Copper-based materials for enhanced CO₂ electroreduction towards hydrocarbons

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**COPPER-BASED MATERIALS FOR ENHANCED CO₂
ELECTROREDUCTION TOWARDS HYDROCARBONS**

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SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

2016

COPPER-BASED MATERIALS FOR ENHANCED CO₂ ELECTROREDUCTION TOWARDS HYDROCARBONS

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Abstract

The research of this thesis is to develop copper (Cu) based materials with various strategies for CO₂ electroreduction towards hydrocarbons. The generation of hydrocarbons is enhanced through taking advantages of modifiers as well as supports.

Firstly, we developed a general amino acid modification approach on Cu electrodes for selective electroreduction of CO₂ towards hydrocarbons. Remarkable enhancement in hydrocarbon generation was achieved on these modified copper electrodes, regardless of the morphology of the Cu electrodes. A density functional theory (DFT) calculation revealed that the key intermediate CHO* was stabilized by interacting with $-\text{NH}_3^+$ of the adsorbed zwitterionic glycine. Our results suggested that amino acids and their derivatives were promising modifiers in improving the selectivity of hydrocarbons in CO₂ electroreduction.

Secondly, Cu doped diamond-like carbon (DLC) film electrodes were synthesized under various potentials. Among all tested electrodes, Cu-DLC film prepared under -1200 V obtained the highest sp³ carbon content, and proved to have the best performance to generate hydrocarbons. DFT simulations indicate that the H atom adsorbed on diamond would be a better source for direct hydrogenation of adsorbed CO, compared to shuttling water as well as H adsorbed on Cu. The results showed that DLC is a good co-catalyst to help Cu producing more hydrocarbons.

Thirdly, a Cu doped carbon aerogel was prepared through carbonization of phenolic resin precursor. The Cu-carbon aerogel had an extremely high Cu loading of 25.8%, with large surface area. All these properties brought about improvements in FE of hydrocarbons as well as decrease of overpotential.

Cu-based composite materials are proved to be promising towards CO₂ electroreduction. The strategy could be expanded to other types of materials, like metal-organic framework compounds, intermetallics as well as other chemically modified materials.

Keywords: copper electrode, modification, support, amino acid, diamond-like carbon, carbon aerogel, density functional theory calculation, CO₂ electroreduction

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List of Abbreviations

AES	Atomic emission spectrometry analysis
ATR	Attenuated total reflection infrared spectroscopy
Cu-DLC	Cu doped diamond-like carbon
CV	Cyclic voltammetry
DFT	Density Functional Theory
DLC	Diamond-like carbon
EDX	Energy dispersive X-ray spectroscopy
EQCM	In-situ electrochemical quartz crystal microbalance measurement
EIS	Electrochemical impedance spectroscopy
FE	Faradaic efficiency
FESEM	Field emission scanning electron microscopy
FTIR	Fourier-transform infrared spectroscopy
GC	Gas Chromatograph
GDE	Gas diffusion electrode
HPLC	High performance liquid chromatography
HER	Hydrogen evolution reaction
NDD	Nitrogen-doped nanodiamond
NDDL	Nitrogen-doped nanodiamond prepared under lower temperature
NDDH	Nitrogen-doped nanodiamond
NMR	Nuclear magnetic resonance prepared under higher temperature
NW	Nanowire
ORR	Oxygen reduction reaction
PAW	Projector-augmented wave
PBE	Perdew-Burke-Ernzerhof
RDE	Rotating disk electrode
SEM	Scanning electron microscopy
SHE	Standard hydrogen electrode
SPE	Solid polymer electrolyte
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
VASP	Vienna ab initio simulation package
XPS	X-ray photoelectron spectroscopy
XRD	X-ray powder diffraction

Chapter 1. Introduction and Scope of Thesis

1.1. Introduction

Carbon Dioxide (CO₂), a gas that only makes up no more than one one-thousandth of earth's atmosphere, is the most important part of carbon cycle and greatly affect the climate,¹⁻² leading to drastic environmental concern.³ As the most-known greenhouse gas, the concentration of CO₂ kept rising and falling in a range of 150 to 300 ppm in the last four hundred thousand years, until modern times. However, human beings started to exploit and consume fossil fuels massively from industrial revolution, which caused a dramatic rise of CO₂ concentration to 400 ppm.⁴⁻⁶ The anthropogenic CO₂ emission has contributed to a series of climate change, and the most serious issue is the global warming.⁷ Recent research indicated that the CO₂ emission might have to be reduced by up to 80%, basing on the emission scale in 2000, to keep the increase of global temperature within 2.0-2.4 °C.⁸ Attempt of totally replace current energy consumption to renewable sources is our long-range objective, but still unrealistic in a foreseeable future. Among all alternative technologies, capture and reduction of CO₂ would be the most promising ones.⁹⁻¹¹ The former could gather the CO₂ in atmosphere, while the latter could transform the CO₂ to fuels and fine chemicals. A combine of both capture and reduction of CO₂ could realize the artificial carbon cycle to reduce the CO₂ concentration in atmosphere directly.

At present, the technique of CO₂ capture is relatively mature and turned into application. Smoking absorber of various kinds of absorption liquid is now

used in some of thermal power plant, where the carbon emission is intensive.¹² Meanwhile, the reduction of CO₂ is in an initial development period and expected to be a package solution to utilize new energy resources and to eliminate CO₂ emission simultaneously.¹³ As a matter of fact, we would better to regard CO₂ as important industrial raw materials rather than waste gas. The world annual demand for CO₂ is estimated to be 200 million tons,¹⁴⁻¹⁵ and some of developed technologies like Fischer-Tropsch synthesis have been already applied in this area.¹⁶⁻²¹ The manufactured products from CO₂ reduction are a series of fine chemicals (Figure 1.1).

Figure 1.1 Conversion of CO₂ into more valuable commodity chemicals. Reprinted from Ref. 14, with permission of Royal Society of Chemistry, Copyright 2012.¹⁴

The feasible proposals for CO₂ reduction are varied, including hydrogenation reduction,²² photochemical reduction²³ and electroreduction.²⁴ On the other hand, scientists have developed a series of efficient renewable energy plants, like photovoltaic device, wind farm and tidal power plant, etc. However, all these devices are unable to generate power consistently with high voltage at present, so it is difficult to input these devices into the grid.²⁵ Making use of such unstable electric power to reduce CO₂ to fuels would also be an effective way for renewable electrical energy storage.²⁶⁻²⁸ Considering all these factors, scientists are now casting more interests on electrochemically reducing of CO₂.

As the CO₂ is such a kinetic stable molecular and hard to cleave, an obvious barrier to overcome is the high overpotential of CO₂ electroreduction, which would cause considerable energy loss in this process. The extremely negative potential could bring about a series of technological difficulties. First, the existing typical process of CO₂ electroreduction is to electrolyze saturated CO₂ aqueous solution, thus the high negative potential could lead to hydrogen evolution as side reaction. It contaminates the final products while waste the current. Second, as many types of common electrode materials are unstable under inevitable high negative potential, like most of metallic oxide and metal sulfide, the choice of cathode material is limited. Last but not least, deactivation of cathode driven by deposition of impurities or final products could be even more serious. To deal with all these problems, fundamental work has involved various facets and factors of the process, mainly about the cathode electrocatalyst and electrolyte composition.²⁹ Besides analysis of material and products, more tools need to be introduced to reveal the

detail of reaction and the mechanism, like in-situ FTIR or DFT theoretical calculation.³⁰⁻³¹ Some of the proven technologies from related area such as gas diffusion electrode (GDE)³²⁻³⁴, three-phase electrodes³⁵⁻³⁶ and solid polymer electrolyte (SPE)³⁷⁻³⁹ are also introduced to improve the performance.

Many kinds of metal and non-metal materials have been tested as the cathode material for CO₂ electroreduction.⁴⁰ However, Cu is the only one to produce hydrocarbons so far.⁴¹ Some early studies done by Hori illustrated the behavior of polished pure Cu electrode, that methane and ethylene are the only products.⁴²⁻⁴⁴ The mechanism of CO₂ electroreduction route on Cu surface has also been studied by Norskov, with DFT calculations.^{31, 45} Some of the important intermediates like CHO* have been proposed, which would be helpful to reduce the energy barrier and design new catalysts.

1.2. Scope of the thesis

The study in this thesis is mainly to develop new strategies to improve the selectivity of hydrocarbons on Cu electrodes in CO₂ electroreduction, through making use of modifiers or supports.

Chapter 1 provides a brief introduction about the background of how CO₂ affect the environment, the importance of utilize CO₂, the reason why CO₂ electroreduction is promising and selected as the objective of this research.

Chapter 2 gives detailed instruction of multiple aspects of CO₂ electroreduction, including fundamental theory, common used electrocatalysts, mechanism and challenges we face right now.

In Chapter 3, we prepare 3 kinds of different Cu electrodes, namely, Cu nanowire (NW) film, polished Cu foil and annealed Cu plate. A strategy of using modifiers is applied on all kinds of Cu electrodes, and it is found that the amino acid with certain concentration could enhance the selectivity towards hydrocarbons during CO₂ electroreduction. -NH₃⁺ end of zwitterionic amino acids is regarded as the active site to stable the intermediate CHO, thus increase the final products.

In Chapter 4, Cu doped diamond-like (DLC) carbon film electrodes are prepared under different deposition potentials. The electrode prepared under -1200 V is proved to have high sp³ carbon contents and highest activity to electroreducing CO₂ towards hydrocarbons. The H atom adsorbed on diamond carbon is suggested to be a better source for hydrogenation.

In Chapter 5, Cu doped carbon aerogel is prepared, with high selectivity towards hydrocarbons, high current density and low overpotential for CO₂ electroreduction.

At last, Chapter 6 summarizes the results of this work and raises plans as well as outlook for the future work.

Chapter 2. Literature Review

2.1. Fundamentals of CO₂ electroreduction

CO₂ electroreduction aims at obtaining fuels and other chemicals by using electric energy, which could be derived from renewable energy sources. When we regard CO₂ as the carbon source, the first difficulty is that the CO₂ would be one of the most stable carbon based substance. Although the CO₂ electroreduction could be realized under a relatively mild condition compared to CO₂ thermal hydrogenation, there still exists a significant overpotential resulting from the large energy barrier, thus 60%-70% of the energy could be wasted during CO₂ electroreduction.⁴⁶⁻⁴⁷ However, with the development of the electrochemical theory as well as the novel materials, CO₂ electroreduction would make considerable progress in both efficiency and selectivity after receiving more attention. Fundamental studies of this area initiated at early 20th century,⁴⁸ and were further boosted by scientists in recent few decades. In line with this, we would like to introduce the fundamental theory of CO₂ electroreduction in the first section.

2.1.1 Electrochemical equilibrium

CO₂ molecule is chemically inert, so it may seem counterintuitive that equilibrium potentials of CO₂ electroreduction towards all reduced products are not so negative. Table 2.1 shows that standard electrode potential of CO₂ electroreduction to CH₄, the simplest hydrocarbon, is only -0.24 V vs. SHE. As a

comparison, the standard electrode potential of hydrogen evolution reaction (HER) is -0.42 V vs. SHE, which is much more negative. However, the CO₂ electroreduction only occurs at much more negative potential, always with HER as a nonnegligible side reaction. A recognized reason is that CO₂^{•-}, the intermediate of the first step of CO₂ electroreduction, requires an extremely negative potential (-1.90 V vs. SHE as calculated) to generate.

Table 2.1 Selected electrochemical equilibriums of CO₂ electroreduction. (in water solution, pH=7.0, 25 °C, 1 atm.)⁴⁹

Equilibrium of CO ₂ Electroreduction	E ⁰ /V vs. SHE
CO ₂ + 2H ⁺ + 2e ⁻ → CO + H ₂ O	-0.53
CO ₂ + 2H ⁺ + 2e ⁻ → HCOOH	-0.61
CO ₂ + 4H ⁺ + 4e ⁻ → HCHO+H ₂ O	-0.51
CO ₂ + 6H ⁺ + 6e ⁻ → CH ₃ OH + H ₂ O	-0.38
CO ₂ + 8H ⁺ + 8e ⁻ → CH ₄ + 2H ₂ O	-0.24
2CO ₂ + 12H ⁺ + 8e ⁻ → C ₂ H ₄ + 4H ₂ O	-0.34
CO ₂ + e ⁻ → CO ₂ ^{•-}	-1.90
2H ⁺ + 2e ⁻ → H ₂	-0.42

The equilibriums above indicate that the CO₂ electroreduction in aqueous solution could be enhanced with the decrease of pH, as the H⁺ is at the side of reactant. However, the practical situation would be more complicated. One reason is that the CO₂ dissolved in water could generate carbonic acid, which could affect the pH of electrolyte. Another one is that the side reaction HER could be dramatically enhanced by increasing the concentration of H⁺. Considering all these factors, alkaline electrolyte is always used and after saturated with CO₂, it could

become weakly alkaline, so the studies of CO₂ electroreduction is generally in ~7.0 pH aqueous solution.

When strong base solution like NaOH or KOH are used and purged with CO₂, species of H₂CO₃, HCO₃⁻ and CO₃²⁻ could coexist with multiple equilibria. Considering the following equilibrium (with standard condition, p (CO₂) = 1 atm):

As concentration of CO₂ in solution accords with the Henry law (Henry constant $h = 3.38 \times 10^{-2} \text{ mol l}^{-1} \text{ atm}^{-1}$), for reaction (1),

$$\text{pH} = \text{pK}_{a1} - \log h + \log[\text{HCO}_3^-] - \log P(\text{CO}_2) = 7.82 + \log[\text{HCO}_3^-] - \log P(\text{CO}_2) \quad (3)$$

For reaction (2),

$$\text{pH} = \text{pK}_{a2} + \log ([\text{CO}_3^{2-}]/[\text{HCO}_3^-]) \quad (4)$$

When reaching the equilibrium with 1 atm CO₂ gas, the dominant species is HCO₃⁻, whose concentration roughly equals to that of Na⁺ or K⁺. Therefore we may conclude that regardless of whether the initial solution is hydroxide, carbonate or bicarbonate, the pH is only determined by the concentration of Na⁺ or K⁺, which equals to the final concentration of HCO₃⁻. For instance, the pH of 1 M KHCO₃

solution saturated with CO_2 could be calculated to be 7.82, according to equation (3). Thus the KHCO_3 has been selected as the most commonly used electrolyte for the reasons above.

2.1.2 Electroactive species in CO_2 electroreduction

From the chemical equilibrium in electrolyte we know that there are various carbon(IV) species existing in electrolyte. When discussing CO_2 electroreduction, it is important to make sure that which species is reduced directly on the surface of electrode. Since the solubility of CO_2 in water is extremely low (~ 30 mM in 1 atm and room temperature)⁵⁰, electroreducing HCO_3^- directly seems to have much more advantages, as we could simply improve the reaction efficiency by increasing the concentration of bicarbonate. Besides that, it is also economically feasible to capture CO_2 and convert it to bicarbonate with existing proven techniques.⁵¹ However, although there are still some controversies, most scientists in this area agree that the electroactive species in CO_2 electroreduction is molecule form of CO_2 or H_2CO_3 , rather than CO_3^{2-} or HCO_3^- ions.⁵²

There were still some articles claiming that bicarbonate could be directly electroreduced, at nanodiamond electrodes⁵³, Hg electrodes⁵⁴⁻⁵⁶ or Pd electrodes⁵⁷⁻⁵⁸. All these electrodes had something in common, that the current densities were relatively low and the products were carboxylic acid. In response to this argument, Fujii has made an investigation, and clearly pointed out that the H_2CO_3^* (sum of dissolved CO_2 and H_2CO_3) was the electroactive species in CO_2 electroreduction, by using quantitative analysis.⁵⁹⁻⁶⁰ He also illustrated that HCO_3^- with high

concentration could decompose and generate $\text{CO}_2(\text{aq})$ by itself, thus the electrolysis of bicarbonate could also generate CO_2 reduction products like formic acid with relatively lower current density on Cu electrode. Hori and Suzuki also tested electroreduction of NaHCO_3 and Na_2CO_3 on Hg electrode without CO_2 bubbling, and found that the current density first increased with the negative potential, then reaching a limiting value of $\sim 0.5 \text{ mA cm}^{-2}$ at -1.9 V vs. SHE , which was much lower than that of ordinary CO_2 electroreduction.⁶¹ All these results confirm that during electroreduction of HCO_3^- , the actual reduced species is molecular CO_2 or H_2CO_3 , and the rate determine step is the decomposition of HCO_3^- to CO_2 , which is much slower than the diffusion of CO_2 towards electrode surface. The conclusion also indicates the importance of continuous gas CO_2 supply in its electroreduction process.

2.1.3 Cathode catalyst poisoning

The poisoning of catalyst for CO_2 electroreduction was reported frequently in previous articles, especially for Cu electrode in producing hydrocarbons.⁶² Generally, a fresh-prepared polished Cu electrode could lose most of the capability of producing CH_4 and C_2H_4 within 1 hour continuous CO_2 electroreduction, while the hydrogen evolution is gradually enhanced and become the dominant reaction on Cu surface. Au or Ag electrodes were also illustrated to have a decrease in producing CO after a period of CO_2 electroreduction.⁶³⁻⁶⁵ The reasons of deactivation phenomenon are in dispute, and would probably be a combined one. Vielstich⁶⁶, Bard⁶⁷, and Lee⁶⁸ all reported that after electroreduction of CO_2 , the Cu

electrode would become black, partly or totally. Bard analyzed the surface of Cu electrode after CO₂ electroreduction, by X-ray photoelectron spectroscopy (XPS), and found the existence of carbon. As the contamination of carbon from air or human body for XPS sample is so common, Lee verified the Cu surface with various and more accurate methods, including atomic emission spectrometry analysis (AES), In-situ electrochemical quartz crystal microbalance measurement (EQCM) and field emission scanning electron microscope measurement (FESEM). The AES and EQCM results pointed out that the carbon content on Cu surface was beyond normal standard, and amorphous carbon was observed by FESEM. It was suggested that the amorphous carbon is also one by-product of CO₂ electroreduction. Tributsch⁶⁹, Kyriacou⁷⁰ and Augustynski⁷¹ reported the absorption of organic species on electrode, which could be the contaminate or products of CO₂ electroreduction. This phenomenon was also reported in some relevant research. For example, the deactivation of Pb electrodes for oxalic acid electroreduction towards glyoxylic acid was ascribed to the absorption of product on Pb surface.⁷²

Hori attributed the poisoning of catalyst to contamination of trace heavy metal impurities or organic impurities, which could be aggravated during electrolysis.⁷³ He suggested that the impurities was introduced by original chemicals used in electrolyte, like bicarbonate and water, and designed a series of experiments to simulate real situations.⁷⁴ By using purified reagent in electrolyte, the Cu electrode roughly kept its performance in producing hydrocarbons by ~2 h. However, after adding 0.1 μM Fe²⁺ or Zn²⁺, the deactivation curve of FE vs. time

nicely fit that of using common reagent. By using CV scan Hori proved that the trace impurity metal could be electrodeposited on the surface of electrode and poison it. Besides that, he also verified that absorption of trace amount trimethylamine, which would exist in the ion exchange membrane, could also decrease the capability for Cu electrode to produce hydrocarbons. The trimethylamine test indicated that organics like surfactant in electrolysis would also affect the activity of electrode.

In addition to using reagent with high purity for electrolyte preparation, scientist has also raised some strategies to delay or even eliminate the catalyst poisoning in CO₂ electroreduction. Among which the most feasible one recommended by Hori was pre-electrolysis.⁷⁴ By using a Pt black electrode as cathode and electrolyzing with a high current density, the heavy metal impurities could be deposited on Pt black and removed from electrolyte, thus the life of catalyst could be extended to that of using high purity reagent. It was also reported that intermittent anodic polarization or pulses would be useful for maintaining the performance of Cu electrode in producing hydrocarbons, and the proposed mechanism could be that the anodic treatment temporarily removed the impurities and generate fresh surface.^{71, 75-76} In recent works, the nanostructure electrodes with large specific surface area seemed to have better performance in long-term electrolysis.⁷⁷ It could be ascribed to that large surface area possesses high tolerance of impurities.

2.2. CO₂ electroreduction on various cathode materials

CO₂ electroreduction is a complicated process with various products. As aforementioned, products generated from the CO₂ electroreduction process are strongly dependent on the materials used at the electrode. Different metals and nonmetals can act as catalysts during the reaction, as they possess different adsorption affinities for the various intermediates thus affect distribution of final products. According to the products selectivity, materials are classified to four parts as illustrated in Table 2.2. Note that products other than dominant one are still exist, and the applied potential would also affect the product distribution to some extent.

Table 2.2 Classification of cathode materials in CO₂ electroreduction.⁷⁸

Metal	Significant Property	Main Product
Pb, Hg, In, Sn, Cd, Tl, Bi	High hydrogen overvoltage	HCOOH
Ni, Fe, Pt, Ti	Low hydrogen overvoltage	H ₂
Au, Ag, Zn	Weak CO adsorption	CO
Cu	Generate hydrocarbon products	Hydrocarbons

Metals with extremely high hydrogen overvoltage like Pb, Hg, Sn, etc. tend to produce HCOOH with high faradaic efficiencies. On the other hand, the side product, H₂, dominates for metals with low hydrogen overvoltages such as Ni and Pt. Au, Ag and Zn could adsorb little CO and therefore produce CO as the main product. Of all the metals investigated, Cu is unique for its ability to produce

hydrocarbons through a relatively complicated reaction pathway, and it will be emphatically discussed later. For nonmetal materials, like carbon and silicon, the main products would be CO or HCOOH, depending on material forms. Besides, composite materials are also developed, like metal oxide, metal sulfide and metal-organic framework, with various properties in CO₂ electroreduction.⁷⁹⁻⁸¹ In this section we would like to illustrate the previous research of different materials, classified by their selectivity.

2.2.1 Materials with carboxylic acid selectivity

For electroreduction of CO₂, formation of CO₂^{•-} through a one electron transfer to the CO₂ molecule is regarded as the initial step.⁸² As shown in Table 2.1, this requires an extremely high potential, up to -1.90 V vs. SHE. Therefore, this step is also considered as the rate determining step. CO₂^{•-} could accept a proton and an electron to form HCOO⁻, and it has been regarded as the direct intermediate of HCOOH formation when the CO₂ electroreduction were carried out on various metal electrodes like Pb, Hg, In, Sn, Cd, TI and Bi.⁸³ As evidence, CO₂^{•-} was detected on the Pb electrode during electroreduction of CO₂, by using ultraviolet spectroscopic (UV) measurements.⁸⁴ The common characteristic of these metals is high hydrogen overvoltages. Furthermore, when verifying the so called *Volcano curve* in Figure 2.1, a plot illustrating the relationship between current densities (*i*₀) and metal-hydrogen bond energy which is important for exploration of HER, we may find that most materials with HCOOH selectivity have weak M-H bond

strength, which indicates that low adsorption density of atomic H benefits the carboxylic acid products.⁸⁵

Figure 2.1 Volcano plot for $\log i_0$ values for the HER as a function of M-H bond energy. Reprinted from Ref. 85, with permission of Elsevier, Copyright 2015.⁸⁵

An Sn based gas diffusion electrode was used for CO₂ electroreduction to produce HCOOH.⁸⁶ In this case, Sn was electrodeposited on carbon paper to make

a cathode, and worked at a potential of -1.6 V at 40 °C for 1h with a constant flow of 50 ml min⁻¹ CO₂. Pt coil was used as the anode with H₂ (10 ml min⁻¹) + N₂ (90 ml min⁻¹) while Ag/AgCl was used as the reference electrode. The Sn electrode generated a FE of 18% which is relatively lower than that of the Pb electrode. However, the Sn GDE maintains a stable performance even at long reaction time (maintained about 12% after 1 h). Recently Meyer's group prepared nanostructured Sn electrodes through a facile hydrothermal method. These electrodes produced HCOOH at overpotentials as low as ~340 mV, while FE surpassed 93%.⁸⁷ The high performance may be due to high active surface area. Furthermore, nanostructured metal electrodes would also have increased the efficiency of HCOOH formation.

Figure 2.2 Applied electrolysis potential dependence of total current densities (red squares) and Faradaic efficiencies (blue circles) for formate production on reduced nano-SnO₂ loaded on carbon black. Reprinted from Ref. 87, with permission from the American Chemical Society, Copyright 2014.⁸⁷

Kanan has developed Sn and Pb oxide derived electrodes with enhanced performance in producing formic acid, compared to corresponding polycrystalline metal foil.⁸⁸⁻⁸⁹ After oxidation treatment, the FE of HCOOH increases from ~60% to nearly 100% on Pb, while that of both HCOOH and CO increase for 3-4 times on Sn, in overall potential region. Kanan attributed the suppression of H₂ evolution and enhancement of CO₂ electroreduction to the metastable adsorption layer of corresponding metal oxide or hydroxide, which could be formed at grain boundaries of nanostructure surface.

Figure 2.3 Comparison of CO₂ reduction on metal foil and oxide-derived (OD) metal foil in CO₂ saturated 0.5 M NaHCO₃. (A) Plot of HCOOH Faradaic efficiency vs potential for Pb foil (■) and OD-Pb (●). (B) Faradaic efficiencies for HCOOH and CO at various potentials on Sn foil and in-situ deposited Sn/SnO_x thin-film electrodes. Reprinted from Ref. 88 and Ref. 89, with permission from the American Physical Society, Copyright 2012 & 2015 American Chemical Society.⁸⁸⁻

Some types of carbon based electrodes developed recently were also proved to possess carboxylic acid selectivity. Quan has used microwave plasma enhanced chemical vapor deposition (CVD) to prepare nitrogen-doped nanodiamond (NDD) array electrodes on silicon substrate⁹⁰, which illustrated rare selectivity towards formate as well as acetate.⁵³ NDD electrode prepared under low temperature (450 °C, denoted as NDD_L) and relatively high temperature (500 °C, denoted as NDD_H) have different performances which illustrated in Figure 2.4 A. Through XPS analysis, Quan found that high preparation temperature increased the content of N-sp³C, which would benefit the generation of carboxylic acid. By adjusting the reactant gas ratio (N₂:CH₄:H₂) of CVD process, the N contents could also be changed, and it was illustrated that production rates of acetate and formate could increase with the N contents in Figure 2.4 B.

Figure 2.4 (A) Production rates of acetate and formate on NDDL/Si RA and NDDH/Si RA electrodes obtained from electrochemical reduction of CO₂ for 3 h at -0.55 to -1.30 V (CO₂ saturated 0.5 M NaHCO₃). (B) Production rates of acetate and formate on NDDL/Si RA electrodes with N contents of 0.93, 2.12, and 3.68 atom % (-1.0 V). Reprinted from Ref. 53, with permission from the American Chemical Society, Copyright 2015.⁵³

Meyer reported that the polyethylenimine-enhanced nitrogen-doped carbon nanomaterials, like nitrogen doped carbon nanotube⁹¹, were also able to electroreduce CO₂ to formate with high performance. From Figure 2.5, we might conclude that the nitrogen doping could invest inert CNT with catalytic activity of CO₂ electroreduction, and modification of polyethylenimine could double the partial current density as well as FE compared to bare NCNT.

Figure 2.5 (a) Cathodic linear sweep voltammetry scans at 50 mV/s in a CO₂-saturated aqueous 0.1 M KHCO₃ solution. (b) Plot of Faradaic efficiencies for formate production vs applied potential at CNT/GC, NCNT/GC, and PEI-NCNT/GC electrodes. Reprinted from Ref. 91, with permission from the American Chemical Society, Copyright 2014.⁹¹

2.2.2 CO selectivity

Au, Ag and Zn produce CO as the main product when CO₂ is reduced in aqueous solution at various potentials. Alloys of Cu and Cd also produce CO as the dominant product as well.⁹² For Au, Ag and Zn, the ability of producing CO is reduced when modified with metal adatoms, like Cd, Sn, In, Pb and Tl.⁹² CO₂^{•-} is also the intermediate during CO formation, but the reaction route is different. CO is attained at relatively lower potentials compared to HCOOH. Hori suggests that this is because CO₂^{•-} is greatly stabilized by adsorption on Au, and the onset potential is only -0.8V vs. SHE.⁹³ Results of Tafel slope measurements also show that the generation of CO on Au surface was not affected by pH of the solution.⁹³ For Ag

electrodes, the (110) single crystal face shows the best performance for obtaining CO.⁹⁴

Figure 2.6 FEs for CO and HCOO⁻ production on oxide-derived Au and polycrystalline Au electrodes at various potentials between -0.2 and -0.5 V in 0.5 M NaHCO₃, pH 7.2. Dashed line indicates the CO equilibrium potential. Reprinted with Ref. 95, with permission from the American Chemical Society, Copyright 2012.⁹⁵

Recently, many groups have focused their investigations on nanostructured metals electrodes as means to reduce the overpotential and enhance efficiency of CO production. Kanan's group reported an oxide-derived Au nanoparticle (np) electrode, which reduced overpotential by about 0.15 V compared to polycrystalline Au electrodes, and provided almost 100% CO selectivity.⁹⁵ Qi Lu,

etc. reported that Ag nanoparticle electrodes prepared by dealloying of an Ag-Al precursor enlarged the reduction current density for more than 10 times at -0.60 V vs. RHE, and reduced the overpotential as well.⁹⁶

Figure 2.7 Electrocatalytic performance of np-Ag. CO₂ reduction activity of np-Ag and polycrystalline silver at -0.60 vs. RHE. Total current density versus time on (left axis) and CO Faradaic efficiency versus time (right axis). Reprinted from Ref. 96, with permission from the Nature Publishing Group, Copyright 2014.⁹⁶

Pd has been long used as an efficient HER electrocatalyst, thus the bulky Pd is regarded as a terrible catalyst for CO₂ electroreduction because of the high H₂ selectivity. However, Pd electrodes with certain structure have displayed unexpected capability to convert CO₂ towards CO.⁹⁷⁻⁹⁸ Wang reported that the FE

of CO on Pd electrocatalyst could be controlled by size of Pd nanoparticle.⁹⁹ When the diameter of Pd particles decrease from 10.3 nm to 2.4 nm, the FE of CO increase from less than 10% to almost 100%. Through DFT theoretical calculation it was found that different facets of Pd possessed different performance in reducing free energy for intermediates, like adsorbed COOH*. Within a narrow size range of 2.4–10.3 nm, smaller Pd nanoparticles obtain more corner and edge sites, which were more active than terrace sites toward CO₂ electroreduction. As it is widely known that Pd could adsorb CO easily thus result in a catalyst poisoning, a stablization test would be necessary for further developing of Pd catalyst for CO₂ electroreduction.

Figure 2.8 (A) Applied potential dependence of Faradaic efficiencies for Pd nanoparticles with different diameters. (B) Adsorption of intermediate COOH and free energy diagrams for CO₂ reduction to CO on Pd(111), Pd(211), Pd55, and Pd38. Reprinted from Ref. 99, with permission from the American Chemical Society, Copyright 2015.⁹⁹

Ionic liquid and organic solvent could be used to increase the solubility of CO_2 ¹⁰⁰⁻¹⁰³, but could not provide the proton which is necessary for the formation of reductive products. A mixture of ionic liquid, organic solvent and water could be a method to combine the merits of all contents. Rosenthal prepared a Bi electrode from $\text{Bi}(\text{OTf})_3$, which illustrated performance of producing CO in a mixture of 1-butyl-3-methylimidazolium based ionic liquid and acetonitrile solution, surpassing that of bulky Au or Ag electrodes.¹⁰⁴ Carbon nanofibre and molybdenum disulphide electrode developed by Kumar both manifested excellent selectivity of CO in CO_2 electroreduction, in EMIM- BF_4 water solution.

A common characteristic of metals which preferentially generate CO is their low CO adsorption ability. CO is an important intermediate in electroreduction of CO_2 for the formation of more thoroughly reduced products, like alcohol or hydrocarbons. Thus, for metals which are unable to adsorb CO, it is not further reduced to other products on electrode surface, thus leading to a high selectivity to CO. Metals like Cu could also produce CO as the dominant product at low potential.¹⁰⁵

2.2.3 H_2 selectivity

Metals with low hydrogen overpotentials, like Ni, Fe, Pt and Ti mainly produce H_2 instead of CO_2 reduction products. In truth, the overpotential of CO_2 electroreduction is not high on Pt or Ni,⁹² however, H_2 generation is extremely active on these metals, which overtakes the electroreduction of CO_2 completely. Another possible reason is that the CO molecules, generated from CO_2

electroreduction, could strongly adsorb on metals of Pt and Ni.¹⁰⁶⁻¹⁰⁷ The adsorption layer of reduced species would block the active sites of CO₂ electroreduction, and only left hydrogen evolution reactive centers. H₂ is also a common byproduct on other metal electrodes. For example, on the Cu electrode, faradaic efficiency of H₂ can reach to 80% at low potentials.⁴¹

2.2.4 Alcohol selectivity

Frese's group has demonstrated that when semiconductors are used at the cathode, they are able to efficiently convert CO₂ to methanol.¹⁰⁸⁻¹⁰⁹ n-GaAs, p-GaAs and p-InP were tested on different crystal faces in electroreduction of CO₂ with potentials from -1.2 to -1.4 vs. SCE. For n-GaAs, the FE of methanol generation reached almost 100% on the As(111) crystal face with a high current density of 160-200 $\mu\text{A cm}^{-2}$. However, performance of the As(111) crystal face in p-GaAs was relatively lower, with FE of 52%-57% and current density of 80-100 $\mu\text{A cm}^{-2}$. For p-InP, the active crystal face was P(111), which provided a 69%-80% FE and lowest current density 60-66 $\mu\text{A cm}^{-2}$. Current densities generated by semiconductor electrodes are relatively lower compared to ordinary metal electrodes like copper or gold electrodes. However, their ability to convert CO₂ to methanol with extremely high efficiency is attractive. We conclude that for semiconductors, the nonmetallic crystal faces tend to have better performance for electrochemical reduction of CO₂. Mo is special among pure metal materials in electroreduction of CO₂, owing to its ability to convert CO₂ to methanol in water solution. Frese's group demonstrated that one of the significant advantages of this

material is its extremely low overpotentials during electrolysis.¹¹⁰ They proved that if the electrode could be pretreated by cycling between -1.2 V to +0.2 V vs. SCE, FE of reduction could reach 370% at -0.8 V vs. SCE. As the reported alcohol FEs were always extremely high, the repeatability would need further confirmation, and the substance of the electrode might be consumed during electrolysis process.

2.2.5 Hydrocarbons selectivity on Cu electrode

Cu is a unique electrode material for the electroreduction of CO₂, owing to its ability to produce hydrocarbons like CH₄, C₂H₄ and C₂H₆ in aqueous solution, which are most reduced products. However, the products are more complex. The selectivity of products is affected by electrolyte, potential, temperature, pressure of CO₂ and surface treatment or modification of Cu electrode.

Figure.2.9 shows the product distribution of CO₂ electroreduction in 0.1 M KHCO₃ solution under different potentials, on a polycrystalline Cu electrode.¹⁰⁵ At low potentials, the main product is H₂, which changes less in current density with the growth of potential. Current density of CO increases from the initial potential -0.8V vs. SHE, and reaches the peak between -1.2 V to -1.4 V vs. SHE, with a maximum current density of around 0.2 mA cm⁻², and then drops. HCOOH is generated at around -1.0 V vs. SHE, while C₂H₄ and CH₄ are generated at -1.1 V and -1.2 V vs. SHE respectively. Products of the abovementioned increase rapidly with increasing negative potentials.

Figure 2.9 Partial current data of different products generated on Cu electrode. Conditions: 0.1M KHCO₃, 19 °C, CO₂ bubbled. Reprinted from Ref. 105, with permission from the Royal Society of Chemistry, Copyright 1989.¹⁰⁵

Crystal face of Cu is also a significant factor to determine the distribution of products. Many kinds of single crystal Cu electrodes have been tested in order to evaluate the performance. Frese reported that hydrocarbons are favored on low index crystal face like Cu(111), Cu(110) and Cu(100).¹¹¹

When the surface treatment was applied on Cu electrode, the performance and selectivity changed significantly. Many recent works focused on preparation of nanostructure metal materials in electroreduction of CO₂ to obtain better performance. Cu electrodes prepared by annealing oxidation and in situ electroreducing could produce C₂H₄ as well as C₂H₆, which was rarely seen in

products produced by polycrystalline Cu electrode, with low overpotential and relatively high faradaic efficiency.^{77, 112} A similar oxide-derived nanocrystalline Cu electrode was also applied in electroreduction of CO, an important intermediate in CO₂ reduction reaction, and could produce liquid products like ethanol, acetate and n-propanol with up to 57% FE.¹¹³ One kind of electrodeposit honeycomb-like Cu electrodes were prepared as well, with a similar performance in producing both C₂H₄ and C₂H₆.¹¹²

Figure 2.10 Comparison of faradaic efficiencies for CH₄, C₂H₄ and C₂H₆ vs potential, between polycrystalline Cu and Cu annealed at 500 °C for 12 h. Data for polycrystalline Cu is literature data obtained in 0.1 M KHCO₃/CO₂. Reprinted from Ref. 61, with permission from the American Chemical Society, Copyright 2012.⁷⁷

2.3 Mechanism of CO₂ electroreduction

It has been proposed that the formation of CO₂^{•-} radical, which is generated by single electron transfer to adsorbed CO₂ on electrode, is the initial step of CO₂ electroreduction.^{82, 114} The conversion from linear triatomic molecule CO₂ towards CO₂^{•-} with trigonal planar geometry demands high activation free energy¹¹⁵, which has been illustrated in Table 2.1. CO₂^{•-} has been detected on various kinds of electrodes in aqueous or nonaqueous electrolyte during CO₂ electroreduction, through ultraviolet (UV) spectroscopic and in-situ Fourier transform infrared spectroscopy (FT-IR) measurements.^{53, 84, 116} A study of SCF (ab initio) molecular orbital energies and atomic population analysis of free CO₂^{•-} shown that at the highest occupied orbital of molecule, the unpaired electron density is localized at carbon atom, which makes CO₂^{•-} a nucleophilic reactant. However, the following steps from CO₂^{•-} to more reduced products would branch, which are demonstrated in Figure 2.11.

Figure 2.11 Proposed stepwise reaction mechanism of CO_2 electroreduction, on different groups of materials in aqueous solution. Reprinted from Ref. 40, with permission from the Wiley & Sons, Inc., Copyright 2016⁴⁰

For the metals like Sn, Hg, Pb and In with HCOO^- selectivity, it is found that the coverage of adsorbed reduced species is low,¹¹⁶⁻¹¹⁷ which indicated that most of generated $\text{CO}_2^{\bullet-}$ would be close to the electrode, but free in the solution. As mentioned above, free $\text{CO}_2^{\bullet-}$ is a nucleophilic reactant which could be attacked by a proton from water on carbon atom, forming a $\text{HCOO}^{\bullet}$, and further reduced to HCOO^- .

Other metals with high $\text{CO}_2^{\bullet-}$ adsorption would have a different route. As $\text{CO}_2^{\bullet-}$ was proposed to adsorb on metal surface with carbon atom,¹¹⁸ the protonation could only occur on oxygen atom to form adsorbed COOH^* intermediate, and lose OH^- anion to become adsorbed CO. Most of metals with high $\text{CO}_2^{\bullet-}$ adsorption like Au, Ag or Zn cannot stabilize CO molecular on surface, hence, the CO would be the preferred product. Till now, only Cu has a unique

property with moderate CO adsorption and could stabilize further reduced species, thus the hydrocarbons formation could be achieved.

2.3.1 Tafel slope studies

In order to compare the activity and explore the mechanism of electrocatalysts for HER, ORR as well as CO₂ electroreduction, Tafel analysis is usually introduced. In Tafel analysis, the relationship between $\log j$ (j represents the current density) and η (which represents the overpotential) is plotted, and the slope of plots' liner part is the so called Tafel slope, which could be used to identify the rate determining step of the corresponding reaction on electrode.

The reaction of CO₂ electroreduction is complex with multiple products. For each products, the Tafel slope needed to be calculated independently with $\log j_o$ (j_o represents the partial current density of corresponding product), and the different results may indicate different rate determining steps.

Generally, the process of initial electron transfer to CO₂ forming adsorbed CO₂^{•-} intermediate is regarded as the rate determining step, with a Tafel slope of ~118 mV dec⁻¹. This value could be acquired by using the partial current density of CO on many types of Ag, Au or Cu electrodes,^{77, 105} proving that the CO formation follows the mechanism.

Figure 2.12 CO partial current density Tafel plots for polycrystalline Cu and for annealed Cu electrodes, obtained in M KHCO₃/CO₂ electrolyte. Reprinted from Ref. 61, with permission from the American Chemical Society, Copyright 2012.⁷⁷

However, for the hydrocarbon formation there seems to be a larger energy barrier. The electroreduction of CO does not involve the formation of CO₂^{•-}, but Hori found that larger Tafel slopes of ~176 mV dec⁻¹ were observed in electrolyte with various pH.¹¹⁹ With an assumption that the partial current density would be related to activity of proton in solution, the value of Tafel slope indicate that the rate determining step for formation of C₂H₄ as well as other hydrocarbons could be the second electron transfer to adsorbed CO to form another intermediate, COH or CHO.

Figure 2.13 Partial current densities for the formation of ethylene in CO electroreduction vs. applied potential in electrolyte with different pH: pH 6.0-6.3 ($\circ$), pH 7.1-7.7 (Δ), pH 8.0-8.6 ($\square$), pH 8.7- 8.9 ($\times$), pH 9.0-9.3 ($\bullet$), pH 10.5-11.3 ($\blacktriangle$), pH 12.2 ($\blacksquare$). Reprinted from Ref. 119, with permission from the American Chemical Society, Copyright 1997.¹¹⁹

For the generation of formate, various Tafel slopes are obtained on various materials. For CO selective material, the increase of formate partial current density with potential is low, which makes the Tafel slope extremely larger and meaningless. For formate selective material, especially the electrodes with

nanostructure, the Tafel slopes were reported to be smaller than 118 mV dec^{-1} and much close to 59 mV dec^{-1} , involving an electron transfer from HCO_3^- or CO_2 towards $\text{CO}_2^{\bullet-}$.⁸⁸⁻⁸⁹

2.3.2 Theoretical study of hydrocarbons formation on Cu

It is complicated to explain why only Cu obtains repeatable property in producing hydrocarbons. In general, formation of hydrocarbons needs appropriate adsorption of specific species. For instance, Au lacks the ability in adsorbing CO, which makes it difficult for CO to be further reduced on the surface of Au electrodes.¹²⁰ On the other hand, if adsorbed CO is more stable than adsorbed hydrocarbons, it means that formation of hydrocarbons needs more activation energy. CO has a moderate adsorption on Cu surface, which is beneficial for gathering and conversion of CO.

Over the past several decades, many mechanism studies focus on its microscopic structure aiming at revealing details of CO_2 electroreduction. From computational chemistry research, we may find the mechanism of CO_2 electroreduction in each step at the surface.^{31, 121-122} The research would not only explain why the Cu is unique, but also illustrates the possibilities of making more efficient electrodes.

The CHE model calculation research of the CO_2 reduction on Cu surface by Norskov's group illustrates the reaction occurs on the Cu(211) crystal face, which could probably be a stepwise process with decreasing in energy.¹²¹ Figure 2.14 shows lowest energy route for the formation of H_2 , HCOOH , CO, and CH_4 from

reduction of CO₂ on Cu surface. In this figure, each step (from left to right) on any route represents the transfer of one proton-electron pair. The free energy at 0 V vs. RHE are shown in black while that at selected potential are shown in red.

Figure 2.14a shows the generation of H₂, and CO₂ does not participate in this reaction route. The first step of proton adsorption is the potential-limiting step. The reaction pathway is calculated by the CHE model on the Cu (211) surface with an onset potential of around -0.03 V vs. RHE. In practice, a more negative potential like -0.3 V vs. RHE is needed, in order to eliminate the oxide sited on Cu surface which will lead to significant overpotential of H₂ generation.

Figure 2.14b shows the formation of HCOOH. In this route, one adsorbed CO₂ molecule combines with a proton-electron pair to form a carboxyl species (COOH). Then the combination of another proton-electron pair with carboxyl results in a HCOOH. The formation of carboxyl is the potential-limiting step, on a potential of -0.41 V vs. RHE calculated by the CHE model.

Route of carboxyl species to CO is also illustrated in Figure 2.14c, which starts at -0.41 V vs. RHE by the CHE model as well. From the onset potential we could find that this reaction pathway is also limited by the formation of carboxyl species. As mentioned before, CO is moderately adsorbed on Cu surface, making a balance between free CO and surface adsorbed CO.

Compared to the general view that the formation of CO₂^{•-} is the rate determining step, the calculation of Norskov's group suggests that there would be another key enabling step, which is the protonation of adsorbed CO to form adsorbed CHO at -0.74 V vs. RHE calculated by the CHE model, since it is the

first step of the formation of hydrocarbons from CO_2 . Figure 2.14d shows the lowest-energy pathway to CH_4 . After the formation of adsorbed CHO , another proton-electron pair combines with CHO to form adsorbed formaldehyde (HCHO). Then HCHO would further protonated to form adsorbed methoxyl (OCH_3) and then combine with a proton in solution to produce CH_4 . Another model also suggested that the first H atom would bond with O to form COH as another possible intermediate.¹²³ Besides that, CHO was also regarded as the key intermediate to form C2 hydrocarbons.⁴⁵

All these calculation results explain why Cu is more effective than other kinds of metals. According to the calculation, the ideal catalysis material could adsorb CO in a certain extent, and further stabilized CHO on surface with higher extent.

Figure 2.14 Calculation of free energy diagrams. Free energy diagrams for the lowest energy pathways to (a) H_2 , (b) HCOOH , (c) CO , and (d) CH_4 . In each diagram, the black (higher) pathway represents the free energy at 0 V vs. RHE and the red (lower) pathway the free energy at the indicated potential. Reprinted from Ref. 121, with permission from the American Chemical Society, Copyright 2012.¹²¹

2.3.3 Approaches to improve selectivity based on theoretical study

The calculation provides us several possible routes to promote the performance of Cu electrodes, which are shown in Figure 2.15. All these methods focus on enhancing the conversion of adsorbed CO to adsorbed CHO or COH in order to compete hydrogen evolution reaction, through stabilizing these two kinds of intermediates.

Figure 2.15 Suggested decoupling strategies exploiting the geometric differences between adsorbed CHO and adsorbed CO. Reprinted from Ref. 121, with permission from the American Chemical Society, Copyright 2012.¹²¹

Alloying is a traditional method in altering the property of catalyst surface. Various kinds of Cu-based alloys, formed with Au, Ag, Ni, Fe, Pb, Pd, Sn, Cd and so on, have also been tested.¹²⁴⁻¹²⁹ However, in previous work, almost all kinds of Cu-based alloys could not exceed pure Cu in terms of producing hydrocarbons during electrolysis, with a certain improvement in generating of H₂, CO or formic acid. With the increasing of heterogeneous metals coverage on Cu, the selectivity of hydrocarbons usually decreases.¹³⁰

Ligand stabilization refers to a series of strategies called molecular electrocatalysts. Many kinds of complexes which contain Cu, Pd, Ni or Co as metal center have been reported to obtain abilities in catalyzing the electroreduction of CO₂. Some of metal complexes can even produce highly reduced products like methanol.¹³¹ Cu complexes obtain the ability to fixate CO₂ from air when the pH is above 7.¹³²⁻¹³³ Angamuthu prepared one kind of dinuclear Cu complex, which could fixate and electroreduce CO₂ under -0.03 V vs SHE to produce oxalate.¹³⁴ Monodentate palladium complexes were used in electroreduction of CO₂ to produce hydrogen and formic acid, but no CO was detected.¹³⁵ Nickel cyclams are highly selective in producing CO,^{106, 136} while macrocyclic nickel complexes tends to electroreduce CO₂ to oxalate.¹³⁷ Immobilisation of Co complexes to a dual-film electrode could produce methanol, ethanol, acetone and lactic acid, with potential of only -0.60 V vs. SHE in aqueous solutions.¹³⁸⁻¹³⁹ Pyridinium was also found to be able to reduce CO₂ efficiently, with low potentials. Methanol could be generated with efficiencies of around 30% when facilitated with hydrogenated palladium electrodes, at -0.76 V vs. SHE, while formaldehyde could be generated at -1.00 V

vs. SHE.¹⁴⁰ All these ligand stabilization methods require extra co-catalyst, and none of them could produce hydrocarbons so far.

Tethering and promoters strategies require modification or functionalization of electrodes. Researchers have tried to chemically modify Cu electrodes to alter the properties of surface, in order to improve the performance compared to bare Cu. Oxidized Cu electrodes have been tested in electroreduction of CO₂ directly, and several dramatically high Faradaic yields of ethanol product have been reported.¹⁴¹⁻¹⁴² However, the performance could not maintain a steady state and was difficult to reproduce,⁷⁸ since both CuO and Cu₂O would be reduced to Cu at negative working potential during electroreducing CO₂ in aqueous solution. Other modifications of Cu electrodes with sulfur or halogen atoms have been reported as well.¹⁴³⁻¹⁴⁴ Compared to bare Cu electrode, Cu electrodes modified with halogen atom have better selectivity in producing ethylene, and those treated with Na₂S could produce more C₂ products as well. However, just like CuO and Cu₂O electrode, Cu modified with halogen and sulfur obtain similar shortcoming of instability.¹⁴³⁻¹⁴⁷ Finding a stable and effective modifier, which could attach on Cu surface even in cathodic process and interact with intermediates of CO₂ electroreduction, would be a feasible strategy to enhance the generation of hydrocarbons.

Chapter 3. Amino Acid Modified Copper Electrodes for the Enhanced Selective Electroreduction of Carbon Dioxide towards Hydrocarbons

3.1. Introduction

CO₂ electroreduction towards hydrocarbons is attractive due to its high conversion efficiency and desirability of the hydrocarbon-based products that can be obtained.^{41, 148-151} Many electrocatalysts including metal and molecule pyridine catalysts have been investigated for CO₂ reduction in the past decades.^{87, 95, 152-162} Of all the metals examined hitherto, only copper (Cu) has shown a unique ability to produce hydrocarbons with reasonable Faradaic efficiency (FE).¹⁶³⁻¹⁶⁴ Achieving high efficiency in the Cu-catalyzed CO₂ reduction process requires Cu electrodes with sufficient active sites.¹²⁴ Various nanostructured Cu electrodes have thus been reported to enhance the activity and selectivity.^{113, 165-168} Nevertheless, the overall selectivity towards hydrocarbons is still very limited.¹⁶⁹ Particularly, the final hydrocarbon mixtures obtained are mostly composed of methane (CH₄) and ethylene (C₂H₄).¹⁷⁰⁻¹⁷³ Typically, only very small amounts of ethane (C₂H₆) are produced, and high carbon products like propene (C₃H₆) are even rarer.¹⁷⁴

Theoretical calculations reveal that effective catalysts must be capable of efficiently catalyzing the protonation of adsorbed CO to adsorbed CHO or COH and exhibit simultaneous poor activity for the competitive hydrogen evolution reaction.¹⁷⁵⁻¹⁷⁶ It is further proposed that the presence of certain ligands on the

catalyst surface would stabilize such adsorbed intermediates (CHO or COH) over CO, the selectivity to hydrocarbons could then be improved.¹²¹ Unfortunately, no experimental evidence has ever been reported to support such theoretical prediction. Along this direction, we describe our recent efforts in developing amino acid modified Cu electrodes for enhanced hydrocarbon production. To demonstrate the validity of this novel modification approach and to rule out any possible Cu morphology effect, we examined three different types of Cu electrodes, namely, Cu nanowire (NW) film, smooth Cu foil, and annealed Cu electrode.⁷⁷ The choice of amino acid to modify Cu surface is based on the fact that amino acids and their derivatives have been used to modify metal catalysts for hydrogenating carbonyl compounds, and the enhanced interaction between certain functional groups of amino acids and intermediate CHO.¹⁷⁷⁻¹⁷⁸

We demonstrate herein that the remarkably enhanced Faradaic efficiency (FE) of total hydrocarbons, including C2 hydrocarbons (C₂H₄ and C₂H₆) and a small amount of C3 hydrocarbon (C₃H₆), increases by up to 100% for glycine modified Cu NW film. Similar trends are also observed on the other two types of Cu electrodes, where the FEs of total hydrocarbons on the modified Cu foil and annealed Cu electrodes have also more than doubled. To the best of our knowledge, this is the first report to realize the enhanced selectivity of Cu electrodes in producing hydrocarbons via the surface modification method. The mechanism of such enhancement is further illustrated by theoretical calculation. Excellent adsorption stability of amino acids on Cu surface during the electrochemical process is also demonstrated.

3.2. Experimental Section

3.2.1 Preparation of electrodes

Potassium persulfate ($\geq 99.0\%$), phosphoric acid (≥ 85 wt. %), potassium bicarbonate (99.7%), 1-aminoanthraquinone (97%), sodium nitrite (97%), Acetonitrile (99%), and tetrabutylammonium tetrafluoroborate (99%) were purchased from Sigma-Aldrich. Glycine ($\geq 99\%$), DL-alanine ($\geq 99\%$), DL-leucine ($\geq 99\%$), DL-tryptophan ($\geq 99\%$), stearic acid (≥ 98.5) were purchased from Sigma. Copper foil (0.025mm thick, 99.98%), DL-tyrosine (99%), DL-arginine ($\geq 98\%$), 1-dodecyl mercaptan ($\geq 98\%$) and o-nitroaniline (98%) were purchased from Aldrich. Sodium hydroxide (97%) was purchased from Alfa Aesar. Hydrochloric acid (37%) was purchased from Merck. Carbon dioxide gas (99.8%) was 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 (Millipore). Cu foils (20 mm $\times$ 20 mm) were first electropolished in 85 wt. % phosphoric acid at 0.5 V vs. Ag/AgCl for 500 s. Polished Cu foils were washed with deionized water, and then immediately immersed into a chemical bath, which is prepared with sodium hydroxide (2.0 g), potassium persulfate (0.81 g) and deionized water (20 mL). After 4 h, a film of copper hydroxide (Cu(OH)₂ NW film) were generated, and then it was washed with deionized water. Cu(OH)₂ NW film was electrochemical reduced in 0.1 M KHCO₃ solution at -2.0 V for 500 s in to obtain Cu nanowire file electrodes (Cu NW film). Annealed-reduced Cu electrodes were prepared by annealing at 500 °C

under the air for 12 h in muffle furnace, and then *in-situ* electrochemical reducing at -2.0 V for 500 s in our cell according to the previous report.⁷⁷ In this process, the Cu electrodes were first oxidized to Cu₂O film and then reduced to Cu electrode. For the modification part, all kinds of amino acids (glycine, DL-alanine, DL-leucine, DL-tryptophan, DL-tyrosine and DL-arginine) were dissolved in deionized water, and 1-dodecyl mercaptan as well as stearic acid was dissolved in ethanol to prepare solution with certain concentrates: 0.1 mM, 0.5 mM, 1.0 mM, 2.5 mM and 10 mM. Electrodes modified by amino acids, mercaptan or stearic acid were prepared by transferring 20 μ L solution on each side of one Cu NW film electrode (40 μ L in total), then kept for 15 mins and dried under nitrogen flow. Cu foil electrodes were modified through immersing one electropolished Cu foil into ~10 mL water solution which contained 5×10^{-8} mmol glycine. The solution was bubbled with nitrogen for 0.5 h in advance. Diazo salts of anthraquinone and o-nitrobenzene were prepared through typical diazotization of corresponding amine, 1-aminoanthraquinone and o-nitroaniline. Amine was first dissolved in 50 mL HCl (37%), and then 1 mmol NaNO₂ is dissolved in 50 mL of deionized water. NaNO₂ solution was added into amine solution slowly under ice bath. After stirring for 10 h, 2 μ L of reaction mixture containing diazo salt was added into 30 mL acetonitrile solution with 0.1 M NBu₄BF₄. Cu NW film electrodes were electroplated in diazo salt solution at -0.3 V vs. Ag/AgCl for 300 s and then washed with acetonitrile for 3 times to obtain diazo salt modified electrodes.

3.2.2 Thickness calculation

The thickness of the film is estimated to be 0.8 μm via the equation: $\text{thickness} = Q \cdot M / n F \rho$ (Q: charge for reducing $\text{Cu}(\text{OH})_2$ film per cm^2 , in our test is $\sim 0.55\text{C}$; $M(\text{Cu}(\text{OH})_2) = 97.5\text{g mol}^{-1}$; $n = 2$; $\rho = 3.37\text{g cm}^{-3}$; $F = 96485\text{C mol}^{-1}$).

3.2.3 Electrochemical active surface measurements

The electrochemically active surface area of electrodes was measured through determination of double-layer capacitance at various scan rates. CVs were obtained for a potential range in which only double-layer adsorption and desorption occurred. The current densities were obtained by integrating area of CV curves, and then plotted against the scan rates of the CV. The slope of the linear regression gave the capacitance. Cu NW film electrodes in 0.05 M H_2SO_4 provided a capacitance of 1.25 mF cm^{-2} . As a comparison, polished Cu foils gave out a capacitance of $1.15 \times 10^{-2}\text{ mF cm}^{-2}$.

3.2.4 Current densities measurements

A Cu disk electrode (diameter 2.0 mm) was polished with 0.01 μm aluminum and washed with deionized water under ultrasonic condition. Cu disk electrodes were immersed into 1.0 mM and 0.01 mM glycine solution for various duration (1 min or 15 mins) to prepare modified ones. Modified Cu disk electrodes and bare Cu disk electrodes were used for scanning between -0.4 V and -1.9 V vs.

Ag/AgCl (scan rate: 0.1 V s^{-1}) in 0.1 M KHCO_3 solution, before test the electrolyte was bubbled by with N_2 for 1 h.

3.2.5 CO_2 electroreduction experiments

An original design H-type cell separated by NAFION N117 ion exchange membrane, and an Autolab potentiostat/galvanostat (Model PGSTAT-72637) workstation at ambient temperature were used for all electrochemical experiments and tests. 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 AgCl) electrodes were used as working electrodes and reference electrodes in the cathode cell. Before electroreduction of CO_2 , CO_2 gas was passed through the electrolyte for at least 1 hour to ensure saturated. Headspace of cathode cell was directly linked to a gas chromatograph (Agilent 6890N-G1540N) equipped with a thermal conductivity detector, Porapak Q column and Molecular Sieve 5A column to analyze gas products.

3.2.6 Characterization

Electrochemical impedance spectroscopy (EIS) was used to prove the stability of absorbed amino acids during electrolysis. A Cu NW film electrode, a modified Cu NW film electrode modified with glycine by immersing into 1.0 mM glycine for 15 mins, and a modified Cu NW film electrode prepared as above

which had already worked for 6 h at -1.9 V vs. Ag/AgCl in 0.1 M KHCO₃ solution were tested. Each sample was firstly immersed into 0.5 M NaCl solution for 30 mins, and then impedance measurements were carried out for each sample at open circuit potential, in a frequency range of 10 kHz – 20 mHz and amplitude of 5 mV peak-to-peak using as signals. Powder 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 the materials. The morphology and microstructure of the products were further studied by transmission electron microscopy (TEM; JEOL, JEM-2010, 200 kV). Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer, equipped with an ATR detector) and attenuated total reflection infrared spectroscopy (ATR) were used to obtain the transmission and reflection infrared spectrum of samples. Tyrosine was used instead of glycine, for its signals of phenyl is obvious. Contact angle analyzer (FTA200 Dynamic Contact Angle Analyzer equipped with an APPRO camera) was used to measure the contact angle of samples. X-ray photoelectron spectroscopy (XPS; VG ESCALAB MKII instrument) with an Mg K α X-ray source was used for analyzing the surface properties of the samples.

3.2.7 Theoretical calculations

Density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP)¹⁷⁹ with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.¹⁸⁰ Ionic cores were treated using the projector-augmented wave (PAW) method.¹⁸¹ The Cu(110) surfaces were chosen to model the experimental systems due to their enhanced activities towards CO₂ and CO electroreduction.¹⁶³ We modeled the surfaces with a 3×3 supercell and 4 metal layers. During the structure optimization, two layers of the adsorbate and the topmost were allowed to relax while the bottommost two layers were kept fixed. Wave functions of valence electrons were expanded using plane wave basis sets with a kinetic energy cutoff of 400 eV. The Brillouin zones were sampled using Monkhorst-Pack scheme with 5×7×1 grids.¹⁸² The Fermi level of surfaces was smeared by the Methfessel-Paxton approach with a Gaussian width of 0.2 eV. To address the solvation effect in the electrochemical environment, we obtained the free energy changes in the proton-coupled electron transfer (PCET) steps using the well-documented computational hydrogen electrode (CHE) model.¹⁸³ Solvation corrections of -0.25 eV for ROH and -0.10 eV for carbonyls were applied arising from our test molecular dynamics (MD) simulations including two water layers. The zero-point energies (ZPE) and vibrational contributions to the entropy for different adsorbates were considered within the harmonic oscillator approximation.

3.3 Results and Discussion

3.3.1 Characterization of electrocatalyst, before and after modification

The Cu NW film is obtained by electrochemically reduction of $\text{Cu}(\text{OH})_2$ NW film on Cu foil in KHCO_3 solution. The thickness of the film is estimated to be 0.8 μm through the calculation method in 3.2.3. Figure 3.1A shows field-emission scanning electron microscopy (FESEM) image of $\text{Cu}(\text{OH})_2$ NW film, the entire Cu foil surface is uniformly coated with $\text{Cu}(\text{OH})_2$ NW. FESEM image obtained at a higher magnification (inset of Figure 3.1A) further reveals that nanowires formed are 100-200 nm in diameter and tens of micrometers in length. After electrochemical reduction, the Cu NWs retain their one-dimensional morphology, however, the straight nanowires become sinuous while the surfaces of nanowires are roughened (Figure 3.1B). The structure of the Cu NWs is further investigated by transmission electron microscope (TEM). Figure 3.1C shows the porous surface of an individual Cu NW. The porous structure and the rough surface should result from dehydration of $\text{Cu}(\text{OH})_2$ NW during the reduction process. Selected-area electron diffraction (SAED) pattern (inset of Figure 3.1C) of single Cu NW shows concentric rings, composed of bright discrete diffraction spots, indicative of high crystallinity. High resolution (HR) TEM image reveals Cu NW has a lattice fringe with interplane spacing of 0.209 nm, corresponding to the (111) plane of Cu. The Cu NW film is also monitored with X-ray diffraction (XRD) and energy dispersive X-ray (EDX) techniques (Figure 3.1D and Figure 3.2). After treatment of Cu foil in NaOH and $\text{K}_2\text{S}_2\text{O}_8$ chemical bath, diffraction peaks in XRD pattern and EDX

analysis indicate the formation of $\text{Cu}(\text{OH})_2$ phase. However, peaks ascribed to metallic $\text{Cu}(0)$ are still present, indicating that the $\text{Cu}(\text{OH})_2$ NW film is not dense enough to completely cover the entire surface of Cu foil base without leaving microvoids. Only $\text{Cu}(0)$ peaks are observed after the electroreduction, demonstrating that the $\text{Cu}(\text{OH})_2$ NW film was completely reduced.

Figure 3.1 FESEM of $\text{Cu}(\text{OH})_2$ NW film (A) and Cu NW film (B). TEM of an individual Cu nanowire (C), the insets in (C) show the selected area electron diffraction (SAED) and HRTEM of Cu NW. XRD patterns (D) of $\text{Cu}(\text{OH})_2$ NW film and Cu NW film.

Figure 3.2 FESEM images and EDX patterns of Cu(OH)₂ (A, B) and Cu NW film (C, D).

Modification of the Cu NW film electrodes is realized by dropping the corresponding modifiers onto the electrode surface. The X-ray photoelectron spectroscopy (XPS) patterns in Figure 3.3 show the successful modification of glycine on the Cu NW film. Figure 3.3B shows that bare Cu NW film reveals no signal of nitrogen species while the glycine modified Cu NW film shows a peak at ~400 eV in N1s scan, corresponding to -NH₂ group. Such peak is still present on the modified Cu NW film after operating at -1.9 V vs. Ag/AgCl for 6 h, indicating that the modification group is stable during the harsh electrochemical testing. On

the bare Cu NW film, there is only one weak peak at ~283 eV in C1s scan, attributing to the sp^2 C–C of trace graphite contaminant. In contrast, there are obvious peaks at ~284, ~286 and ~289 eV in the spectrum of the operated glycine modified Cu NW film electrode, indicating the existence of sp^3 C–C, C–O and –COOH, respectively (Figure 3.3C). Besides that, peaks at ~532 and ~533 eV in O1s scan for the used glycine modified Cu NW film also suggest the existence of organic O species (Figure 3.3D). For O1s scan of bare Cu NW film, there is only a weak peak at ~530 eV, which corresponds well to the characteristic peak of metal oxide and indicates that a small quantity of Cu has been oxidized in the air. The presence of all these signals indicates the existence of –COOH and –NH₂ functional groups on the modified Cu NW film and further confirms that the adsorption of glycine is stable.

Figure 3.3 XPS patterns of Cu NW film and modified Cu NW film (pre-electrolysis). (A) Comparison on full range, (B) N1s scan, (C) C1s scan and (D) O1s scan.

Fourier transform infrared spectroscopy (FT-IR) and attenuated total reflection infrared spectroscopy (ATR-IR) patterns in Figure 3.4A also confirm the successful modification on copper surface. Peaks observed at $\sim 3000\text{ cm}^{-1}$ are ascribed to the stretching vibration of N-H and vibration of associated -COOH . In Figure 3.4B, the electrochemical impedance spectroscopy (EIS) also proves the absorption of amino acids on the Cu NW film. After modification with glycine, an

obvious semicircle impedance loop appears in the high-frequency region. As the radius of semicircle is related to the charge transfer resistance at the interface of electrode and electrolyte, thus the increase of semicircle diameter (charge transfer resistance) indicates that a stable glycine layer is successful absorbed onto the surface of the Cu NW film by occupying some surface sites.

Figure 3.4 (A) Fourier transform infrared spectroscopy (FT-IR) of amino acid (tyrosine) KBr pellet, attenuated total reflection infrared spectroscopy (ATR) of Cu NW film and ATR of amino acid modified Cu NW film. (B) Electrochemical impedance spectroscopy (EIS) results of Cu NW film and modified Cu NW film at open circuit potential.

Furthermore, contact angle measurements of the modified Cu NW film in Figure 3.5 also indicates that the electrode surface is modified, but still maintain its hydrophilicity after the modification. In contrast to the hydrophobic Cu foil surface (109.14° , Figure 3.5A), porous Cu NW film exhibits a hydrophilic surface property (31.3° , Figure 3.5B). The hydrophilic nature of Cu NW film is very important for

producing uniformly modified Cu NW films. After modification with 40 μL , 1.0 mM glycine solution, contact angle increases slightly (55.78° , Figure 3.5C). However, the surface remains hydrophilic. This is advantageous for electro-reduction of CO_2 as it ensures sufficient contact area between the electrode and the electrolyte. Modification with large amount of glycine results in a hydrophobic Cu NW film surface (116.26° , Figure 3.5D) which would block the transfer of dissolved CO_2 during electrolysis.

Figure 3.5 Contact angles of Cu foil (A), Cu NW film (B), 20 μL 1mM glycine modified Cu NW film (C), large amount of glycine modified Cu NW film (D).

3.3.2 The performance of modified electrocatalysts

The FEs of various products obtained on Cu NW film with and without the modification of glycine are shown in Figure 3.6A (products analyses through GC are shown in Figure 3.7-3.9). C2 products (C_2H_4 and C_2H_6) with high FEs as well as some C3 products (C_3H_6) are observed on the bare Cu NW film electrode, which is quite different from previously reported results on various Cu electrodes^{68, 77, 112, 124, 165, 167, 170-171, 174, 184} (Table 3.1). The generation of C3 product is rare, which could be related to the thick and porous nanowire layer. After the glycine modification, hydrocarbon generation is further enhanced while hydrogen evolution is suppressed. The FEs of C_2H_4 and C_2H_6 increase with the decrease of the potential while that of C_3H_6 remains unchanged. At -1.9 V, the total FE of hydrocarbons on the Cu NW film modified with glycine reaches 34.1%, which has almost doubled from the bare Cu NW film electrode (17.8%). Furthermore, the FE of H_2 drops at each potential for the modified electrodes, in alignment with the increasing selectivity towards hydrocarbons. Potentials more negative than -1.9 V are not applied in experiment because the absorbed glycine would detach from the surface at such negative potentials. To evaluate the effect of modification degree, the FEs of total hydrocarbons on Cu NW film electrodes at a typical potential of -1.9 V with varying glycine amounts are examined (Figure 3.6B). The FEs of total hydrocarbons first increased and then decreased with the increase of glycine amount. The FE reaches the maximum of 34.1% at $40\ \mu\text{L} \times 1.0\ \text{mM}$ glycine ($4 \times 10^{-5}\ \text{m mol}$), corresponding to a glycine loading of $4.55 \times 10^{-8}\ \text{m mol cm}^{-2}$ on Cu NW film (based on electrochemical active surface area). The electrochemical active

surface area of Cu NW film increased 110 fold compared with the Cu foil, as verified by the measured capacitance difference (1.25 mF cm^{-2} vs $1.15 \times 10^{-2} \text{ mF cm}^{-2}$, Figure 3.10). At such a loading, it is estimated to be only 7.6% of Cu NW film is covered by glycine, assuming 1 amino acid (glycine) molecule occupies 6 Cu atoms.¹⁸⁵ The increased FE of hydrocarbons over that on the bare Cu NW film suggests that the enhanced catalytic effect is driven by an appropriate level of surface modification by glycine on Cu surface. With too high surface coverage, it may block large number of active catalytic sites and lead to the inhibition of CO_2 electro-reduction.

Figure 3.6 Electrochemical CO_2 reduction on Cu NW film electrodes, (A) on full potential range from -1.3 V to -1.9 V. (B) With different concentrations of glycine at -1.9 V.

Figure 3.7 GC measurements of CO. (A) High concentration of CO, around 10%. (B) Standard sample of HCOOH, with a concentration of 101.6ppm±1%. (C) Sample of modified Cu NW Film. (D) Sample of Cu NW Film.

Figure 3.8 GC measurements of C_2H_4 and C_2H_6 . (A) High concentration of C_2H_4 and C_2H_6 , all around 5%. (B) Standard sample of C_2H_4 and C_2H_6 , with a concentration of $101.7\text{ppm} \pm 2\%$, $101.59\text{ppm} \pm 0.5\%$, respectively. (C) Sample of modified Cu NW Film. (D) Sample of Cu NW Film.

Figure 3.9 GC measurements of H_2 . (A) High concentration of H_2 almost 100%. (B) Standard sample of H_2 , with a concentration of 4000ppm. (C) Sample of modified Cu NW Film. (D) Sample of Cu NW Film.

Figure 3.10 CVs of Cu NW film electrodes at various scan rates with double-layer charging and discharging, in a solution of 0.05 M H_2SO_4 solution.

Table 3.1 FEs of hydrocarbon products on various kinds of Cu electrodes.

Electrode	Potential*	Faraday Efficiency (%)				Reference
		CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	
Cu NW film Gly	-1.9	N/A	6.7	13	0.16	This work
Cu foil Gly	-1.9	32	24	N/A	N/A	
Annealed Cu Gly	-1.9	5.3	20	0.4	N/A	
Cu foil	-2.1	20	4	N/A	N/A	Ref. 68
Cu nanofoam	-1.7	0.2	1.4	1.2	0.1	Ref. 174
Reducted Cu ₂ O	-1.6	N/A	4	7	N/A	Ref. 77
Carbon-supported Cu	-1.8	18	38	N/A	N/A	Ref. 171
Copper electrodeposits	-1.9	N/A	10	3	N/A	Ref. 112
Cu ₂ O-derived nanoparticles	-1.75	3	19	2	N/A	Ref. 167
Nanoparticles covered Cu	-1.75	2	36	N/A	N/A	Ref. 165
Sputtered Cu	-1.75	7	22	1	N/A	Ref. 165
Cu nanoparticles 5-15 nm	-1.75	15	7	N/A	N/A	Ref. 184
Cu-Pt overlayers	-1.65	7	N/A	N/A	N/A	Ref. 170
Cu(111) single crystals	-1.9	24	3	N/A	N/A	Ref. 124

* The potential listed is vs. Ag/AgCl reference electrodes.

To find out whether other amino acid will also function in a similar way, various amino acids including DL-alanine, DL-leucine, DL-tyrosine, DL-arginine and DL-tryptophan are also investigated, with same concentration of 1.0 mM. As shown in Figure 3.11A, Cu NW film electrodes modified with all kinds of amino acids perform better in producing hydrocarbons compared to the bare Cu NW film

electrode. Glycine, the simplest amino acid that only contains -COOH and -NH_2 functional groups, provides a relatively higher hydrocarbons FE of 34.1%. DL-alanine just has an extra methyl group compared to glycine, and gets a lower hydrocarbons FE of 24.3%. Other amino acids with larger branch like DL-leucine, DL-tyrosine, DL-arginine and DL-tryptophan also demonstrate enhanced FEs of hydrocarbons at 19.4%, 20.9%, 23.6% and 27.1%, respectively. The results suggest that -COOH and -NH_2 are probably responsible for the enhanced selectivity of CO_2 reduction. Previous reports illustrate that the adsorption of amino acids on Cu surface is achieved through both -COOH and -NH_2 groups.¹⁸⁵ Stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$, RCO_2H), which contains only -COOH group, is selected to identify the role of -COOH . As shown in Figure 3.11B, the production of hydrocarbons is weakened when the electrode is modified with stearic acid. Other modifiers such as α -anthraquinone diazonium salt (AQ),¹⁸⁶ o-nitrobenzene diazonium salt (PhNO_2),¹⁸⁶ dodecyl mercaptane ($\text{C}_{12}\text{H}_{25}\text{SH}$, RSH) which contain neither -COOH nor -NH_2 groups are also investigated, and all these modifiers reduce the amount of hydrocarbons produced. In particular, the AQ-modified Cu NW film electrodes exhibited only 8.7% of total hydrocarbon FE. The negative effects of other modifiers suggest that amino acids are critical for the electrocatalytic reduction of CO_2 to hydrocarbons. It is proposed that amino acids adsorbed on the catalyst surface which introduce the -NH_2 group can simultaneously enhance hydrocarbon generation.

Figure 3.11 Electrochemical CO₂ reduction on Cu NW film electrodes. (A) With different concentrations of glycine at -1.9 V. (B) With different kinds of amino acids at -1.9 V. (C) With different kinds of modifiers at -1.9 V.

As the types of Cu electrodes would affect the selectivity of final products of the CO₂ electroreduction, the modification method is extended to other Cu electrodes in order to further demonstrate the validity of this novel modification approach and to rule out the Cu morphology effect on the CO₂ reduction. First we tested the performance of polished Cu foil (Figure 3.12), before and after modification. Figure 3.13A shows FEs of CH₄ and C₂H₄ of bare and glycine modified Cu foil electrodes from -1.5 V to -1.9 V. Our Cu foil benchmarks well with the previous report.⁶⁸ After modification, the FEs of CH₄ and C₂H₄ of glycine modified Cu foil are clearly higher than those of the bare one at full potential range. The FEs of CH₄ and C₂H₄ achieve 32.1% and 24.0% on the modified Cu foil electrode respectively, while the corresponding FEs of the bare Cu foil electrode are only 16.1% and 9.5%. Similar to the Cu NW electrodes, the largest enhancement of total hydrocarbons FE (30.5%) is also achieved at -1.9 V. Figure

3.13B exhibits an optimized amount 5×10^{-7} mmol of glycine for the Cu foil electrode (20 mm $\times$ 20 mm). The corresponding covering rate is estimated to be 10.4%, which is close to that of the modified Cu NW film. In Figure 3.13C, all kinds of amino acids demonstrate the positive effect in producing hydrocarbons at all tested potentials, while glycine is the best among them (detailed data with total potential range are in Figure 3.14). The investigation of other modifiers containing neither $-\text{COOH}$ nor $-\text{NH}_2$ groups in Figure 3.13D further confirms the critical role of amino acid on the promotion of CO_2 conversion efficiency to hydrocarbons.

Figure 3.12 FESEM image of polished Cu foil.

Figure 3.13 Electrochemical CO₂ reduction on Cu foil electrodes. (A) On full potential range from -1.5 V to -1.9 V. (B) With different amount of glycine at -1.9 V. (C) With different kinds of amino acids at -1.9 V. (D) With different kinds of modifiers at -1.9 V.

Figure 3.14 Total FEs of hydrocarbons on Cu foil electrodes modified with various amino acids in full potential range.

Furthermore, another kind of Cu electrodes derived from oxides with high activity in producing hydrocarbons is also investigated. The morphology as well as XRD pattern are shown in Figure 3.15, which fit the reference well.⁷⁷ Figure 3.16 shows the comparison of FEs for various hydrocarbons on bare annealed Cu electrode and modified counterpart. The FE of total hydrocarbons at -1.5 V vs. Ag/AgCl (~ 0.85 V vs. RHE) on our bare annealed Cu electrode is close to the reported value, offering a good benchmark point.⁷⁷ The FEs of both CH_4 and C_2H_4 on glycine-modified electrode is higher than those of the bare one throughout the overall potential range. The total FE of hydrocarbons reached the highest value of 26.2% and 10.3% with and without glycine at -1.8 V, respectively. However, the largest difference of FE is 17.2% at -1.9 V, as shown in Figure 3.16A. The results in Figure 3.16B obtained from the annealed Cu electrodes modified by different amino acids again confirm this effective approach, and glycine is still the optimal

choice to improve the selectivity of CO₂ conversion to hydrocarbons. Specific FEs of all electrodes under various conditions are illustrated in Table 3.2.

Figure 3.15 FESEM image (A) and XRD pattern (B) of annealed Cu (Cu₂O layer).

Figure 3.16 Electrochemical CO₂ reduction on annealed Cu electrodes. (A) On full potential range from -1.3 V to -1.9 V. (B) With different amount of glycine at -1.9 V.

Table 3.2 Faradaic efficiencies of CO₂ electro-reduction products under different conditions.

Electrode (vs. Ag/AgCl)*	Faradaic Efficiency (%)						
	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	CO	H ₂	Total
Cu NW film Gly (-1.9 V)	N/A	12.7	21.1	0.3	0.9	52.2	87.2
Cu NW film Gly (-1.8 V)	N/A	8.3	18.0	0.3	1.0	69.3	97.0
Cu NW film Gly (-1.7 V)	N/A	5.1	12.4	0.3	1.0	76.5	95.2
Cu NW film Gly (-1.6 V)	N/A	3.5	8.4	0.3	1.1	77.4	90.7
Cu NW film Gly (-1.5 V)	N/A	2.1	5.0	0.2	1.6	79.3	88.2
Cu NW film Gly (-1.4 V)	N/A	1.3	3.3	0.2	2.0	85.4	92.3
Cu NW film Gly (-1.3 V)	N/A	0.8	2.6	0.2	3.3	84.8	91.8
Cu NW film (-1.9 V)	N/A	5.9	11.7	0.2	0.7	76.2	94.7
Cu NW film (-1.8 V)	N/A	5.3	11.1	0.2	0.8	75.9	93.3
Cu NW film (-1.7 V)	N/A	4.0	9.9	0.3	0.8	78.6	93.5
Cu NW film (-1.6 V)	N/A	3.0	6.7	0.2	0.8	82.8	93.5
Cu NW film (-1.5 V)	N/A	2.3	4.5	0.2	1.1	80.0	88.0
Cu NW film (-1.4 V)	N/A	1.4	2.8	0.2	1.6	90.5	96.5
Cu NW film (-1.3 V)	N/A	0.7	1.6	0.2	2.5	89.1	94.1
Cu NW film Leu	N/A	6.1	13.0	0.2	0.6	72.4	92.4
Cu NW film Trp	N/A	8.8	18.0	0.3	0.7	67.3	95.2
Cu NW film Arg	N/A	8.3	15.1	0.2	0.7	63.2	87.5
Cu NW film Ala	N/A	8.8	15.3	0.2	0.7	66.8	91.8
Cu NW film Tyr	N/A	8.8	11.8	0.3	0.7	72.3	93.9
Cu NW film Gly after 2 h	N/A	13.8	20.0	0.3	0.5	63.2	97.8
Cu NW film Gly after 3 h	N/A	12.8	18.7	0.3	0.5	66.8	98.6
Cu NW film Gly after 4 h	N/A	13.0	19.1	0.4	1.0	65.2	98.7
Cu NW film Gly after 5 h	N/A	12.7	17.3	0.7	0.3	64.3	95.3
Cu NW film Gly after 12 h	N/A	9.0	13.4	0.2	3.2	70.9	96.7
Cu NW Gly 4×10 ⁻⁶ m mol	N/A	8.0	13.7	0.2	0.7	74.3	96.8
Cu NW Gly 2×10 ⁻⁶ m mol	N/A	7.1	16.8	0.2	0.7	69.7	94.4

Table 3.2 Continuation

Electrode (vs. Ag/AgCl)*	Faradaic Efficiency (%)						
	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	CO	H ₂	Total
Cu NW Gly 1×10 ⁻⁴ m mol	N/A	5.3	15.0	0.1	0.5	71.5	92.5
Cu NW Gly 4×10 ⁻⁴ m mol	N/A	4.9	9.3	0.1	0.5	79.3	94.2
Cu NW film RCOOH	N/A	3.7	12.1	0.1	0.5	79.6	96.0
Cu NW film PhNO ₂	N/A	2.4	7.3	0.2	0.8	77.1	87.8
Cu NW film AQ	N/A	1.9	6.7	0.2	0.7	83.1	92.6
Cu NW film RSH	N/A	2.8	10.2	0.1	0.8	74.3	88.2
Cu foil (-1.9 V)	16.1	9.5	N/A	N/A	1.1	66.8	93.5
Cu foil (-1.8 V)	8.8	8.2	N/A	N/A	1.2	77.9	96.1
Cu foil (-1.7 V)	2.6	3.3	N/A	N/A	1.9	84.8	92.6
Cu foil (-1.6 V)	1.6	1.9	N/A	N/A	2.0	90.7	96.2
Cu foil (-1.5 V)	0.9	0.6	N/A	N/A	14.9	71.4	87.8
Cu foil Gly (-1.9 V)	32.1	24.0	N/A	N/A	0.6	34.7	91.5
Cu foil Gly (-1.8 V)	20.9	22.4	N/A	N/A	1.0	43.9	88.1
Cu foil Gly (-1.7 V)	12.2	18.0	N/A	N/A	4.1	56.5	90.9
Cu foil Gly (-1.6 V)	6.6	11.3	N/A	N/A	6.9	71.3	96.1
Cu foil Gly (-1.5 V)	4.3	6.9	N/A	N/A	5.8	71.3	88.3
Cu foil Leu (-1.9 V)	16.5	9.0	N/A	N/A	1.0	65.2	91.6
Cu foil Leu (-1.8 V)	12.0	10.2	N/A	N/A	1.7	65.8	89.6
Cu foil Leu (-1.7 V)	6.0	6.6	N/A	N/A	2.5	73.4	88.5
Cu foil Leu (-1.6 V)	3.0	3.6	N/A	N/A	4.8	81.8	93.2
Cu foil Leu (-1.5 V)	1.9	2.0	N/A	N/A	7.9	76.6	88.4
Cu foil Tyr (-1.9 V)	21.3	13.9	N/A	N/A	0.8	57.0	93.1
Cu foil Tyr (-1.8 V)	12.8	12.8	N/A	N/A	1.1	60.5	87.2
Cu foil Tyr (-1.7 V)	9.7	12.4	N/A	N/A	1.7	67.6	91.4
Cu foil Tyr (-1.6 V)	5.7	9.1	N/A	N/A	2.5	75.0	92.3
Cu foil Tyr (-1.5 V)	3.6	6.0	N/A	N/A	3.2	76.3	89.1
Cu foil Arg (-1.9 V)	24.3	15.9	N/A	N/A	1.0	47.1	88.4
Cu foil Arg (-1.8 V)	21.7	17.3	N/A	N/A	0.8	55.1	94.9

Table 3.2 Continuation

Electrode (vs. Ag/AgCl)*	Faradaic Efficiency (%)						
	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	CO	H ₂	Total
Cu foil Arg (-1.7 V)	14.2	15.0	N/A	N/A	3.5	56.8	89.5
Cu foil Arg (-1.6 V)	9.4	9.8	N/A	N/A	4.3	71.5	95.1
Cu foil Arg (-1.5 V)	4.8	5.1	N/A	N/A	3.6	74.1	87.6
Cu foil Ala (-1.9 V)	25.5	18.4	N/A	N/A	2.9	41.6	88.4
Cu foil Ala (-1.8 V)	19.5	18.3	N/A	N/A	1.0	56.4	95.1
Cu foil Ala (-1.7 V)	14.5	15.2	N/A	N/A	2.5	63.1	95.2
Cu foil Ala (-1.6 V)	7.5	9.5	N/A	N/A	6.6	70.9	94.4
Cu foil Ala (-1.5 V)	4.9	5.7	N/A	N/A	5.9	79.4	96.0
Cu foil Trp (-1.9 V)	28.6	11.1	N/A	N/A	1.3	48.0	89.0
Cu foil Trp (-1.8 V)	29.3	11.8	N/A	N/A	2.4	46.7	90.3
Cu foil Trp (-1.7 V)	19.1	11.5	N/A	N/A	4.2	60.2	95.0
Cu foil Trp (-1.6 V)	6.0	5.7	N/A	N/A	4.4	79.0	95.2
Cu foil Trp (-1.5 V)	5.2	4.6	N/A	N/A	6.1	71.2	87.0
Cu foil Gly 5×10 ⁻⁶ m mol	7.1	16.8	N/A	N/A	1.1	63.7	88.7
Cu foil Gly 5×10 ⁻⁸ m mol	27.3	17.6	N/A	N/A	1.1	46.4	92.4
Cu foil RCOOH	12.4	10.4	N/A	N/A	3.9	65.6	92.3
Cu foil PhNO ₂	7.3	5.2	N/A	N/A	1.9	80.6	94.9
Cu foil AQ	7.7	5.1	N/A	N/A	3.5	74.6	90.9
Cu foil RSH	13.2	9.0	N/A	N/A	1.8	71.0	95.1
Annealed Cu Gly (-1.9 V)	5.3	19.7	0.3	N/A	1.1	61.2	87.6
Annealed Cu Gly (-1.8 V)	4.5	21.3	0.4	N/A	1.1	66.5	93.9
Annealed Cu Gly (-1.7 V)	2.8	18.6	0.4	N/A	1.4	65.0	88.2
Annealed Cu Gly (-1.6 V)	1.8	14.6	0.5	N/A	2.8	71.2	90.9
Annealed Cu Gly (-1.5 V)	1.7	11.9	0.6	N/A	2.9	78.1	95.3
Annealed Cu Gly (-1.4 V)	1.1	7.4	0.6	N/A	3.9	78.4	91.5
Annealed Cu Gly (-1.3 V)	1.3	5.6	0.8	N/A	7.5	79.7	94.8
Annealed Cu (-1.9 V)	0.6	7.0	0.5	N/A	1.2	86.8	96.0
Annealed Cu (-1.8 V)	0.6	8.9	0.7	N/A	1.1	84.3	95.7

Table 3.2 Continuation

Electrode (vs. Ag/AgCl)*	Faradaic Efficiency (%)						
	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	CO	H ₂	Total
Annealed Cu (-1.7 V)	0.4	8.8	1.0	N/A	2.1	78.6	91.0
Annealed Cu (-1.6 V)	0.4	7.5	1.1	N/A	3.0	80.0	92.1
Annealed Cu (-1.5 V)	0.4	6.0	1.3	N/A	3.4	79.0	90.1
Annealed Cu (-1.4 V)	0.5	4.5	1.3	N/A	6.6	82.2	95.1
Annealed Cu (-1.3 V)	0.8	3.8	1.4	N/A	12.9	71.1	90.0
Annealed Cu Arg	5.9	12.6	0.2	N/A	1.0	76.9	96.6
Annealed Cu Leu	1.3	9.4	0.5	N/A	1.2	79.2	91.5
Annealed Cu Tyr	2.3	10.8	0.5	N/A	1.2	75.8	90.6
Annealed Cu Trp	1.5	18.7	1.1	N/A	1.3	67.5	90.0
Annealed Cu Ala	2.8	18.1	0.7	N/A	1.3	67.3	90.3

* For the applied potentials not indicated, they are -1.9 V vs. Ag/AgCl.

3.3.3 Mechanism of enhanced performance driven by modification

The current density (j), which represents the production rate, is further investigated. After modification, the total current density (j_{total}) during the electrolysis decreases. Previous work reported the nanostructured metal electrocatalysts could suppress the hydrogen evolution while enhancing the CO₂ electroreduction, through the complex interplay between surface structure, electrode mesostructure, and the electrolyte composition.¹⁸⁷ In our case, we hypothesize that the current decrease is mainly due to the coverage of modifiers on catalytic active sites for hydrogen evolution reaction, while having minimal influence on hydrocarbon generation (Figure 3.17). In contrast to the total current

density, partial current densities of hydrocarbons (j_{CxHy}) are even higher than that of the bare electrodes, in spite of the partial coverage of active sites by functional molecules. For Cu NW film, Cu foil and annealed Cu electrodes, both j_{CxHy} and the differences of j_{CxHy} between the modified and bare electrodes increase with the decrease of potential. j_{CxHy} shows over 100% increase at -1.9 V for all three kinds of electrodes, as illustrated in Figure 3.18. The results indicate that the rise of FEs is due to not only the drop of side reaction current density (like hydrogen evolution current density), but also a clearly enhanced capability in producing hydrocarbons after modification. The enhanced selectivity of hydrocarbons is probably related to the strong interaction between -NH_2 groups in amino acids and formyl (CHO). The interaction plays a significant role in stabilization and transform of formyl (CHO), which is the most important intermediate of CO_2 electroreduction towards hydrocarbons. Nørskov proposed that the ligands tethered to the electrode surface would interact with the adsorbed CHO and stabilize it, the energy barrier for the formation of CHO would be reduced and subsequent hydrocarbon formation could be facilitated.

Figure 3.17 Linear sweep voltammograms for the bare and modified Cu disk electrodes (2.0 mm in diameter) in N₂ bubbled 0.1 KHCO₃ solution. Range: -0.4 V ~ -1.9 V vs. Ag/AgCl. Scan rate: 0.1 V s⁻¹.

Figure 3.18 Partial current density of hydrocarbons: (A) Cu NW film electrodes. (B) Cu foil electrodes. (C) Annealed Cu electrodes (A-Cu).

A Tafel plot, consisted of potential vs. the log of CO current density, is also extracted from the data in an attempt to get more information about the possible mechanism. At lower current density, a Tafel slope of $\sim 0.13 \text{ V dec}^{-1}$ indicates the CO_2 electroreduction is at the 1st order with respect to CO_2 , and the rate determining step of the reaction is the first electron transfer to CO_2 to form $\text{CO}_2^{\bullet-}$.

⁴³ Before and after modification of the Cu NW film electrodes, the slopes of linear parts are 0.124 and 0.120 V dec^{-1} , respectively (Figure 3.19A-B). It indicates the modification process do not change the Tafel slopes of Cu NW electrodes. The constant Tafel slopes reveal that the modification would not decrease the overpotential of CO_2 electroreduction while only increasing the hydrocarbons yield. Furthermore, the measurement of Tafel slopes on Cu foil and annealed Cu electrodes are also carried out (Figure 3.19C-F). The Tafel slopes of Cu foil and annealed Cu electrodes are 0.122 and 0.119 V dec^{-1} , respectively. After modification process, the Tafel slopes remain unchanged, which are 0.119 V dec^{-1} and 0.125 V dec^{-1} , respectively. All these results are consistent with the previous reported values in similar overpotential range and also indicate the modification process of copper electrode will not change the rate determine step ($\text{CO}_2 \rightarrow \text{CO}_2^{\bullet-}$) in the CO_2 reduction process.^{78, 95}

Figure 3.19 CO partial current density Tafel plots for Cu NW film electrode(A) and modified Cu NW film electrode(B) CO partial current density Tafel plots for Cu foil electrode (C), modified Cu foil electrode (D), annealed Cu electrode (E) and modified annealed Cu electrode (F).

To further unveil the underlying mechanism, the free energy change of CO₂ and CO protonation on bare and glycine modified Cu surface are calculated (Figure 3.20). Consistent with previous calculations, the key step of CO₂ electroreduction

towards hydrocarbon products is the CO^* (* denotes adsorbed species) hydrogenation to CHO^* with a free energy change of 0.79 eV .^{31, 122}

Figure 3.20 The DFT calculated free energy change of CO_2 and CO protonation without glycine (blue line) and with zwitterionic glycine (red line).

Due to the fact that glycine will partially transfer from neutral to zwitterionic form in the aqueous environment and the experimental pH range, we take into account both glycine forms.¹⁸⁸⁻¹⁹⁰ In its neutral form, glycine adsorbs on Cu(110) with its -NH_2 end while negligible free energy changes are found during CO_2 and CO protonation. However, the -NH_3^+ end of zwitterionic glycine exhibits strong hydrogen-bond like interaction with both COOH^* and CHO^* adsorbate, leading to a stabilization of ~ 0.50 eV and ~ 0.20 eV, respectively (Figure 3.21). Therefore, amino acids adsorbed on the catalyst surface would introduce the -NH_3^+ group, stabilize CHO^* and simultaneously enhance hydrocarbon generation.

Figure 3.21 Hydrogen-bond like interaction between adsorbed amino acid and: (A) COOH^* ; (B) CO^* ; (C) CHO^* .

The stability of glycine modified as well as bare Cu NW film electrodes is also evaluated in the electrochemical operation (Figure 3.22). FE of hydrocarbons remains largely stable for at least 6 h electrochemical reduction of CO_2 , and keeps more than 2/3 after 12 h operation. The hydrocarbons FE of glycine modified Cu NW film at 12 h (22.6%) is still obviously larger than that of bare Cu NW film

electrode at 1 h (16.7%). Moreover, current density has also remained roughly unchanged at $\sim 11 \text{ mA cm}^{-2}$ for the modified Cu NW film electrode and at $\sim 14 \text{ mA cm}^{-2}$ for the bare Cu NW film electrodes during such a long electrochemical operation period. The similar trend of FE and current density changing demonstrates that the modification would be stable.

Figure 3.22 Electrocatalytic stability of modified Cu NW film (A, B) and bare Cu NW film (C, D) in CO_2 saturated KHCO_3 solution at -1.9 V : (A, C) Faradaic efficiencies; (B, D) the response of current density.

The stable adsorption of amino acids on Cu NW film electrodes during electrolysis is further supported by the XPS results (Figure 3.23). The retained Cu NW morphology (Figure 3.24A) and similar EIS results (Figure 3.24B) further

prove the robust structure. Both of the robust structure and stable adsorption of amino acids assure the excellent electrochemical stability during the CO₂ reduction.

Figure 3.23 XPS pattern (N1s scan) of the modified Cu NW film, after long time electrolysis at -1.9 V.

Figure 3.24 (A) FESEM image of the modified Cu NW film surface after long time electrolysis at -1.9 V. (B) EIS of the modified Cu NW film, at initial condition and after electrolysis at -1.9 V in CO_2 saturated KHCO_3 solution.

3.4 Conclusions

In summary, we developed a general and effective approach of amino acid modification on Cu electrodes for the enhanced electroreduction of CO_2 towards hydrocarbons. To demonstrate the validity of this novel modification approach and to rule out the possible Cu morphology effect, we examined three different types of Cu electrodes, namely, Cu NW film, polished Cu foil and annealed Cu electrodes. The Cu NW film demonstrated an excellent activity for the generation of C_2 and C_3 hydrocarbons in the CO_2 electroreduction. Remarkable enhancement in faradaic efficiency as well as partial current density of hydrocarbons is observed for all kinds of Cu electrodes after proper modification. This modification method would suppress hydrogen evolution and improve the efficiency of the total hydrocarbons

generated. Theoretical calculations reveal that the hydrogen bond formation between CHO^* and $-\text{NH}_3^+$ end of zwitterionic glycine leads to an extra stabilization of CHO^* , which would contribute to the enhanced selectivity for CO_2 reduction. The results reveal that amino acids and their derivatives are promising modifiers in improving the selectivity of hydrocarbons in CO_2 electroreduction, and this strategy has potential to be extended to other important electrocatalytic reactions.

3.5 Declaration

The work presented in this chapter has been published in Energy and Environmental Science. Reproduced by permission of The Royal Society of Chemistry.

Amino Acid Modified Copper Electrodes for the Enhanced Selective Electroreduction of Carbon Dioxide towards Hydrocarbons. **Ming Shi Xie**, Bao Yu Xia, Yawei Li, Ya Yan, Yanhui Yang, Qiang Sun, Siew Hwa Chan, Adrian Fisher, and Xin Wang, *Energy Environ. Sci.*, 2016, 9, 1687-1695.

Chapter 4. Cu Doped Diamond-like Carbon Film

Electrode for Enhanced CO₂ Electroreduction

towards Hydrocarbons

4.1 Introduction

Cu (copper) has been proved to be the unique one to convert CO₂ to hydrocarbons with considerable Faradaic efficiency (FE). Cu electrodes with various morphologies and selectivity have thus been reported. However, the overall efficiency to produce hydrocarbons is still dissatisfactory, thus to prepare Cu based composite material would be a promising strategy to obtain better selectivity towards hydrocarbons in CO₂ electroreduction.

Alloying treatment has been long used to alter the catalytic properties of metal catalysts, and nearly all kinds of Cu based alloys have been tested in CO₂ electroreduction. For instance, Cu-Au alloy has been proved to possess better selectivity towards CO^{124, 191}, while Cu-Pb alloy illustrated a higher FE of formic acid¹⁹². Preparing composite material would be effective to enhance the performance of producing CO compared to both polycrystalline Cu or Au. However, all Cu based alloy performed worse than pure Cu in generating hydrocarbons during CO₂ electroreduction. Even 1% of Au existing in Cu alloy could suppress the generation of hydrocarbons significantly. Another typical kind of composite material is the carbon-supported material, which has been widely used in catalytic, photocatalytic and electrocatalytic process. Cu nanoparticles

supported on carbon black, Ketjen Black and single-wall carbon nanotubes (SWNT) were evaluated in CO₂ electroreduction. With a quite negative potential at -2.2 V vs. Ag/AgCl, the Cu particle with a diameter of ~20 nm on SWNT demonstrated FEs of 42% C₂H₄ and 32% CH₄. These types of carbon supported Cu particles favored C₂ products just like other nanostructured Cu electrodes.¹⁷¹ However, an appreciable amount of CH₄ was observed as well, and the phenomenon would be attributed to hydrogen spillover from carbon supports. The carbon would also raise the hydrogen evolution reaction (HER) during electrolysis.

To suppress the side reaction of hydrogen generation in CO₂ electroreduction, introducing material with higher overpotential of HER could be a feasible strategy. Diamond-like carbon (DLC) or nanodiamond is such a kind of material which obtains extremely negative hydrogen evolution potential and could be used in organic electroreductive reaction, like debromination of polybrominateddiphenyl ethers.⁹⁰ Besides that, the nitrogen doped nanodiamond film on silicon rod array via microwave plasma enhanced chemical vapor deposition has been reported to be a unique material to electroreduce CO₂ to acetate.⁵³ The diamond like carbon is also a possible modifier to enhance the performance of Cu electrodes. In line with this, we prepared Cu doped diamond like carbon (Cu-DLC) film by electrodeposition on Si substrate. As a composite material, the Cu-DLC film demonstrated an excellent activity with higher FE compare to traditional Cu electrode. Quite unexpectedly, the diamond-like carbon does not act as a hydrogen inhibitor, but becomes a proton donor to make Cu

particle produce more hydrocarbons. The mechanism is further explored through DFT calculation.

4.2 Experimental Section

4.2.1 Preparation of electrodes

Silicon wafers with resistivity of 5-7 Ω cm was cut into pieces (10 mm $\times$ 10 mm) as electrode substrates. All Si substrates were washed with 10 M NaOH solution for 1 min, 1 M hydrofluoric acid under ultrasonic for 1 min and then rinsed with DI-water for 3 times. A treated Si substrate and a graphite plate (20 mm $\times$ 30 mm) were connected to the cathode and anode side of a high voltage direct current (HVDC) power supply (Haokexing Ltd. Model HKXDY), respectively. The two electrode slices were parallel to each other with a distance of 10 mm in the cell. 25 mL volume of anhydrous analytically pure acetonitrile was placed in a single compartment electrolytic cell and used as electrolyte. The cell was putted in a container with cooling water to prevent the boiling of electrolyte during electrodeposition. The Cu doped DLC films were prepared by electrodeposition at -1000 V, -1100 V, -1200 V, -1300 V and -1400 V, respectively, at room temperature. During electrodeposition, 0.1 M $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4/\text{CH}_3\text{CN}$ solution was continuously dropped into the electrolyte to maintain the current density at $\sim 10 \text{ mA cm}^{-2}$ for 20 min. DLC films on Si substrate were also prepared under -1200 V in pure CH_3CN solution, without $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ salt.

4.2.2 Electrochemical experiments

A custom-made H-type electrolytic cell with its cathode chamber and anode chamber separated by NAFION N117 ion exchange membrane, and a CHI potentiostat (Model PGSTAT-72637) were used for all electrochemical experiments. 0.1 M potassium bicarbonate and 0.05 M sulfuric acid electrolyte was prepared with corresponding analytical pure chemicals and deionized water. Platinum net electrode (20 mm×20 mm), Cu-DLC electrodes and Ag/AgCl (saturated KCl) electrode were used as the counter electrode, working electrodes and reference electrode. Before electroreduction of CO₂, electrolyte in cathode chamber was bubbled with pure CO₂ gas for at least 1 hour to ensure saturation. There is a gas-tight tube on the headspace of cathode cell to lead the gas into a gas chromatograph (Agilent 6890N-G1540N), 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 balance.

4.2.3 Characterization

Powder 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 for the Cu-

DLC films. Field-emission scanning electron microscopy (FESEM; JEOL, JSM-6701F, 5 kV) equipped with energy dispersive X-ray spectroscopy (EDX) was used to confirm the morphology and elemental composition of the films. The morphology and microstructure of the products were further studied by transmission electron microscopy (TEM; JEOL, JEM-2010, 200 kV). Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer) was used to get the transmission infrared spectrum of samples. 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 Raman measurements.

4.3 Results and Discussion

4.3.1 Characterization of Cu-DLC film

The Cu-DLC films are obtained by high voltage electrodeposition in CH₃CN solution with [Cu(CH₃CN)₄]ClO₄ as copper source. During 20 min direct-current electrodeposition, the Si wafer is gradually covered with dark brown film. The film possesses high adhesion strength towards the substrate, and the thickness is then observed to be ~1 μ m (Figure 4.1). Figure 4.2 illustrates the field-emission scanning electron microscopy (FESEM) images of all kinds of Cu-DLC films, which show that the morphology of the film changes with the deposition potential. Under lower potential (-1000 V), the Cu-DLC film is formed by intensive

nanoparticles with a diameter of ~ 100 nm. When the potential becomes more negative, the nanoparticles accumulate to a dendritic structure which makes the film to be porous. After increase the potential to as negative as -1400 V, the nanoparticles further gather to be larger lumps with an average size of ~ 1 μm .

Figure 4.1 FESEM of Cu-DLC film obtained at -1200 V, viewing the thickness from a cutting off side.

Figure 4.2 FESEM of Cu-DLC films obtained under various potentials. (A) and (B): -1000 V. (C) and (D): -1100 V. (E) and (F): -1200 V. (G) and (H): -1300 V. (I) and (J): -1400 V.

In order to investigate how the Cu and carbon formed the structure of Cu-DLC film jointly, the transmission electron microscope (TEM) is further used to illustrate the inner structure. Figure 4.3A shows the magnified FESEM image of Cu-DLC film. As a comparison, the TEM images in Figure 4.3B and Figure 4.3C show that in the Cu-DLC film formed at -1200 V, the ~ 100 nm nanoparticles is accumulated by smaller Cu nanoparticles, with a diameter of only ~ 10 nm, and the Cu nanoparticles are surrounded with carbon film. In high resolution TEM image (Figure 4.3D), there is only CuO lattice fringe with interplane spacing of 0.238 nm and 0.292 nm, which represent CuO(111) and CuO(110) lattice planes, respectively. The lattice fringe of carbon is not observed which indicate that the carbon is in amorphous state. Selected-area electron diffraction (SAED) pattern (insert of Figure 4.3B) of Cu nanoparticle illustrates clear diffraction concentric rings, which indicate its high crystallinity. The innermost 3 rings correspond to interplanar crystal spacing of 0.292 nm, 0.238 nm and 0.208 nm, which could be ascribed to CuO(111), CuO(110) and Cu(111) lattice planes, respectively. The result also implies that the Cu nanoparticle has an oxidized surface and a homojunction metal core.

Figure 4.3 (A): Magnified FESEM image of Cu-DLC film. (B) and (C): TEM image of Cu-DLC film, the insets of (B) show the selected area electron diffraction (SAED). (D): The high resolution of accumulated Cu particles.

The Cu-DLC film is further monitored with X-ray diffraction (XRD) to validate the form of Cu. Figure 4.4 illustrates the XRD pattern of Cu-DLC film which displays peaks at $\sim 33^\circ$, $\sim 37^\circ$ and $\sim 51^\circ$ and $\sim 44^\circ$, which could be assigned to the CuO(110), CuO(111), CuO(112), and Cu(111) planes respectively. The

diffraction peaks reveal that the Cu nanoparticles contain both Cu phase and CuO phase, which is consistent with the result of SAED. As the Cu(111) peak is the dominate one in XRD pattern, we could draw the conclusion that the Cu nanoparticle is generated at first during electrodeposition, then oxidized partially in a short time when exposed to the air as the particle size is only ~10 nm. The film on Si substrate is also monitored with energy dispersive X-ray (EDX) techniques, which confirms that the films prepared under various potentials contain only copper and carbon components. EDX analysis (Figure 4.5) shows that the atomic percentage of Cu is 75%, 82%, 92%, 91%, and 78%, for the Cu-DLC films prepared under the potentials from -1000 V to -1400 V, respectively. The elemental analysis illustrates that the copper is the dominate component in the Cu-DLC film, which indicates that the growth of Cu particle is faster than that of carbon film.

Figure 4.4 XRD pattern of Cu-DLC film obtained under -1200 V (on Si substrate).

Figure 4.5 EDX pattern of Cu-DLC films obtained under various potentials: -1000 V (A), -1100 V (B), -1200 V (C), -1300 V (D) and -1400 V (E).

Figure 4.6 shows the Raman spectroscopy mainly for qualitative measurement of carbon in the film as the existence form would be an important factor to affect the performance of Cu-DLC film. The shoulder peak at 1340 cm^{-1} is the D band which indicates the amorphous sp^3 carbon, while the peak at 1560 cm^{-1} is the G band which could be attributed to sp^2 carbon. Besides that, a broad peak at $\sim 300\text{ cm}^{-1}$ is related to CuO. Thus the Raman shows the film consists

of copper and diamond-like carbon. Fourier transform infrared spectroscopy (FT-IR) patterns in Figure 4.7 also reveal that the hydrogen is contained in the diamond-like carbon, as the peaks at 2840 cm^{-1} and $2900\text{--}3000\text{ cm}^{-1}$ correspond to the vibration of sp^3 carbon-hydrogen bonds. The sp^2 carbon ($\text{C}=\text{C}$ bonds) and sp^3 carbon ($\text{C}-\text{C}$ bonds) also correspond respectively to peaks at $\sim 1600\text{ cm}^{-1}$ and $\sim 1300\text{ cm}^{-1}$.

Figure 4.6 Raman spectroscopy of Cu-DLC film obtained under -1200 V .

Figure 4.7 FT-IR spectroscopy of Cu-DLC film obtained under -1200 V.

As Cu-DLC film is used as the electrocatalyst for CO₂ reduction, it's more important to analyze the surface composition compared to the overall distribution of elements. In order to quantitatively analyze copper/carbon content and the sp³/sp² ratio of carbon in Cu-DLC films obtained under different conditions, X-ray photoelectron spectroscopy (XPS) is used to measure the surface composition (Figure 4.8 and Figure 4.9). The spectrum illustrates the characteristic peaks of carbon and copper in Cu-DLC film prepared under various potentials. Despite the peak of contaminate organic carbon at around 288.5 eV, the C 1s peaks of all the samples could be decomposed to two peaks at ~284.5 eV and ~285.5 eV, which indicate the sp² and sp³ carbon, respectively. The CuO is also confirmed by Cu 2p peaks at ~933.0 eV (2p^{3/2}) and ~953.0 eV (2p^{1/2}), as well as O 1s peak at ~530.0 eV. When calculating the content of carbon and copper through XPS atomic sensitivity factors (0.25 for C 1s and 6.3 for Cu 2p) and area of peaks, we could

draw the conclusion that for Cu-DLC films obtained under the potential of -1000 V, -1100 V, -1200 V, -1300 V, -1400 V, the atomic number percentage of Cu/(Cu+C) is 42%, 44%, 38%, 46%, and 41%, respectively. By such analogy, we could also reach that the atomic number percentage of sp^3 C/(sp^2 C+ sp^3 C) is 20%, 36%, 39%, 28%, and 24%, respectively. With increasing negative potential for preparation of Cu-DLC film electrodes, the content of copper present a rough trend to decrease at first and then increase, while the percentage of sp^3 carbon would first increase and then decrease. Compared to EDX results, the Cu content on surface is much lower than overall Cu content for all samples prepared under different potentials. All these results indicate that during electrodeposition, the Cu nanoparticles would grow rapidly on the surface of substrate, with the diamond-like carbon is generated at the same time and wrap on them. The carbon will cover part of Cu surface and could bond to the Cu nanoparticles together to form morphology of dendritic structure or even larger lumps.

Figure 4.8 XPS splitting peaks of Cu-DLC films obtained under -1200 V. (A): Cu 2p scan. (B): C 1s scan.

Figure 4.9 XPS comparison of Cu-DLC films obtained under various potentials, from -1000 V to -1400 V. (A): Cu 2p scan. (B): C 1s scan.

Figure 4.10 shows the CO₂ electroreduction current vs. potential curves of Cu DLC film electrode and DLC film electrode in 0.1 M KHCO₃ solution, which are obtained from [Cu(CH₃CN)₄]ClO₄/CH₃CN solution and pure CH₃CN solution, respectively. There is a tiny peak at ~ -1.05 V vs. Ag/AgCl for Cu DLC film, which could be ascribed to an inhibition of the electroreduction due to the adsorption of generated CO, and -1.05 V could be regarded as the onset potential of this electrocatalyst for CO₂ reduction. Compared to previous Cu electrodes, the Cu-DLC film has an obvious decreasing of onset potential.¹²⁴ In a region from -1.05 V to -1.9 V, the current density of Cu-DLC film is ~ 50 times larger than that of DLC film. Such remarkable difference indicates that the CO₂ reduction mainly occurs on the Cu active sites, thus it is reasonable to use pure Cu electrode to estimate the electrochemical active areas of Cu-DLC electrodes.

Figure 4.10 CV curves of Cu DLC film electrode (A) and DLC film electrode (B) in CO₂ saturated 0.1 M KHCO₃ solution. (Scan rate: 100 mV s⁻¹)

The surface areas of Cu-DLC film prepared under different potentials are compared by measuring the electric double-layer capacitance in 0.05 M H₂SO₄ solution under a scan rate of 100 mV s⁻¹, from -0.04 V to -0.105 V vs. Ag/AgCl. (Figure 4.11) For the electrodes prepared under voltages from -1000 V to -1400 V, the capacitance are 56.2, 77.8, 83.0, 70.7 and 41.3 $\mu\text{F cm}^{-2}$, respectively. As a standard, the capacitance of polished Cu disk electrode with a diameter of 2 mm is measured to be 15.5 $\mu\text{F cm}^{-2}$. It could be concluded that Cu-DLC film with dendritic structure obtain larger surface area, and agglomerated particles could lead to a decrease of electrochemical active sites.

Figure 4.11 Surface areas measurements through CV scan.

4.3.2 The performance of Cu-DLC film in CO₂ electroreduction

The FEs of hydrocarbon products of various Cu-DLC film electrodes are shown in Figure 4.12 and Figure 4.13. All types of Cu-DLC film electrodes show the specific selectivity towards C₂H₄ while bare Cu electrodes prefer CH₄ product⁶⁸, which could be attributed to the small Cu particle size¹⁸⁴. For all the electrodes the FE increase with the negative potential and onset potentials to generate hydrocarbons are all at ~ -1.2 V vs. Ag/AgCl. However, when we compare the performance in producing hydrocarbons under same potential, there is notable difference among Cu-DLC film electrodes prepared under different conditions. For the Cu-DLC film electrode prepared under -1200 V, the FE of total hydrocarbons reaches up to 73.5% (21.4% for CH₄ and 52.1% for C₂H₄) at ~ -1.9 V vs. Ag/AgCl,

better than that of electrodes prepared under more positive or negative potential. As a comparison, Cu-DLC prepared under -1400 V only gives 19.4% FE of total hydrocarbons at -1.9 V.

Figure 4.12 (A): FE under different potential, for Cu-DLC film electrodes prepared under -1200 V. (B): Comparison of performance at -1.9 V vs. Ag/AgCl, for all Cu-DLC film electrodes prepared under various potentials from -1000 V to -1400 V.

Figure 4.13 FE under total potential range, for Cu-DLC film electrodes prepared other than -1200 V. (A): -1000 V (B): -1100 V. (C): -1300 V. (D): -1400 V (E).

The stability of Cu-DLC film electrode prepared at -1200 V is also evaluated in an electrolysis operation as long as 8 h. (Figure 4.14) For the first 4 h, the FE of hydrocarbons remains roughly stable, and maintains more than 60% performance until 8 h. Besides that, the current density is keeping at 13-14 mA cm⁻².

Figure 4.14 Stability test for Cu-DLC film electrodes prepared under -1200 V. (A): FE for 8 h. (B): Current density for 8 h.

The factors which could probably affect the performance of Cu-DLC film electrode in CO₂ electroreduction would be the surface area, the copper content and the carbon content. According to the measurement electrochemical active surface areas mentioned above, the electrochemical active surface areas of Cu-DLC films are only 2.8-5.4 times of polished Cu, which are relatively smaller than previous Cu nanostructure electrode.^{167, 174} Generally, the morphology of material only plays a major role in changing the distribution of C1-C2 hydrocarbon products, but not always increasing the overall FE of hydrocarbons. When considering the Cu content, Cu-DLC film with best performance prepared under -1200 V is the sample with the least Cu content on the surface. However, there is a positive correlation between the amount of carbon in Cu-DLC film and the FE of hydrocarbons, especially the sp³ species. It is suggested that the factor which obviously enhances the FE of hydrocarbons could be the synergistic effect between copper and diamond-like carbon on its surface.

4.3.3 Mechanism explored by DFT calculation

To unveil the underlying mechanism for preferred C1-C2 hydrocarbons formation on the Cu nanoparticles embedded diamond-like carbon film, density functional theory (DFT) calculations were applied to acquire the reaction free energies and kinetic barriers of the crucial reaction steps. Explicit water molecules were included during the calculation of potential-dependent reaction barriers, which was similar to the practice in previous theoretical works.^{123, 193} Owing to the deficiency of standard DFT in describing supported large Cu clusters, supported Cu stripes were modeled instead, as shown in Figure 4.15a, which were proved to be effective in describing oxide-supported Au clusters.¹⁹⁴

Previous experimental and theoretical works have proved that CO is the most important intermediate during CO₂ electroreduction to hydrocarbons.^{31, 121} Furthermore, the selectivity towards CH₄ or C₂H₄ has been found to be controlled by the preferential production of *CHO or *COH on different Cu facets.¹⁹⁵ Therefore, we focus primarily on the kinetic barriers of *CHO/*COH formation on Cu (111) and diamond supported Cu stripe surfaces. Figure 4.15b illustrates that on Cu (111), *COH formation is preferable due to the relatively lower barrier of hydrogen shuttling by the water molecule, compared to that of direct hydrogenation of *CO to *CHO by the atomic H adsorbed on Cu (111). When H and CO both adsorb on the Cu stripe surface, the barriers for both *CHO and *COH formation are similar to that on Cu (111). Nevertheless, when considering the hydrogen source as terminated *H on diamond (100), direct hydrogenation of *CO will become dominant with respect to protonation of *CO by the shuttling water, as

illustrated by the lowered barrier for $^*\text{CHO}$ formation and the elevated barrier for $^*\text{COH}$ formation. Therefore, the better selectivity for C1-C2 hydrocarbons on diamond film supported Cu nanoparticles can be ascribed to a synergistic effect of diamond and Cu in the interface region.

Figure 4.15 (a) Top view and side view of the stripped model used to describe the Cu nanoparticle/diamond film interface. (b) The energy level of CO hydrogenation to CHO (solid line) and COH (dashed line) on Cu (111) (red), stripped Cu with H adsorbed on Cu (green) and stripped Cu with H adsorbed on C (blue).

4.4 Conclusion

As a conclusion, we prepared Cu-DLC film electrodes under different potentials through a simple method of high voltage direct current electrodeposition. $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ is used as organic copper sources with CH_3CN ligands, which makes the Cu nanoparticles integrate into the carbon film and well disperse when generated. As a composite material, the Cu-DLC film prepared under certain voltage demonstrated an excellent activity to generate hydrocarbons when used as electrode for CO_2 reduction, compared to conventional pure copper electrodes. By comparing the morphology as well as composition of Cu-DLC films and their performance, we may conclude that the content of sp^3 carbon would be the key factor which enhances the FE of hydrocarbons like methane and ethylene. DFT theoretical calculations reveal that when consider absorbed $^*\text{H}$ on diamond structure carbon as the hydrogen source, the $^*\text{CHO}$, which is the most important intermediates for CO_2 electroreduction towards hydrocarbons, would have a lower barrier to generate, thus the FEs of methane and ethylene are obviously increase. The results reveal that diamond-like carbon is an excellent support to enhance the Cu electrocatalysts in selectivity towards hydrocarbon products, and the metal-carbon composite materials would be promising to further improve the efficiency of CO_2 electroreduction.

Chapter 5. Carbon aerogel supported Cu nanoparticles for CO₂ electroreduction with low overpotential

5.1 Introduction

Cu is the unique catalyst to produce hydrocarbons reliably in CO₂ electroreduction. Recent studies have found that the performance of Cu electrodes, including products distribution and onset potential to produce hydrocarbons, correlate with the surface structure obviously. For instance, the Faradaic efficiency of hydrocarbons was proved to be increasing with the enlarged particle size of Cu nanostructured electrodes, and it has been attributed to the increasing content of Cu (100) and Cu (111) facets.¹⁸⁴ Nanostructured Cu electrodes also had the advantage to decrease the overpotential for ~0.1 V in generation hydrocarbons and favored higher carbon number products, both compared to polished Cu polycrystalline electrode.

Besides altering the surface structure, composite Cu materials were also prepared for enhanced CO₂ electroreduction. O, S or halogen were introduced as adatoms for changing the properties of Cu electrodes, but there was no solid evidence to prove that the adatoms could still exist at the surface of electrodes after a period of cathodic reduction process.¹⁴⁴ A stable modification of amino acids was proved to be a feasible strategy for enhanced CO₂ electroreduction, and its probable mechanism could be that the key intermediate CHO* is stabilized by -NH₃⁺ group.¹⁹⁶

Another typical strategy to reduce the amount of metal catalyst while maintaining the performance is to introduce carbon support, which is always used for support noble metal catalyst like Pt or Pd. Cu nanoparticles supported on carbon black, Ketjen Black and single-wall carbon nanotubes (SWNT) illustrated similar product distribution like nanostructured Cu electrodes, with desirable FE of hydrocarbons.¹⁷¹ However, the carbon support would not be inert in CO₂ electroreduction system and may intensify the hydrogen evolution reaction to compete the hydrocarbons generation. In line with this, we expect to develop a new type of carbon-support-copper electrocatalyst, with properties of better Cu dispersibility, large specific surface area as well as lower selectivity towards H₂.

Carbon aerogel prepared by corresponding hydrogel has long been used as catalyst or catalyst support, for isomerization reaction of 1-butene, decomposition of isopropanol, CO decomposition and oxygen reduction reaction, etc.¹⁹⁷ Its porous structure could be conducive to enlarge the electrochemical surface area and capable of preparing gas diffusion electrode to enhance the mass transfer if needed. In this work we prepared the precursor hydrogel by using dihydroxybenzoic potassium, whose K⁺ could be simply replaced by Cu²⁺, to achieve a high loading amount and good disperse of Cu in final aerogel.

5.2 Experimental Section

5.2.1 Preparation of material.

Cu-Carbon aerogel was prepared based on previous method. 1.37 g K_2CO_3 (10 mmol) was first dissolved in 100 mL deionized water, and then 2.93 g 2,4-dihydroxybenzoic acid (19 mmol) was added into the solution under continuous stirring. The acid would convert to potassium salt and dissolve gradually in a few hours. 2.85 mL 37 wt. % formaldehyde (38 mmol) water solution was then dropped in. The mixture was poured into 10 mL glass sample vials, sealed, and cured one day at room temperature, followed by three days at 80 °C. The solution would become red during curing, and finally the brown phenolic hydrogel would be generated, with a reduced volume compared to the original solution in the vial. The hydrogel were soaked in 0.1 M CuSO_4 solution, and solution was replaced every 24 hours for three times to make Cu^{2+} display K^+ in the hydrogel. The resultant Cu loaded hydrogel was washed with deionized water, frozen in -80 °C refrigerator and then freeze-dried under -40 °C for 24 hours to form the phenolic aerogel. Finally, the aerogel was carbonized at 900 °C for 5 hours under nitrogen flow, with a heating rate of 5 °C min^{-1} to prepare Cu-Carbon aerogel.

5.2.2 Electrochemical experiments.

A self-design double chamber electrolytic cell was used as CO_2 electroreduction reactor. The anode compartment and cathode compartment were separated by NAFION N117 ion exchange membrane to avoid the possible

oxidation of products. 0.1 M potassium bicarbonate solution was prepared as electrolyte, with deionized water and analytical pure potassium bicarbonate. To make the system saturated with CO₂, the electrolyte in cathode compartment was aerated with 20 mL min⁻¹ CO₂ for 1 hour in advance. A custom-made L type glassy carbon disk electrode (Tianjin Aidai, 7 mm in diameter) was used as working electrodes to support the electrocatalyst, as it was easy to release the generated bubble from surface compared to traditional glassy carbon disk electrode. The Cu-Carbon aerogel was mixed with methanol and then ultrasonicated for 1h to prepare a solution with 2 mg mL⁻¹ concentration. 20 µL electrocatalyst dispersion mixed with 5 µL 0.05 wt % Nafion solution was dropping onto the polished L-type glassy carbon electrode, and then dried in a 50 °C oven. A platinum net electrode (Tianjin Aidai, 20 mm×20 mm), and Ag/AgCl electrode with saturated KCl (Tianjin Aidai) were used as counter electrode and reference electrode, respectively. A CHI electrochemical work station (Model PGSTAT-72637) was used to introduce all electrochemical tests. The head space (no more than 30 mL) of cathode compartment was linked to the automatic sampler of a gas chromatograph (GC, Agilent 6890N-G1540N) through a sealing tube. The hydrocarbon products were quantified by flame ionization detector (FID), while other products responded on thermal conductivity detector (TCD) in GC. Hayasep column and Molecular Sieve 5A column were used to separate all gas components.

5.2.3 Characterization.

Powder X-ray diffraction (XRD) patterns were acquired using a Bruker diffractometer, equipped with Cu K α radiation (D8 Advance X-ray diffractometer, Cu K α , $\lambda = 1.5406 \text{ \AA}$, 40 kV, and 40 mA) to get the phase composition of the Cu-carbon aerogel. Field-emission scanning electron microscopy (FESEM; JEOL, JSM-6701F, 5 kV) equipped with energy dispersive X-ray spectroscopy (EDX) was used to acquire the morphology as well as elemental composition of the Cu-carbon aerogel. The microstructure and existence form of doped Cu were further studied by transmission electron microscopy (TEM; JEOL, JEM-2010, 200 kV). Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer) was used to acquire the transmission infrared spectrum of Cu-carbon aerogel. A RENISHAW Raman microscope with WIRE 2.0 software and 514.5 nm emission line of laser was used to irradiate the sample to illustrate the form of carbon in aerogel. X-ray photoelectron spectroscopy (XPS; VG ESCALAB MKII instrument) with an Mg K α X-ray source was used for analyzing the surface composition through C 1s, O 1s, and Cu 2p spectra. Thermogravimetric analysis (TGA) in air flow was used to obtain the ratio of carbon/metal in the sample.

5.3 Results and Discussion

5.3.1 Characterization of Cu-carbon aerogel

The Cu-carbon aerogel is prepared through carbonization of Cu doped phenolic aerogel. Figure 5.1 illustrates the field-emission scanning electron microscopy (FESEM) images of phenolic aerogel and carbon aerogel. The Cu doped phenolic aerogel (before carbonization) consists of uniform-sized nanoflowers, and the Cu-carbon aerogel roughly sustains the morphology after carbonization. However, the Cu-carbon aerogel become more dispersed and have more emptiness inside, which could be ascribed to that the carbonization process eliminate most of the hydrogen and oxygen component of phenolic aerogel. The Cu-doped carbon nanoflowers have similar diameters of 3-5 μm , and are constituted by nanoflakes with ~ 100 nm width. There is no obvious aggregated Cu particle on the carbon nanoflower, which indicate that the Cu is finely dispersed in carbon support after thermal treatment.

Figure 5.1 FESEM of Cu doped phenolic aerogel before carbonization (A, B) and Cu-Carbon aerogel after carbonization(C, D).

To further investigate the existing form of Cu in the Cu-carbon aerogel, the transmission electron microscope (TEM) is used to illustrate the detailed microstructure. Figure 5.2 shows that in carbon support, the Cu particles are ~20 nm in size and uniformly distributed. There is no apparent agglomeration at highest Cu loading. There is only interplane spacing of 0.275 nm in high resolution TEM

image, which demonstrates the existence of CuO(110) lattice plane in the Cu nanoparticle. Selected-area electron diffraction (SAED) pattern is also used to show the crystalline form of Cu-Carbon aerogel. The brightest diffraction concentric ring correspond to crystal spacing of 0.277 nm, which could be ascribed to CuO(110) lattice planes. There are still some fainter rings inside and outside the brightest one, indicating the interplanar spacing of 0.360 nm, 0.321 nm and 0.208 nm, and corresponding to CuO(100), CuO(111) and Cu(111) lattice planes, respectively. From the distribution of different crystal forms we may conclude that the carbon aerogel contain both Cu(II) and Cu(0) after carbonation treatment. Figure 5.3 illustrate the XRD pattern of Cu-Carbon aerogel. The diffraction peaks also confirm that the Cu nanoparticles contain both Cu and CuO phase, which is in accordance with the result of SAED. From both TEM and XRD measurement, there is no lattice plane or diffraction of carbon observed, which indicates that the carbon in the aerogel would be amorphous.

Figure 5.2 TEM of Cu-carbon aerogel with Cu particle embedded in carbon (A), the High resolution TEM of Cu particle(B), and the selected area electron diffraction (SAED) of Cu-carbon aerogel (C).

Figure 5.3 XRD pattern of Cu-carbon aerogel.

The Cu-Carbon aerogel is monitored with energy dispersive X-ray (EDX) techniques to ensure the elements it contains (Figure 5.4). After ion exchange and thermal treatment, there only exists Cu, O and C elements, which confirms that almost all potassium ions have been changed to copper ions in previous steps. More accurate composition could be obtained through thermogravimetric analysis (TGA) result, which is shown in Figure 5.5. When setting the initial weight of the sample as 100%, the weight of dried sample is 96.8% after heating to 100 °C. From 200 °C the weight decreases dramatically, which could be attributed to the carbon part of the aerogel starts to burn up in the air flow. After heating to over 450 °C, the weight of sample keeps roughly stable at ~31.2% g until 800 °C, and we could conclude that the dry sample (from 100 °C) loses 67.8 % of its weight, and the leftover would be only CuO. Through the TGA results we could calculate the weight percentage of copper is 25.8%.

Figure 5.4 EDX of Cu-Carbon aerogel.

Figure 5.5 TGA curve of Cu-Carbon aerogel.

Figure 5.6 shows the X-ray diffraction (XPS) data which could be used to approximately calculate the surface elemental composition of Cu-Carbon aerogel through XPS atomic sensitivity factors and peak area of copper, carbon and oxygen. The Cu $2p^{1/2}$ peak and Cu $2p^{3/2}$ peak ensure that the existence form of copper on the sample surface is CuO. O 1s signal could be fitted to 3 peaks:

oxygen in Cu-O at 531.3 eV, in C-OH at 532.1 eV and in C=O at 534.9 eV, while C 1s signal could also be split to 3 peaks: carbon in amorphous form at 281.5 eV, in C-OH at 282.8 eV and in C=O at 284.1 eV. The estimate distribution of each species is shown in Table 5.1. After normalization we could calculate that the ratio of different element atoms on surface is Cu: O: C = 7.4%: 30.2%: 62.4%. From atom ratio we could calculate the surface weight percentage of copper is 27.8 %, thus the Cu content on surface of catalyst is close to the overall Cu content, compared to TGA results.

Figure 5.6 XPS peaks of Cu-Carbon aerogel. (A) Cu 2p scan, (B) C 1s and (C) O 1s scan.

Table 5.1 XPS peak separation results.

Elements	Factors*	Species	Peak areas	Species composition**	Elements composition***
Cu	6.3	Cu in CuO	22460.51	3565.16	3565.16
		O in CuO	2132.49	3231.05	
O	0.66	O in C-OH	4673.32	7080.79	14539.14
		O in C=O	2790.02	4227.3	
C	0.25	amorphous C	4477.59	17910.36	30113
		C in C-OH	1853.36	7413.44	
		C in C=O	1197.3	4789.2	

* XPS atomic sensitivity factors.

** Relative species atomic composition.

*** Relative elements atomic composition, sum of Species composition (Relative species atomic composition).

The XPS data indicate that there exists functional groups on carbon surface, and it is further confirmed by Fourier transform infrared spectroscopy (FT-IR) illustrated in Figure 5.7. Peaks observed at $\sim 1300\text{ cm}^{-1}$ are ascribed to the C-OH which could be the residue of phenolic hydroxyl groups, while the one at 1720 cm^{-1} is the characteristic peak of C=O. However, we could still conclude that the degree of carbonization is high. Besides that the XPS data shows the dominate species of carbon on surface is amorphous carbon, Raman spectrum (Figure 5.8) also gives more accurate information of the sample. Two strong board peaks at $\sim 1350\text{ cm}^{-1}$ and $\sim 1550\text{ cm}^{-1}$ identify Raman D bands and G bands, respectively. Therefore the aerogel is supposed to be constituted by copper particle and amorphous carbon.

Figure 5.7 FT-IR of Cu-Carbon aerogel.

Figure 5.8 Raman of Cu-Carbon aerogel.

Figure 5.9 shows the CO₂ electroreduction current vs. potential curves of Cu-Carbon aerogel film electrode and carbon aerogel film electrode, which are obtained from hydrogel precursor with and without ion exchanging process of Cu²⁺. For the CV of Cu-Carbon aerogel film electrode, there is an obvious peak at ~ -1.0 V vs. Ag/AgCl for Cu DLC film, which is supposed to be caused by adsorption CO generating from initial step of CO₂ electroreduction. The -1.0 V

could be identified as the onset potential of Cu-Carbon aerogel for CO₂ electroreduction, which is obviously more positive than that of common polycrystalline Cu electrodes, at around -1.35 V.¹⁷¹ In CO₂ electroreduction potential region from -1.0 V to -1.9 V, the current density of carbon aerogel film without Cu doping is no more than 5% of Cu-carbon aerogel current density, proving that the carbon aerogel is relatively inert for both CO₂ electroreduction and water splitting, compare to Cu-Carbon aerogel. The extreme difference of activity between aerogel with and without Cu doping makes it possible to estimate the surface area of Cu-Carbon aerogel film electrode based on only Cu component. The electroactive surface area of Cu-Carbon aerogel film supported on glassy carbon electrode is measured by electric double-layer capacitance under a series of scan rates, i.e., 20, 40, 60, 80 and 100 mV s⁻¹, from -0.04 V to -0.105 vs. Ag/AgCl. From simple linear regression we could obtain the result that the capacitance is 186.1 μF cm⁻². With exactly the same procedure above, the capacitance of polished Cu disk electrode with a diameter of 2 mm is also measured to be 15.5 μF cm⁻², as a standard. Therefore it could be estimated that the electroactive surface area of Cu-Carbon electrode is ~12 times larger than polished Cu (Figure 5.10).

Figure 5.9 CV curve of Cu-carbon aerogel electrode (A) and carbon aerogel electrode (B) in CO_2 saturated 0.1 M KHCO_3 solution.

Figure 5.10 Surface areas measurements through CV scan. (A) Cu-Carbon aerogel electrode. (B) Polished Cu electrode.

5.3.2 The performance of Cu-Carbon aerogel electrode in CO_2 electroreduction

The FE results of various hydrocarbon products obtained on Cu-Carbon aerogel supported on glassy carbon electrode are shown in Figure 5.11. High FEs of C_2H_4 and CH_4 are observed while there are still trace C_2H_6 product generated, and left part of FE is occupied by H_2 . With the increase of negative potential, the FEs of CH_4 and C_2H_4 both increase and peak at -1.8 V, then slightly decrease at -

1.9 V vs. Ag/AgCl. At -1.8 V, the FE of CH₄, C₂H₄ and C₂H₆ are 11.5%, 34.8% and 0.44%, respectively. The largest current density emerges at -1.9 V, with 35.6 mA cm⁻² in total and 15.0 mA cm⁻² for hydrocarbons partial current density. The distribution of hydrocarbon products generated from Cu-Carbon aerogel electrode is similar to that from Cu structured electrode as previous report.^{77, 184} However, the total FE of hydrocarbons is significantly improved when compared to that of conventional Cu electrode, and even more than 10% FE of hydrocarbons is observed at as low as -1.2 V, which indicated an extremely low overpotential for CO₂ electroreduction on Cu-Carbon aerogel electrodes. The stability of Cu-Carbon aerogel electrode is evaluated through an electrolysis operation at -1.8 V, the potential with highest FE, for as long as 6 h. (Figure 5.12) In first 3 h, the FE of total hydrocarbons remains stable, and then slightly decrease with the extension of time, mainly due to the drop of C₂H₄ FE. However, the electrode still maintains more than 70% of the performance until 6 h, which the current density holding at ~35 mA cm⁻². The result indicate that the electrode obtains a well stability in long time process.

Figure 5.11 FEs under different potential, for Cu-Carbon aerogel electrode.

Figure 5.12 Stability test for Cu-Carbon aerogel electrode. (A): Current density for 6 h. (B): FE for 6 h.

5.4 Conclusions

A Cu particle doped carbon aerogel was prepared as electrocatalyst for CO₂ reduction, through carbonization of phenolic resin aerogel loaded with Cu²⁺. Phenolic resin aerogel was prepared through vacuum drying of phenolic resin hydrogel precursor, in order to maintain the nanostructure with larger surface area. Loading Cu²⁺ onto precursor was realized through repeatedly ion exchange, which resulted in a theoretic maximum Cu loading of 25.8%, confirmed by TGA of final product. The aerogel consisted by uniform carbon nanoflowers and well dispersed ~20 nm Cu nanoparticle illustrated high performance in generating hydrocarbons. Compared to polycrystalline Cu electrode, the Cu-Carbon aerogel preferred C₂H₄ products with a Faradaic efficiency of up to 34.8%, and there still existed other minor products like CH₄ and C₂H₆. A significant decrease for onset potential for hydrocarbons was observed, through a 0.35 V shift of CO₂ reducing peak in CV curve as well as considerable FE of hydrocarbons at -1.2 V. The large electroactive surface area of Cu-Carbon aerogel also brought about large current density, and the nanoporous structure made it possible to prepare gas diffusion electrode with this material in future application.

Chapter 6. Conclusions and Recommendations for Future Work

6.1. Conclusions

In this thesis, we developed a series of electrocatalysts based on Cu for CO₂ electroreduction. All electrocatalysts illustrated enhanced performance in producing hydrocarbons compared to pure Cu electrodes, mainly due to the effect of modifiers or supports. During screening for appropriate strategies to enhance the performance of pure Cu electrodes for CO₂ electroreduction, we revealed that i) amino acids with proper coverage rate could increase the FE of hydrocarbons on various type of Cu electrodes, and glycine had the best property among them. ii) diamond-like film (DLC) doped with Cu nanoparticles prepared under -1200 V electrodeposition performed extremely high selectivity towards hydrocarbons, which could be attributed to the hydrogen shuttling by diamond. iii) Cu nanoparticle supported on carbon aerogel prepared through carbonization of Cu doped phenolic gel had a lower overpotential and higher selectivity towards hydrocarbons.

However, the modifiers as well as supports tested hitherto were much more than demonstrated in this thesis, and most of them could not provide positive results. From all these successful and unsuccessful attempts we could conclude that:

(1) The introduction of modifiers would enhance the performance of Cu electrode obviously, but the type and quantity are critical. Other modifiers like

mercaptans, long-chain aliphatic acid, grafted diazonium salt, etc. could decrease the Cu electrode performance of producing hydrocarbons. Overload of the modifiers could also result in electrocatalyst poisoning.

(2) Till now, $-\text{NH}_3^+$ group of zwitterionic amino acid is identified as the only active site to stabilize the important intermediate CHO through hydrogen-bond like interaction, which promotes the generation of hydrocarbons. Glycine, the simplest amino acid, has been proved to be the most efficient modifier.

(3) The microstructure of Cu electrode would greatly affect the selectivity during CO_2 electroreduction. However, in most cases, the modifiers or supports would just enhance the FE rather than changed the distribution of hydrocarbon products.

(4) For the DLC-Cu electrodes, the content ratio of sp^3 carbon, which is affected by the deposition potential, would be the critical factor to enhance the generation of hydrocarbons. DFT theoretical simulations indicate that the H adsorbed on diamond structure carbon is a better hydrogen source for CO_2 electroreduction compared to H adsorbed on Cu surface, which decreases the energy barrier for generation of important intermediate CHO.

(5) For Cu particle doped carbon aerogel, the larger electrochemical surface area leads to high current density, while a significant decrease for onset potential for hydrocarbons is observed. Although more evidences are needed, the surface oxygenic functional groups of carbon support might change the property of Cu nanoparticle thus enhance the performance for producing hydrocarbons.

6.2. Recommendations for future work and expectations

We have illustrated that Cu is the unique catalyst for CO₂ electroreduction, as it is the only cathode material which could produce hydrocarbons hitherto. In order to promote the technique of preparing hydrocarbons through CO₂ electroreduction to a practical level, we need to enhance the Cu electrodes from 3 aspects: extending the service life, enlarging the current density and increasing the efficiency. The technical approaches towards former two aspects are relatively more straightforward. The service life of Cu electrode could be prolonged by using purified electrolyte or electrical pulse during CO₂ electroreduction, while the current density could be increased by using gas diffusion electrode or electrode with rough surface. However, to increasing the efficiency of CO₂ electroreduction involves complicated mechanism and has more significance in practice, as it could save electrical energy and inhibit by-products. For that reason, we believe that increasing the efficiency of CO₂ electroreduction on Cu based electrodes could be a lasting and the most important topic in this area.

In order to increase the CO₂ electroreduction efficiency there could be several kinds of strategies:

(1) Increasing the solubility of CO₂ in electrolyte. We could easily increase the solubility of CO₂ by increase the CO₂ partial pressure or use electrolyte with lower temperature, and it can certainly benefit the generation of hydrocarbons. Another way is to use solution with high pH, and it could also suppress the generation of hydrogen by decreasing the H⁺ concentration in solution. However, the purging of CO₂ usually neutralizes the alkaline electrolyte, thus decreases the

pH. Removing bicarbonate and adding potassium/sodium hydroxide continuously would be a solution.

(2) Adjust the selectivity of Cu crystal face. As high index crystal face of Cu has better HER selectivity, and lower index crystal face could benefit the generation of hydrocarbons⁷⁸, it is possible to prepare Cu electrode with optimized crystal face to have better efficiency. However, we still prefer to use nanostructured Cu electrodes rather than use single crystal one, as rough face of electrode could decrease the overpotential and generate more complex hydrocarbons, with a better stability. Using proper modifiers to selectively adsorb on high index crystal face would be a good strategy; however, we still need more relevant research to see whether it is feasible.

(3) Develop more Cu-based composite material. The works illustrated in this thesis mainly use this strategy, and we do develop several kinds of material with better performance. Our future work would also focus on this direction.

The planed work is shown as the following:

(1) According to Chapter 3, amino acid is the only effective modifier for Cu electrode to enhance the generation of hydrocarbons during CO₂ electroreduction, and DFT calculation reveals that -NH_3^+ group was the active site. The fact that the simplest amino acid glycine has the best performance strongly suggests that small size of modifier would be conducive to CO₂ electroreduction, which might be attributed to better mass transfer. This line with this we could design different strategies. One is trying to bond other kinds of small molecules with amino group, like 2-aminoethanethiol or diazophenylamino. We could also introduce other

functional group in the modifier to adjust the polarity of N–H bond or limit the position of $-\text{NH}_3^+$ group to control the performance. The other way is to combine the support strategy illustrated in Chapter 4 and 5. More specifically, we could introduce nitrogen functional groups in carbon support or use nitrogen-doped carbon support to load dispersive Cu, and the nitrogen might change the property of Cu in CO_2 electroreduction. The challenge would be that whether the functional group could be stable on cathode.

(2) As CO_2 electroreduction always occurs under extremely negative potential, many modification methods like simply introducing O, S or halogen adatom could not be applied, as plenty of modifiers are unstable on the cathode. Considering all these facts, Cu-based alloy is still worth studying, although there are only negative results so far. In Chapter 3 we have demonstrated that only low coverage of amino acid (below 10% of Cu surface) could increase the generation of hydrocarbons, while overloading the modifiers could poison the electrocatalyst, which might be ascribed to blocking too many active sites of Cu. In line with this, we think that the alloy method should meet the following conditions: strictly control the amount of additional metal other than Cu; increase the dispersion of additional metal in Cu. The challenge we would face is that if the crystalline grains of additional metal are too big, the performance of alloy could only be between two kinds of pure metal rather than enhancing the Cu. Intermetallic compound might be the most promising material, and we may need DFT calculation to give instructions to narrow the screening scope of possible alloys.

For the future expectations in this research field, we believe that more types of composite materials need to be synthesized and screened for CO₂ electroreduction, as the performance of most pure metal and simple alloys have been investigated already. Modification would improve the performance of original material, or even provide new reaction route beyond expectation. A potential electrocatalyst for CO₂ electroreduction should obtain low HER activity and high stability under negative potential. The DFT calculation would be a useful tool for forecasting the properties and explore new mechanism of new electrocatalysts. Another promising research direction is to use new electrolyte like ionic liquid or solid electrolyte, which could increase the solubility of CO₂ while decrease the concentration of H₂O, thus suppressing the HER. A promising electrolyte should obtain large electrochemical window and low adsorption on electrodes.

Publications and Manuscripts during Ph.D. Candidate

1. Amino Acid Modified Copper Electrodes for the Enhanced Selective Electroreduction of Carbon Dioxide towards Hydrocarbons. Ming Shi Xie, Bao Yu Xia, Yawei Li, Ya Yan, Yanhui Yang, Qiang Sun, Siew Hwa Chan, Adrian Fisher, and Xin Wang, Energy and Environmental Science, 2016, 9, 1687-1695. (Impact factor: 20.523)
2. Cu Doped Diamond-like Carbon Film Electrode for Enhanced CO₂ Electroreduction towards Hydrocarbons, as manuscript.
3. Carbon aerogel supported Cu nanoparticles for CO₂ electroreduction with low overpotential, as manuscript.
4. Copper-Modified Gold Nanoparticles as Highly Selective Catalysts for Glycerol Electro-Oxidation in Alkaline Solution. Larissa Thia, Mingshi Xie, Dr. Zhaolin Liu, Dr. Xiaoming Ge, Dr. Yizhong Lu, Prof. Wenmei Eileen Fong, Prof. Xin Wang, ChemCatChem, 2016, DOI: 10.1002/cctc.201600725
5. Improving electron trans-inner membrane movements in microbial electrocatalysts. Tao Le, Xie Mingshi, Chiew Geraldine Giap Ying, Wang, Zhijuan, Chen Wei Ning, Wang Xin, Chemical Communications, 2016, 52, 6292-6295.
6. Improving mediated electron transport in anodic bioelectrocatalysis. Le Tao, Haibo Wang, Mingshi Xie, Larissa Thia, Wei Ning Chen and Xin Wang. Chemical Communications, 2015, 51, 12170-12173.

7. Strategies on the Design of Nitrogen-Doped Graphene. Haibo Wang, Mingshi Xie, Larissa Thia, Adrian Fisher, and Xin Wang, The Journal of Physical Chemistry Letters, 2014, 5 (1), 119-125.
8. A review on the electrochemical reduction of CO₂ in fuel cells, metal electrodes and molecular catalysts. Rern Jern Lima, Mingshi Xie, Mahasin Alam Sk, Jong-Min Lee, Adrian Fisher, Xin Wang, Kok Hwa Lim, Catalysis Today, 2014, 233, 169-180.

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