOFs of several hypothetical catalysts, assuming they are targeted to the same reduction reaction. The plateau of each curves represents the TOF_{max} for each catalyst. The relative capability of catalytic performance for each catalyst can be used to demonstrate the maximum catalytic capability of specific catalyst. When $\eta=0$, the TOF here can be regarded as a criterion for benchmarking the intrinsic catalytic capability.⁸³

$$i_{cat}/i_p = \frac{1}{0.446} \sqrt{\frac{RTk_{app}}{zFv}} \quad (2.5)$$

$$TOF = \frac{TOF_{max}}{1 + \exp\left[\frac{F}{RT}(E_{CO_2/P}^0 - E_{cat/2} - \eta)\right]} \quad (2.6)$$

Figure 2.9 Plot of TOF as a function of the applied overpotential η for hypothetical catalysts C_1 , C_2 , and C_3 related to the same reduction reaction. Reprinted with Ref. ¹⁹, with permission from American Chemical Society, Copyright 2018.

With respect to the mechanistic investigations on heterogeneous catalysis of CO_2 reduction, despite the complexity of the product distributions combined with side variables like pH, there is some way to uncover the mechanisms regarding specific CO_2 reduction reaction. Tafel analysis, in some cases, can be introduced to illustrate the rate determining step under certain circumstances.

In Tafel analysis, the logarithm of j_x (partial current density of product x) can be plotted with η (overpotential) to obtain a Tafel plot. During the linear part of the plot, a slope called Tafel slope was extracted. With specific value of this Tafel slope, one could readily identify the rate determining step of the specific CO_2 reduction to product x on electrode.

As the product for specific reduction reaction with specific rate determining step may vary. Therefore, for specific product, the Tafel plot was supposed to be derived individually with $\log j_x$, as various results may represent different rate determining steps.

In principle, the process of initial charge transfer to CO_2 generating the anion intermediate CO_2^- is recognized as the rate determining step for most of the heterogeneous catalysts, with a Tafel slope of $\sim 118 \text{ mV dec}^{-1}$. Such value is alternatively obtained by using the partial current density of CO on various electrodes like Ag, Au or Cu electrodes.⁸⁴⁻⁸⁵ Based on this fact, CO_2 conversion to CO may obey this rule with a fast and kinetically favorable CO evolution may follow the rate determining charge transfer on those electrodes. Christina et al. have reported an air-annealed Cu electrocatalyst for robust reduction of CO_2 under low overpotentials.⁸⁵ The Tafel plot in Figure 2.10 presented a slope of 116 mV/dec , which is consistent with CO_2^- mechanism.²⁰

Figure 2.10 Partial CO current density plotted with overpotential for polycrystalline Cu and annealed Cu electrodes, obtained in CO_2 saturated 0.5 M NaHCO_3 electrolyte. Reprinted from Ref. ⁸⁵, with permission from the American Chemical Society, Copyright 2012.

2.2.2 Spectroelectrochemistry (SEC) studies

Coupling specific spectroscopic techniques with electrochemical experiment, in situ identification and detection of products and intermediates formed during the electrolysis process can be enabled. Techniques such as UV-vis SEC and IR SEC have been successfully applied and become the most widely used in probing the active species during electroreduction of CO₂ in terms of the appropriate photo energy range, which can cover most of the electronic and optical transitions within molecules, as well as the relatively simple set-up for the apparatus.⁸⁶ Metal carbonyl complexes are a common type of catalyst or intermediate serving in the electrochemical CO₂ reduction. IR SEC is thus frequently applied as the characterization method as the carbonyl related ligands, as well as the catalytic intermediates, even chemisorbed CO₂ can produce strong infrared absorbance in nature. During the catalysis process, the depletion of CO₂ during the electrolysis can be monitored by recording the intensity variations of its signature signal near 2350 cm⁻¹.⁸⁷

Charles et al. utilized IR-SEC to investigate the electrochemical behavior of a molecular catalyst Mn(CN)(bpy)(CO)₃ at the first reduction under inert atmosphere.⁸⁸ From the left section of Figure 2.11, at the original state (black trace), four IR bands were recorded, which were ascribed to CN, CO, CO and CO, from left to right, respectively. When the potential reached where the first reduction occurred (red trace), on the one hand, the stretches of CN and CO ligands underwent a red shift due to electron uptake. On the other hand, the newly formed triplet of CO stretches was presented consistent with a two-electron reduced species [Mn(bpy)(CO)₃]⁻ which was supposed to emerge at the second reduction. A low-intensity band at 2007 cm⁻¹,

however, indeed suggested the product $[\text{Mn}(\text{CN})(\text{bpy})(\text{CO})_3]^-$ after one-electron reduction, suggesting there could be a disproportionation occurred on one-electron products here. To verify this issue, the author used a reductant CoCp^*_2 instead of applied voltage to chemically reduce the initial molecular catalyst. Shown in the section on the right-hand side in Figure 2.11, same trend was presented as the experiment applied with voltage, indicating that the initial substrate was reduced into the two-electron product at the first reduction.

Figure 2.11 Infrared spectra transitions of $\text{Mn}(\text{CN})(\text{bpy})(\text{CO})_3$ at controlled potentials (left) and with added chemical reductant CoCp^*_2 (no voltage applied; right) under inert atmosphere. Reprinted from Ref. ⁸⁸, with permission from American Chemical Society, Copyright 2015.

When the molecular catalyst was applied in electrolysis of CO_2 , IR-SEC can also assist the investigations of the insights on the catalysis process. In Figure 2.12A, before CO_2 sparging, the initial state was recorded as the same results of the black trace in Figure 2.11A. After applying CO_2 and proton source PhOH and starting the electrolysis at -1.9V (spectra recorded from black trace to orange trace with time), the peak intensity of PhOH became more negative at 1607 cm^{-1} (due to a subtract on background), indicating the consumption of the proton source. Moreover, the broad peaks at 1654 cm^{-1} (water) and 1587 cm^{-1} (PhO^-) were intensified, indicating these

two species were produced during the electrolysis following the process of $\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$. No reduced species were detected as they were rapidly consumed by catalytic reduction of CO_2 . When increasing the potential to -2.1 V, the spectra in Figure 2.12B showed same consumption of PhOH. However, the reduced $[\text{Mn}(\text{bpy})(\text{CO})_3]^-$ began to appear and accumulate, indicating a faster reduction of the catalyst than catalytic reduction of CO_2 .

Figure 2.12 Infrared spectra of $\text{Mn}(\text{CN})(\text{bpy})(\text{CO})_3$ at -1.9 V (A) and then -2.1 V (B) vs Fc/Fc^+ under CO_2 saturated electrolyte and 0.5 M phenol. Spectra were recorded roughly every minute (black to orange). Reprinted from Ref. ⁸⁸, with permission from American Chemical Society, Copyright 2015.

2.2.3 Theoretical computational studies

In some cases, experimental studies just cannot be capable of measuring the exact thermodynamic or kinetic parameters for required catalysis process, while owing to the development of recent advanced technologies, computational modeling and calculation can be crucial to assist the explorations of the insights on specific reaction mechanisms.^{42, 89} Numerous works are taking the advantage of this technique

for either deeper understandings on mechanisms or better guidance for subsequent experimental design.⁹⁰⁻⁹¹ Among heterogeneous catalysts, like nanoparticles, active sites for CO₂ reduction as well as for the competing HER can exist in the same time. Various of active site favor different catalysis processes, rendering a broad spectrum of product distribution, making it difficult to perform the optimization for specific product.

Seoin *et al.*, has applied density functional calculations (DFT) on investigations on the free energies for CO₂ and relevant intermediates within the conversion to CO (including compete HER pathways) on facet, corner, edge sites of Au or Ag nanoparticles.⁹² The free energy (G) diagrams for CO₂ reduction were shown in Figure 2.13A, B. For Ag, the energy level for *COOH on edge sites showed lowest, indicating edge sites were the most active towards CO₂ reduction. While for Au, the most active sites were placed at corner sites. In both diagrams, the facet sites were the least active for CO₂ reduction, suggesting low-coordinated sites with high index are favorable. From Figure 2.13C&D, Au was more active towards HER than Ag in view of each type of active sites. It is also noteworthy that the Au corner site presented the least activity towards HER while the best towards CO₂RR, expecting good selectivity towards CO production here.

Figure 2.13 Free energy diagrams for CO₂ reduction to CO (A, B) and HER (C, D) on Ag (A, C) and Au (B, D) nanoparticles. Reprinted from Ref. ⁹², with permission from the American Chemical Society, Copyright 2015.

Yuan Pan et al. has designed a type of heterogeneous Co-N₅ active sites which performed well in CO₂ electrocatalysis to produce CO.⁹³ DFT with calculations computational hydrogen electrode model was carried out to investigate the superiority of the precursor CoPc and derived Co-N₅ sites over Cu, Fe and Ni analogue precursors.

Figure 2.14 (a) Optimized structures for the stepwise transition state within CO₂ reduction process. (b) Calculation results for free energy of CO₂RR (red short dash line, the desorption free energy level of CO). Reprinted from Ref. ⁹³, with permission from the American Chemical Society, Copyright 2018.

Figure 2.14(a) showed structural and optimizations of Co-N₅ sites for each step of CO₂ reduction, indicating two successions of proton-coupled electron (H⁺+e⁻) transfers. The free energy calculation results were presented in Figure 2.14(b), among which the first H⁺+e⁻ transfer on Cu- and Ni-based precursors presented significantly higher energy barrier than Fe- and Co-based precursors, indicating no activity towards CO₂ reduction on Cu and Ni counterparts. After construction of Co-N₅ sites from Co precursor, the first H⁺+e⁻ showed lower energy level, indicating a more favorable CO₂ reduction than the Co precursor itself, which was consistence with the experimental results.

2.3 Cathode materials of CO₂ electroreduction

In this section, electrocatalysts for CO₂ reduction will be classified into metallic, non-metallic and molecular categories. Each session will be described with examples.

2.3.1 Metallic electrocatalysts

(1) Mono-metallic electrocatalysts

Figure 2.15 Stepwise reaction scheme of electrochemical CO₂ reduction on metal electrodes in aqueous solutions. Reprinted from Ref. ¹⁸, with permission from the Wiley & Sons, Inc., Copyright 2016.

According to different binding capability to different CO₂ related intermediates, metallic electrocatalysts can produce a wide spectrum of products. As summarized in Figure 2.15, Au, Ag, Zn or Pd can generate CO.⁹⁴ Sn, Hg, Pb and In tend to produce formate species.⁴⁰ While Cu can further hydrogenate and reduce *CO intermediates to hydrocarbons and other advanced products.⁵⁴ The specific mechanism for the formation of C-H and C-C bonds have been discussed in section 2.1.1.

However, it is worth noting that when Cu nanoparticles (Cu NPs) were applied to CO₂RR, as reported by Reske et al., the size effect of NPs could play an important role on product distribution.⁹⁵ Figure 2.16A showed a relationship between diameter of the CuNPs with faradaic efficiency towards products. From the results, when the size decreased, HER became dominant, while the hydrocarbons suffered from low efficiency. In addition, CO had noticeable efficiency compared to the bulk Cu foil, indicating that the reaction rate towards CO hydrogenation became slower than the desorption of *CO. The author explored the relationship between the

population of surface Cu atoms with specific coordination number (CN) and the NP diameter. Shown as Figure 2.16B, small-sized CuNP tended to expose more low-coordinated sites, which was not favorable towards production of hydrocarbons.

Figure 2.16 (A) Faradaic efficiencies of major products of CO₂ electroreduction on Cu NPs with various of diameters. (B) Population of surface atoms with a specific CN versus particle diameter. Reprinted from Ref. ⁹⁵, with permission from the American Chemical Society, Copyright 2014.

(2) Bimetallic electrocatalysts

Combination of several types of metallic materials can bring about unique and synergetic effect on the product distribution regarding CO₂ reduction.

Sarfraz et al. has attempted to electrodeposit Sn to Cu surface to achieve a Cu-Sn bimetallic system.⁹⁶ It was found that, during CO₂ electrolysis, such Cu-Sn bimetallic system produced CO in high efficiency and selectivity, with a little H₂ and HCOOH as byproducts, displayed by Figure 2.17b. The Cu basis, however, presented a broad product distribution, including H₂, CO, HCOOH and CH₃COOH, with poor selectivity (Figure 2.17a). While single Sn just tended to promote HER (Figure 2.17c). The author also investigated the effect of the Sn deposition amount to the product

distributions under different potential (Figure 2.17d,e), showing the optimal deposition amount for producing CO was around $3.9 \sim 4.4 \mu\text{mol}/\text{cm}^2$. High Sn deposition amount could enhance the overall catalytic current, but too high or too low Sn deposition amount could promote HER and production of formate under the tested potentials.

Figure 2.17 Faradaic efficiency results of (a) treated Cu basis, (b) Cu-Sn, and (c) Sn deposited on the Sn sheet at applied potentials. Effect of Sn deposition amount on the Cu basis on CO₂ electroreduction performance at (d) -0.6 V and at (e) -0.8 V vs RHE. The round dots represent steady-state current densities. Reprinted from Ref. ⁹⁶, with permission from American Chemical Society, Copyright 2016.

2.3.2 Non-metallic electrocatalysts

Non-metallic materials contain various types. Metal oxides,⁹⁷ metal sulfides⁹⁸ and even some metal phosphides⁹⁹ can be capable to catalyze CO₂ reduction to various product even C₄ species. Other types of nonmetallic materials, such as

MOFs¹⁰⁰ and COFs,¹⁰¹ are great candidates and precursors for robust CO₂ electrocatalysis to CO.

Most interestingly, metal-free materials such as nitrogen doped graphene quantum dots (NGQDs), can also serve as a catalyst for CO₂ reduction even to some hydrocarbons. As usual, transition metal sites are regarded as the active elements for CO₂ catalysis. Wu et al. reported that their nanosized NGQDs could catalyze CO₂ into hydrocarbons with comparable efficiencies and current densities at low overpotentials.¹⁰² From the FE results shown on Figure 2.18, for NGQDs, the catalytic capability started to appear at very low overpotential. From Figure 2.18a, at high overpotentials, this material could catalyze CO₂ into producing C₂H₄, CH₄, EtOH, AcO⁻, even n-propanol, besides CO and formates. Compared with graphene quantum dots (GQD, Figure 2.18b) and N-doped reduced GOs (NRGOs, Figure 2.18c), the capability of catalyze CO₂ reduction to various advanced products like hydrocarbons, alcohols and acids with low HER level was superb. The Tafel slope depicted in Figure 2.18d of NGQDs were lower than that of GQDs and NRGOs, reflecting the fastest kinetics among all the samples tested. They claimed that the unique nanostructure along with the exposure of hetero-doped N edge sites made up NGQDs' unique performance for CO₂ catalysis.

Figure 2.18 (a) FEs of CO, CH₄, C₂H₄, HCOO⁻, EtOH, AcO⁻ and n-propanol at applied cathodic potentials for NGQDs. (b) FEs of CO₂ reduction products for pristine GQDs. (c) FEs to CO₂ reduction products for NRGDs. (d) Tafel plots of partial current density of CO₂ reduction. Reprinted from Ref. ¹⁰², with permission from Springer Nature Publishing AG, Copyright 2016.

2.3.3 Molecular electrocatalysts

Numerous investigations have been applied on molecular catalysts. Most of the homogeneous molecular catalysts are transition metal complexes, where metal centers can be ascribed to the monofunctional sites which can bond with CO₂ and its relevant intermediates. A typical example showing general reaction scheme during CO₂ catalysis has been displayed in Figure 2.1³. Based on plenty of work, homogeneous active molecular catalysts for CO₂ reduction can be categorized into mainly three types: metal complexes with bipyridine-based ligands (bipyridine, terpyridine, phenanthroline...), macrocyclic ligands (cyclams, porphyrins,

phthalocyanines...), and phosphide-based ligands.¹⁰³ Due to limitations on homogeneous catalysis, plenty of work started to heterogenize or immobilize active molecular catalysts onto appropriate supporting materials to eliminate diffusion-controlled process and enhance the charge transfer between the active moieties with the electrode. Therefore, carbon-based material like graphene or carbon nanotubes (CNTs) can be great candidate of the supporting basis.⁷⁷ Furthermore, manually design of single-atom catalysts (SAC) rendering metal-nitrogen coordination sites (MN_x) embedded in carbon materials is emerging as an effective approach for CO_2 catalysis in high efficiency. The monofunctional MN_x sites can also be regarded as a moiety coming from molecular catalyst.¹⁰⁴⁻¹⁰⁵ In this session, homogeneous molecular catalysts and heterogenized catalyst comprising molecular moieties will be discussed separately.

(1) homogeneous molecular catalysts

As mentioned above, transition metal complexes with bipyridine-, macrocycle- and phosphide-based ligands are the mostly investigated monofunctional catalysts for CO_2 -to- CO conversion. $Mn(I)^{106}$ and $Re(I)^{107}$ bipyridine complexes have been widely discussed as active species mostly for catalyzing CO_2 conversion to CO . However, several works have reported other products like formic acid can also be detected by tuning the structure of the ligands. Pendant groups with intramolecular local proton source on the such bipyridine ligand can play an important role on the catalysis process. Franco et al. has developed an $Mn(I)$ complex with a bipyridine ligand containing a phenol pendant group, showing remarkable capability to catalyze CO_2 to CO (70% FE) and $HCOOH$ (22% FE) without adventitious proton source added.⁷² Other than CO , formate was also found in a

comparable efficiency within the products, indicating local proton source could affect the reaction pathway.

Cu complexes for catalyzing CO₂ reduction are seldom reported in very few of literatures in that the first proton-coupled electron of CO₂ on single Cu site (in CuN₄ site) presented an extremely high energy barrier, shown in Figure 2.14b (black trace). However, Angamuthu et al. has constructed a Cu complex coordinated with N and S, which was active in catalyzing CO₂ into oxalates.¹⁰⁸ From Figure 2.19, the initial Cu(II) species, denoted as [Cu₂(L-L)(CH₃CN)₂]²⁺, was reduced under -0.03 V vs NHE into Cu(I) species [Cu₂(L-L)]²⁺. Under CO₂ atmosphere, two [Cu₂(L-L)]²⁺ could reduce CO₂ into oxalates, giving [Cu₄(L-L)₂(C₂O₄)₂]⁴⁺, with Cu sites bridged by C₂O₄²⁻. The C₂O₄²⁻ can be precipitated by Li⁺ in CH₃CN solvent. Such binuclear Cu complex was able to render C-C coupling under such aprotic condition. Another work accomplished by Pokharel et al. also reported a binuclear copper complex catalyzing CO₂ reduction to oxalates,¹⁰⁹ verifying the capability of coupled copper sites can manage C-C formation.

Figure 2.19 Simplified scheme for the reported¹⁰⁸ binuclear Cu complex catalyzing CO₂ reduction to oxalate. Reprinted from Ref. ¹⁹, with permission from American Chemical Society, Copyright 2018.

(2) Molecular catalysts as an active unit for heterogeneous electroreduction of CO₂

Plenty of attempts have been focused on immobilization molecular catalysts on carbon support either through covalent bonding between ligands of specific molecular catalyst and carbon materials¹¹⁰ or through noncovalent bonding via π - π stacking between the carbon support and the target catalyst molecule¹¹¹.

Besides, construct 2D materials from molecular catalysts along with building blocks has been always a challenge. Lin et al. has developed a covalent organic framework (COF) from a cobalt porphyrin molecular catalyst [Co(TAP)], which presented high activity to catalyze CO₂ producing CO at 90% efficiency with 9400 h⁻¹ of TOF in aqueous condition, 26-fold improvement compare with the initial molecular catalyst. Figure 2.20A shows a general synthesis scheme, applying two types of building blocks with different length to control the porosity size for the final COF. The CV curve obtained under inert gas or CO₂ in Figure 2.20B has verified the catalytic activity under CO₂ atmosphere. Moreover, by controlling the amount of Co active sites (doped with Cu sites), it was found that the COF with larger amount active Co revealed inferior catalytic performance regarding the low TONs collected after each time period, shown in Figure 2.20C. The better performance towards COFs originated from the molecular Co(TAP) catalyst could be ascribed to the faster kinetics after the formation of COF, according to relatively flat Tafel slopes compared to the monomer, depicted in Figure 2.20D.

Figure 2.20 (A) Rough synthesis scheme for the metalloporphyrin derived COFs. (B) CV curves obtained under N_2 or CO_2 in pH 7.2 aqueous potassium phosphate buffer (0.2 M) with 0.5 M KHCO_3 under CO_2 or 0.5 M NaClO_4 under N_2 at 0.1 V/s for COF-366-Co and COF-367-Co. (C) Comparisons of TONs of COF-367 with various amount ratio of Co/Cu sites, obtained under electrolysis condition at -0.67 V vs RHE. (D) Tafel slopes of COFs vs the monomer Co(TAP). Reprinted from Ref. ¹⁰¹, with permission from American Association for the Advancement of Science, Copyright 2015.

Chapter 3. Selective Electrochemical Reduction of CO₂ to Ethylene on Nanopores Modified Copper Electrodes in Aqueous Solution

3.1 Introduction

Increasing amount of carbon dioxide emission from utilizing fossil fuels into atmosphere results in a worldwide threat to the climate change.¹¹² Therefore, to alleviate the negative influence on excessive CO₂ emission, multiple approaches that can immobilize and consume the stable greenhouse gas have drawn more attention nowadays.¹¹³⁻¹¹⁹ The conversion of CO₂ into fuels and feedstocks can be one of the promising methods for such purpose. However, owing to the outstanding stability of CO₂, it is difficult and energy-intensive to convert CO₂.¹²⁰⁻¹²³ Traditional catalytic hydrogenation of CO₂ must be conducted at high pressure and high temperature.¹²⁴⁻¹²⁷ The relatively low conversion, unsatisfactory selectivity and non-economic costs can be considered as the major shortcomings of this approach.^{126, 128} Alternatively, the conversion of CO₂ via electrochemical reduction can be considered as another possible candidate to yield fuels and meanwhile overcome the shortcomings related to traditional catalytic hydrogenation of CO₂.¹²⁹⁻¹³⁰ Electrocatalytic reduction of CO₂ has become a cutting-edge area for its several advantages: (1) controllable experimental process and tunable ambient conditions when conducting the reaction; (2) recycled electrolytes and electrodes in some cases; (3) clean electricity power such as solar and hydro- energy without extra CO₂ production; (4) compact, modular and customizable reaction systems and apparatus, possible to be scaled up to practical

production.¹³¹⁻¹³² Through electrocatalytic process, CO₂ can be adsorbed and reduced to various fuels and valuable chemical feedstocks such as CO,⁹⁴ CH₄,¹³³ C₂H₄,¹³⁴ C₂H₆,¹³⁵ HCHO,³⁸ CH₃OH³⁹ and HCOOH³⁸ with the judicious selection of catalysts under moderate ambient temperature and pressure. Nevertheless, challenges still remain in terms of slow kinetics and competitive hydrogen evolution reaction which would lower the energy efficiency of the whole electrocatalytic process. Hence, low performance of some electrocatalysts is recognized as a hindrance of CO₂ electroreduction. It becomes meaningful to overcome the low catalytic activity, poor selectivity and insufficient stability of the electrocatalysts by means of modification, reconstruction, incorporation with novel structures, doping with extraneous atoms and so on.¹³²

To efficiently manage the formation of ethylene during CO₂RR process is an attractive approach to synthesize multi-carbon products in a sustainable manner. For instance, commercial polycrystalline copper manifests a comparative activity of methane and ethylene.¹³⁶ However, there are abundant low-cost accesses to methane such as exploiting natural gases and biogases.¹³⁷ In that case, tuning the selectivity of copper for ethylene over methane is rather more important when considering ethylene is also an indispensable chemical feedstock applied in industry.¹³⁸ Previous studies show that the selectivity between methane and ethylene can be strongly influenced by crystalline orientation.¹³⁹ It is also reported that Cu (111) favors methane whereas Cu (100) is highly active for C-C coupling. In addition, high index facets prefer the ethylene evolution as well.¹³⁶ Thus, it seems to be promising to regulate the morphology of catalysts to expose more crystalline facets that can facilitate the ethylene formation.

Based on this feature of copper related electrodes, this work aims to explore morphological effects on CO₂RR at copper electrodes in aqueous KHCO₃ solution, and most importantly, to tune the selectivity towards useful hydrocarbon fuels and chemical feedstocks, especially ethylene. Meanwhile, it is equally essential to figure out how the morphology of copper electrodes influences the catalytic activity and selectivity towards specific product, including changes on active sites, the adsorption of CO₂ and intermediates and the potential-dependent reaction pathways.

At the beginning, inspired by the method provided by Falong Jia et al.,¹⁴⁰ we obtained a nanoporous surface morphology on a Cu foil through a handy preparation scheme which presented selective ethylene production over methane in 0.1M KHCO₃. A surface alloying-dealloying process was involved to enlarge the surface area and regulate surface morphology for a polycrystalline copper electrode. The surface-polished copper foil was first *in situ* electro-deposited with a layer of zinc, followed by heating under inert gas to form a layer of Cu-Zn alloy. Nanoporous surface morphology was achieved by removing the Zn content from Cu-Zn alloy layer. Investigations on such samples with a thickness gradient of nanoporous layer (including bare Cu foil) were conducted by means of electrochemical measurements and characterization techniques. Sufficient thickness of nanoporous layer on the surface can effectively suppress the evolution of methane during the electroreduction process.

3.2. Experimental Section

3.2.1 Preparation of electrodes

Copper foil (99.98%, 0.025mm), zinc foil (99.95%, 0.1mm), zinc chloride (anhydrous, $\geq 98\%$), phosphoric acid (≥ 85 wt. %), potassium bicarbonate (99.7%), potassium chloride ($\geq 99.5\%$), sodium hydroxide ($\geq 98\%$), Hexadecyltrimethylammonium bromide (CTAB, powder, $\geq 98\%$) and hydrochloric acid (37%) were purchased from Sigma-Aldrich. Ethanol (99%) was purchased from chemicals testing & calibration laboratory. Carbon dioxide gas (99.8%), nitrogen gas (99.9995%) and argon gas (99.9995%) were purchased from Air Liquide. Chemicals were all used without purification. Chemical bath and electrolyte solution were prepared with deionized water, which is produced by Milli-Q Gradient A10 system ($18.2 \text{ M}\Omega \text{ cm}^{-1}$, Millipore).

The commercial Cu foil was first polished in 85 wt % phosphoric acid under the potential of +0.5 V vs Ag/AgCl for 500 s, followed by rinsing with DI water, dried in the vacuum, and saved as a counterpart without nanoporous surface.

The nanoporous Cu foil can be obtained readily by an alloy-dealloy process according to the previously reported work. The general preparation scheme was depicted in Figure 3.1A. In the beginning, the polished Cu foil was electrodeposited to be covered by a $1 \text{ cm} \times 1 \text{ cm}$ zinc layer immersed in the electrolyte, containing 30 g/L ZnCl_2 ($\geq 98\%$), 150 g/L KCl ($\geq 99.5\%$) and 5 g/L CTAB. This in situ electrodeposition process was conducted under a specific cathodic current density of 20 mA cm^{-2} through a three-electrode system, among which a $1 \text{ cm} \times 1 \text{ cm}$ Zn foil (99.95%) served as counter electrode, the polished copper foil as working electrode and Ag/AgCl as the reference. To investigate the effect on different values of thickness of nanoporous layer, we first controlled the deposition time i.e. the depth

of the Zn coating. The final nanoporous samples obtained initially by deposition for 30, 60 and 120 seconds were denoted as 30s, 60s and 120s, respectively.

To obtain different depths of the Cu-Zn alloy layer, 30s, 60s and 120s were respectively heated up to 150 °C in Ar atmosphere for 2, 4 and 8 h, with the heating rate of 2.5 °C/min. By finishing this annealing process, silvery Zn coating was turned into a golden manner, which indicated the formation of Cu-Zn alloy layer. These samples were then rinsed by DI water and EtOH and transferred into 1M NaOH with 0.2wt% CTAB immediately to let the alloyed Zn part dissolve during room temperature. After the dealloying process with proper durations, these samples were taken out and rinsed by DI water and EtOH in turn. Followed by vacuum drying, the as-prepared samples were ready for the measurement and analysis afterwards. Before carrying out the electroreduction, these samples were needed to be immersed in diluted H₂SO₄ aqueous solution with pH value of 4 for 5 min to remove residual impurities.

3.2.2 Instrumentations

X-ray diffraction (XRD) patterns were obtained by using a Bruker diffractometer with Cu K α radiation (D8 Advance X-ray diffractometer, Cu K α , λ = 1.5406 Å, 40 kV and 40 mA) to get the crystallographic information of the materials. Field emission scanning electron microscopy (FESEM; JEOL, JSM-6701F, 5 kV) equipped with energy dispersive X-ray spectroscopy (EDX) was used to observe the morphology and elemental composition of these electrode materials. X-ray photoelectron spectroscopy (XPS; VG ESCALAB MKII instrument) with an Mg K α X-ray source was used for analyzing the surface chemical properties of the samples.

3.2.3 Electrochemical measurements

The description of electrode preparation can be found in the supporting information. An original designed H-type cell separated by NAFION N117 ion exchange membrane, and a CHI660E potentiostat/galvanostat workstation at ambient temperature were used for all electrochemical experiments and tests. The 0.1 M potassium bicarbonate was prepared with deionized water and used as electrolyte. A Platinum electrode was used as counter electrode in the anode cell, while various Cu electrodes and Ag/AgCl (saturated with KCl, iR corrected) electrodes were used as working electrodes and reference electrodes, separately, in the cathode cell. Before electroreduction of CO₂, the cell was bubbled with CO₂ at the flow rate of 20 mL/min passing through the electrolyte for 30 min to ensure saturation. The system was kept being stirred with a magnetic stirrer. Fresh electrode sample and electrolyte were used for each electrochemical test under a specific potential. Headspace of cathode cell was directly linked to a gas chromatograph (Agilent 7890B) equipped with a thermal conductivity detector, Porapak Q column and Molecular Sieve 5A column to analyze gas products. The gaseous samples were fed into GC system every 15.6 min. The final faradaic efficiency under certain potential was obtained by calculating the average of the data from 3rd to 6th samples.

3.3 Results and discussions

3.3.1 Formation of nanoporous surface structure

The formation of Cu-Zn alloy layer was an essential procedure leading to the nanoporous morphology. Heat treatment at a relatively low temperature was reported

to favor the diffusion of the Zn atoms into the crystal lattice of Cu.¹⁴⁰ To investigate whether the alloy layer was formed under specific heating condition, we compared the X-ray diffraction (XRD) patterns obtained after specific procedures of an untreated copper foil. After polishing, the copper foil was deposited with zinc layer and subsequently heated at 150 °C for 4h under Ar atmosphere and finally dealloying in NaOH aqueous solution. Figure 3.1B showed the pattern of untreated copper foil with zinc overlayer. Two characteristic peaks of hexagonal zinc (002) and (100) evidenced the existence of isolated zinc component. This sample was obtained after a 60-second electrodeposition in the electrolyte mentioned above without thermal treatment. Figure 3.1B has validated the alloy layer formation after a 4-hour annealing process under the protection of inert gas atmosphere. The characteristic peak of solid solution phase CuZn appeared at 2θ of 78.4°, accompanied with the depletion of isolated Zn phase. In addition, there were no visible peaks suggesting the existence of zinc phase or solid solution phase after a 12 hours dealloying process, which was almost consistent with the polished copper foil. The peaks near 43°, 50° and 74° correspond to (111), (200) and (220) planes of Cu. It is noticeable that the peak near 43° presented a tiny shift towards left from the deposition procedure. Peak shift can be explained by deposition and thermal treatment, rendering the formation of multiple alloy species. Additionally, Cu-Zn alloy species have peaks flocked together at this location, so it is difficult to distinguish the compositions here precisely. However, the left-shift occurred even after dealloying process, which was supposed to contain no zinc species. Analysis of this sample indicated that the annealed sample only consisted of copper component after dealloying. Figure 3.2 shows the XPS pattern of a specific sample before and after dealloying, suggesting

that zinc component was eliminated on the electrode surface after the whole preparation process.

Figure 3.1 (A) The schematic diagram of the preparation process. (B) Typical X-ray diffraction (XRD) patterns of a polished Cu sample in different stages of synthesis with standard patterns included for reference (vertical line on the bottom). (C) Typical XRD patterns of all types of the as-prepared samples.

Figure 3.2 Typical XPS spectra of Cu 2p and Zn 2p scan for the sample of 120s before and after dealloying process.

To further verify whether zinc part was dissolved completely after etching in alkaline solution, anodic linear sweep voltammetry (Figure 3.3) was measured in N₂ bubbled 0.1 M KHCO₃ solution. The potential window was ranged from -1.0 to 0.2 V vs RHE, with the scan rate of 10 mV s⁻¹ (scan positively). The zinc foil had an oxidation peak at -0.45 V. While the copper foil covered with zinc layer showed a peak located at the same potential, showing that the zinc layer began to be oxidized.

However, a peak at -0.4 V appeared on the alloyed sample, indicating that a different phase was formed after the thermal treatment. At -0.1 V, the dealloyed sample exhibited a feeble peak, which should be attributed to the oxidation of Cu. There was no significant oxidation peak of barre copper foil throughout such potential range, indicating that nanostructured Cu is more reactive than bulk Cu. Combining the results conveyed by Figure 3.1B and Figure 3.3, we can conclude that thermal treatment on the zinc covered copper foil can lead to the formation of Cu-Zn alloy species. Subsequent dealloying in alkaline solution was proved to be feasible for the strip of zinc ingredients. In Figure 3.1B, it is noteworthy that there was a slight left shift of Cu (111) peak on the dealloyed sample, which denotes the d-spacing of (111) was enlarged. The lattice distortion of (111) orientation of copper component after the zinc part was dissolved can be the relic for the entrance and exit of Zn atoms.

Figure 3.3 Anodic linear sweep voltammetry (LSV) of Cu-Zn samples treated under different synthesis stages. Tested in N_2 bubbled 0.1M $KHCO_3$ solution. Scan rate: 0.01 V s^{-1} .

Therefore, it is convincing that proper thermal treatment can result in the diffusion of surface deposited Zn into Cu substrate to form CuZn alloy layer. The as-prepared samples were subsequently chemically etched by 5 wt % NaOH aqueous solution, which proved that the zinc component can be removed effectively. The etching time was determined by the amount of deposited Zn. Noted that the resulting zinc overlayer could completely or partially diffused into Cu substrate based on specific thermal treatment condition but the total amount of zinc would remain constant, we therefore controlled the zinc amount through tuning the duration of electrodeposition time for 30 seconds, 60 seconds and 120 seconds. The nanoporous samples obtained correspondingly are denoted as 30s, 60s and 120s, respectively. To ensure the deposited zinc could infiltrate into Cu substrate adequately, the thermal treatment durations of these samples were set at 2h, 6h and 12h, respectively,

followed by around 6-, 12- and 24-hour dealloying treatment. Erlebacher et al.¹⁴¹ had attempted to explain the mechanism of this process. In this case, the alloy is separated by the selective dissolution of zinc. Initially, the surface zinc layer was dissolved, and island-like morphology was formed through the diffusion of the residual copper component. Afterwards, with the increasing amount of dissolved zinc, the Cu islands could develop along with two dimensions, and finally tend to become an interconnected and porous structure, deeper inside the copper substrate and vaster throughout the surface. In addition, it is also worth noting that excessive etching duration can lead to the oxidation of surface Cu, which might have an impact on the surface morphology. Thus, once the sample surface becomes dark, it is time to pick it out of the alkali solution. The dealloying time settings mentioned above was just an estimated value.

The surface morphology after different stages of treatment was investigated by field emission scanning electron microscopy (FESEM). Polished copper foil (Figure 3.4A) shows almost uniform flat surface with less obvious steps., since the choices of ramp time and target temperature were the same to all the samples prior to their thermal treatment, we could assume that all the samples shared the same diffusion mechanism. The 30s started with the least amount of zinc alloyed with copper substrate and the thinnest alloy layer. From Figure 3.4B, it was evident that the island-like areas were formed with the diameter ranging from hundreds of nanometers to several microns in the final morphology. The morphology almost turned out to be consistent with the theory proposed by Erlebacher et al..¹⁴¹ Zinc atoms near the surface were dissolved whereas the copper atoms realign to generate discrete areas. With the increasing thickness of alloyed layer, shown as 60s (Figure 3.4C), the

discontinuous copper areas began to crosslink with each other into ligament structure, which built the nanoporous manner at the same time. Moreover, the diameter of these pores varied greatly from hundreds of nanometers to a few microns, while the diameter of the ligaments ranged from tens to hundreds of nanometers. It is apparent that a few isolated copper areas still existed, which can be considered as an evidence for the trends of morphological change. Regarding 120s, this sample surface was covered by a large amount of nanoscaled pores with the uniform size around 300 nm (Figure 3.4D), resulting in the huge augment of surface area, compared to the two previous samples. The residual copper formed a universal skeleton structure, with the diameter around 100 nm. Investigating Figure 3.4B, C and D, the trend of morphological change was readily exhibited. Increasing the thickness of Cu-Zn alloy could allow the alkali to enter deeper down from the sample surface. It is not difficult for us to tell the difference of the etching depths as per the difference of the SEM contrast ratio shown in these pictures. Meanwhile, the residual copper would rearrange and restructure gradually to form a universal and relatively stable configuration with the depletion of zinc. The copper blocks formed at first could be elongated to connect or swallow the small particles and therefore a crosslinked framework structure began to develop.

Figure 3.4 Typical plan-view scanning electron microscopy (SEM) images of A) polished copper foil, B) sample 30s, C) sample 60s and D) sample 120s. The inset image on A) showed polished Cu foil with alloyed surface with Zn.

3.3.2 Products from electroreduction of CO₂ on various electrode samples

Cathodic linear sweep voltammetry tests of polished copper foil, 30s, 60s and 120s were measured in CO₂ saturated KHCO₃ solution to investigate the electrocatalysis of these electrodes on full potential range. From Figure 3.5, it was obvious that the faradaic current density of the polished copper foil was significantly lower than that of any nanoporous sample at a specific potential, showing different catalytic reactivity between these copper electrodes. In principle, higher current density indicates higher reaction rate. Larger surface area and more reactive sites might be obtained by means of surface treatment in this experiment.

Figure 3.5 Cathodic linear sweep voltammetry of samples with different surface morphology. Tested in 0.1 M KHCO₃ solution saturated with CO₂ under scan rate 0.1 V s⁻¹.

Moreover, it is likely that entirely different types of active sites might show up after treatment, resulting in the change of selectivity of specific product. It is noteworthy that the faradaic current density among nanoporous species turned higher with the increasing of depth of the nanoporous structure under certain potential, which is probably due to the increment of surface area and active sites.

A considerable amount of research work has drawn the interest on the mechanism for the unique production of hydrocarbons on bulk copper surface. Adsorbed CO₂ was believed firstly ordered in the reduction into CO₂⁻.¹⁴² The adsorbed CO (*CO), which was originated from the reduction of CO₂⁻, was considered to be the key intermediate for the hydrocarbon formation. Tafel plots can help gain insights into possible kinetics of such electrocatalysis reactions. In this case, the Tafel plot was obtained by extracting the data from CO₂ electroreduction under low overpotentials, containing the potential as a function of logarithm of CO partial

current density. As shown in Figure 3.6, at lower current density, all the slopes were around 0.12 V dec^{-1} , which suggested the CO_2 reduction was at first order with its rate determining step of first electron transfer to $\text{CO}_2^{\cdot-}$.¹⁴²⁻¹⁴³ The constant Tafel slopes further demonstrated that the surface modification would not change the onset overpotential of CO_2 electroreduction,¹⁴⁴ but merely the selective behavior towards specific products.

Figure 3.6 CO partial current density Tafel plots for polished copper foil, sample 30s, sample 60s, and sample 120s.

On polished copper foil, the electroreduction of CO_2 was carried out under the potential range of -0.5 to -1.5 V vs RHE . The faradaic efficiencies of the major products are shown in Figure 3.7A. The dynamic initial point of -0.5 V was determined by the inflection point of the linear sweep voltammetry (LSV) curve (Figure 3.5). At this potential, formic acid formation began to appear as a satellite reaction of hydrogen evolution reaction (HER), with the total current density around

2 mA/cm². When such low potentials (-0.6 to -0.8V) were applied, CO₂RR could not be catalyzed effectively, with HER becoming dominant. Under modest overpotentials (-0.8 to -1.0V), formic acid became predominant, with the Faradaic efficiency (FE) of around 35%. Meanwhile, the hydrocarbons (methane and ethylene) started to be detectable. The total FE of hydrocarbons could reach up to its top value of 45% at -1.3 V, with 30% of methane and 15% of ethylene.

Figure 3.7 Faradic efficiencies for CO₂ electrochemical reduction products as function of potentials: (A) Polished copper foil, (B) sample 30s, (C) sample 60s, (D) sample 120s. (E) FEs for hydrocarbons obtained on different electrodes under -0.9 to -1.5V vs RHE. (F) FE ratios of ethylene to methane on all types of the samples.

By controlling the zinc deposition time, nanostructured surface layers with variant thicknesses were obtained and exhibited different product distribution. The electrochemical reduction of CO₂ on nanoporous foils was conducted within the potential range of -0.9 to -1.5 V vs RHE in 0.1 M KHCO₃ solution with CO₂ bubbled.

The potential range was chosen to shed the lights on the hydrocarbon evolution. The potential of -0.9 V was observed to be the onset point of the generation of hydrocarbons for all these nanoporous samples, and similar results as the polished copper electrode were observed. Under low overpotentials (-0.9 V, -1.0 V), HER and formic acid production dominated, which was the same case for both 30s (Figure 3.7B) and 60s (Figure 3.7C). On the case of 120s, however, CO production became predominant when such potential was applied. Starting from -1.1 V, CO evolution was suppressed, and the production of formic acid increased steeply. For 30s and 60s, there were no considerable amounts of CO detected. The selectivity to the evolution of HCOOH or CO depends on the adsorption energy for these two species on the exposed copper surfaces.⁴² With regard to 120s, more complicated skeleton structures and larger numbers of pores can contribute huge augment of specific surface area. Hori et al.¹³⁹ reported that the formation of C₂ compounds could be optimized by the introduction of (111) steps to Cu (100) basal plane, leading to the formation of high-indexed Cu[n(100) × (111)] crystal series, which could be able to promote the dimerization of *CO located on Cu surfaces with such right-angled arrangement. As shown in Figure 3.8A, higher ethylene partial current density on each sample with nanoporous surfaces under a potential range from -1.1 to -1.3V could possibly be explained by the increasing number of active sites along with the highly restrained evolution of methane.

The activity is certainly related to the surface roughness of these samples. The electrochemically active surface area (ECSA) is used as an expression of surface roughness, which was measured by determination of double-layer capacitance of each sample in 0.05 M H₂SO₄ aqueous solution. As exhibited in Figure 3.8B, polished

copper foil gave a capacitance of 0.11 mF cm^{-2} , while 30s, 60s and 120s provided about 5, 9 and 18 times of the capacitance of polished copper foil respectively. Combining higher ECSA and higher ethylene partial density after surface treatment, we can conclude that more reactive sites for ethylene production were brought in by increasing surface area.

Figure 3.8 (A) Partial current densities for ethylene and methane obtained at different potentials for all types of as-prepared samples when conducting the CO₂ electroreduction. (B) Current densities of each as-prepared sample as a function of scan rates with double-layer capacitances indicated by the slope of each curve.

Single crystal work demonstrated that Cu (100) favors the production of ethylene (FE ~40%). The ethylene formation is further facilitated by the introduction of (111) or (110) steps to the (100) basal plane.¹³⁹ In our case, Figure 3.8A exhibits that the production of methane was suppressed increasingly with the degree of the surface treatment. The high ratio of the ethylene FE to methane FE of specific sample (especially 120s) may be the evidence for the introduction of large amount of exposed crystalline steps and edges on the basis Cu (100), i.e. high-indexed crystal facets such as Cu(211), Cu(511).¹⁴⁵ Herein, we applied totally identical procedure to a single

crystal copper foil of (111) orientation. After such treatment, a tiny peak suggesting (200) facets of copper emerged after examined by XRD (Figure 3.9A). Note that the properties of (200) facets are identical to (100) except *d-spacing*. This result can provide an evidence for the transfer of some (111) facets into (100) facets during this treatment, indicating the abundance of (100) as well as stepped and edged atoms may increase on such nanoporous structure, which may account for the selectivity of ethylene over methane.

As shown in Figure 3.7F, the samples with higher extend of surface treatment exhibited higher selectivity towards ethylene over methane along with higher current densities, which remarked higher reaction rate. However, HER was promoted as its partial current density displayed an increasing tendency with higher overpotential, indicated in Figure 3.7. This observation may probably be ascribed to the exposure of more undercoordinated atoms. Atoms with low coordination number are deemed to bind atomic hydrogen more strongly than Cu atoms on a planar surface.¹⁴⁶ Additionally, such atoms are most likely located at edges and steps on the surface. Therefore, facilitated HER can be considered as another evidence for the existence of surface steps and edges.

As a key intermediate of CO₂RR to hydrocarbons, CO should be adsorbed on Cu surface neither too strongly nor too weakly, so that it can be further hydrogenated into hydrocarbon species.⁴² DFT calculations have predicted that Cu (100) terrace preferred ethylene due to its much lower energy barrier for dimerization of *CO than the close-packed (111) facets under proper potential regimes,⁶² which is in alignment of Hori's hypothesis on the mechanism of the *CO dimerization.¹³⁹ The considerable evolution of CO under lower overpotentials on 120s (Figure 3.7D) can be the

evidence for the abundance of exposed (100) terraces. In this case, the applied potential could not facilitate *CO dimerization effectively on such terraces. Due to the mediocre binding capability between *CO and (100) facet, CO could escape from the interface of the electrode into the solution due to mass transfer. Different from 120s, 60s presented little CO production while formate predominated under similar low overpotentials. Besides, as presented in Figure 3.7D, CO production took the lead against formate formation at -1.0 V vs RHE, but an entirely different story at -1.1 V vs RHE. The formation of formate species would compete with the CO evolution under such potentials.¹⁴⁵ Once the electrode was covered by *CO, the *CO would block the electrode surface.¹⁴⁷ If the given overpotential was not sufficient, neither *CO desorption from Cu sites through mass transfer nor dimerization of *CO into hydrocarbons will occur. Formate production would take place instead at this moment. This reported reaction mechanism was shown in Figure 3.9B, demonstrating that there are two major pathways for CO₂ reduction, one leading to formate, the other leading to hydrocarbons.

Figure 3.9 (A) Comparisons on XRD patterns for single crystal Cu (111) foil before (black) and after treated with the same alloy-dealloy procedures (red). (B) Proposed reaction pathways occurred on the copper electrode surface.

Figure 3.10 (A) Electrocatalytic stability performance of the ethylene production on Sample 120s. Measured in CO₂ saturated 0.1 M KHCO₃ solution at -1.3 V vs RHE for 8 hours. SEM images of Sample 120s show the retained nanopored morphology before (B) and after (C) the 8-hour electrocatalysis for the stability test.

The electrocatalytic stability of nanopore modified sample (120s) was also evaluated following the same electrochemical condition at -1.3V vs RHE (Figure 3.10A). The efficiency of ethylene production remained on a same level (~30%) after an 8-hour electrocatalysis. Moreover, the current density has also remained stable during such period (~45mA/cm²). The outstanding steady performance could be

ascribed to the retained nanopored surface morphology (Figure 3.10B and C) before and after such long period of electrocatalysis.

3.4 Conclusions

In situ alloying-dealloying process was used to modify the surface of polished copper foils so as to generate nanoporous morphology. Tuning the thicknesses of the nanostructured surface layer can influence the selectivity of products drastically. With the increasing thickness of nanoporous overlayer, the production of ethylene becomes more efficient. The Faradaic efficiency of ethylene can reach up to dozens of times compared to that of methane, i.e. 35% of ethylene to 0.6% of methane. Material characterization and morphology analysis suggested that the electro-deposited Zn layer could be successfully alloyed with Cu substrate through suitable thermal treatment regimes. The chemical dealloying process was accompanied with the diffusion and reconstruction of residual Cu atoms, which brought in the alternation of the crystalline orientation on the surface. The high selectivity towards ethylene was believed to be due to multiple factors including the exposed crystalline facets, the abundance of (100) facets transited from CH₄ favored (111) facets, along with the possible existence of stepped and edged atoms. This work can give inspirations on *in situ* modification of surface morphology on electrodes used in electrocatalysis. However, further experiments and theoretical methods are still needed to obtain more reliable evidence for the proposed reaction pathways and mechanisms. For example, in-depth characterization of high-indexed crystal facets on the surface would be of great importance.

Chapter 4. Heterogenization of a Monofunctional Molecular Rhenium Complex onto Graphene for CO₂ Electroreduction to CO

4.1 Introduction

Transition metal complexes have drawn intensive attention on electrochemical reduction of CO₂ to carbon monoxide (CO)¹⁴⁸⁻¹⁵⁰ or formic acid (HCOOH)¹⁵¹⁻¹⁵³. Metal bipyridine-type (bpy) complex, especially with Mn(I)^{66, 77} and Re(I)^{103, 154-156} as the metal core, were proved as efficient and selective catalyst for CO₂ reduction to CO¹⁵⁷ or formate⁷⁷. Derivatives of bipyridine ligand such as functional group substituted on the pyridine ring and phenanthroline analogues¹⁵⁸ can be utilized for other catalyst integration. Such monofunctional molecular complex is capable of fine-tuning towards the metal core or the structure of the peripheral ligand to manually control the activity¹⁵⁹ and selectivity¹⁵¹ of specific product on CO₂ reduction. Numerous investigations have been applied into [Re(bpy)(CO)₃Cl] systems for reduction of CO₂ since the initial discovery by Lehn's group¹⁶⁰. Changing the nature of the substituents on the **bpy** ligand can draw massive impact on the activity originated from the electron induced effect¹⁰³. Electron-withdrawing groups (-ethynyl)¹⁵⁰ could reduce the overpotential for the reduction, as well as the catalytic capability. On the contrary, electron donating groups (-tBu) can boost the catalytic while at higher overpotential.¹⁰³

Mounting these molecular catalysts onto electrodes from homogeneous to heterogeneous electrocatalysis can benefit from plenty of aspects. First, solubility

problem of target molecular catalyst can be totally ruled out. Such hybrid materials after heterogenization are allowed to perform in universal electrolytes like water, free of expensive aprotic electrolytes.^{101, 161} Second, the accessible usability can boost the recycle rates of the electrode and the electrolytes, along with a simpler process on separation of the products during catalysis. Moreover, limitations from diffusion-controlled electrocatalysis with catalysts in the bulk solution can be overcome through immobilization process.¹⁶¹ In terms of this aspect, graphene sheets can be appropriate for the heterogenization of these metal complexes in view of the high specific surface area and conductivity,¹⁶²⁻¹⁶³ which presents excellent charge transfer properties for the tethered species.¹⁶⁴ Bearing a π -electron enriched substituent like pyrene species onto the complex became a feasible strategy of catalyst immobilization on graphene matrixes via π - π interaction.⁷⁷

Here, aldehyde substituted bpy was applied for the functional ligand for the formation of Re(I) tricarbonyl complex *fac*-[Re(bpy-CHO)(CO)₃Cl] (**bpyCHORe**) that allow the subsequent integration of pyrene tethering unit for heterogenization on the graphene matrix. The pyrene-free complex was first studied homogeneously in MeCN under both inert and catalytic conditions using cyclic voltammetry (CV) and found the catalytic performance was comparable to the non-substituted [Re(bpy)(CO)₃Cl]¹⁰³ but with much lower overpotential to reach the maximum turnover frequency. The heterogenized graphene composite was applied into aprotic MeCN and fully aqueous electrolytes. It was found that in aqueous condition, HER can compete with the reduction of CO₂, leading to a distinct drop of the faradaic current for the CO evolution.

4.2 Experimental Section

4.2.1 Synthesis of **bpyCHORe**

Scheme 4.1 The molecular structure of **bpyCHORe**.

30mg (0.14mmol) of 2,2'-bipyridine-4,4'-dicarbaldehyde (**bpyCHO**) (AppTec) was dissolved in 20ml toluene. 36.2mg (0.1mmol) $\text{Re}(\text{CO})_5\text{Cl}$ (Sigma Aldric) was then added into this mixture, which was heated to reflux for 2h under Ar. During the heating process, the Re precursor $\text{Re}(\text{CO})_5\text{Cl}$ began to dissolve around 50 °C. The colour of the solution turned to red when the temperature reaches around 80 °C. A deep burgundy-colored solid started to precipitate after refluxing for 30 minutes. The solid was then obtained through filtration, rinsing with cold ethanol, and vacuum drying. 47.2mg of the product was collected, giving a yield of 91.5%. Elemental analysis: calculated for $\text{C}_{15}\text{H}_8\text{ClN}_2\text{O}_5\text{Re}$: C, 34.79; H, 1.56; N, 5.41. Found: C, 34.45; H, 1.48; N, 5.36. ^1H NMR (300 MHz, DMSO-d_6) δ 10.27 (s, 2H), 9.37 (s, 2H), 9.36 (d, $J = 2.6$ Hz, 2H), 8.19 (d, $J = 8.8$ Hz, 2H).

4.2.2 Synthesis of **PyrbpyRe**

Scheme 4.2 The molecular structure of **PyrbpyRe**.

41.4mg (0.08mmol) **bpyCHORe** was added into 10ml anhydrous ethanol. The suspension was moved to heat to reflux under Ar till the solid dissolved. Once the suspension became clear, the heat was removed, and the solution was allowed to cool to 50 °C. Then, 26.7mg (0.1mmol) of 1-pyrenemethylamine hydrochloride (Sigma-Aldric) was dissolved in 10ml anhydrous ethanol with the addition of 1 eq Et₃N (VWR) to neutralize the hydrochloride, which was added to the Re complex solution. The mixture was then heated to reflux under Ar for 24h. An orange solid was formed after a few hours of refluxing. Upon cooling to room temperature, the supernatant was filtered off. The solid was obtained by rinsing with hot methanol and ethanol after recrystallization. After drying under vacuo, 44.8mg of product was obtained, giving the yield as 76.6%. Elemental analysis: calculated for C₃₂H₁₉ClN₃O₄Re: C, 52.57; H, 2.62; N, 5.75. Found: C, 52.45; H, 2.81; N, 5.69. ¹H NMR (300 MHz, DMSO-d₆) δ 10.89 (s, 1H), 9.47 (d, J = 9.4 Hz, 1H), 8.97 (d, J = 3.4 Hz, 1H), 8.95 (d, J = 3.2 Hz, 1H), 8.74 (s, 1H), 8.68 (d, J = 4.6 Hz, 1H), 8.65 (d, J = 4.7 Hz, 1H), 8.57 (t, 1H), 8.54 (s, 1H), 8.53 (d, J = 6.2 Hz, 1H), 8.50 (d, J = 2.8 Hz, 1H), 8.47 (d, J = 2.4 Hz, 1H), 8.26 (d, J = 5.4 Hz, 1H), 8.23 (d, 1H), 8.03 (d, J = 5.1 Hz, 1H), 8.00 (d, J = 4.1 Hz 1H), 7.98 (d, J = 3.7 Hz, 1H), 2.13 (s, 2H).

4.2.3 Synthesis of reduced graphene oxide (G)

Graphene oxide (**GO**) water dispersion was first synthesized after modification on Hummers' method as reported.¹⁶⁵ A 10mg/ml GO dispersion was diluted to 2mg/ml with DI water and transferred into Teflon autoclave and heated at 160 °C for 10h. The black solid was obtained as the reduced graphene oxide (**G**), which was

filtered and rinsed with DI water, ethanol, and isopropanol. The product was then dispersed in isopropanol to give a concentration of 5mg/ml.

4.2.4 Electrode material preparation for CV, CPE and instrumentations

For homogeneous electrochemistry testing, the 3mm (diameter) glassy carbon electrode was first polished with 1 μ m Al₂O₃ powder. Then this glassy carbon electrode was rinsed with DI water and ethanol. Additionally, the electrode was then immersed in ethanol and treated with ultrasonication for 1 minute. After drying under ambient condition, the electrode was ready for use.

For testing the graphene composite samples in heterogeneous ways, the electrodes were prepared as follows: 3 μ l of ~5mg/ml **G** isopropanol dispersion was dropped casting onto a 3mm glassy carbon electrode. The electrode was then dried under IR lamp for 30 minutes, which was subsequently immersed in a DMF solution of **PyrbpyRe** with the concentration of 10mg/ml (13.7mmol/L) for 2h at room temperature under Ar. The electrode was then rinsed with pure DMF and ethanol and dried under vacuo for 30 minutes, which can be used for later testing.

For bulk electrolysis and instrumental characterizations, 1ml of ~10mg/ml DMF dispersion of **G** was added into 10ml 10mg/ml DMF solution of **PyrbpyRe**. The mixture was stirred at room temperature for 2h under Ar. The **G** composite was obtained by filtration and rinsing with pure DMF and isopropanol to remove the loosely bonded molecules. The sample was then dispersed in isopropanol to give the concentration of ~5mg/ml (content of **G**). 100 μ l (10*10 μ L) of this dispersion was evenly cast onto one side of glassy carbon sheet (1cm*1cm) and dried under vacuo.

4.2.5 Electrochemistry

A custom-made H-type electrolytic cell with its cathode chamber and anode chamber separated by NAFION N117 ion exchange membrane, and a CHI660E potentiostation were used for all electrochemical experiments.

Solutions of 0.05M Tetrabutylammonium tetrafluoroborate (TBAB) in anhydrous acetonitrile (ACN) and dimethylformamide (DMF) were prepared as electrolytes for following use respectively. For electrolysis in aqueous phase, 0.1M KHCO_3 solution was used as the electrolyte.

Mesh-type Teflon-Platinum electrode (10mm×10mm) was used as the counter electrode. $\Phi=3\text{mm}$ glassy carbon electrode was applied as the working electrode. For heterogeneous catalysis, the graphene composite would be cast onto the same working electrode. With respect to the preparation of Ag/Ag^+ reference electrodes for nonaqueous electrochemistry, the filling electrolytes should be the same as above-mentioned. AgNO_3 was then added, brought up to the concentration of 10mM, and stored in the absence of light. There would be an -0.01V difference versus Fc/Fc^+ reference. Therefore, to convert the voltage value vs Ag/Ag^+ to Fc/Fc^+ , a difference of 0.01 should be added. For electrolysis in aqueous electrolytes, Ag/AgCl (saturated with KCl) electrode were applied as the reference instead. Electrode potentials corrected for the uncompensated Ohmic loss (iR), where the internal resistance was determined by the workstation itself.

Before CV scans, the electrolyte was saturated with Ar or CO_2 by bubbling the gas for 15min with stirring. Once starting the tests, the gas inlet was raised above the electrolyte. Magnetic stirring was also stopped. The data was collected after 5 cycles, when the curve became stable and repeatable.

Before controlled potential electrolysis (CPE) under CO₂, the electrolyte in cathode chamber was bubbled with pure CO₂ gas at the flow rate of 20 ml/min for 30min to ensure saturation. A gas-tight tube was installed on the headspace of cathode cell, acting as the gas outlet and connected with a gas chromatograph system (Agilent 7890B), which is equipped with flame ionization detector (FID), thermal conductivity detector (TCD), Hayasep column and Molecular Sieve 5A column to analyze gas products. A Hayasep Q and a Mol Sieve 5A column were used for separation of all components of mixture gas. All CO₂ reduction experiments were carried out at room temperature and the electrolytic reaction time before each injection is more than 1000 s to ensure that headspace had achieved the equilibrium. The duration for single run of this GC system was around 830 s (13.7 min).

4.2.6 Characterizations

Nuclear magnetic resonance (NMR) was performed by Avance 300 NMR (Bruker, 300MHz) for confirmation of the molecular structure of the synthesized catalysts. Elemental analysis (EA) was conducted on CHNS Elemental Analyser (Elementar) to determine the content of C, H, and N within the complexes along with the ligands. X-ray diffraction (XRD) patterns were obtained by using a Bruker diffractometer with Cu K α radiation (D2 Phaser, Cu K α , $\lambda = 1.5406 \text{ \AA}$, 40 kV, and 40 mA) to investigate the crystallographic information for the **G** sheets. Transmission electron microscopy (TEM; JEOL, JEM-2010, 200 kV) equipped with energy dispersive X-ray spectroscopy (EDX) was used to confirm the morphology and elemental composition of the electrode materials. Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer) was used to characterize the structure and composition of the synthesized catalysts and **G** composites. X-ray photoelectron

spectroscopy (XPS; VG ESCALAB MKII instrument) with an Mg K α X-ray source was used for analyzing the surface elemental composition and valence state of the films. A RENISHAW Raman microscope with WIRE 2.0 software and 514.5 nm emission line of laser was used for investigation on the **G** related materials.

4.3 Results and Discussion

4.3.1 Characterization of ligands, relevant complexes and immobilization on graphene basis

Scheme 4.3 Synthetic route of the complex **PyrbpyRe**. Condition i): Re(CO)₅Cl, toluene, reflux, Ar; ii): 1-pyrenemethylamine hydrochloride (**NH₂Pyr**), Et₃N, ethanol, reflux, Ar.

PyrbpyRe was synthesized using Schiff base condensation from amine and aldehydes. Pyrene groups were imbued with π electrons, which can attach to other π - π conjugated structures like graphene, carbon nanotubes and even carbon black through π - π stacking interaction. Therefore, pyrene groups can be grafted onto active molecules as a tether to immobilize those dissociative catalysts onto electrode surface. However, this intermolecular interaction is not as strong and stable as

covalent bonds. The synthesized compounds were first characterized by $^1\text{H-NMR}$ and EA.

To investigate the metalation of bipyridine groups by Re precursor $\text{Re}(\text{CO})_5\text{Cl}$, FTIR was applied to confirm the absorbance of CO coordinating the Re center. The dispersion of each sample was dropped and cast onto KBr slices and dried under vacuum before use. Figure 4.1A presented the IR absorbance of each reactants and products. Combining Figure 4.1B, the Re complex **bpyCHORe** showed 3 separate absorbance bands regarding CO ligands, located at 2025cm^{-1} , 1938cm^{-1} and 1906cm^{-1} . After grafting with pyrene basis, the absorbance bands were shifted to 2019cm^{-1} , 1906cm^{-1} , and 1890cm^{-1} , respectively. These varying shifts were caused by electron donating/withdrawing effect on the bipyridine ligand. The pyrenemethylamine group substituted the $-\text{CHO}$ group, lowering the electron withdrawing effect of pyridine ligand, giving a red shift of CO absorbance. Same shifting trends were demonstrated on the literatures¹⁰³ ($[\text{Re}(\text{bipy-tBu})(\text{CO})_3\text{Cl}]$, 2023cm^{-1} , 1916cm^{-1} , 1898cm^{-1} ; $[\text{Re}(\text{bipy})(\text{CO})_3\text{Cl}]$, 2025cm^{-1} , 1918cm^{-1} , 1902cm^{-1} ; $[\text{Re}(\text{bipy-COOH})(\text{CO})_3\text{Cl}]$, 2037cm^{-1} , 1935cm^{-1} , 1911cm^{-1}). Immobilization of the compounds onto reduced graphene oxide (**G**) was also confirmed through FTIR. The control sample **G|bpyCHORe** was obtained following the same method to immobilize **PyrbpyRe**. Briefly, **bpyCHORe** was dissolved in DMF along with dispersed **G**, the mixture was then stirred at room temperature. The sample was then rinsed with DMF and isopropanol for several times and dispersed in isopropanol. Figure 4.1C compared the bare **G**, control sample **G|bpyCHORe** and the sample **G|PyrbpyRe**, which revealed that there was no clear absorbance at $\nu(\text{CO})$ regarding the bare **G** and the control sample. On the contrary, the sample with pyrene grafted

Re complexes showed distinguishable absorbance within the range of $\nu(\text{CO})$, indicating the Re complexes were successfully anchored onto graphene sheets. Therefore, grafting of π electron enriched structures, especially polycyclic aromatic hydrocarbons like pyrene is essential for anchoring dissociated small molecular catalysts.

Figure 4.1 FTIR transmittance spectra of all the reactants and products (A), enlarged view for determining absorbance of CO regarding Re complexes (B), and comparison of immobilizing Re complexes onto **G** before and after grafting with pyrene basis (C).

Raman spectroscopy was also utilized to investigate the interaction between the complexes and the **G** substrate. Raman spectra for the pristine and composites loaded with Re complexes were obtained with 514nm laser applied (shown in Figure 4.2). The peak located around Raman shift 1340cm^{-1} , 1580cm^{-1} and 2700cm^{-1} can be assigned to D band, G band and 2D (G') band respectively.¹⁶⁶

The G band represents the sp^2 carbon vibration regarding graphene related materials, while D band is attributed to the defects, grain boundaries and other disorders. The satellite on D band (indicated by the green arrow) of the sample with catalyst immobilized indicated adventitious species, which intensified the disorder and defect of π conjugated sp^2 C-C backbone compared to the bare graphene, demonstrating the attachment of extraneous molecules.

Figure 4.2 Raman spectra of bare graphene (black) and the graphene composite loaded with Re complex (**G|PyrbpyRe**, red).

Surface element content and valence status was analyzed by X-ray photoelectron spectroscopy (XPS). Figure 4.3 showed the results of broad scan (Figure 4.3A) of all

samples, and the comparison of narrow scan for the selected Re 4f and Cl 2p of all samples including the blank and the control sample. From the comparison results of Re 4f and Cl 2p scans, the control showed little loading capacity of Re species (atomic ratio of Re: 0.03%). Constrained by the sensitivity of Cl detection, there was even no noticeable signal regarding the control. With respect to the graphene loaded with Re complex grafted by pyrene tether, the integrated peak area of Re 4f was around 20 times (atomic ratio of Re: 0.55%) as the control, indicative of the effectiveness of this immobilization strategy.

Figure 4.3 Broad XPS survey (A) and narrow scans of Re 4f (B) and Cl 2p (C) results of bare graphene (dark), the graphene composite (blue) and the control sample containing Re complex without pyrene grafted (red).

In order to investigate the element content of the graphene composite **G|PyrbpyRe**, narrow scans of Re 4f, Cl 2p and N 1s were differentiated and fitted respectively. From Figure 4.4A, a couple of peaks at 44.3eV and 42.0eV can be attributed to Re 4f_{5/2} and Re 4f_{7/2} respectively, which is consistent with the Re(I) species within reported Re(L)(CO)₃Cl complexes. Cl 2p scan presented 2 types of Cl, which may result from the isomerism. Cl can be located in or perpendicular against the plane determined by Re core and bipyridine ligand (Re-bpy). When Cl atom in plane with Re-bpy, its electron density could become reduced due to the conjugated effect from the ligand, compared with the one vertical to the Re-bpy plane. Organic form of Cl is not as electron-enriched as chlorides (Cl⁻). Therefore, different Cl species indicated by the XPS results can be originated from the existence of isomers.

With respect to N 1s scan, pyridinic N dominated in the content of N species. The -C=N- bond generated from *Schiff* base condensation can also be attributed to pyridine-like N. The minor content graphitic (sp³) N may come from the residual of the solvent DMF.

Figure 4.4 XPS peak identification and analysis of Re 4f, Cl 2p and N 1s within the graphene composite **G|PyrbpyRe**.

The morphology along with the elemental distribution of this composite was investigated by TEM and EDX. From the TEM images of different magnifications, this composite displayed that the graphene sheets were slices with the diameter no larger than hundreds of nanometers. When zoomed in, the porous structure of graphene slices was presented (Figure 4.5D). Elemental mapping of the selected C, O, N, Re and Cl indicated that the Re complexes were attached uniformly on the graphene supports (Figure 4.6).

Figure 4.5 TEM images obtained from different positions under different magnifications of G|PyrbpyRe graphene composite.

Figure 4.6 Mapping images for the composite **G|PyrbpyRe** obtained from EDX equipped HRTEM regarding the selected elements (A) C, blue; (B) O, purple; (C) N, teal; (D) Re, red; (E) Cl, green; (F) mixed results.

4.3.2 Electrochemical studies

The electrochemical response of complex **bpyCHORe** was examined through cyclic voltammetry (CV). Without pyrene basis grafted, it is better to investigate the electrochemical properties in homogeneous way. Therefore, this complex was first dissolved in acetonitrile to form a 0.5mM solution with 0.05M NBu₄BF₄ as the supporting electrolyte. CV was conducted first under Ar with a bare 3mm glassy carbon working electrode. Shown by the black trace in Figure 4.7, the Re complex exhibited a quasi-reversible redox response at:

$$(1) {}^1E_{1/2} = -1.14\text{V (vs Ag/AgNO}_3, -1.13\text{V vs Fc/Fc}^+);$$

Followed by an irreversible reduction process at:

$$(2) E_p = -1.44\text{V (vs Ag/AgNO}_3, -1.43\text{V vs Fc/Fc}^+);$$

A quasi-reversible redox at:

$$(3) {}^2E_{1/2} = -1.97\text{V (vs Ag/AgNO}_3, -1.96\text{V vs Fc/Fc}^+).$$

These redox events were assigned to (1) first reduction of the complex into radical anion with added electron; (2) dissociation of the anion Cl⁻; (3) metal-based reduction, including possible dimerization to generate -Re-Re- bond.¹⁵⁵ As the electron-withdrawing effect of -CHO groups on bipyridine ligand, this complex presented a less negative reduction potential of metal center compared to the complexes with electron-donating ligands such as [Re(vinyl)(CO)₃Cl] (-2.06 V vs Fc/Fc⁺)¹⁵⁰ and [Re(t-Bu)(CO)₃Cl] (-2.22V Fc/Fc⁺)¹⁶⁷.

The catalytic performance was investigated under CO₂ atmosphere. A negative shift of the potential for each reduction event has been found probably due to a CO₂-involved process such as adsorption and coordination on the metal center. Under catalytic condition, the dimerization may not occur as the CO₂ could occupy the vacancy left by Cl⁻. A distinct enhancement of peak current under catalytic condition (i_{cat}) was assigned at reduction process (3), indicating that the complex was active towards reduction of CO₂. The ratio of i_{cat}/i_p (i_p denotes the peak current under inert conditions) was extracted from the CV curve to obtain the constant k_{obs} of this catalytic process, according to Equation 4.1. Under same ambient conditions, higher i_{cat}/i_p ratio means higher catalytic activity.¹⁹

$$i_{cat}/i_p = \frac{1}{0.446} \sqrt{\frac{RTk_{obs}}{zFv}} \quad (4.1)$$

Figure 4.7 CV curves of **bpyCHORE** obtained under Ar (black) and CO₂ (red). Blank scans without addition of Re complexes was also included for comparison under Ar (blue) or CO₂

(green). Condition: 0.1 V s⁻¹, 0.05M NBu₄BF₄/MeCN. Redox events were labelled. The pink arrow indicated the peak shift under CO₂ atmosphere.

In Equation 4.1, R is the molar gas constant; T is the ambient temperature; z is the number of electrons transferred during a molar catalytic reaction (in this case, CO₂ to CO, $z=2$); F is the Faradaic constant; v is the scan rate (in this case, 100 mV s⁻¹).

The i_{cat}/i_p ratio was found to be 12 from the CV curve. The catalytic reaction constant k_{obs} was then calculated to be 223.5 s⁻¹ accordingly. This value was considered as the TOF_{max} regarding the catalytic Tafel plot (TOFs vs applied overpotential η) according to Equation 4.2, where $E_{CO_2/CO}^0$ is the thermodynamic potential of CO₂ conversion to CO. In MeCN, the potential was reported at -0.75V vs NHE,¹⁶⁸ i.e., -1.55V vs Ag/Ag⁺. $E_{cat/2}$ was assigned to half-wave potential of the catalytic wave. In this case, the value of $E_{cat/2}$ was observed as -2.0V. Hence, the benchmark results regarding the catalytic Tafel plots of Re bipyridine complexes with different 4,4'- substituent groups can be determined by using plotting Equation 4.2 with overpotential η as the variable (Figure 4.8).¹⁶⁹

$$TOF = \frac{TOF_{max}}{1 + \exp\left[\frac{F}{RT}(E_{CO_2/CO}^0 - E_{cat/2} - \eta)\right]} \quad (4.2)$$

Figure 4.8 Benchmark of homogeneously catalytic Tafel plots of Re bipyridine complexes with various 4,4'-substituent groups as -CHO (black, this work); -tBu (red, ref.¹⁶⁷); -CH₃ (blue, ref.¹⁶⁷); -H (green, ref.¹⁶⁷); -ethynyl (yellow, ref.¹⁵⁰) and -vinyl (purple, ref.¹⁵⁰).

After being grafted by pyrene groups, the electrochemical properties of the complex were also tested under homogeneous conditions regarding both inert and catalytic atmosphere. To increase the solubility of the grafted complex in MeCN, DMF was added into the electrolyte to form the concentration of 1M. Thus, $E_{CO_2/CO}^0$ would not give too much of the difference in this electrolyte. To test the potential offset of $E_{CO_2/CO}^0$ in this mixed electrolyte, non-grafted Re complex **bpyCHORe** was also dissolved in this solution. CV was performed under Ar and it was found that there was almost no potential shift of the redox events. Afterwards, the electrolyte containing 0.5mm **PyrbpyRe** was applied for CV scans under Ar or CO₂. From the CV diagrams in Figure 4.9A, the electrochemical response became more sophisticated after grafted with pyrene basis. Referred to non-grafted **bpyCHORe**, the complex should undergo a ligand-based reduction first, followed by a possible

dimerization and metal-based reduction. The electrochemistry of the ligand became more complicated since not only the *Schiff* base linkage (-C=N-) but the π -electron enriched pyrene group would also display a sensitive manner towards charge transfer and/or proton transfer. Indicated by CV curves obtained under Ar and CO₂, CO₂ can be reduced at the potential where the reduction of Re center could occur. Under inert condition, the reduction of Re center can be assigned to the reduction at -2.2 V vs Ag/Ag⁺. A quasi-reversible redox right before the metal reduction at $E_{1/2} = -1.8$ V became irreversible under catalytic condition, indicating that it was the first ligand-metal charge transfer.¹⁰³ This area was emphasized by a grey box on Figure 4.9A, which was selected to determine the scan rate dependence kinetics under inert condition subsequently.

Scan rate dependence of the peak current was also resulted from a series of CV scans with various scan rates from 0.02 V s⁻¹ to 0.6 V s⁻¹ within the selected potential window (Figure 4.9B). The peak current was shown to follow a proportional relationship (intercept=0) regarding the square root of the scan rates (Figure 4.9B inset), suggesting a diffusion-controlled redox process, corresponding to homogeneous electrochemistry. *Randles Sevcik Equation*¹⁷⁰ (Equation 4.3) has unveiled this i_p -scan rate dependency for diffusion-controlled processes, where i_p = peak current of redox wave, F = Faradaic constant, R = universal gas constant, T = temperature, D = diffusion coefficient, n = # of electrons transferred, ν = scan rate, A = geometric area of the working electrode, and c_{cat} = catalyst concentration.

$$i_p = 0.4463 n F A c_{cat} \sqrt{\frac{n F D \nu}{R T}} \quad (4.3)$$

The ratio of i_{cat}/i_p has dropped to 6, leading to a drop of TOF_{max} down to 55 s^{-1} .

The inferior homogenous catalytic activity may be subjected to the decreased diffusion coefficient according to Equation 4.3.

Figure 4.9 (A) CV curves of Pyr bpyRe under Ar and CO₂ at 0.1 V s^{-1} in $0.05\text{ M NBu}_4\text{BF}_4/\text{MeCN}$ containing 1 M DMF . (B) Scan rate dependence of peak current of the redox at -1.8 V , determined under Ar in $0.05\text{ M NBu}_4\text{BF}_4/\text{MeCN}$ containing 1 M DMF . Inset: linear fittings of peak current vs square root of scan rate.

However, when anchored on the electrode surface, this complex can still retain active towards catalytic reduction of CO₂ regardless of this diffusion barrier.

Heterogenized catalysts will perform charge transfer directly with the electrode, not confined by diffusion kinetics any further. The graphene composite loaded with the complex or bare graphene was dropped onto a glassy carbon working electrode with the diameter of 3mm. CV scans were performed under Ar or CO₂ in 0.05M NBu₄BF₄ in MeCN. From the results shown in Figure 4.10, under inert atmosphere, an irreversible reduction peak was recorded at -1.68V, which can be ascribed to ligand-metal charge transfer. Compared to the results collected under homogeneous condition, the peaks regarding the responses of the ligand disappeared. This fact can account for a direct charge transfer from the electrode to the metal center. After saturated with CO₂, an irreversible peak was observed at -1.36V, indicating the adsorption of CO₂. The reduction at -2.1V showed catalytic activity under CO₂. It is noteworthy that if the lower limit of the potential window reached more negative than -2.5V, a distinct deactivation could be observed starting from the second scan, which could be ascribed to unexpected damage to the complex due to the high cathode voltage.

Figure 4.10 CV scan results of the graphene composite G|PyrbpyRe under Ar or CO₂. For comparison, the bare graphene was also included based on the same conditions.

The electrochemical response obtained by CV can help determine whether the active complexes were heterogenized onto graphene base. Under inert conditions, the scan rate dependence of the peak current was performed through the same method mentioned above (Figure 4.11A). At -2.5V vs Ag/Ag⁺, a reversible redox emerged, which can be ascribed to the dimerization for the formation of Re-Re bond, which could not be produced in the presence of CO₂ since the reaction of [Re(Pyrbpy)(CO)₃]⁻ with CO₂ is much faster than electron transfer from the cathode.¹⁵⁵ Such high cathode voltage could destroy the activity of the catalyst under CO₂. The peak current of this redox was chosen to confirm the scan rate dependence, which presented proportional to the scan rate. This fact demonstrated that this redox was a surface-controlled process, indicating that the active components were immobilized on the electrode surface, unveiled by Equation 4.4,¹⁷¹ where i_p = peak current of redox wave, F = Faradaic constant, R = universal gas constant, T = temperature, n = # of electrons transferred, ν = scan rate, and Γ = catalyst loading.

$$i_p = \frac{n^2 F^2 \Gamma \nu}{4RT} \quad (4.4)$$

Compared with Equation 4.3, the peak current during the heterogeneous process does not contain any parameters relating to diffusion kinetics, indicating that this catalytic process contains direct charge transfer with the working electrode.

Figure 4.11 (A) Broad CV scans of the graphene composites immobilized with active complexes with a series of scan rates. (B) Scan rate dependence of the reduction peak current regarding the redox at -2.5V vs Ag/Ag⁺.

The catalyst loading on the surface of the composites can be calculated on the basis of CV peak area, according to the equation below, where Q = charge extracted from integration of redox waves in CV; z = # of electrons required for redox event, in this case, $z=2$; F = Faradaic constant; $A_{\text{electrode}}$ = geometrical area of the electrode = 0.07 cm²; Γ = catalyst loading.

$$\Gamma = \frac{Q}{zFA_{\text{electrode}}} \quad (4.5)$$

The charge was calculated regarding two oxidation waves at around -2.4V ($Q_1 = 5.4 \mu\text{C}$) and -1.7V ($Q_2 = 3.9 \mu\text{C}$) based on the CV in the scan rate of 0.15 V s^{-1} . The difference between these two values revealed the disparity of the electrochemical activity towards different redox event. Taking into account that the potential applied during CPE was around -2.0V, Q_2 was suitable for the subsequent TOF estimation. Therefore, the surface coverage Γ and the active amount n_{cat} of catalysts can be obtained as $0.29 \text{ nmol cm}^{-2}$ and 0.02 nmol , respectively.

4.3.3 Controlled Potential Electrolysis (CPE) Under CO_2

CPE was conducted at -2.1 V vs Ag/Ag^+ in CO_2 bubbled acetonitrile containing 0.05M NBu_4BF_4 for 5000 s. The graphene composite was applied onto one side of a glassy carbon piece with the immersed area of 1 cm^2 . The faradaic efficiency (FE) became stable after 1660 s of CPE, probably because of the initial consumption of the residual moisture taken up by the electrolyte. The faradaic efficiency for producing CO was stabilized at ~92% after running CPE for 2500 s while the current was keeping decreased throughout the entire process of CPE, which would be subject to partially deactivation and the falling-off of the catalyst from the graphene basis. From Figure 4.12, the maximum TOF during the CPE can be calculated as 35 s^{-1} (marked red on Figure 4.12B) after running for 1660 s (the second run of the GC sequence), according to the equation below,¹⁰¹ where i is the current, FE is the Faradaic Efficiency for the desired product, z is the number of electrons required for redox event ($z=2$ for CO_2 conversion to CO), F is Faradaic constant and n_{cat} is the loading amount of the catalyst.

$$TOF = \frac{i \times FE}{z \times F \times n_{cat}} \quad (4.6)$$

Figure 4.12 Above: CPE I-t curve between the catalyst and the bare graphene on the glassy carbon working electrode (blank); Below: Faradaic efficiency of CO₂ reduction to CO during the CPE process on the catalyst immobilized on the graphene.

Unlike Mn(I) analogues, Re(I) bipyridine complexes were found active towards CO₂ reduction without the existence of proton. However, it does not signify that the addition of proton source such as water, trifluoroethanol and phenol would have nothing to do with the CO₂ reduction performance.¹⁶⁷ Here, CPE was applied in fully aqueous condition to investigate the CO₂ reduction activity. CV response of this graphene composite indicated a catalytic process starting from -1.2V (vs Ag/AgCl) (Figure 4.13A). Under CO₂, the faradaic current was obtained an enhancement. Apart from HER, this material would be capable for CO₂ reduction. The potential for CPE was fixed at -1.5V vs Ag/AgCl, keeping the same level as -2.1V vs Ag/Ag⁺ in aprotic solvents.

Figure 4.13 (A) Comparisons of CV curves obtained from aqueous solution regarding the catalyst material and graphene basis under inert and catalytic atmosphere. Condition: 0.1M KHCO₃, 0.1 V s⁻¹. (B) I-t curve applied for CPE and the FEs for hydrogen and CO. Condition: -1.50V vs Ag/AgCl, CO₂ bubbled 0.1M KHCO₃.

Under fully aqueous condition, the CPE was also performed in 0.1M KHCO₃ bubbled with CO₂. With maximum of 28% faradaic efficiency for CO generation, the main process was still presented to be hydrogen evolution (Figure 4.13B). The I-t curve showed that the current density was stabilized at ~ -1.0 mA cm⁻² shortly after starting the CPE. No significant decrement of the reactivity was found during the CPE process, probably due to the hydrophobic nature of graphene surface, which may impede the catalyst migration through the interface between the electrode and bulk electrolyte. Compared to the result from aprotic condition, the mean faradaic current for CO production has dropped from 1.4 mA cm⁻² to 0.28 mA cm⁻².

4.4 Conclusions

The Re(I) bipyridine tricarbonyl complexes were proved to be an active homogeneous catalyst towards CO₂ electroreduction in aprotic electrolytes. In this work, Re(I) tricarbonyl complex with 4,4'-aldehyde group substituted bipyridine as the ligand was investigated firstly for homogeneous catalysis and found active towards CO₂ reduction. By grafted with π electron enriched polycyclic groups, such as pyrene in this case, this complex can be successfully anchored onto carbon substrate like graphene through π - π stacking effect, which can be applied as a heterogeneous catalyst for CO₂ electroreduction.

In aprotic electrolytes, the graphene composite as the catalyst material showed considerable reaction rate to reduce CO₂ to CO with the efficiency of 92% and the TOF of up to 35 s⁻¹. Amount loss of complex immobilized was observed. Some loosely bonded complexes could migrate into the bulk electrolyte, leading to the decrement of the Faradaic current. In fully aqueous electrolytes, the HER would compete with CO₂ reduction and became dominant throughout the CPE process, bringing about a 28% efficiency for producing CO.

In sum, this method is practical for tethering simple single-sited molecular catalyst onto carbon support with high specific surface area and considerable conductivity. This heterogenization process can avoid unexpected diffusion course resulting from homogeneous catalysis.

Chapter 5. Highly Robust CO₂ Reduction to CO in Aqueous Solution on Graphene Electrode Modified by Iron Porphyrins Comprising Intramolecular H-bond Donor

5.1 Introduction

Introduced by the previous chapter, molecular catalysts for electrochemical CO₂ reductions can be systematically modified to achieve expected activity and selectivity^{66, 172-176}. Plenty of molecular catalysts comprising macrocycle ligands, coordinated with transition metals¹⁷⁷⁻¹⁷⁸, have been proved to be effective and robust mainly towards CO₂-to-CO conversion particularly in organic aprotic media¹⁷⁹. Transition metal coordinated porphyrins towards CO₂ reduction prevailed from 1980s¹⁸⁰⁻¹⁸¹. Since the global energy issues have been raised in recent years, the interest towards the use of those chemicals for CO₂ reduction has arisen again¹⁸². Iron porphyrins were also proved to be effective for CO₂ reduction to CO without exception. Particularly, iron(0) sites under catalytic condition can bond CO₂^{179, 182-183}. Coupling of electron transfer and proton transfer, the C-O bonds of CO₂ can break, giving rise to CO release¹⁸². Unlike some molecular catalysts, such as Re(bpy)CO₃Cl¹⁶⁷, proton transfer was confirmed to be essential in the catalysis process based on iron porphyrin. Research done in organic media with addition of Brönsted acid has presented a sustainable reaction retaining high catalytic efficiency¹⁷⁹. Moreover, modification of the porphyrin ligands with OH groups on particular sites can bring about high local proton concentration, boosting the catalytic performance.¹⁷⁹

Inspired from the mechanism of catalytic routes of CO₂ conversion on iron porphyrins and knowing that the proton source is essential, there could be a possibility to perform CO₂ reduction in aqueous solutions based on these metalloporphyrins, which are proved to be stable in water.¹⁸⁴ Most of the investigations on such catalysts are performed homogeneously in organic solvents with Brönsted acid as an additive. In water-based electrolytes, however, porphyrin species are usually solids, showing little solubility. Moreover, these solids are still not appropriate to be directly used as electrode material because of the poor conductivity. Herein, heterogenization of these compounds onto proper support materials should be inevitable.

Anchoring these molecular catalysts onto electrodes in heterogeneous manner instead of homogeneous catalysis can benefit from plenty of aspects as demonstrated by the previous chapter. Heterogeneous catalysis in water-based electrolytes can be more economic and accessible in most cases.¹⁰¹ However, fully aqueous condition can intensify the competition with hydrogen evolution (HER),¹⁸⁵⁻¹⁸⁶ which may be demanding for large amount molecular catalysts. In general, graphene sheets can be appropriate for the substrate to support π -electron enriched porphyrin analogues via π - π interaction in view of the high specific surface area and conductivity of graphene,¹⁶²⁻¹⁶³ which also presents excellent charge transfer properties for the surface bonded species.¹⁶⁴

In this work, a type of modified porphyrin ligand with *ortho*-sited NH₂ groups on the phenyl rings of tetraphenyl porphyrin (TPP) was allowed to be coordinated with iron. In both homogeneous and heterogeneous conditions, this molecular catalyst exhibited great capability of CO₂ reduction to CO. After heterogenized onto

graphene, this compound was able to suppress HER in a significant degree in aqueous media, with the Faradaic efficiency for CO production more than 99%, much higher than the iron coordinated variants of bare tetraphenyl porphyrin and *para* positioned -NH₂ modified tetraphenyl porphyrin. Preliminary computational results reveal that the NH₂ groups on ortho sites can play a role of H-bond donor for stabilizing bonded Fe(0)CO₂ sites, which may benefit further protonation and C-O bond cleavage, rendering CO generation.

5.2 Experimental Section

5.2.1 Synthesis of iron porphyrins with different phenyl substituents on *meso* position

Scheme 5.1 Molecular structure of iron porphyrins to be prepared.

0.05mmol metal-free porphyrin ligand [*i.e.* 5,10,15,20-(tetra-4-aminophenyl)porphyrin (TAP), 5,10,15,20-(tetra-2-aminophenyl)porphyrin (oTAP) and 5,10,15,20-(tetraphenyl)porphyrin (TPP) (PorphChem)] was dissolved in 15ml dimethylformamide (DMF, Sigma) mixed with 10ml of chlorobenzene (Sigma), respectively. 41.0mg (0.15mmol) FeCl₃·6H₂O (Sigma Aldric) was added into the abovementioned solution, which was then moved to reflux at 120 °C for 12h under

argon flow. After being cooled to room temperature, the mixture was applied to a rotary evaporator to remove the solvents. Excessive amount of pure water was then added into this highly concentrated mixture to render the targeted precipitation. The mixture was filtered off and rinsed with pure water and a small amount of cold ethanol. After recrystallization in a mixed solution of dichloromethane and ethanol, the solids were collected and dried under vacuo. For synthesis of FeTAP, 2ml of 37% HCl solution should be injected to the reactor every 3 hours during the refluxing to prevent the para-NH₂ coordination with Fe³⁺.

5.2.2 Synthesis of reduced graphene oxide (**G**)

The reduced graphene oxide (**G**) was obtained as shown in Part 4.2.3, which was filtered and rinsed with DI water, ethanol, and DMF. The product was then dispersed in DMF to give a concentration of 10mg/ml.

5.2.3 Electrode material preparation for CV, CPE and instrumentations

For homogeneous electrochemistry testing, the 3mm (diameter) glassy carbon electrode was prepared for readily use as shown in Part 4.2.4.

For testing heterogeneous samples, the electrodes were prepared as follows:

2ml DMF dispersion of **G** was mixed with 0.01mmol of iron porphyrins. DMF was added to keep the total volume at 10ml (The concentration of iron porphyrins would be 1mmol/L). The mixture was stirred at room temperature for 12h. Upon finished, the mixture was applied on suction filtration. The filter cake was rinsed by DMF and ethanol till the filtrate became clear. Then, the filter cake was collected and subsequently dispersed into isopropanol to form the concentration of 2mg/ml (in graphene terms). The dispersions of these iron porphyrin graphene

composites were dropped and pasted onto carbon fiber paper for preparation of the electrode material, which can be used for later testing after drying under IR lamp.

5.2.4 Electrochemistry

A custom-made H-type electrolytic cell and the CHI660E potentiostation were configured to the same specs as described in Part **4.2.5**.

Solutions of 0.05M Tetrabutylammonium tetrafluoroborate (TBAB) in DMF were prepared as electrolytes for following use respectively. For electrolysis in aqueous phase, 0.1M KHCO_3 solution was used as the electrolyte.

Mesh-type Teflon-Platinum electrode (10mm×10mm) was used as the counter electrode. $\Phi=3\text{mm}$ glassy carbon electrode was applied as the working electrode. For heterogeneous bulk CO_2 catalysis, the carbon fiber paper coated with catalysts would be installed onto a supporting clamp as the working electrode. With respect to the preparation of Ag/Ag^+ reference electrodes for nonaqueous electrochemistry, please see Part **4.2.5**. In this case, there was no distinguishable potential difference after calibration using Fc/Fc^+ . Therefore, in this case, when converting the voltage value to which versus SHE, a difference of +0.75V should be added towards the original value vs Ag/Ag^+ (calibrated with Ag/AgCl). For electrolysis in aqueous electrolytes, Ag/AgCl (saturated with KCl) electrode were applied as the reference instead. Electrode potentials corrected for the uncompensated Ohmic loss (iR), where the internal resistance was determined by the workstation itself. When necessary, the potential value would be converted versus RHE by adding a difference of +0.6V on which recorded vs this Ag/AgCl reference.

For procedures when performing CV scan, please see the descriptions in Part 4.2.5. For controlled potential electrolysis (CPE) under CO₂, the procedure along with the calibration of GC system will remain the same as Part 4.2.5.

5.2.5 Characterizations and theoretical computational details

LC-MS (Liquid chromatography–mass spectrometry) was performed on Agilent 6130 LCMS to confirm the molecular weight of the complex synthesized. The signals include a broad scan and a simulated signal window that only display the exact molecular weight. Samples were dissolved in DMF with the concentration of 0.1mM. The mobile phase of LC was chosen to be a mixture of 5 vol% water with 95 vol% acetonitrile. For MS, protonation mode was selected as the given molecular weight should be added with 1. The maximum runtime was capped at 7 minutes.

Elemental analysis (EA) was conducted on CHNS Elemental Analyser (Elementar) to determine the content of C, H, and N within the samples.

X-ray diffraction (XRD) patterns were obtained by using a Bruker diffractometer with Cu K α radiation (D2 Phaser, Cu K α , $\lambda = 1.5406 \text{ \AA}$, 40 kV, and 40 mA) to investigate the crystallographic information for the **G** sheets.

Transmission electron microscopy (TEM; JEOL, JEM-2010, 200 kV) equipped with energy dispersive X-ray spectroscopy (EDX) was used to confirm the morphology and elemental composition of the electrode materials.

Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer) was used to characterize the structure and composition of the synthesized catalysts and **G** composites.

X-ray photoelectron spectroscopy (XPS; VG ESCALAB MKII instrument) with an Mg K α X-ray source was used for analyzing the surface elemental composition and valence state of the films.

Quantitative analysis of metal ions was measured on a Teledyne Leeman Labs Inc. Prodigy High Dispersion Inductively Coupled Plasma (ICP).

UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer with the wavelengths ranging from 800nm to 200nm.

The calculations were performed with Gaussian 09D package. DFT functional B3LYP have been selected with consideration of Greeme GD3(BJ) Van der Waals correction for gas phase model. The geometry configurations were obtained with def2-SVP for C, H, N, O atoms, and def2-TZVP for Co. The frequencies were obtained at the same level. In order to obtain high-level results, the basis set used for energy calculation was increased to def2-TZVP for all the atoms.

5.3 Results and Discussions

5.3.1 Characterizations of iron porphyrin complexes

Iron porphyrins were synthesized by refluxing the porphyrin ligand with iron source, i.e. iron(III) chloride in appropriate solvent. The solvent was chosen to be a mixture of DMF and chlorobenzene of 1:1 volume ratio.¹⁰¹ This method could render a five-coordinated iron complex with a halogen (in this case, Cl) atom connected with the central metal atom. These metalloporphyrin species were first characterized by EA. Elemental analysis results has shown on Table 5.1.

Table 5.1 EA data of the iron metalloporphyrin samples.

Elemental weight %	FeTPP		FeTAP		FeoTAP	
	C ₄₄ H ₂₈ FeClN ₄		C ₄₄ H ₃₂ ClFeN ₈		C ₄₄ H ₃₂ ClFeN ₈	
	Calculated	Found	Calculated	Found	Calculated	Found
C	75.07	75.17	69.17	68.87	69.17	68.64
H	4.01	3.91	4.22	4.33	4.22	4.29
N	7.96	7.77	14.67	14.34	14.67	14.18

From the EA data listed above, we can roughly claim that the expected products were obtained as the error between the experimental and theoretical value was negligible. These iron metalloporphyrins also showed the evidence for the existence of a chlorine atom within a molecule. Assuming the sample included no Cl, the data would display a gain which was noticeable and could not be ignored. Taking FeTPP as the example, the elemental weight could be turned to 79.05, 4.22 and 8.38 for C, H and N, respectively. If the iron atom did not coordinate with the porphyrin, the difference would become even larger.

To further investigate whether these complexes were obtained properly, the molecular weight was examined by means of LC-MS. The signals were obtained from LC-MS include two channels. The SIM channel is based on the targeted molecular weight. While the Scan channel shows the results from a broad scan. In this case, the range for broad scan was determined as 500 to 800, containing possible impurities, such as porphyrin free-base and multi-sited coordinated metalloporphyrins. The solvent peak was deducted as a part of background. Figure 5.1 showed the spectra of two channels for the iron porphyrin samples. For FeTPP, the single peak that indicated its exact molecular weight appeared at around 40s. With respect to FeTAP and FeoTAP, each characteristic singular peak emerged at 1 minute. Within a specific iron

porphyrin sample, the position of the peaks of both two channels was matched well, indicating that the Scan channel included mainly the species filtered by SIM channel.

Figure 5.1 LC-MS spectra of SIM and Scan channels on protonation mode for each iron porphyrin samples.

To investigate the formation of iron porphyrins, FTIR was applied to examine the porphyrin free base and iron-coordinated counterparts. These samples were grinded with KBr template with the weight ratio at around 1:200, followed by tableting process, the samples were ready for the test. Figure 5.2 showed the FT-IR spectra of those porphyrins before and after metalation by iron. At 967cm^{-1} , shown in the insets for enlarged view, the absorption peak expresses the rocking vibration of

the abovementioned pyrrolic N-H bond ($\delta_{\text{N-H}}$). These peaks would disappear after coordination with iron. As the consequence of iron occupying the center site of the porphyrin, all four N atoms will coordinate with Fe atom, meanwhile two H atoms bonded with N atom will be substituted. Therefore, the two characteristic peaks indicating the vibrations of N-H would be muted afterwards. A relatively strong adsorption peak at 998cm^{-1} ($\nu_{\text{Fe-N}}$) would appear to be the evidence of the successful bonding of Fe-N. From Figure 5.2, for the amino-modified porphyrins, the N-H rocking vibration ($\delta_{\text{N-H}}$) sited on the internal pyrrolic ring disappeared, accompanied with $\nu_{\text{Fe-N}}$ generated at 998 cm^{-1} , corresponding to the formation of Fe-N bonds. However, it is noteworthy that regarding the existence of anilino groups on *meso*-sites, $\nu_{\text{N-H}}$ of internal pyrrolic N-H was covered over by those adventitious amino groups for the rest amino-modified porphyrin derivatives.

Figure 5.2 FTIR transmittance spectra of all the porphyrin free bases and iron coordinated derivatives. Insets for each window are zoomed view of the shaded ranges from 1100 to 900 cm^{-1} , aiming to show a regression of $\delta_{\text{N-H}}$ after metalation with FeCl_3 .

To further investigate the properties of porphyrins with their metalation derivatives, UV-vis spectroscopy was utilized as a sound approach to observe the variations before and after iron modification. All the samples were dissolved in DMF, rendering a universal concentration of 0.01mM. Samples were scanned with a range from 800nm to 200nm. According to the theory raised by Gouterman *et. al.*¹⁸⁷, the absorbance of porphyrin species could be ascribed to the electron transition (π - π^* transition) in between the LUMOs and HOMOs. These transitions could present two

sets of the absorbance bands, i.e. Soret bands and Q bands. Soret bands reflected linear coupling those π - π^* transitions, showing intensive absorbance. While Q bands presented the neutralization of those transitions, showing relatively low absorbability.

To verify the formation of iron coordinated porphyrins, besides the porphyrin free base and the as-prepared iron porphyrin species, control sample of a mixture of porphyrin free base and equimolar iron precursor (FeCl_3) should be included (denoted as XXX-Fe on Figure 5.3). Hence, three sets of UV-vis spectra were obtained regarding three types of porphyrin basis. From Figure 5.3, when comparing the absorbance of the free base with the control sample containing FeCl_3 additives, no distinguishable difference was found. The absorbance of intrinsic FeCl_3 (yellow trace) was presented in Figure 5.3A, showing little absorbance within the entire range of the wavelengths. Therefore, the significant difference of the spectra of between the porphyrin free base with iron additives and iron coordinated species confirmed the fact of the generation of entirely different species after reaction regarding porphyrin basis with iron sources.

Figure 5.3 UV-vis spectra of bare porphyrin bases, iron coordinated species and control samples, each containing porphyrin free base added with iron precursor. Solvent: DMF (solvent background deducted).

Table 5.2 UV-vis absorption peak identifications for each sample.

Samples	Soret band, λ_{max} / nm	Q band, λ_{max} / nm
TPP	417	514, 549, 591, 646
FeTPP	418	576, 623 (shoulder)
TAP	436	529, 577, 667
FeTAP	435	638
oTAP	419	518, 554, 594, 649
FeoTAP	420	694

From the absorbance spectra and the table content (Table 5.2) for each porphyrin free base (Figure 5.3D), the Soret band comes at around 417nm for TPP, 419nm for oTAP and 437nm for TAP. For TAP, due to the electron-releasing (conjugative effect) nature and para-positioning for -NH₂, central π electron density has been increased when compared to TPP, which accounting for the red shift of the Soret band. For oTAP, ortho-positioning effect could arise a distortion of the planar conjugative structure because of the steric hindrance, impeding the transfer of electron-feeding effect from -NH₂. However, owing to that structural distortion, the π -conjugated electron density has been reduced. Hence, a slight red shift was still found in oTAP. In visible region of UV-vis, the Q band, containing 3 to 4 absorption peaks for each porphyrin free base, stacked in the range from 500nm to 700nm. After the metalation with iron, the amount of absorption peaks was reduced significantly. Moreover, the intensity of the absorbance for iron porphyrins showed a distinct regression. The center of the porphyrin ring was occupied by Fe³⁺, meanwhile substituted the proton of -NH- the pyrrolic ring after metalation. The molecular symmetry has been enhanced. A closer molecular energy level emerged after the iron coordination, which deciphered the decrease in the number of absorption peaks and absorbance intensity.

With respect to the Soret band for metalloporphyrins, intensity degradation also can be observed compared to the corresponding free base, which is evidential for the formation of metalloporphyrin. However, no significant red/blue shift found on these iron porphyrins, indicating no structural distortion after iron coordination. Within UV region, the absorption level of specific iron porphyrin was apparently higher than its free base, which can be subject to metal-to-ligand charge transfer

(MLCT) of these species, which is exclusive for those porphyrins coordinated with metal ions.

5.3.2 Characterization of iron porphyrin graphene composites

The composite was obtained by stirring the mixture of graphene dispersion with 0.1mM of iron porphyrin solution in DMF for 12 hours under room temperature. First, the graphene sheet was applied as the support for the loading of the catalysts in view of its excellent electron conductivity with extensive π - π stacking properties, which is beneficial to the immobilization of molecular catalysts with conjugated macrocycles like porphyrins. The graphene sheets were prepared followed with a modified method from literature.¹⁸⁸

The prepared graphene sheets were confirmed by X-ray diffractions. From the patterns shown below, the GO, which was used as the precursor, displayed typical peaks at $2\theta = 11^\circ$ and 43° , which can be ascribed to plane (002) and (100).¹⁸⁹ After a 5-hour hydrothermal reduction, the signature peak for (002) at 11° for GO has shifted to $2\theta = 23^\circ$, indicating a decreased *d-spacing* for the plane (002), which can be evidential to the formation of rGO. From figure 5.4, after loaded with iron porphyrin catalysts, the graphene basis could retain its original property. The adsorbed iron porphyrins did not crystallize on the surface of such graphene support.

Figure 5.4 XRD patterns for GO, rGO, and iron porphyrin loaded graphene composites.

In order to investigate the surface element content of the iron porphyrin graphene composites, X-ray photoelectron spectroscopy (XPS) scan was conducted with regard of several elements containing Fe 2p and N 1s. From Figure 5.5A, the peak fittings of Fe 2p narrow scan for all the samples showed similar results. The fitting for Fe 2p_{3/2} presented a single peak at 711.4 eV, which can be evidenced that the iron existed mainly in +3 valence within those porphyrin complexes as the binding energy of Fe 2p_{3/2} for Fe(III) usually ranged from 711 to 712 eV. No other components can be fitted into this area like Fe(II). For similar Fe(II)N₄ coordination species, the binding energy for Fe(II) 2p_{3/2} was positioned at around 709 to 710 eV.¹⁹⁰⁻¹⁹¹ with respect to Fe(0) species, the binding energy is even lower than Fe(II) species, at around 707 eV.¹⁹⁰ Moreover, the binding energy of Fe 2p_{1/2} in this case was fitted at 724.6 eV, typical for Fe(III) species.¹⁹²

With respect to N 1s scan, N species should come from porphyrin ligand. For FeTPP graphene composite, as iron atom occupied the center of the porphine ring of TPP, the protonated N would turn unprotonated after the coordination by Fe, indicating that this composite should present single component of N species. The scan

results verified such assumption, with single peak at 399.8 eV, representing the pyrrolic N.¹⁹³ Other than just singular peak configuration, FeTAP and FeoTAP graphene composites contained another amino N from the phenylamino group at *meso* position of porphine ring, indicated by the peaks at 401.1 eV, which is characteristic for protonated N species.¹⁹³

In view of XPS results, the iron porphyrin species were immobilized onto the graphene support, with their own features kept in an intact manner. This is meaningful as the intrinsic properties of iron porphyrins can be inherited into heterogenized composite material among which the iron porphyrins can act as the reactive component. The properties of iron porphyrins, such as capability to catalyze CO₂ reduction and other own features like molecular configurations that could influence the catalytic performance, can be tuned in molecular dimension but perform in a heterogenized and accessible way, which will be elaborated below.

Figure 5.5 XPS peak identification and analysis of (A) Fe 2p and (B) N 1s with respect to all the iron graphene composites along with (C) comparisons of all the composites with bare graphene sheets (blue) regarding Fe 2p, N1s and Cl 2p scan.

The morphology investigations along with the elemental distributions of those graphene composites were performed by TEM with EDX equipped. From the TEM images with the element mapping images, this composite displayed that the typical shapes of graphene nanosheets, hundreds of nanometers in diameter, with iron porphyrins embellished on. It also can be noticed that the typical morphology of

graphene sheet with thin layers and wrinkles retained after the loading process with iron porphyrins, suggesting that the high specific surface area, high conductivity and other superior properties of graphene could be restored and beneficial to the catalytic activity of such composites as the electrode material of reduction of CO₂. From the mapping results in Figure 5.6, the selected elements were evenly distributed on the surface of these graphene composites. The atomic ratio of those elements showed a trend of C>N>Fe≥Cl, which was reasonable regarding the composition of those graphene composites.

To confirm the iron content within those graphene composites in a more accurate manner, ICP was applied as the prescription. The graphene composite sample should be leached completely with concentrated sulfuric acid (98%) and nitric acid (70%) at 120 °C. Each sample can be totally dissolved after leaching for a few days and was capped up to 20ml with dilution with water.

Table 5.3 ICP testing results for iron species among all the iron graphene composites. The iron porphyrin loading capacity for graphene base was also calculated accordingly.

Sample Name	Sample Weight (mg)	[Fe ³⁺] (mg/L)	Iron Porphyrin Loading Capacity (μmol/mg)
G FeTPP	3.2	3.97	0.44
G FeTAP	5.8	6.00	0.37
G FeoTAP	5.4	4.06	0.27

Figure 5.6 TEM images with element mapping results regarding the selected elements of C, N, Fe, Cl for (i) graphene composite with FeoTAP, (ii) graphene composite with FeTAP and (iii) graphene composite with FeTPP, respectively.

The iron porphyrin loading for the graphene basis was also calculated from the concentration of iron species obtained from ICP results, which can be useful for the following calculations of TOFs.

5.3.3 Electrochemistry studies

The electrochemical response and catalytic activity regarding each iron porphyrin was examined by means of cyclic voltammetry (CV). Without immobilization on the graphene basis, it is better to investigate the electrochemical properties in homogeneous way. Therefore, those iron porphyrins were dissolved in DMF (5M water should be added when necessary) to form a 0.5mM solution with 0.05M NBu₄BF₄ as the supporting electrolyte.

CV was first conducted under inert condition to observe the intrinsic electrochemical response of possible redox pairs of each iron porphyrin. The tests were performed under argon with a bare glassy carbon ($\Phi=3\text{mm}$) as the working electrode, DMF with 5M water as the solution, and 0.05M NBu₄BF₄ as the supporting electrolyte. From Figure 5.7A, for FeTPP, the two reversible pairs of redox events took place at -1.22V vs Ag/Ag⁺ (-0.47V vs SHE) and -2.20V vs Ag/Ag⁺ (-1.45V vs SHE). These two redox events can be ascribed to Fe(II)→Fe(I) and Fe(I)→Fe(0), respectively.¹⁸² On the contrary, the XPS results indicated that Fe species existed in valence of +3. However, the starting potential in this case was at -0.5V, where Fe(III) would be transformed into Fe(II) immediately (Fe(III)→Fe(II), $E^0 = \sim -0.1\text{V}$ vs SHE),¹⁹⁴ along with the detachment of Cl⁻. Similarly, for FeTAP and FeoTAP, these two redox events also occurred and could be determined in terms of the CV curves. With respect to the first charge transfer, *i.e.* Fe(II) + e⁻ → Fe(I), compared to FeTPP,

the peak current of this redox was presented much higher in FeTAP. Moreover, the potential of this redox shifted in negative direction, which might result from the effects of the para-NH₂ substituents. With respect to FeoTAP, the first reduction of Fe(II) was detected at -1.13V vs Ag/Ag⁺ (-0.38V vs SHE), a positive shift observed. However, the peak current was not as comparable as FeTPP or FeTAP, which may be affected by its twisted, nonplanar molecular structure.

Figure 5.7 (A): CV scanning curves of iron porphyrins obtained under inert conditions (Scan rate: 0.1 V s⁻¹; Electrolyte: 0.05M NBu₄BF₄, DMF, 5M H₂O, 1 atm argon). (B): Comparisons

of catalytic currents under 1 atm CO₂ (green) and Brönsted acid (*i.e.* water) added (purple) with the peak current from inert conditions (orange). (C): Enlarged view of CV curves corresponding to (B) of potential range from -2.6V to -0.8V under inert (orange) and catalytic (purple) condition. Oxidation waves for Fe(I)→Fe(II) transitions under both inert and catalytic condition have been labelled.

The second redox event for the samples tested was observed at around -2.2V to -2.25V vs Ag/Ag⁺, which was denoted as the second reduction of iron center, from Fe(I) to Fe(0). Under catalytic condition, it was apparent that the reduction of CO₂ was coupled with the redox Fe(I) to Fe(0). Without addition of Brönsted acid, only keep fluxing with CO₂, no catalytic current was supposed to be found as the charge transfer must be coupled with proton transfer during CO₂ reduction process in metalloporphyrins. If no local proton source existed, the catalytic reaction would be interrupted, lacking essential reactant. However, other than FeTPP, two iron porphyrins with amino groups was found to present an obvious current gain on the site where Fe(I) to Fe(0) occurred (green lines from Figure 5.7B). Limited by our operation conditions, the anhydrous electrolyte may still contain a small amount of water and even other Brönsted acid that can provide protons. Besides, the iron porphyrins with amino groups may also absorb moisture from ambient conditions, which can be used as a local proton source. After addition of water till 5M to the dry DMF based electrolyte (volume ratio of H₂O:DMF = 1:10), all the sample showed significant catalytic current gain at the potential for the conversion of Fe(I) to Fe(0). Moreover, under high overpotentials, the catalytic current of FeoTAP presented the highest among the three variants, showing its higher turnover frequency under specific potential.

In consequence, two conclusions can be set based on analysis of CV results presented in Figure 5.7. On the one hand, proton source is essential for the catalytic capability of CO₂ reduction on the iron porphyrins. Therefore, in many cases, addition of weak Brönsted acid will be recommended to boost the CO₂ reduction. On the other hand, the catalytic reduction of CO₂ was related with the redox Fe(I)→Fe(0), indicating the Fe(0) porphyrins can be the active state to bind CO₂. The cleavage of C-O bond can be activated with the assistance of the proton source. Hence, a simplified universal reaction scheme towards homogeneous CO₂ catalytic reduction on iron(0) porphyrins was proposed as follows:^{179, 182}

Scheme 5.2 Simplified universal reaction scheme towards CO₂ catalytic reduction on iron(0) porphyrins. Porphyrin ligands and charges of the complexes were omitted. HA: Brönsted acid.

This scheme contains 4 steps with the rate determining step of first charge transfer of CO₂ → CO₂⁻, conveyed by Step (2). With the knowledge that Fe(II) porphyrin species can strongly bond with CO.¹⁸² Homogeneously, Fe(II)CO porphyrin species would tend to generate at a more negative oxidation potential than Fe(I) → Fe(II) transition under inert conditions. The oxidation waves have been highlighted on Figure 5.7C. The significant shift of the oxidation wave of Fe(I)→Fe(II) transitions in catalytic and inert situations has shown the strong stability of iron (II) CO porphyrin adducts.

5.3.4 Controlled potential electrolysis (CPE) Under CO₂

CPE was conducted at variations of potentials from -1.1V to -1.4V vs Ag/AgCl (-0.5V~-0.8V vs RHE) in CO₂ bubbled 0.1M KHCO₃ solution. The graphene composite suspension was applied on both sides of carbon fiber paper, which was used as the support for electrode materials. The geometric area of the pated materials was controlled to be 1cm² (2×0.5cm×1cm). The amount of the applied graphene composite from its suspension onto the electrode support was kept at 0.12 mg (60 μL×2mg/mL). The value of Faradaic efficiency (FE) was recorded after the GC starting to run stably.

Before CPE investigation on the reduced products from CO₂, LSV (linear sweep voltammetry) was conducted under the same electrolyte under bubbling CO₂ to probe the onset potential for CO₂RR of each iron porphyrin graphene composite within the potential window from 0 to -0.8V (vs RHE) with the scan rate of 0.02 V s⁻¹. From Figure 5.8A, the onset potential for each electrode presented similarly at around -0.5V vs RHE (before conversion, -1.1V vs Ag/AgCl). The onset potential in homogeneous condition was -2.1V vs Ag/Ag⁺ (-1.55V vs Ag/AgCl), which was performed at a 450mV more negative potential. Such gap of overpotential may result from a necessary driving force for the catalyst diffusion and a higher energy barrier for charge transfer between the catalyst and the electrode in homogeneous catalysis. In heterogeneous circumstances, catalysts are usually immobilized onto certain supporting material, like graphene, where catalysts no longer need to diffuse to the phase interface to perform charge transfer and so on.

As the potential went more negatively, the catalytic current of the graphene composite variants all increased but showing different slopes, suggesting different

capability of reducing CO₂ under specific potential here. Among all those electrode materials, graphene composite with FeoTAP displayed the steepest slope regarding the current gain vs potential increment. Therefore, the superior performance of this variant can be expected.

During the electrolysis, CO was found to be the main product from CO₂ reduction. However, graphene composite with iron porphyrin variants presented completely different activity and selectivity. Figure 5.8B has summarized the Faradaic efficiency results during the CPE. For graphene composite loaded with FeTPP, HER still presented to outperform CO₂RR in fully aqueous electrolytes. At -0.7V vs RHE (-1.3V vs Ag/AgCl), Faradaic efficiency for CO₂ reduction to CO reached highest (46%) within the whole tested potential range. The half of the catalytic current still served as HER. In addition, shown by Figure 5.8C, the catalytic current density (j) of FeTPP graphene composite in total was not comparable with other graphene composite variants with different iron porphyrins. For the FeTAP variant, the catalytic current density showed a significant increase compared with G|FeTPP. Moreover, CO production outperformed HER this time with 75% to 85% faradaic efficiencies applied with different potentials. Surprisingly, with respect to graphene composite with FeoTAP, CO production was highly dominant against HER, which was almost completely suppressed with only 3%-4% faradaic efficiency, even below 1% at certain potential (-0.7V vs RHE). Meanwhile, the catalytic partial current density for CO remained in a much higher level (2.5~3mA/cm²) than FeTAP and FeTPP graphene composites (~1mA/cm² and ~0.3mA/cm², respectively) within the whole potential range, shown by the inset in Figure 5.8C.

It is worth noting that the decline of catalytic current with increasing runtime was found regarding all the samples but in different degrees. For FeoTAP graphene composite, the decline of CO partial current density was the most visible among those variants. According to Scheme 2, the last reaction step [Step (4)] was much faster than Step (3) and (2). In heterogeneous case, the diffusion of the catalysts could be constrained in some dimensions, resulting in the accumulation of generated Fe(II)CO porphyrin adducts with high stability, further causing catalyst poisoning.

To further quantify the catalytic performance of such iron porphyrin graphene composites, turnover frequency (TOF) or turnover numbers (TON=TOF*Reaction time) was applied. From the equation below, TOF can be calculated given the faradaic current ($i \times FE$), electron transferred per reaction ($z=2$), Faradaic constant ($F = 96485$ C/mol) and the catalyst loading amount (n_{cat}):

Figure 5.8 (A) LSV results of all samples in CO₂ bubbled 0.1M KHCO₃. Scan rate: 0.02V/s. (B): Faradaic efficiencies of CO and H₂ as the main products during CPE from -0.5V to -0.8V vs RHE of all samples. (C): Typical I-t curves recorded during CPE at -0.7V vs RHE of all samples. Inset: partial current density of CO from all samples under CPE at -0.7V (vs RHE) according to the last 3 runs examined by GC. (D) Average TOFs of all the samples obtained from potentials applied for CPE.

$$TOF = \frac{i \times FE}{z \times F \times n_{cat}} \quad (5.1)$$

Referring to the data ICP results shown in Table 5.3, the loading amount of Fe species for FeTPP, FeTAP and FeoTAP graphene composites can be worked out as 0.0528 μmol, 0.044 μmol and 0.0324 μmol. The average TOFs along with TONs for 1 h can be obtained shown as the table below:

Table 5.4 TOFs and TONs for 1-hour CO₂ reduction to CO of iron porphyrin graphene composites with potential profile.

Potential/ V vs RHE	G FeTPP		G FeTAP		G FeoTAP	
	TOF (s ⁻¹)	TON (1h)	TOF (s ⁻¹)	TON (1h)	TOF (s ⁻¹)	TON (1h)
-0.5	0.0039	14.0	0.0223	80.4	0.0708	254.9
-0.6	0.0159	57.3	0.0909	327.3	0.2688	967.8
-0.7	0.0284	102.1	0.1488	535.7	0.5310	1911.6
-0.8	0.0367	132.1	0.1802	648.8	0.6277	2259.7

The TOFs/TONs data from the table showed remarkable catalytic capability of **G|FeoTAP**. The TOFs increases, however, not linearly with the increased overpotential, transpiring by Figure 5.8D. The growth rate of TOFs for CO generation slowed down at high overpotentials as HER would take advantage again in aqueous

solutions if the sufficiently high potential applied. Shown by Figure 5.8B, at -0.7V (vs RHE), the reaction selectivity towards CO₂ conversion to CO was presented as the sweetest point for all the tested graphene composites.

5.3.5 Elementary insights based on theoretical and experimental studies

By introducing functional groups onto the porphyrin ligands, the catalytic performance can be promoted dramatically. For FeoTAP, the amino groups located in the *ortho* sites of the phenyl on *meso* position of the porphine ring may provide a possibility of H-bond bridge to stabilize *COOH intermediates bonded with Fe(0) sites before the cleavage of one of the C-O bonds.

Figure 5.9 DFT computations of (A): Gibbs energy level for each iron porphyrins coupled with CO₂-related intermediates for each reaction step during catalysis. (B): Structural optimizations of FeoTAP variant coupled with *COOH (white: H, blue: N, grey: C, red: O).

From DFT results shown on Figure 5.9A, FeoTAP coupled with *COOH showed the lowest Gibbs energy level among all the porphyrin variants, revealing its great affinity to bond with CO₂ and proton. Combined with the CV result from Figure 5.7C, the observed reduction wave of Fe(I) conversion to Fe(0) in FeoTAP may be ascribed to the stable FeoTAP-COOH adduct. The structural optimizations of

FeoTAP-COOH species have been accomplished by DFT computations as well. Depicted by Figure 5.9B, at least one of the H atom from the ortho-sited amino group on the phenyl tended to associate with one oxygen atom from *COOH through H-bond. The distance between H and O atom was revealed at 2.14Å, proven to be sufficiently close for the formation of H-bond.¹⁹⁵ Therefore, it is the hydrogen bond that can account for the unexpected stability of FeoTAP-COOH intermediate. After a cleavage of C-O bond, the intermediate of iron porphyrins coupled with *CO can be formed subsequently, among which the FeoTAP-CO remain the highest Gibbs energy level, providing a preferable scheme for releasing CO. Therefore, CO production rate can be boosted on FeoTAP variant. In addition, FeTPP-CO presented lowest energy level here, showing high stability, which may give the cause for the worst performance among these variants.

As to the similar model proposed by C. Costentin *et. al.*^{179, 183}, they investigated the iron(0) porphyrin with *ortho* OH groups on the phenyls. The pre-reduction wave emerged closely before the catalytic process, including the transition from Fe(I) to Fe(0), bonding with CO₂, first protonation by intramolecular OH groups, and second protonation which occurred on deprotonated OH groups by the added Brönsted acid. The story may be a little different in terms of our case. Amino groups lack of ability to donate the proton to Fe-CO₂ site. Therefore, the adduct Fe-CO₂, which was stabilized by H-bond from NH₂ groups, would also be quickly protonized by water for subsequent C-O bond break. For FeTAP and FeTPP, the reduction of Fe(I) will be submerged by catalytic current in that such intermediate state is not stable enough to be detected. It is observed that FeTAP outperformed FeTPP. The

possible explanations may be originated from the tuning of hydrophilicity and electron density within FeTAP molecular dimension from the pendant amino groups.

5.4 Conclusions

Metalloporphyrins are effective agents towards the conversion of CO₂ to CO in plenty of application scenarios, such as photocatalysis, electrocatalysis and photoelectrocatalysis. Owing to the nature that the proton is a necessity coupled with charge transfer during CO₂-to-CO conversion, appropriate proton source can be applied. Moreover, these molecular catalysts can be immobilized onto reliable supporting materials, rendering heterogeneous catalysis based on aqueous solutions, which would be more accessible and convenient compared with homogeneous catalysis in aprotic solvents.

In this case, three variants of iron porphyrins have been synthesized and characterized (FeTPP, FeTAP and FeoTAP). They presented catalytic activity towards CO₂ reduction without exception in homogeneous catalysis. After immobilized onto graphene, those composites were applied to perform CO₂ electrolysis in aqueous solution. In consequence, the FeoTAP variant presented the highest catalytic performance with more than 99% of Faradaic efficiency and above 2000 h⁻¹ turnover frequencies towards CO₂-to-CO conversion at -0.7V vs RHE, far better than the other two variants. One possible explanation has been established by experiments coupled with theoretical computations. The ortho-sited -NH₂ groups in oTAP ligand may offer the conditions to form H-bonding to stabilize the *COOH intermediates on Fe(0) sites. Combined with high energy level after adsorbed with CO, the FeoTAP variant can render a boost both in selectivity and catalytic activity for CO production.

Chapter 6. Conclusions and Prospects for Future Work

6.1 Conclusions

Based on all the work mentioned above, a series of strategies have been employed in order to adjust the selectivity performance regarding heterogeneous electrocatalysts CO₂ reduction to specific products.

(1) *In situ* alloying-dealloying process was applied to modify the surface of polished commercial copper foils to generate nanoporous morphology. The Faradaic efficiencies (FEs) of ethylene production can reach up to 35% against 0.6% of methane production at -1.9V vs Ag/AgCl on proper nanoporous copper electrode. For comparison, FEs of ethylene and methane were observed as 17% and 35% respectively on untreated copper foil. The chemical dealloying process, accompanied with the diffusion and reconstruction of residual Cu atoms, could bring in the alternation of the crystalline orientation on the surface. The high selectivity towards ethylene was believed to be due to multiple factors including the exposed crystalline facets, the abundance of (100) facets, along with the possible existence of stepped and edged atoms.

(2) Re(I) tricarbonyl complex with 4,4'-aldehyde group substituted bipyridine as the ligand was investigated firstly for homogeneous catalysis and found active towards CO₂ reduction. By grafted with π electron enriched polycyclic groups, such as pyrene in this case, this complex can be successfully anchored onto carbon substrate like graphene through π - π stacking effect, which can be applied as a heterogeneous catalyst for CO₂ electroreduction, showing 92% and 28% of Faradaic efficiencies for CO₂ conversion to CO in aprotic and aqueous conditions respectively.

This method has been verified practical for tethering simple monofunctional molecular catalyst onto carbon support with high specific surface area and considerable conductivity. This heterogenization process can avoid unexpected diffusion course resulting from homogeneous catalysis.

(3) Variants of iron porphyrins have presented catalytic activity towards CO₂ reduction without exception in homogeneous catalysis. However, the catalytic current varied between each other, among which the iron porphyrin with ortho-NH₂ groups modified ligand (FeoTAP) presented the highest catalytic current. After immobilized onto graphene, those composites were applied to perform CO₂ electrolysis in aqueous solution. In consequence, the FeoTAP-graphene composite presented the highest catalytic performance with more than 99% of Faradaic efficiency and above 2000 h⁻¹ turnover frequencies towards CO₂-to-CO conversion at -0.7V vs RHE, several times better than the other two variants. One possible explanation has been established by experiments coupled with theoretical computations that the ortho -NH₂ groups on phenyl rings within oTAP porphyrin ligand may act like a bridge by offering the H-bonding to stabilize the *COO intermediates adsorbed on Fe(0) center, rendering a boost in terms of the selectivity and catalytic activity for CO production.

In sum, morphology tuning can be effective and essential on selectivity optimization of CO₂ electroreduction on heterogeneous catalysts with nanostructured configurations, allowing the adjusts of active sites favorable of specific product. On the other hand, creation of heterogenized composites with monofunctional active units derived from molecular catalysts can also prove to be promising in reducing byproducts. Further tuning on the molecular structure on the active molecular units can boost the performance to a higher level.

6.2 Recommendations for future work and expectations

The attention on the unique feature of hydrocarbon production on copper-based cathode materials for CO₂ reduction has never shown any regression.

In view of what has been achieved on first work, there are still plenty of further research can be carried on regarding the selectivity enhancement. It is noticeable that the hydrogen evolution level was still relatively high on those modified copper electrodes. Therefore, the first issue we have to deal with is to suppress HER level. This issue can be addressed from several aspects. In the beginning, the pH value of the buffer electrolyte can play an important role on proton-coupled charge transfer during catalysis, which can be tuned by controlling the concentration of KHCO₃, rendering different buffer capacities. Moreover, various types of buffer systems such as KH₂PO₄-K₂HPO₄ system can be applied for comparison. In terms of electrode preparation process, further modification can also be applied, such as additions of different surfactants to adjust the surface reconstruction process. Meanwhile, doping with inert heteroatoms like carbon during the morphological formation process can be practical in that the introduction of heteroatoms can effectively regulate the coordination number of surface atoms, beneficial to selectivity optimization. Furthermore, during the alloy-dealloy process, replacements like Sn and Al rather than Zn can also be applied as the component for the initial alloying with Cu since variations on atomic diameters of alloy components can result in different crystalline transitions, bringing about different final surface constructions.

With respect to the second work mentioned above, there are still plenty of improvements to be done. It is noteworthy that this noncovalent bonding based on π -

π stacking could not manage the longevity of the composite catalysts. More stable grafting techniques for immobilizing active molecular units should be included using covalent bonding. First, the carbon-based support material should be functionalized prior to the subsequent grafting. Second, screening and selection of appropriate ligands with functional groups should match with the functionalized support. The most popular functional group couples which can connect with each other can be amino-carboxylic systems and amino-aldehyde systems, owing to the mild operational conditions and accessibility of relevant ligands. Other approaches rendering covalent bonding between the molecule catalyst and the support like electrochemical reduction of diazonium pendant units to directly bond with CNTs, glassy carbon electrodes and graphene without functionalization. Immobilization of diazonium moieties, derived from -NH_2 pendant groups reacting with nitrites, have been proved effective and feasible. Such heterogenization process will become more meaningful and necessary if targeting the active molecular units with less developed conjugated structure (such as metal cyclam complexes, metal bipyridine complexes, etc.), which are not capable of stably interacting with support materials before the covalently tethering. Other macrocyclic molecules like porphyrins and phthalocyanines contain developed and large scoped π -electron conjugation system, exhibiting high affinity to highly conjugated carbon supports.

More work can be involved in the future regarding the work mentioned in Chapter 5. Since intramolecular H-bond donor based on -NH_2 and -OH groups can stabilize the CO_2 intermediate chemisorbed in metal sites, such groups can also be introduced to other monofunctional molecular catalyst to investigate if the performance boost still exists, especially for those catalysts following the pathway of

proton-coupled electron transfer. Besides, effectiveness on various of metal sites other than Fe should also be examined to give a relatively universal feasibility of this strategy, since the energy barrier of binding CO₂ along with the bonding energy regarding different metal sites can vary drastically. On the other hand, in situ techniques like IR-SEC should be applied for observation of those intermediates to further verify this mechanism.

Considering the advances of recent achievements regarding CO₂ electroreduction, other forms of catalysts can be constructed for pursuing higher efficiency and selectivity. Novel nanostructured metallic copper electrodes are of great importance to obtain hydrocarbons. Single atom catalysts containing coordinated metal sites like CoN₄ and NiN₄ moieties have been proved to be a robust and stable catalysts serving the similar function as molecular catalysts comprising similar metal coordinated moieties like cobalt porphyrin (CoN₄) and nickel cyclam (NiN₄) but present better overall performance regarding higher current densities with higher TOFs and stability. Construction of conductive MOFs and COFs based on active molecular moieties is an alternative way to achieve high-performance heterogeneous electrocatalysts without the application of conductive carbon supporting materials.

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