



齐鲁工业大学  
QILU UNIVERSITY OF TECHNOLOGY

本科毕业论文

**Electrocatalytic Unsaturated Hydrocarbon  
Reaction**

**电催化不饱和烃反应**

学院名称 化学与化工学院  
专业班级 应用化学（国际班）17-1  
学生姓名 戚建国  
导师姓名 陈建宾

2021年 5 月 20 日

# Electrocatalytic Unsaturated Hydrocarbon Reaction

## 电催化不饱和烃反应

作者姓名	<u>戚建国</u>
专    业	<u>应用化学（国际班）</u>
指导教师姓名	<u>陈建宾</u>
专业技术职务	<u>教授</u>

## 齐鲁工业大学本科毕业设计（论文）原创性声明

本人郑重声明：所提交的毕业设计（论文），是本人在指导教师的指导下独立研究、撰写的成果。设计（论文）中引用他人的文献、数据、图件、资料，均已在设计（论文）中加以说明，除此之外，本设计（论文）不含任何其他个人或集体已经发表或撰写的成果作品。对本文研究做出重要贡献的个人和集体，均已在文中作了明确说明并表示了谢意。本声明的法律结果由本人承担。

毕业设计（论文）作者签名：

年 月 日

## 齐鲁工业大学关于毕业设计（论文）使用授权的说明

本毕业设计（论文）作者完全了解学校有关保留、使用毕业设计（论文）的规定，即：学校有权保留、送交设计（论文）的复印件，允许设计（论文）被查阅和借阅，学校可以公布设计（论文）的全部或部分内容，可以采用影印、扫描等复制手段保存本设计（论文）。

指导教师签名：\_\_\_\_\_

年 月 日

毕业论文作者签名：

年 月 日

## Content

Abstract.....	3
Chapter 1 Introduction.....	5
1.1. Background.....	5
1.2. Development.....	8
1.3. Electrochemical application.....	11
1.3.1. Battery.....	11
1.3.2. Fuel cell.....	13
1.3.3. Electrosynthesis .....	14
1.3.4. Plating .....	16
1.3.5. Capacitor.....	17
Chapter 2 Electrocatalytic Unsaturated Hydrocarbon Reaction ...	18
2.1. Introduction.....	18
2.2 Experimental Sections .....	19
2.2.1. Experimental Reagents .....	19
2.2.2 Experimental Instruments .....	20
2.3. Experimental Procedures .....	20
Chapter 3 Conclusions.....	22
3.1. Results.....	22
References .....	24
Acknowledgment.....	27

## Abstract

Electrochemistry is a new research approach which is developed since recent several decades. Although the emergence of the scientific research method is not a long period, electrochemistry becomes a new science hot spot at the present. Electrochemistry can be used to obtain data, verify reaction mechanism, observe experimental phenomena which is an extremely important branch of physical chemistry. The principles of electrochemistry are commonly and widely applied in the battery production, metal plating, capacitors, organic synthesis and advanced manufactures.

Especially, organic synthesis field is one of the most important applications because that electrocatalyst has many observed superiorities comparing with traditional metal catalysts illustrated in the following.

1. The approach of electrocatalyst is matched with the concept of Green Chemistry which is beneficial to environment in which reduces to use and produce toxic compounds during the reactions.
2. The reaction conditions are not harsh which reactions are usually conducted under room temperature and normal press.
3. The rate of reactions is easy to control just by changing current or voltage.
4. The approach has large-scale influence which can be large-scaled copied in the industrial production.

Beside these advantages mentioned above, electrocatalyst has plenty of other excellent respects in the procedure of electrochemical reactions.

The paper is to find and solve a serious of electrochemical problems according to a few basic knowledges of electrochemistry by making experiments in the laboratory and explore the applications of the reaction in the production and life. The scheme of the experiment is that a unsaturated hydrocarbon compound (6-Chloroimidazo [1,2-b] pyridazine) as substrate to synthesis a new product under the condition of constant current or voltage.

**Key words:** imidazo [1,2-b] pyridazine, electrocatalyst, synthesis, unsaturated hydrocarbon

## 摘 要

电化学是最近几十年才被发展的一种新的研究方法。尽管这种科学研究方法的出现没有很长的时间，但是电化学在现在已经成为了一个新的科学热点。电化学是物理化学中一个极度重要的分支，可以被用来获取数据、验证反应机理和观察实验现象等。电化学的原理被普遍而且广泛的应用在电池的生产、金属电镀、电容器、有机合成和高端制造业。

尤其地，有机合成领域是最重要地应用之一，因为电催化具有许多显而易见的优点相比较与传统的金属催化剂，这些优点如下列所示：

1. 电催化的方法符合绿色化学的观念，它对环境有益通过在反应过程中减少使用和生成有毒的化合物。
2. 反应条件不严苛，反应通常可以在室温和常压条件下就可以进行。
3. 反应速率可以简单地通过改变电流和电压进行控制。
4. 这种方法具有规模效应的影响，可以被大规模地复制在工业生产中。

除了以上这些被提及的优点，电催化还有许多其他优秀的方面在电化学反应的过程中。

这篇论文是为了发现和解决一系列电化学的问题根据一些基础的电化学的知识通过在实验室里做实验并探究该反应在生产生活中得应用。这个实验的方案是一个不饱和烃（6-氯咪唑并[1, 2-b]吡嗪）作为反应底物来合成一个新的产物在恒定电流或电压的条件下。

**关键词：**氯咪唑并[1, 2-b]吡嗪 电催化 合成 不饱和烃

## Chapter 1 Introduction

### 1.1. Background

Nowadays, energy problem and environment problem start to become a popular topic appeared in the daily life. On the one hand, the rapidly consumption of fossil energy including coal, petroleum and natural gas results into the stock of natural resources decreasing day by day. On the other hand, a great deal of fossil sources burning in the industries and cities release huge amount of greenhouse gas (carbon dioxide) and polluted gas leading to environmental pollution deterioration. Those are the reasons why shortage of resource and deterioration of environment have vast influence on humankind work and life gradually. Therefore, it is extremely urgent to explore a kind of sustainable, green and economical new resources instead of traditional fossil sources. After persisting efforts by countless scientists, a series of new energy form like wind energy, solar energy and nuclear energy have been widely developed and applied in the life.<sup>[1]</sup> The forms of these energy are quite different on the surface, but in essence the forms of energy have to be transferred into electricity and finally be consumed at the terminals which it is impossible the new form energy is used directly except switching them into electricity. In the chemistry field, electrochemistry develops according to the basic principles.

In essence, electrochemistry reaction is a combination of oxidation reaction and reduction reaction or directly called oxidation reduction reaction which reacts in the two relative separated sections together. In the electrochemistry, copper-zinc battery is usually one of the easiest and simplest battery model to explain some basic principles of electrochemistry. Generally, a whole oxidation reduction reaction of copper-zinc battery has several five main compositions including cathode, anode, salt bridge,  $\text{CuSO}_4$  solution,  $\text{ZnSO}_4$  solution. The function of salt bridge is that connecting two parts of solution and moving dissociated ions to keep cations and anions balance of solution. In the primary cell, two reaction cells existing corresponding solution are connected by two electrodes and a salt bridge consisting of electrochemistry reaction solution which all the parts construct a complete current together. Two electrodes conduct different type reactions which oxidation reaction is occurred at anode or

copper electrode, while reduction is occurred at cathode or zinc electrode. At the same time, many ionization reactions also occur on the surface of electrodes with the processing of oxidation reduction reaction and produce a variety of intermediates, such as radical cations at anode and radical anions at cathode which is solved into the corresponding solutions.<sup>[2]</sup> For the more, it is likely that various secondary reactions maybe appear after some radical ions diffused in the solution <sup>[3]</sup>.

Electrolytes as a most crucial composition, a wide range of acceptable materials to produce it which includes platinum (foil, wire or foil), stainless steel, carbon rod and RVC. RVC is an abbreviation of reticulated glass carbon which is a unique glassy carbon combined the characters of glass and carbon together. Comparing with other electrolyte materials, RVC has many observed advantages, for example, high specific surface area, high porosity and chemical resistance which is benefit for electrochemical transformation. Electrodes are usually made of nonmetal like carbon rod and metal like lead, zinc and platinum. In the reactions, the materials of anode and cathode can be different is different experiments vary from specific conditions. In any electrochemical reactions, it is very vital to think about the selection of electrodes, electrolytes, solvents and current densities before starting a experiment to achieve an optimized scheme, because that anyone parameters have an important impact on final experimental results.

Electrochemistry is an efficient and wonderful synthetic approach in the field of organic chemistry which can reduce environment pollution and achieve sustainable development in the way because that electron is a sustainable green redox media <sup>[4]</sup>. Electrocatalyst plays a critical role in the electrochemistry not only in the pharmaceutical molecules but also suitable for synthesis of a variety of intermediates <sup>[5]</sup>. Electrocatalyst is similar to traditional catalyst which can achieve catalytic activity under some conditions like a certain current. There is no denying that it is observed that electrocatalyst has many obvious advantages comparing with normal catalyst.

Electrochemical protocol does not acquire the usage of dangerous and toxic oxidants compare with common oxidative reactions. These conventional synthetic protocols particular suffer from limitations including toxic and rare reagents, the usage of excess strong oxidants, harsh reaction conditions (high temperature, high press and



etc.), low atom efficiency and high economical costs.<sup>[6]</sup> Therefore, electrocatalyst is an efficient and practical approach for the synthesis of all kinds of desirable substances <sup>[6]</sup><sup>[7]</sup>.

Electrocatalyst is a more economical and environment friendly approach to synthesis aimed producers which is consistent with the concepts of Green Chemistry. Green Chemistry is a new popular theory at the present defined by the following twelve items.

- (1) Inherent instead of circumstantial: chemists should to assure that energy inputs and energy output of all the raw materials as not inherently toxic and dangerous as possible.
- (2) Prevention instead of treatment: it is better for humankind to prevent waste before starting experiment rather than dispose or treat them after the waste is already produced in the reactions.
- (3) Design for separation: the process of purification and separation should be designed that consumption of energy and usage of reagents of reactions should keep as less as possible
- (4) Efficiency maximization: reagents, procedures, conditions and mechanism have to keep the most economical and efficiency of time, space and energy when an experiment is designed.
- (5) Output pulled instead of input pushed: procedures, systems and productors ought to be output pulled in the reactions in the replace of input pushed when raw stuff and energy is used during the experiments.
- (6) Save complexity: complexity and entropy have to be discussed when design some beneficial and recyclable disposition reactions.
- (7) Durability instead of immortality: a designed experiment should pay more attention to durability rather than immortality.
- (8) Keep enough but minimize excess: a wonderful experiment should be signed that all reagents are just enough and minimize excess without unnecessary capacity and capability solution.
- (9) Raw material diversity Minimization: minimize experimental equipment and involved drugs in multicomponent products to promote disassembly and value retention.

- (10)Energy flows and integrate material: The expected experimental design of system, procedures and products must consist of interconnectivity with integration and available materials energy flows.
- (11)Commercial design for the future: the commercial design of systems, procedures and products should have further and prospected thinking which focus on future rather than just current.
- (12)Renewable instead of depleting: the choice of reagents or materials in the reactions should be provided by some renewable or recyclable stuff easily to keep sustainable rather than depleting.<sup>[8]</sup>

The twelve regulations mentioned above are the most basic principles of Green Chemistry. In the work of laboratory or industry, the concept of Green Chemistry should become a guiding ideology so that retain natural environment more sustainable and coordinated development.

## **1.2. Development**

Electricity is one of the most awesome phenomena and magical natural force. There is no doubt that electricity already changed the whole world which not only great effect on electrochemistry field but also abroad applications in the all respects of life. From ancient times to the present, innumerable scientists who would like to reveal the mysterious of the natural force have already be attracted by electricity. Electricity is produced by inner specific atom construction which is made up of a positive charged nuclear and many negative charged electrons orbit around the middle nuclear. Nuclear is composited of positive charged particles named protons and uncharged particles called neutrons. In the normal situation, electric current flows when the particles are positively charged and the particles are negatively charged are transferred through some forms of medium, which creates an electric current.<sup>[9]</sup>

The discovery of electricity can be dated back a few centuries ago and the 17<sup>th</sup> century is a milestone for expiration of natural electric phenomena in the scientific history. In the period, William Gilbert is the first person to point out the terminologies “electric

force” and “electric attraction” and explained the two words. In addition, William Gilbert coined a new Latin word about electricity from accent Greek language: electron. In the later period of the 17<sup>th</sup> century, Robert Boyle invented that electric force could be transmitted through vacuum by a lot of experiments. In 1733, Charles Francois Du Fay clarified inexplicable phenomena and drew the conclusions that there were two different types of electric charges in the nature which is identified positive and negative nowadays.

Coulomb suggested the approach of electrostatic attraction try to study the charge suppression approach proposed by Joseph Priestley in 1781. And in 1791, current Dynamics published the special phenomenon which made frogs' leg muscle to twitch. It is possible that electrochemistry is the first time to be considered <sup>[10]</sup>. In 1799, based on his electroplating work, he invented the "electropile" of different wet paper metal plates, now known as the "volt reactor". This is a prototype of a chemical power source. Before the invention of the DC motor, various chemical power sources were the only chemical power sources that could provide a steady current. The quantum foundation of electrochemistry was laid by Faraday's discovery of electrolysis in 1834.

In the 19<sup>th</sup> century, Gibbs and Helmholtz proposed the battery "energy" (now called "electrical energy") which had clear thermodynamic significance; In 1889, the relationship between the substance concentration of electrode reaction and electrode potential was derived by thermodynamic method. In 1923, Debye and Hook proposed the widely accepted electrostatic theory of dilute solutions with strong electrolytes which greatly promoted the development of electrochemistry both theoretically and experimentally. Since the 1940s, the application and development of transient electrochemical techniques, electrochemical methods, and the combination of optical and surface techniques have made it possible to study complex electrode reactions and provide molecular information at the electrode interface.<sup>[11]</sup>

The combination of chemistry and electricity provides us with the field of electrochemistry, which is defined as the study of the interactions between conductive different materials <sup>[9]</sup>. Electrochemistry tends to study the electrical interface region where two materials with different levels of electrical conductivity meet. The

electrolyte comes into contact with the cathode or anode material, where the cathode or anode comes into contact with the collector. These areas are usually only a few nanometers thick. These are the interface areas where ions and electrons transition from one material to another. [9]

In recent decades, electrochemistry has achieved rapid development in the advanced scientific research fields. For example, bubble formation is an ordinary phenomenon in many electrochemical procedures, but electrochemistry of nanobubbles attracts many chemists' attention at the recent years. In 2007, atomic force microscopy (AFM) has been used to image the formation and growth of H<sub>2</sub> nanobubbles on highly oriented pyrolytic graphite first time and subsequent studies show that O<sub>2</sub> nanobubbles may also be generated on highly oriented pyrolytic graphite with lower yield than H<sub>2</sub> nanobubbles. [12]

Local pH measurements are important in various fields of electrochemistry, from corrosion to bioelectrochemistry and electrocatalysis. Different techniques can be used to perform these measurements and offer many possibilities in terms of spatial and temporal resolution, sensitivity and precision. In electrochemistry, the local concentration of protons in solution plays an important role in the reactions in different fields and is a function of the base geometry, current density, mass transfer, and electrolyte buffer capacity. Anodic oxidation corrosion is usually associated with the dissolution and hydrolysis of metals, thus producing protons locally. [13]

Electrochemistry of nucleic acids was discovered about 40 years ago. In the first 15 years, electrochemistry brought the early evidence of DNA prefusion and DNA double helix polymorphism. Currently, electrochemical methods using fixed electrodes are able to detect DNA at attomol, in some cases even at low levels. In recent years, great progress has been made in the development of electrochemical sensors for DNA hybridization and DNA damage, indicating that these sensors will soon become important tools in medicine and other areas of real life in the 21st century. [14]

Optical fibers gained significant attention in electroanalytical chemistry over the last decade, as they become increasingly useful for imaging of micro- and nanoscopic

surfaces in a variety of industrial and biological processes. The use of Optical fibers in combination with micro- and nanoelectrodes enables the quantification of various processes down to a resolution at the nanoscale. Optical fibers consist of an inner core, surrounded by cladding of a lower refractive index than the core material, followed by a buffer and jacket. <sup>[15]</sup>

The emergence of nanoscale electrochemistry has brought many problems that were only discovered when microelectrodes began routine laboratory experiments about 25 years ago. The main theoretical problems at the time seemed mostly to be related to the difficulty of dealing with edge effects under steady and quasi-steady electrochemical conditions and the consequences of diffusion and interfacial diffusion layers amalgamation to points. Monomolecular electrochemistry was created more than 20 years ago. This method utilizes the current generated when a feedback mode is established between two closed electrodes which illustrates the well-known principle of REDOX cycles between two closed electrodes. <sup>[16]</sup>

### **1.3. Electrochemical application**

Electrochemistry is one of the oldest activation methods in use in the laboratory which can be dated back to the 19th century. Electrochemistry is so widely applied on many various fields that its shadow is everywhere no matter how in the industries or humankind daily life. Electrochemical energy storage devices remain one of the most common applications of electrochemistry, and the market continues to grow exponentially with the increasing popularity of portable electronics and more recently larger scale applications such as electric vehicles or grid energy storage <sup>[17]</sup>. There are a few common applications about electrochemistry are introduced simply in the following paper.

#### **1.3.1. Battery**

Battery is a special saving energy device which can switch inner chemical energy into

electricity used by terminals. Nowadays, batteries have huge and common application in the storage of energy, for example, electrical power system, electric vehicles, portable resource due to safety performance and high capacity. [18]

Both industrial application and consumer usage boost fast evolvement of battery design. Consumer devices are different from the application in the industry and not used to operate in the industrial surroundings. Hundreds and thousands of consumer batteries are produced in the factories every year on the whole world which are used in various electronic product like cell phones, laptops, cameras and portable source. In general, the consumer batteries are classified into recharged batteries and non-recharged batteries (primary batteries). Handheld products are always equipped with easily replaced or recharged consumer batteries which are designed to normally work at approximate room temperatures and normal press. It is observed that the batteries applied on the electronic products such as cell phones or laptops are upgraded in the one or two years, and phone or laptops get out of style in the short time. As a consequence, the life cycle of rechargeable batteries at consumer grade is about 2-3 years which is equalled to about 500 full recharging circulates. The dried batteries are suitable for toys, remoter and alarm use cheap raw materials and substances which can work between 0 and 40 centigrade with about 3-year lifespan. [19]

The applications in the industries are totally different from the consumer applications, the devices used to in the factories are usually located in the distant and hard to touch places where the industrial equipment has to be powered supported by itself. And it is unlikely that these industrial batteries are replaced and charged with a high frequency. Therefore, the designers must pay more attention on battery durability and reliability in industrial applications while consumer products are focus on high energy density of battery to achieve slim and flexible designs. As a result, consumer batteries are slimmer and more flexible than industrial batteries but the service life is much shorter than industrial batteries. The characteristics of both are different due to their usage diversity respectively.

Consumption of industrial electricity is a most important purpose which has signification for industrial production. In the meantime, energy efficiency is a critical

factor in reducing environment pollution and production costs. The factors also effect on battery production. With the continuous development of society, the demand of battery is steadily and gradually increasing due to e-productors universal and electrical vehicles extension.

In order to meet the growing demand for batteries, production capacity is increasing correspondingly, which in turn raises the question of energy demand and energy efficiency. The production of battery can be divided into three main procedures which are electrode manufacturing, battery assembly and battery finishing. However, because of the high sensitivity of the materials involved to moisture, the cell assembly has to take place in a dry room. Operating dry rooms requires complex and energy-intensive building technology services. It is well known that electrode drying and drying chamber facilities are major energy consumers in battery production. [20]

The development of batteries is required by our need for life. Therefore, with the development of various technical products and various portable electronic products, as well as the requirements of environmental protection, the ecological potential of existing batteries will change greatly in the future.

### **1.3.2. Fuel cell**

Fuel cells are also called continuous batteries which is an alternative energy technology that converts the chemical energy of fuel directly into electric energy. With in-depth research in materials engineering, nanotechnology, transport phenomena and electrocatalyst engineering. Fuel cell technology is gradually developing, and these systems can be used in many fixed and portable applications. [21]

Fuel cells are at the forefront of alternative energy because that they promise and deliver high energy conversion efficiency without harming the environment. In a fuel cell, the energy loss is smaller than in an internal combustion engine because the chemical energy of the fuel is converted directly to electrical energy in these systems, which do not contain moving parts that can cause friction loss. In addition, each

section has distinct operating temperatures, power output, energy efficiency and capacity to meet the requirements of any application that requires energy. [22]

In addition, to achieve a higher efficiency, using fuel cells as a power source offers a number of other advantages over traditional internal combustion engines. The products released from electrochemical reactions are mostly environmentally friendly because they do not contribute to greenhouse gas emissions. The product is only water, if pure hydrogen is used in the reaction. Products maybe vary depending on the species of fuel used. They work quietly because there are no moving mechanical parts, which is especially preferred in defence and security-related applications. This feature also makes the fuel cell easier to operate, and the durability issues associated with friction are no longer a concern. The modularity of fuel cell systems allows us to achieve high power densities, even for small systems without debasing energy efficiency. Dynamic load response characteristics are sensitive to any changes in the system. Fuel cells can operate at different power ranges that vary according to the purpose of the application. The hydrogen, methanol, methane, propane, natural gas, hydrocarbons and other hydrogen generated in the reforming process in the fuel cell and the hydrogen generated by the alcohol in the liquid fuel cell can be used; Therefore, this provides great flexibility for the utilization of these systems [22].

The fuel cell usually converts chemical energy of fuels into electrical energy directly by the approach of electrochemistry in the electrochemical cell under the conditions of a voltage and certain current. It is a typical oxidation reduction reaction which oxidation reacts at the anode and reduction reacts at the cathode. In the whole reactions, ions produced at the anode is allowed to complete the circuit to cathode through a polymer electrolyte membrane which separates solution into anode and cathode parts. At the same time, electrons are generated at the anode and move to cathode by the form of electricity in the outside circuit. They bind to protons reaching the cathode and participate in the reduction of the oxidizing agent. [23]

### **1.3.3. Electrosynthesis**



Electrosynthesis is a modern technology widely applied in the organic synthesis and production of pharmaceuticals. Electrosynthesis is similar with common chemical synthesis but one of the most distinctions about both is the different types of catalyst. An ordinary definition about catalyst is as follows: a catalyst is a special material is used to increase or decrease the rate of a chemical reaction without taking part in the allover stoichiometry of the reaction. Catalyst is not related to reacted allover stoichiometry, but it does not present that catalyst never participates in the reactions. Honestly, catalyst is an extremely key substance which is involved on the surface of in the middle according to species of reactants. Catalyst can first react with the part of reactants and produce an intermediate which can react with the rest of reactants to create products. The rate of reactions can be increased or decreased by controlling intermediated reaction rate. Herein, draw the conclusion that catalyst forms someone intermediate which provides an easier alternative method in the catalytic process and the catalyst is not consumed any more in the whole reactions. [24]

In the electrosynthesis, the voltage or current affected on electrolyte solution plays the same role of conventional catalyst in the reactions: catalysis. A complete reaction of electrosynthesis needs an electrolyte, a galvanic cell, a solvent, a potential, a separated or unseparated cell and two electrodes. In the organic synthesis, electrochemistry can be used in amination, C-H activation, hydrogenation, halogenation and so on. Especially, electrocatalytic strategies have been conveniently used to achieve C-C, C-O, C-N and C-S bond formation reactions. Despite these advances, the formation of electrochemical C-X (Cl or Br) bonds has rarely been reported. [6]

Synthetic organic chemists are always looking for new techniques and methods to improve selectivity and productivity to construct molecules essential for drugs. Electrochemical organic synthesis is experiencing a Renaissance in recent years as the pharmaceutical industry increasingly demands green chemistry and engineering. Electrochemical organic synthesis can reduce the use of chemicals, reduce waste, and improve cost, safety, and sustainability by using electrons directly from the power source to achieve REDOX conversion. Almost all synthetic organic electrochemical methods use a constant voltage or current to drive chemical transformations. Under the conditions of constant current and voltage, the current only can flow in a stationary direction named direct current solution. Alternating current (AC)

electrolysis has been poorly studied because its charge flow periodically changes direction. [25]

#### **1.3.4. Plating**

Electroplating is a technique to produce a thin metal film on the outside surface of products. The principle is that an electroplated product as a cathode which is dipped into an electrolyte containing corresponding metal ions, while another appropriate material as an anode connecting with the cathode. Then apply a direct current on the cathode to gain the electroplated products. Electroplating can improve the luster of objects, achieve a beautiful effect, prevent corrosion. For example, tin on the metal surface to prevent corrosion and hard chrome plating can improve the surface hardness and resistance of the product.

In the industry, electroplating copper is known as one of the most important technologies in recent years. At present, copper coating is widely used in copper foil electrolysis of printed circuit board materials, copper metallization process of VLSI, copper bump processing, printed circuit board perforation electroplating, etc. Copper metal film has a variety of electroplating deposition processes including electroplating method or electrodeposition copper which has the advantages of low cost, high yield, high quality and strong hole filling ability.

Electroless plating is another electrochemical method of depositing thin film metal layer. The approach mainly adopts autocatalytic chemical reaction, since that the metal ions in the electrolyte generates layer of precipitation on the surface of product without outside environmental influence. The reaction process of electroless plating is similar to electroplating, but the electrons are not transferred through external wire instead of conducting on the surface of products directly. Because REDOX reactions occur only on solid surfaces with active materials so that electroless plating does not affected by the shapes, sizes, or conductivity of products [26]. Therefore, electroless plating is a convenient and effective method for depositing a metal layer on a non-conducting surface, such as silicon or plastic.

### 1.3.5. Capacitor

The positive and negative charges can be attracted with each other when a voltage is applied on the two separated parallel electrodes. The paralleled electrodes or called capacitor is constructed by two parallel double electrodes with a tiny thickness where electrolyte and electrodes contact with each other at the interface dielectric layer. The charges are accumulated in the dielectric layer when a voltage is applied on the electrodes, then charges move into the electrolyte solution to neutralize the extra charges and release energy when voltage disappears. The system between two electrodes is like the discharge process of a secondary battery.

The above structure is called a double-layer capacitor because that its energy is stored in the double-layer electrodes. This type of capacitor is also known as ultrahigh capacitor because of its high discharge capacity, fast charging time and hundreds of times of capacitance more than conventional capacitors.

A distinct from secondary battery, the ultra-high capacitance absorbs the charges from solution on the electrode surface during the process of charging and discharging without causing any attendant chemical reactions. Therefore, it charges and discharges quickly with a high current. Nowadays, double-layer capacitors can be used not only as power units with currents of 1 A or less, but also as power units with currents of 1 A or more. Ultra-high capacitors have stable charge-discharge characteristics over a wide temperature range, unlike batteries which have strict temperature limits. It has many great characters such as safety, economic and environment friendly. The development of double-layer capacitors has gradually made batteries possible in some cases, or the combination of double-layer capacitors and batteries can be used in products such as home appliances and computers that require high power and large current.

## Chapter 2 Electrocatalytic Unsaturated Hydrocarbon Reaction

### 2.1. Introduction

Electrochemical synthesis has enjoyed a renaissance in the chemical field due to its green and sustainable synthesis mechanism since the last decades [27]. The oxidation reduction reaction always plays an important role in organic chemistry, petrochemical industry and biomass conversion [28]. Especially, the non-covalent interaction  $\pi$  of unsaturated hydrocarbons which has homonuclear bonds or heteronuclear halogen bonds has become a researched hot spot [29]. The representing non-covalent interactions get an important position in all the learned intermolecular forces because that they have a great influence on plenty of natural phenomena, for example, the real rate state of matter, the understanding of atmospheric environment and the biological identification process [30].

Imidazole pyridazine is one of the important unsaturated hydrocarbon with non-covalent bonds and 6-Chloroimidazo [1,2-b] pyridazine is one kind of them in this experiment. Imidazole pyridazine consisting of an imidazole ring ortho fused to a pyridazine ring which shows a wide range of biological and therapeutic activities and forms the basis of a deal with of medicines in humankind and animal drugs [31]. Imidazole is an important class of nitrogen containing heterocycle and some heterocycle-linked imidazole derivatives exhibited potential antimicrobial and antifungal activities such as imidazole [1,2-a] pyrazine, imidazole[1,2-a]pyridine, imidazole[1,2-a]pyrimidine and pyrazolo-[1,5-a] pyrimidine illustrate significant antifungal activity against human pathogenic microorganisms and [1,2,4] triazolo[1,5-a] pyrimidine derivatives show certain antifungal activity against plant pathogenic fungi [32]. Beside agriculture, imidazole also has abroad application pharmacy as cefozopran, Iclusig, Vardenafil and cilazapril contain pyridazine moiety. In addition, the pyridazine portion also has great biological importance with the same as imidazole. Pyridazine is present in a number of important biological building blocks, such as histidine and the hormone histamine and the ring is present in many drugs such as the antifungal nitroimidazole and the sedative midazolam [33].

Because that imidazole and pyridazines play a series of extremely important role in the biological, pharmacological and agriculture fields so that a quantity of scientific researches have been conducted on the synthesis of some bicyclic and tricyclic systems based on kinds of pyridazines, various imidazole pyridazines and some tricyclic azazo analogs [34], [35], [36].

## 2.2 Experimental Sections

### 2.2.1. Experimental Reagents

Number	Name	Formula	molecular mass	State	Specification	SPEC	Producer
1	6-Chloroimidazo [1,2-b] pyridazine	C <sub>6</sub> H <sub>4</sub> ClN <sub>3</sub>	153.57	s	1g	AR	Leyan
2	Cerium chloride	CeCl <sub>3</sub>	246.48	s	25g	AR	Bide Medicine
3	Lithium perchlorate	ClLiO <sub>4</sub>	106.39	s	500g	AR	
4	Magnesium chloride hexahydrate	Cl <sub>2</sub> H <sub>12</sub> MgO <sub>6</sub>	203.30	s	500g	AR	Hushi
5	Acetonitrile	CH <sub>3</sub> CN	41.05	l	500mL	AR	Fuyu
6	Methanol	CH <sub>3</sub> OH	32.04	l	500mL	AR	Fuyu
7	Petroleum ether	-	-	l	500mL	AR	Fuyu
8	Ethyl acetate	CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	88.11	l	500mL	AR	Fuyu

Table 1 Reagents Information

## 2.2.2 Experimental Instruments

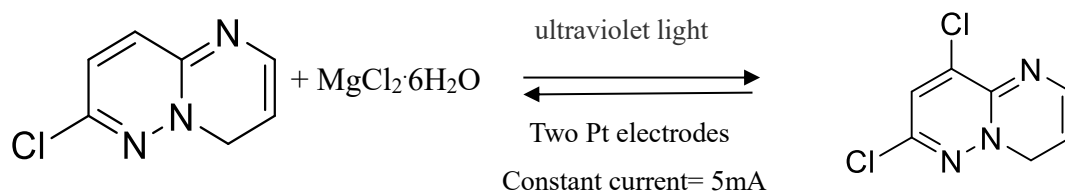
Number	Name	Specification	Producer
1	Platinum electrode	10*10*0.2mm	Shanghai yueci Electronic Technology Co., Ltd
2	Analytical Balance	QUINTIX224-1CN	Sartorius scientific instruments (Beijing) Co., Ltd.
3	Glass Sample Capillary	0.3mm*100mm	Instrument factory of West China University of Medicine
4	Portable ultraviolet analyzer	WFH-204BS	Hangzhou qiweiwei Instrument Co., Ltd
5	Potentiostat	DJS-292B	Shanghai Xin Rui instrument and Meter Co., Ltd.
6	Intelligent magnetic stirrer	ZNCL-BS 140*140	Gongyi Yuhua Instrument Co., Ltd
7	Rotary Evaporator	YRE-2000B	Gongyi Yuhua Instrument Co., Ltd
8	CNC ultrasonic cleaner	KQ3200DB	Kunshan Ultrasonic Instrument Co.,Ltd.

Table 2 Instruments Information

## 2.3. Experimental Procedures

1. First weight 6-chloromidazo [1.2-b] pyridazine 30.7 mg (0.2 mmol),  $\text{CeCl}_3$  2.5 mg (5%),  $\text{LiClO}_4$  63.6 mg (3eq) and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  120 mg(3eq) by the analytical balance and the reagents are located into a cleaned three-necked flask. Next put a suitable size of magneton in the flask before 6 mL MeCN and 0.5 mL MeOH are dropped into the flask by pipette gun. Then insert two Pt electrodes in the middle part and a balloon on the side of the flask and seal with rubber plugs. Finally locate the prepared flask on the above of intelligent magnetic stirrer and mix up until all reagents are dissolved in the solution totally.

2. Fill the balloon connected to flask with nitrogen as protective gas to empty air by the method of exchanging gas.
3. Fasten the three-necked flask above the intelligent magnetic stirrer set 400 r/min and put a ultraviolet source surrounding the flask. The electrodes are connected by certain constant current. When all power switched on, the reaction starts and the reaction is conducted for 12 hours under the conditions of room temperature and constant current.
4. When the reaction ends, all solution including three-time flask flush liquid is transferred into a distillation bottle which is poured with about 5 mL silica sand at the same time. Then the bottle is conducted the process of rotary stream on the rotary evaporator and gain dry sample.
5. The sample is placed in a prepared system of column chromatography while the dissociating agent is mixed by petroleum ether: ethyl acetate = 5:1. Make dissociating solution drop out continuously and test reaction timely by the method in which iodine plate are propped by tiny filter liquor. If iodine plate dropped liquid appears black spots under ultraviolet light, it suggests that the producer occurs. Now, save the aimed solution between black spot occurring and disappearing.
6. The above aimed solution is transferred to another cleaned distillation flask which is already weighted by the same analytical balance. Neat the solution is conducted to the second procedure of rotary evaporator and gain final producer. The last, weight the total weight of bottle and producer and calculate real productivity. And the chemical reaction equation of the experiment is as follows.



## Chapter 3 Conclusions

### 3.1. Results

The final weight of bottle attached the producer is  $m_2$ , while the initial net weight of cleared bottle is  $m_1$ . Weighing by analytical balance for three times, the average results are showed as following.

$$m_1 = 68.4117\text{g}$$

$$m_2 = 68.4366\text{g}$$

Known,

$$M_1 = 153.57\text{g/mol}$$

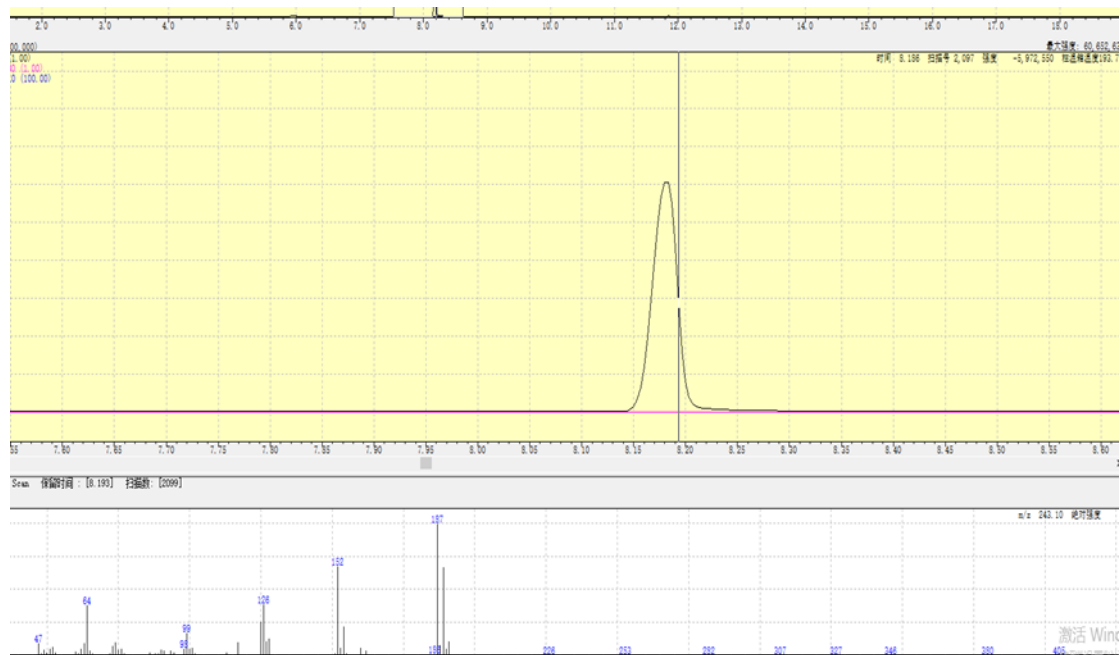
$$M_2 = 188.07\text{g/mol}$$

So,

$$\eta = \frac{m_1/M_1}{(m_2-m_1)/M_2} = 63.83\%$$

The final productivity of the reaction in the experiment is 66.2%.

In addition, in order to identify if the experiment already produced the aimed producer, the above final producer is tested by a chromatograph and gets the three following Chromatogram figures.





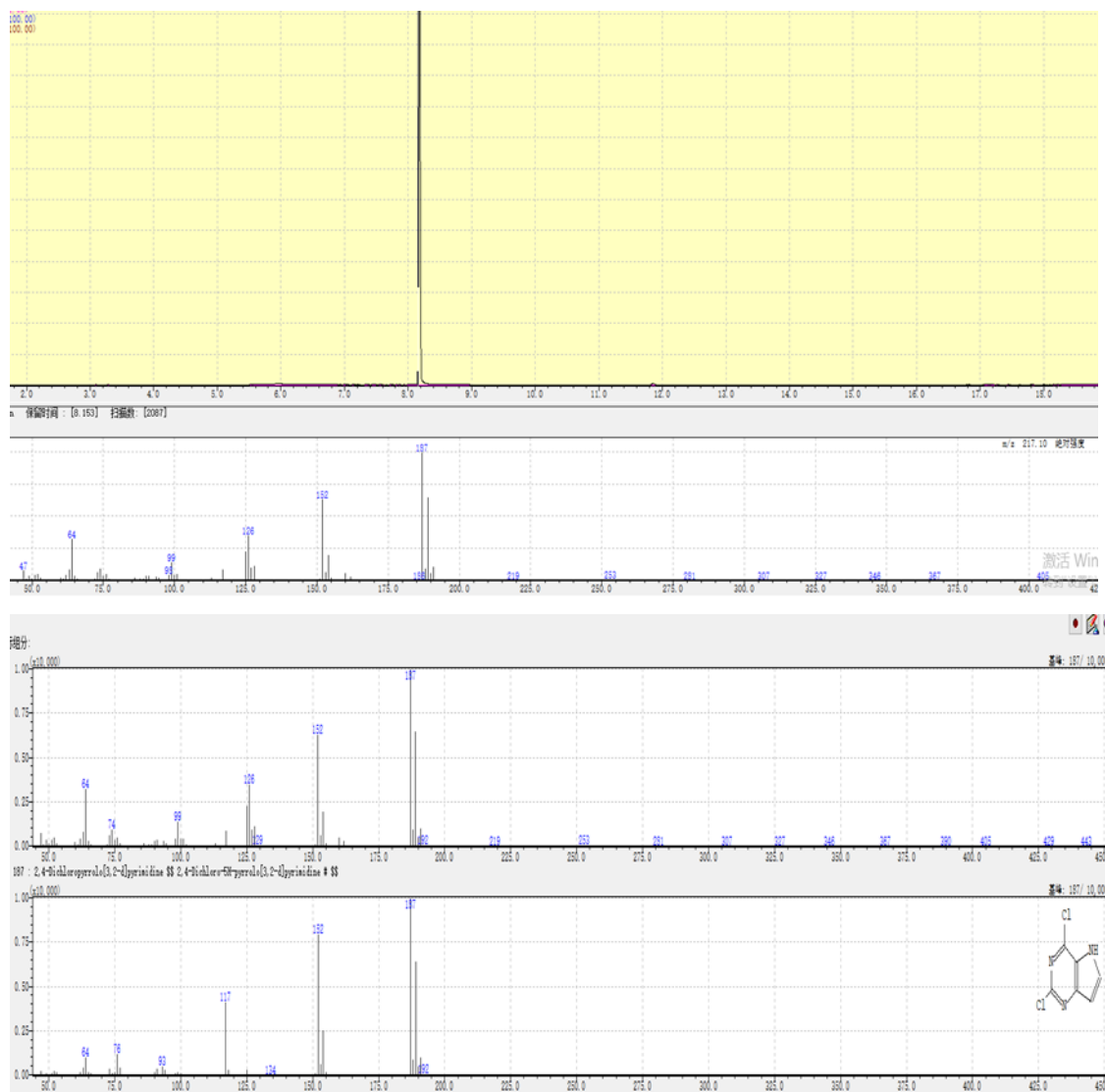
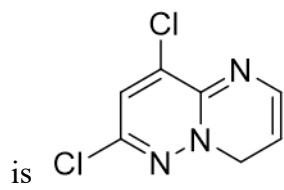


Figure 1,2,3 Chromatograms of producer

Through analysis, the result is that the final producer of this electrosynthesis reaction



, and the productivity is about 66.2% in the experiment.

## References

- [1] Xiaowen Guo, Changyun Chen, Yongcai Zhang, ..., The application of transition metal cobaltites in electrochemistry [J], *Energy Storage Materials*, 2019, Volume 23: Pages 439-465.
- [2] H.-J. Schafer and T. Pienemann, *Synthesis* [M], 1987.
- [3] T. Shono, H. Masuda, H. Murase, ..., *J. Org. Chem.* [M], 1992, 57.
- [4] Siyu Tian, Xiaofei Jia, Ling Wang, ..., Mn-catalyzed paired electrochemical facile oxychlorination of styrenes via oxygen reduction reaction [J]. *Chem. Commun.*, 2019.
- [5] Zhibin Li, Qi Sun, Peng Qian, ..., Electrochemical synthesis of  $\alpha,\alpha$ -dihaloacetophenones from terminal alkyne derivatives [J], *Chinese Chemical Letters*, 2020.
- [6] Xiangtai Meng, Yu Zhang, Jinyue Luo, ..., Electrochemical Oxidative Oxydihalogenation of Alkynes for the Synthesis of  $\alpha,\alpha$ -Dihaloketones [J], *Organic Letters*, 2020, 22 (3), Pages 1169-1174.
- [7] Dan Wang, Zhaohua Wan, Heng Zhang, ..., Electrochemical Oxidative Functionalization of Arylalkynes: Access to  $\alpha,\alpha$ -Dibromoarylketones [J], *Adv. Synth. Catal.*, 2020.
- [8] Béla Török and Timothy Dransfield, *Green Chemistry* [M], Elsevier, 2018.
- [9] John T. Warner, *Lithium-Ion Battery Chemistries* [J], Elsevier, 2019, Pages 17-41.
- [10] T. Shono, T. Soejima, K. Takigawa, ..., *Tetrahedron Lett.* [M], Elsevier, 1994, 35.
- [11] S. H. K. Reddy, K. Chiba, Y. Sun, ..., *Tetrahedron* [M], Elsevier, 2001, 57.
- [12] Ruchirange Ranaweera and Long Luo, Electrochemistry of nanobubbles [J], *Current Opinion in Electrochemistry*, 2020, Volume 22: Pages 102-109.
- [13] Mariana C.O. Monteiro and Marc T.M. Koper, Measuring local pH in electrochemistry [J], *Current Opinion in Electrochemistry*, 2021, Volume 25: 100649.
- [14] Emil Paleček, Past, present and future of nucleic acids electrochemistry [J], *Talanta*, 2002, Volume 56: Pages 809-819.
- [15] Nikita Thomas, Vikram Singh and Sabine Kuss, Optical fibers in analytical electrochemistry: Recent developments in probe design and applications [J], *TrAC Trends in Analytical Chemistry*, 2021, Volume 136: 116196.
- [16] Alexander Oleinick, Irina Svir and Christian Amatore, A few key theoretical issues of importance in modern molecular electrochemistry [J], *Current Opinion in Electrochemistry*, 2019, Volume 13: Pages 33-39.
- [17] Damian Goonetilleke, Jennifer H. Stansby and Neeraj Sharma, In situ studies: electrochemistry and scattering [J], *Current Opinion in Electrochemistry*, 2019, Volume 15: Pages 18-26.
- [18] Miaogen Chen, Shuling Xiang, Wenya Chang, ..., All-carbon-based semimetal for sodium-ion batteries anode material: A first principle study [J], *Physics Letters A*, 2021, Volume 390: 127113.

- [19] Bengt Sundén, *Hydrogen, Batteries and Fuel Cells* [M], Academic Press, 2019, Pages 111-122.
- [20] Marcus Vogt and Christoph Herrmann, Energy efficiency of technical building services in production environments—Application to dry rooms in battery production [J], *CIRP Annals*, 2021.
- [21] Ayşenur Öztürk, Ramiz Gültekin Akay, Serdar Erkan, ..., *Direct Liquid Fuel Cells* [M], Academic Press, 2021, Pages 1-47.
- [22] Bilal Nişancı, In *Advances in Green Chemistry: Nontraditional Activation Methods in Green and Sustainable Applications* [M], Elsevier, 2021, Pages 329-347.
- [23] Ayşe Kübra Erenoğlu, Ozan Erdiñç and Akın Taşcıkaraoğlu, *Pathways to a Smarter Power System* [M], Academic Press, 2019, Pages 1-27.
- [24] Julian R.H. Ross, *Contemporary Catalysis* [M], Elsevier, 2019, Pages 3-38.
- [25] Sachini Rodrigo, Disni Gunasekera, Jyoti P. Mahajan, ..., *Alternating current electrolysis for organic synthesis* [J], *Current Opinion in Electrochemistry*, 2021, Volume 28: 100712.
- [26] D. A. Frey, N. Wu and K. D. Moeller, *Tetrahedron Lett.* [M], Elsevier, 1996, 37.
- [27] Haojiang Shi, Nan Li, Hao-Kuan Lu, ..., *Recent advances in the electrochemical hydrogenation of unsaturated hydrocarbons* [J], *Current Opinion in Electrochemistry*, 2021, Volume 28, 100713,
- [28] Chun Mi, Lu Li, Xiang-Guang Meng, ..., *Highly selective oxidation of unsaturated hydrocarbons to carbonyl compounds by two-phase catalysis* [J], *Tetrahedron*, 2016, Volume 72, Issue 42, Pages 6705-6710.
- [29] Lin Xu, Jian-Wei Zou, Yun-Xiang Lu, ..., *Halogen/ $\pi$  interaction and cooperativity effect between dihalogen molecules and unsaturated hydrocarbons: An ab initio study* [J], *Journal of Molecular Structure: THEOCHEM*, 2009, Volume 897, Issues 1–3, Pages 12-16.
- [30] D.G. Rego and B.G. Oliveira, *The interplay and the formation of  $\sigma$ -hole in the  $\pi \cdots \text{LiX}$  and pseudo- $\pi \cdots \text{LiX}$  ( $X = \text{F}, \text{Cl}$  and  $\text{CN}$ ) lithium bonds involving unsaturated and homocyclic hydrocarbons* [J], *Computational and Theoretical Chemistry*, 2020, Volume 1186, 112899.
- [31] Antonia Sacchi, Sonia Laneri, Francesca Arena, ..., *Research on heterocyclic compounds, XLI. 2-Phenylimidazo[1,2-b]pyridazine-3-acetic derivatives: synthesis and anti-inflammatory activity* [J], *European Journal of Medicinal Chemistry*, 1999, Volume 34, Issue 11, Pages 1003-1008.
- [32] Lingling Fan, Zhongfu Luo, Yi Li, ..., *Synthesis and antifungal activity of imidazo [1,2-b] pyridazine derivatives against phytopathogenic fungi* [J], *Bioorganic & Medicinal Chemistry Letters*, 2020, Volume 30, Issue 14, 127139.

- [33] S. Sharmila Tagore, J. Swaminathan, D. Manikandan, ..., Molecular, vibrational (FT-IR and FT-Raman), NMR and UV spectral analysis of imidazo[1,2-b]pyridazine using experimental and DFT calculations [J], *Chemical Physics Letters*, 2020, Volume 739, 136943.
- [34] A. Pollak and M. Tišler, Synthesis of pyridazine derivatives—III: Formation of some bicyclic heterocyclic systems [J], *Tetrahedron*, 1965, Volume 21, Issue 6, Pages 1323-1326.
- [35] A. Pollak and M. Tišler, Synthesis of pyridazine derivatives—V: Formation of s-triazolo-(4,3-b)-pyridazines and bis-s-triazolo-(4,3-b,3',4'-f)-pyridazines [J], *Tetrahedron*, 1966, Volume 22, Issue 7, Pages 2073-2079.
- [36] B. Stanovnik and M. Tišler, Synthesis of imidazo/1,2-b/-s-triazolo/3',4'-f/pyridazine a new tricyclic azaheterocycle [J], *Tetrahedron Letters*, 1966, Volume 7, Issue 22, Pages 2403-2406.

## **Acknowledgment**

The paper is completely under the guidance of professor Chen Jianbin's team. Professor Chen's rigorous academic attitude, responsible teaching attitude, profound scientific research strength, amiable personality, simple and noble personality charm have a great impact on me. For the thesis, from the topic selection at the beginning, to the experimental research in the laboratory and the writing of the final thesis, every procedure has been patiently known by Mr. Chen. No matter how the general time planning or the specific schedule, Mr. Chen gave me an explanation in the detail. In addition, under the strict supervision of Mr. Chen, I developed a good habit of punctuality and self-discipline which I came to the laboratory on time every day to carry out a day of intense experimental research carefully. For the more, I never forget Mr. Chen's principle of safety first all the time so that I always observed the safety matters of the laboratory and done a good job in personal protection by wearing protecting equipment. Therefore, not only I did master of the basic research approaches, but also I learned the rigorous scientific research attitude which is extremely beneficial for my future work in the research field. Here, I would like to express my highest respect and heartfelt thanks to the professor Chen and all the members in the team!

At the same time, I specially want to thank senior Brother Shao Dongxu for his patient guidance in the laboratory work. Whether it is the experimental steps or instrument operation and he carefully explained and demonstrated to me. Not only that, he always explained the principles or mechanisms of reactions before I conducting. Sometimes, he taught me how to consult the literature and told me some useful precautions and skills in the process of experiment. As a few tiny helps so that I could avoid many detailed mistakes and data errors in my experiment and achieve the accuracy result successfully.

With the time flying unconsciously, the graduation thesis has come to an end and the annual graduation season is coming. Four years of college time is like a snap of the finger and it is running to an end gradually. I am very grateful to Qilu University of technology which a place witnessed my growing. I ever felt sad here while I ever felt lonely, but I struggled more to make my dream come true. At the same time, I would

like to express my heartfelt thanks to all the teachers of Applied Chemistry (international class) in Qilu University of technology. Thanks for your hard work, thanks for your patience and thanks for your tireless teaching.

Here, I would like to thank my classmates and friends meeting in the university. The four-year time of college with you have been the most carefree and happiest period in my life. In the past four years, we have grown up and gone through ups and downs together. At the beginning, we met in Qilu University of technology from all the places of country and start to know in the classroom of Applied Chemistry (international class) and really know each other by every bit of our life together. These for years, we encourage and help each other until we will graduate from university finally together. That is because of your company and encouragement, the youth is more exciting and colorful.

Finally, I would like to thank my parents who not only did provide the best education on me, but also gave me meticulous care in my study and daily life. The successful completion of my graduation thesis also has their silent support and help in the behind. My parents are my dependence in the long road of life and the warmest harbor that can shelter me from the wind and rain. In the future life, I will study and work harder to achieve more brilliant achievements and great career so that I can realize my parents' expectations for me and repay my parents' gratitude for the love and care given from my childhood.

Take dreams as horses and live up to The Zhaohua. Although the college life has ended, a new paragraph of life journey has begun. So look forward to the future bravely without any regrets for the past. I wish I can stick to my original dream when I was young and never give up until forever.