Degradation of Rh B and glycerol using contact glow discharge electrolysis (CGDE)

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Degradation of Rh B and Glycerol Using

Contact Glow Discharge Electrolysis (CGDE)

Master of Engineering

Submitted by: **RAO YUHAN** (G1702524B)

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

**Degradation of Rh B and Glycerol Using
Contact Glow Discharge Electrolysis (CGDE)**

RAO YUHAN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

24/12/2019

Date

Rao Yuhan

Supervisor Declaration Statement

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

24/12/2019

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Huang Yizhong

Authorship Attribution Statement

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

Chapter 4 is published as Separation and Purification Technology, 01 August 2019, Vol.220, pp.328-333 as well as Chemosphere Volume 214, January 2019, Pages 341-348

The contributions of the co-authors are as follows:

- A/Prof Huang Yizhong provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Li Chaojiang and Dr. Cao Xun.
- I co-designed the study with A/Prof Huang Yizhong and performed all the laboratory work at the School of Materials Science and Engineering. In addition, I also collected and analyzed the data.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr Li Chaojiang assisted in the preparation of experiment setting.
- Dr Li Chaojiang assisted in the interpretation of the by Fourier transform infrared data and carried out the spectral interpretation.
- Dr Cao Xun assisted in the collection and provide guidance in the scanning electron microscope data.

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The contributions of the co-authors are as follows:

- Prof Huang suggested the materials area and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised together with Dr. Li and Dr. Cao.
- I performed all the materials synthesis, collected and conducted data evaluation.
- Dr. Li Chaojiang conducted the Rietveld analysis of the interpretation of the by Fourier transform infrared.

24/12/2019

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Summary

In modern society, there is an increasing tendency of requirement for pursuing higher aesthetic abilities. For example, dyeing and chemicals are one of the main perspectives in the creation of industrial pollution. As such, many different chemical methods have been developed to get rid of the pollution through degradation of organic molecules. However, these methods have been still encountering the limit in low efficient process and complex procedures. It is still challenging to discover an approach to the improvement of degradation rate of the polluted organic contents.

In order to increase the degradation of polluted elements, the contact glow discharge electrolysis method was used with Cu and Au-coated Ti foil electrodes. It is the plasma discharge in cathode and the oxidation in anode that work together for chemical degradation.

It is found that a very low CGDE voltage is required to convert the glycerol in the solution in that glycerol is rapidly oxidized and transferred to chemicals such as glyceric acid, glyceraldehyde that are not toxic. The conversion rate is measured up to 81.27% at a concentration of 8mL glycerol.

CGDE enable to cleave the organic molecules either in the plasma zone or on the plasma/solution interface through hydrogen abstraction and electron transfer. Four parallel metal foil electrodes (i.e. Ta, Cu, Ti and Au coated Ti) are proposed and utilized as cathodes in the two-electrode system as above and Rh B molecules are selected organic pollutants. The results show the degradation rates are dependent on the electrical conduction of metal cathodes. During the discharge process, the Ti-based foil produces TiO₂ particles, which then act as catalyst in the electrolyte and perform the photocatalytic process along with the plasma discharge process to degrade organic pollutants. It is of particular interest that gold nanoparticles, generated from Au coated Ti foil film during electrode discharging, are less than 5 nm in size and further enhance the TiO₂ photocatalytic activity. In fact, this bifunctional plasma discharge process to the degradation of water pollutant is

the key finding in this thesis which can also provide an insight into more applications such as chemical conversion, water purification and dust pollution.

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Table Caption

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Abbreviations

%A	Absorptance
%R	Reflectance
%T	Transmittance
Ag	Silver
Ar	Argon
Au	Gold
CF₄	Tetrafluoromethane
CFC	Chlorofluorocarbon
HPLC	High performance liquid chromatography
Cu	Copper
CV	Cyclic voltammetry
CVD	Chemical vapour deposition
DC	Direct current
DSSC	Dye-sensitised solar cell
E_a	Activation energy
EBL	Electron beam lithography
EDX	Energy-dispersive X-ray spectroscopy
EOR	Ethanol oxidation reaction
(FEG-)SEM	Field emission gun scanning electron microscope
(FEG-)TEM	Field emission gun transmission electron microscope
FIB	Focused ion beam
H₂O₂	Hydrogen peroxide
H₂SO₄	Sulphuric acid
HSQ	Hydrogen silsesquioxane
JCPDS	Joint committee on powder diffraction standards
LB	Langmuir-Blodgett
LMIS	Liquid metal ion source
LSPR	Localised surface plasmon resonance

NaOH	Sodium hydroxide
O₂	Oxygen
OM	Optical microscope
ORR	Oxygen reduction reaction
PhL	Photolithography
PMMA	Poly(methyl methacrylate)
PS	Polystyrene
Pt	Platinum
Z	Atomic number

Chapter 1

Introduction

Due to the high social development rate, pollution has been becoming an urgent issue that needs to be resolved to protect the earth. Biodiesel is considered as a sustainable clean fuel to substitute fossil energy, originating from different natural vegetal oils or animal fats. However, biodiesel will contribute large amount of glycerol which is also the major part of the industrial wastewater. The industrial pollution and catalysis are the hottest topics nowadays. Due to the low degradation rate of glycerol pollutant, new catalytic methods and materials are required to be developed. Copper is the one of the cheapest materials which has the high industrial applicability; therefore, this experiment is based on copper in catalytic applications.

1.1 Introduction

The depleting trend of conventional fossil-based fuel and the environmental pollution have triggered research and development on alternative renewable energy [1]. Biodiesel is considered as a sustainable clean fuel to substitute fossil energy, originating from different natural vegetal oils or animal fats [2,3]. Currently, the biodiesel production is expected to increase in the decades to come, leading to a sharp increase of glycerol which is about to be 10% of byproducts of biodiesel production [4-8]. Treatments of glycerol via different reaction pathways such as oxidation, hydrogenolysis, biocatalysts and photo-catalysis has been widely studied [9–11]. Moreover, products from oxidation of glycerol including hydroxypyruvic acid, glyceric acid and glycolic acid can be applied in fine chemical industries [9]. Meanwhile, glycerol, a byproduct during the synthesis of biodiesel, can be widely used in various fields such as food, pharmacy, and cosmetics [12-4]. Due to the depletion of fossil fuel and large requirement of energy resources; the biodiesel production is expected to gradually increase within several years, leading to an increase in the glycerol, which is approximately 10% of byproducts of biodiesel production [15-16]. In addition, impurities such as salts, unreacted alcohol and unused catalyst are included inside the crude glycerol [17,18].

An excessive amount crude glycerol is now regarded as a “waste stream” with a disposal cost associated with it [19-20]. Therefore, if the untreated glycerol directly be discharged into the water way, it will pose detrimental effects to the environment; hence the pre-treatment is required before being discharged [21]. In other aspects, glycerol is also widely considered as the feedstock that can be converted to commodity chemicals and clean fuels [22].

Another common chemical, Rh B, one of the major pollutions of dyeing and textile, is hard to be decomposed naturally. A large amount of Rh B accumulates in the nature and could not be decomposed properly toxic levels reaching to the level which is harmful for living beings.

1.2 Hypothesis/Problem Statement

Rh B, one of the major pollutions of dyeing and textile is hard to be decomposed naturally. While large amount of Rh B accumulates in the nature and could not be decomposed properly toxic levels are reached which is harmful for living beings.

Glycerol, a byproduct during the synthesis of biodiesel, can be widely used in various fields such as food, pharmacy, and cosmetics. Due to the depletion of fossil fuel and large requirement of energy resources; the biodiesel production is expected to gradually increase within several years, leading to an increase in the glycerol, which is approximately 10% of byproducts of biodiesel production.

However, there are still many impurities such as salts, unreacted alcohol, water and unused catalyst consisted inside the crude glycerol which is produced from the biodiesel. In addition, an excessive amount crude glycerol is now regarded as a “waste stream” with a disposal cost associated with it. Therefore, if the untreated glycerol directly be discharged into the water way, it will pose detrimental effects to the environment; hence the pre-treatment is required before being discharged. In other aspects, glycerol is also widely considered as the feedstock that can be converted to commodity chemicals and clean fuels.

1.3 Objective and Scope

Treatment of industrial pollutants via different reaction pathways such as oxidation, hydrogenolysis, and dehydration, photo-catalysis etc. has been investigated extensively over the last decade [21-24]

Most of the methods can convert the pollutants to other smaller products obviously and reach high conversion rate; however, there are also several requirements for enough reaction time and harsh reaction conditions [25-30], such as for glycerol using electrocatalytic oxidation needs 44.5 hours to reach conversion rate just around 38%[26]; while using bi-

ocatalysis oxidation, there are several harsh requirements for experiment condition as pH, temperature, reactant concentration and so on. to guarantee the high conversion rate [24, 31]. According to the previous research from our cooperation group on carbon supported Pt₉Sn₁ nanoparticles as an efficient nanocatalyst for glycerol oxidation, the final conversion rate can typically achieve at 80% while just after 8 hours experiment time [12]. Although the conversion rate is ideal, the time for reaction and preparation of catalyst particles still needs to be improved.

Contact glow discharge electrolysis (CGDE) is a non-Faradaic electrochemical technique which generates plasma directly through the electrical discharge against water [33-34]. In CGDE, various active species such as hydroxyl radicals, hydrogen peroxide were produced either in the plasma zone or on the plasma/solution interface [35-37]. These highly activated species can diffuse into the solution to oxidize the pollutants in water. At present, the CGDE methods with thousands of DC voltage to excitation the gas was reported to degrade organic dye [38-40].

Based on the research done on this field, the oxidation of industrial pollutants induced by CGDE has not been reported so far. Therefore, in order to improve the oxidation efficiency, this work investigates the oxidation of glycerol by means of low voltage CGDE. The fourier transform infrared spectroscopy (FTIR) and the high-performance liquid chromatography (HPLC) were used to determine the standard chemical solution and analysis the experiment products and conversion rate.

1.4 Expected Outcomes/Challenges

Contact glow discharge electrolysis (CGDE) is not wildly discussed in pollution degradation, the energy produced by CGDE is much higher than chemical and biological reactions, which might help chemicals for degradation hence can improve the degradation rates. However, the produce of degradation of dyeing and chemicals is hard to suspect. The resulted production may also be hard to control while the high energy produced in a short time.

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Chapter 2

Literature Review

Pollution degradation as well as the side effects caused by it are the major topics among the high speed of industrial development. Different degradation methods have been discussed and explored in order to reach a higher degradation rate. Contact Glow Discharge Electrolysis (CGDE) is the new technology developed in recent years; it barely has been applied on pollution degradation. Dyeing, the major method that offers different colors for textile industries will cause huge amount of pollution. The happens to the biodiesel fuel industry in which a large number of pollutions will be generated. Therefore, research on CGDE application in pollution degradation is the major motivation of the experiment.

2.1 Industrial pollution

It is necessary for synthesis dyes in various significant industries such as the textile, paper and leather industries for its properties which offer different colors.

Each year, there is approximately 700000 tonnes of various coloring from about 100000 commercially accessible dyes are manufactured [1,6,9,10,16]. Most of dyes have been discarded without further care into the water once they served their purpose. Shown in **Figure 2-0-1**, there are five major industrial which should be responsible for the present dye effluents in the environment.

Figure 2-0-1 Industries responsible for the presence of dye effluent in the environment [25].

The highest dye effluent was contributed by the textile industry (54%) releases which contributing to more than half of the existing dye effluents all around the world. The produce process which other high amounts of dye effluents from various associated processes are paper and pulp industry (10%), dyeing industry (21%), tannery and paint industry (8%) and the dye manufacturing industry (7%). The exact amount of dye effluents ejected by each industry into the environment is unknown but it can be said that the number is quite large to result as a significant environmental issue. Among other dye-utilizing in-

dustries, the textile industry is said to utilize the highest amount of dyestuff at approximately 10 000 tonnes per year worldwide [18]. Besides that, this industry is also known to produce around 100 tonnes of dye effluent per year, the highest amount of dye wastewater from one industry alone [20].

Figure 2-0-2 Discharge percentage of dye mixture from each process of the textile industry [26].

High usage of dyestuff in various processes of textile industries result in generation of huge amounts of dye wastewater. Besides that, textile industries produce high amounts of dye effluents due to the tremendous water requirement by the industry [2, 4, and 5, 19]. For various processes in the textile industry, specific mixtures of chemicals, dyestuff and water is prepared. Once the process is complete, the leftover mixture (dye effluent) is discharged into the environment. For instance, 85% dye effluent is ejected from the dyeing process. This dye effluent is the leftover of the total amount of dye mixture prepared at the beginning of the dyeing process. The percentage of dye mixture ejected at the end of each process of the textile industry is shown in **Figure 2-0-2**. It is deduced that dye effluents from the textile industry exist due to the inability of the dye mixture (dye molecules and chemicals) to completely attach itself onto a fabric or textile [17]. Generally, only a maximum 80% of dye and chemical molecules from dye mixtures are able to be adsorbed by materials intended for coloring [24]. Fabrics in particular, can only absorb a maximum 25% of dye mixture onto its body due to its limited absorption capacity [7].

Figure 2-0-3 Hazardous chemicals used along with dye by dye-utilizing industries.

Dye effluents, better known as dye wastewater, is rich with numerous hazardous chemicals shown in **Figure 2-0-3**. Dye effluents can endanger the lives of animals and humans as they are toxic by nature. It is easy to spot water bodies containing dye effluents as its color gives it away [3, 12]. Presence of dye effluents in water sources are unacceptable as water is required by animals and humans for daily activities such as bathing, cooking, drinking and washing [22]. Nowadays, removal of dye molecules from water sources has not only become a major environmental concern but also a challenge [10, 11, 13]. Techniques of recovering and reusing dye wastewater received the limelight recently as clean water sources might soon begin to deplete rapidly if no dependable solution is found. Developing a fixed solution to permanently eliminate dye particles from textile effluents would greatly benefit the environment [15, 21].

Currently, various dye removal methods have been established in countless research papers claiming successful dye removal. Although there are a variety of applicable dye removal techniques, not all of them are successful or even

Suitable to be practiced due to their disadvantages [8,14]. An ideal dye removal method should be able to efficiently remove large quantities of dye from wastewater in a short time span without producing secondary pollution. It is encouraged to remove pollutants from wastewater with a method that does not produce more hazardous by-products (secondary pollution) [18]. This paper describes different types of dyes as well as dye removal methods biologically, chemically and physically. The focal aim of this paper is to review studies on different dye removal methods according to its dye removal percentage. This paper was composed due to the lack of information on the efficiency of available dye removal methods in literature. Following that, this paper highlights the most suitable dye removal technique based on the review conducted. This paper highlights enzyme degradation (biological) and adsorption (physical) dye removal as these are known as one of the most efficient dye removal techniques these days. The highlighted methods are believed to efficiently remove dye particles from wastewater in a short period of time with no harmful by-products.

2.2 Dyeing and Textile

The use of dye and pattern began in the Paleolithic era (2000 BCE) with cave paintings in Europe and the Americas [27, 28]. Later, humans painted their bodies with minerals or plant-based dyes before using dyes on fabric. Tribes in the Amazon used annatto, derived from the seeds of the achieve tree, as body paint, while Britain's Celts used blue dyes from the wood plant to create blue body paint. Some North American Indian tribes mixed bloodroot with bear grease to make war paint. Gradually people also began to dye the fabrics they wore and used in their homes. Other substances in nature such as clay, mud, or the purple dye made from seashells have also been used to dye fabrics or yarn [29, 30, and 31].

Naturally derived substances have also been used as cosmetics and hair coloring. The first-century CE Roman writer Pliny records the use of black walnut shells to create hair dye [32, 33, 35]. He also mentions the plant weld, which yields a yellow dye that the Romans used for dyeing the robes of vestal virgins and for women's wedding garments [34].

The Egyptians began using leaves from plants, such as indigo, to make dyes. By adding an alkali such as plant ashes, lime water, or urine to the crushed leaves, a blue color was extracted [37, 39]. Henna, a flowering plant, was used to color men's mustaches and beards, horses' tails and manes, and parts of the bodies of mummies [36, 38].

In Asia, printing blocks have been found that are about 5,000 years old. After Alexander the Great invaded India in 327 BCE, new trade routes brought the silks and other fabrics to the rest of Asia, Greece, and Egypt. According to manuscripts of the era, by the fourth century BCE, Indians had begun using indigo as a dye. By the second century CE, Indian fabrics had reached Europe and Africa.

Peru offers the earliest examples (200–100 BCE) of resist dyeing, a process of dyeing that involves wax patterns or designs that resist the dye [38, 40, and 41]. The technique spread into other pre-Columbian civilizations as well. The art of resist dyeing evolved into batik and tie-dye [44].

As people realized that plant-based dyes could be permanent when fermented or mixed with other chemicals, called mordents, techniques advanced. One of the earliest examples of fabric dyeing in Britain can be found in the green wools of the Bayeux Tapestry. Dyers' guilds existed in medieval Italy, and books describing dyeing methods were written [42, 43].

The industry changed with the 1850s creation of mauveine, the first synthetic dye, by British chemist William Henry Perkin. Natural dyes were replaced by aniline dye, made

of coal tar [50, 53]. Although these colors were liable to fade, they were easier to make and use. Contemporary technology allows creation of unusual colors, as well as of pigments that can change color or give off a fragrance in response to light, heat, or stress [44, 47, and 49].

2.2.1 Techniques

Seven steps comprise the direct dyeing process for fabric, which can be adapted for dyeing yarn. First, the fabric must be pre-scoured. To do this, place the fabric into a washing machine and use a hot-water setting [45, 46]. Then, add a teaspoon of Synthrapol SP and a teaspoon of a dye activator for every three yards of fabric. When the cycle ends, the fabric can be dried and put away for later dyeing or placed directly into a solution for soaking. In this second step, a dust mask and rubber gloves are necessary. Wet or dry fabric is placed in a solution of dye activator and salt for 30 minutes to 24 hours. The solution can be reused [48].

Next, the dye is mixed. Instructions come with commercially prepared dyes to give proportions of mix and water. Only after mixing should the protective gloves and mask be removed. The fourth step is the actual dyeing of the fabric, which can be dry, wet, or damp. Fabric should be placed on a protected surface or in a plastic tray [50]. It can be scrunched, folded, or tied; the dye can be squirted or dribbled onto the surface. Curing is the fifth step. This step will take between 30 minutes and 24 hours, and will entail all of the fabric being placed in a plastic bag or covered with plastic to prevent it from drying out [53]. Once it is cured, the fabric can be rinsed in warm water [51, 52].

The final step is the after wash, with another two tablespoons of Synthrapol SP added to a hot cycle. When the fabric has dried, it is ready to become clothing or part of a quilt or other decorative item.

2.2.2 Trends

Concerns have arisen about the environmental impact of the textile industry. Many people are returning to plant-based dyes to create natural colors. Some fabric artists are turning to dyeing their own fabrics or yarns to have more control over the colors or patterns available. Meanwhile, interest in Shinobi continues to grow, with some dedicated fabric artists traveling to Japan to attend workshops and visit well-known artists.

2.3 Biodiesel fuels process and pollution

The search for a variety of energy sources is nearly as old as mankind's need for energy. Increasing industrialization commencing in the 19th century, spurred by the development of machines converting the energy stored in a variety of resources to power, caused this search to intensify. The internal combustion engine, in its two major variations, the spark ignition and compression-ignition (diesel) engines, is a prime example. While fuels obtained from fossil sources were investigated from the onset of these engines, biogenic materials also found some interest, primarily ethanol in the case of the spark-ignition engine [183] and vegetable oils in the case of the compression ignition engine [184]. Due to a variety of factors, petroleum became the major source of fuels for both engines, although research, testing and some use of the "alternative" biogenic fuels continued for many years through approximately World War II and then resumed with ever-increasing intensity, in the late 1970s and early 1980s as a result of the energy crises of the 1970s.

That operational problems were associated with the use of vegetable oils in a diesel engine was recognized early [184], with high viscosity being defined as a major cause of these problems. While one paper states [185] that it is "academically necessary to split off the glycerides and to run on the residual fatty acid," other work goes a step further by interchanging glycerol for ethanol by preparing the ethyl esters of palm oil through a transesterification reaction, with the Belgian patent 422877 probably being the first report of what is termed biodiesel today [186,187] and testing them in an urban bus [188]. This is probably the first documented use of what is now termed biodiesel [189,190], namely the monoalkyl esters of vegetable oils or animal fats or other triacylglycerol-containing feedstocks. This approach was then rediscovered approximately forty years later [191] in

the early stages of renewed interest in vegetable oils and their derivatives as diesel fuel.

Besides preparing biodiesel, several other approaches have been investigated over time with the objective of reducing the viscosity of triacylglycerol-containing materials. These approaches are dilution with petrodiesel, microemulsification, and pyrolysis [192]. Besides these four approaches, more recently another approach based on a catalytic reaction termed hydrodeoxygenation, which affords a mixture of hydrocarbons probably best called “renewable diesel” and simulating the composition of petroleum-derived diesel fuel (petrodiesel), has been developed [193,194]. The present article is, however, concerned with biodiesel and the other approaches are not discussed here.

With ever-increasing research interest as well as production and use of methyl esters of plant oils as biodiesel, especially since the mid- to late 1990s, standards were developed tailored largely toward these methyl esters. The first standard was established in Austria in 1991 followed by other European standards, most notably the German standard DIN 51606. Standards in individual European countries have been superseded by the European standard EN 14214 [195]. In the United States, concurrently the biodiesel standard ASTM D6751 [196] was developed. It may be noted that ASTM D6751 states that biodiesel meeting its specifications is to serve as blend stock for blends with petrodiesel and therefore is applied to neat biodiesel.

Relatedly, the standard ASTM D7467 covers blends at levels of 6–20% biodiesel [197] and an ASTM specification WK52154 for blends >20% is under development [198]. Blends of up to 5% biodiesel with petrodiesel are covered by the petrodiesel standard ASTM D975 [199] with these blends required to meet the specifications for neat petrodiesel. The EN and ASTM standards now often serve as reference standards for other biodiesel standards world-wide. These standards address a variety of fuel quality issues caused by the properties of the major fuel components, the mono-alkyl esters of fatty acids, and by minor constituents (contaminants). It may be noted that viscosity, in the form of kinematic viscosity, as the major issue for using biodiesel instead of vegetable or plant oils, is limited in these standards to ensure that alkyl (usually methyl) esters are indeed

used as biodiesel.

Besides overall favorable properties for use as transportation fuel, biodiesel has numerous other potential uses, although none of these uses can compete with fuel in terms of volume. These uses include heating oil [200,201], power generation [202], lubricants [203], plasticizers [204], high boiling absorbents for cleaning of gaseous industrial emissions [205], as well as various solvent applications, which are also discussed here briefly. It is biodegradable [206-208] and, relatedly, has also been tested as a possible oil spill remediation agent [209-213]. This application relates to the solvent properties briefly discussed at the end of this article. A detailed discussion of the applications of biodiesel other than those discussed here is beyond the scope of this article. Besides the aforementioned driving forces, advantages of biodiesel are low or no sulfur content, no aromatics content, high flash point, inherent lubricity, biodegradability, reduction of most regulated exhaust emissions, miscibility with petrodiesel in all blend ratios and compatibility with the existing fuel distribution infrastructure. Technical challenges associated with biodiesel include reduction of NO_x exhaust emissions and improvement of oxidative stability and cold flow properties. While the biodegradability of biodiesel is frequently cited as an advantage, for example, in case of spills in the environment, this also means that bacterial biomass may grow during storage and form deposits that clog engines and fuel lines [214,215]. The overall environmental benefit or damage derived from the production and use of biodiesel needs to be evaluated on a “cradle-to-grave” basis through life-cycle analyses (LCA). Biodiesel from terrestrial sources is generally computed to have a positive energy balance; i.e., more fuel energy is derived from the product than was consumed to produce it. For example, a life-cycle analysis for soybean-derived biodiesel showed a positive energy ratio [216] and a review of palm biodiesel LCA showed uniformly positive energy ratios with dependence on system boundaries [217]. Aquatic feedstock like microalgae though may result in a negative energy balance. While biodiesel was initially assumed to be “carbon-neutral,” the agricultural inputs needed to grow the feedstock and the incurred carbon debt from land use change often mean that biodiesel use may actually result in greater greenhouse emissions than if petrodiesel were used [217]. Increased agriculture may also have negative impacts on waterways because of ni-

trification from fertilizer runoff. So, while biodiesel has distinct advantages over petrodiesel for the local environment, its impact on the global environment is less clear. LCAs are dependent on system definition and the availability and quality of data. Value judgments will also have to be made on the relative importance of each environmental impact. Which one is more important than the other? Further developments in the assessment of the desirability of a product will be necessary before this question can be answered. The economics of biodiesel have made it often dependent on incentives in the form of subsidies, tax reductions or other regulations to be competitive with petrodiesel. Therefore, it is of interest to investigate other potential applications where biodiesel may be technically and economically competitive. Development of other products from non-oil feedstock components would also be critical, to improve both business and environmental profiles. The business challenges faced by the biodiesel industry have led to the slow adoption of innovative new manufacturing technologies in spite of their many advantages as many of these require significant capital inputs. Thus, while biodiesel has become a widely adopted alternative fuel, there remain many challenges that may prevent it from being more widely used. This article is concerned primarily with fuel properties largely determined by the major components of biodiesel as each component has a different combination of properties. Properties that will be discussed here and how they are affected by the composition of biodiesel from various feedstocks are the cetane number (CN), cold flow, oxidative stability, kinematic viscosity, lubricity, and density. How fuel properties can be influenced by minor constituents will also be addressed. Biodiesel is obtained by transesterifying vegetable oils or other materials are largely comprised of triacylglycerols with monohydric alcohols, most commonly methanol, to give the corresponding mono-alkyl esters (Figure 2-4) [189,190]. Thus, the fatty acid profile of biodiesel corresponds to that of the parent oil or fat from which it is produced. As the least expensive alcohol, methanol has been commonly used to produce biodiesel. Thus, biodiesel is often referred to as the fatty acid methyl esters (FAME) of a vegetable oil or animal fat or other triacylglycerol-containing material. Both moieties, the fatty acid chain and the alcohol functionality, contribute to the overall properties of a fatty ester and therefore the properties imparted by other alcohols (yielding fatty acid alkyl esters; FAAE) that could be used for producing biodiesel should be considered.

Figure 2-4 The transesterification that produces biodiesel. R1, R2 and R3 represent different fatty acid chains. R1, R2 and R3 may or may not be identical. Methanol ($\text{R}' = \text{CH}_3$) is the most commonly used alcohol with sodium methoxide (NaOCH_3) being the preferable catalyst.

2.4 Contact Glow Discharge Electrolysis (CGDE)

Contact glow discharge electrolysis (CGDE) IS a non-conventional electrochemical process in which a plasma is sustained by d c glow discharges between an electrode and the surface of the liquid electrolyte surrounding it. The phenomenon develops at either the anode or the cathode in a spontaneous transition from conventional normal electrolysis at sufficiently high voltages in aqueous, non-aqueous or molten media. A critical investigation of the growth of CGDE in aqueous media [53, 54, 55] has shown that the sequence of events leading to full or true CGDE involves normal electrolysis, solvent vaporization near an electrode by Joule heating, the onset of hydrodynamic instabilities with vapor sheathing the electrode and glow discharges across the vapor sheath. Furthermore, the electrode (1 e anode or cathode) at which the conditions allow easier vaporization and easier onset of hydrodynamic instabilities has been found to be the location of CGDE. The critical voltage for the onset of full glow discharge at an electrode, called the mid-point voltage, is characteristically invariant to external variables. However, the mid-point voltage and the nature of the glow discharges at an anode are quite different from those at a cathode.

A remarkable characteristic of the phenomenon is the strong deviation of the chemical yield at the glow discharge electrode from that expected on the basis of Faraday's law [54-60]. Moreover, the products obtained contain species novel for normal electrolysis.

Thus the formation of H_2O , from H_2SO_4 , and Fe^{3+} from an Fe^{2+} solution, with yields two and eight times respectively of those expected from Faraday's law, during anodic CGDE at 450 V has been reported [53,54] Large deviations have also been noted at a lower voltage of 220 V during cathodic CGDE of several aqueous inert-type electrolytes such as Na or K salts, which liberate cathode gases with volumes two to three times the Faraday law value and containing 15%-20% O_2 by volume [56] However, the yields of anodic CGDE at 220 V in similar electrolytes show smaller deviations the anode gases have volumes 1-1.5 times the Faraday law value and contain 7%-20% H_2 by volume [57] In a further study on the chemical effects of CGDE, It has been found that cathodic CGDE of an I^- solution at 300 V can cause oxidation of I^- at a level of four times that expected from Faraday's law [58] Similar non-faradaic features have also been observed for the chemical effects of anodic CGDE in non-aqueous media, such as liquid ammonia [54,59], acetonitrile and dimethylformamide [60]

Such deviations from Faraday's law are also commonly observed during glow discharge electrolysis (GDE) of aqueous and non-aqueous electrolytes [54], a closely related phenomenon in which the glow discharge electrode is set up in the gas space above the liquid electrolyte However, in the case of molten electrolytes, such deviations, although of significant magnitude in GDE [61, 62], are not observed in CGDE [63]

Figure 2-5 Mechanism of glow discharge plasma

It is usually considered that the yields in significant excess of the Faraday law value for the products of CGDE are due to reactions of the radicals generated by breakup of the solvent molecules in the glow discharges [54-60,64-70]. Indeed, the presence of $\text{H}^\bullet$ and $\text{OH}^\bullet$ radicals generated by GDE of aqueous solutions was confirmed by electron spin resonance (ESR) using 5,5-dimethylpyrrolidine-1-oxide as a spin trap [71]. Because of its potential for generating radicals in high local concentrations, CGDE has been used as a tool to synthesize compounds such as hydrazine [54,59], N,N-dimethylammonioacetamide [8] and amino acids [64-70].

Figure 2-6 Overview of experimental setups (a) CGDE; (b) GDE; (c) Diaphragm glow discharge

The studies described above were primarily concerned with the yield of a particular product either in solution or in the gas phase. Moreover, the results were obtained for CGDE carried out at different voltages where the conditions of glow discharges vary [11]. Thus we cannot correlate the chemical yields of CGDE in solution and in the gas phase observed by different workers. Furthermore, although the solution phase yields of CGDE, such as H_2O_2 , N_2H_4 , Fe^{3+} etc., seem to originate in the solution near the plasma, it is not known whether the origin of the gas phase products, such as H_2 and O_2 , is in the same solution near the plasma or within the plasma itself. A detailed study of the chemical yields of CGDE both in solution and in the gas phase is needed to determine the location of the reaction zones of CGDE and to elucidate the mechanisms of the reactions occurring there.

2.5 Cu and Cu-based nanoparticles

The applications of copper (Cu) and Cu-based nanoparticles, which are based on the earth-abundant and inexpensive copper metal, have generated a great deal of interest in recent years, especially in the field of catalysis. The possible modification of the chemical and physical properties of these nanoparticles using different synthetic strategies and conditions and/or via postsynthetic chemical treatments has been largely responsible for the rapid growth of interest in these nanomaterials and their applications in catalysis. In

addition, the design and development of novel support and/or multimetallic systems (e.g., alloys, etc.) has also made significant contributions to the field. In this comprehensive review, we report different synthetic approaches to Cu and Cu-based nanoparticles (metallic copper, copper oxides, and hybrid copper nanostructures) and copper nanoparticles immobilized into or supported on various support materials (SiO₂, magnetic support materials, etc.), along with their applications in catalysis. The synthesis part discusses numerous preparative protocols for Cu and Cu-based nanoparticles, whereas the application sections describe their utility as catalysts, including electrocatalysis, photocatalysis, and gas-phase catalysis. We believe this critical appraisal will provide necessary background information to further advance the applications of Cu-based nanostructured materials in catalysis.

The catalytic activity of nanoparticles (NPs) represents a rich resource for chemical processes, employed both in industry and in academia.[71,72] NPs have applications in diverse fields, including energy conversion and storage, chemical manufacturing, biological applications, and environmental technology.[73,74] The great interest in catalysis using nanomaterials has prompted the synthesis and investigation of diverse highly functionalized NPs, including graphene-based catalysts, nanocarbon catalysts, core/ shell nanocatalysts, magnetite-supported nanocatalysts, integrated nanocatalysts, and also various metal nanostructures.[75–86] The study of these systems has been facilitated by rapid developments in synthetic methodology that have enabled the preparation of NPs with tunable compositions, shapes, sizes, and structures, either on their own or supported on other materials.[87–94]

Nanomaterials prepared from earth-abundant and inexpensive metals have attracted considerable attention because of their potential as viable alternatives to the rare and expensive noble-metal catalysts used in many conventional commercial chemical processes.[95] These metal NPs often exhibit activity different from that of the corresponding bulk materials because of their different sizes and shapes, which give rise to distinctive quantum properties. In this context, Cu NPs are particularly attractive because of cop-

per's high natural abundance and low cost and the practical and straightforward multiple ways of preparing Cu-based nanomaterials. [96-103]

Despite the strong background on the applications of bulk Cu in various fields (e.g., optics, electronics, etc.), the use of Cu NPs is restricted by Cu's inherent instability under atmospheric conditions, which makes it prone to oxidation. Many efforts to develop the methods and supporting materials that increase the stability of Cu NPs by altering their sensitivity to oxygen, water, and other chemical entities has encouraged the exploration of alternative Cu-based NPs with more complex structures, such as core/shell Cu NPs or systems based on copper oxides. Cu is a 3d transition metal and has some interesting physical and chemical properties.[102] Cu-based materials can promote and undergo a variety of reactions due to Cu's wide range of accessible oxidation states (Cu⁰, Cu^I, Cu^{II}, and Cu^{III}), which enable reactivity via both one- and two-electron pathways. Because of their unique characteristics and properties, Cu-based nanocatalysts have found many applications in nanotechnology, including catalytic organic transformations, electrocatalysis, and photocatalysis.[103–116] The main challenge in the development of catalytic NPs is to prepare nanomaterials that are highly active, selective, stable, robust, and inexpensive.[117,118] One economical way of creating advanced Cu-based nanomaterials for catalysis is to anchor Cu NPs (e.g., Cu, CuO, or Cu₂O) on supports such as iron oxides, SiO₂, carbon-based materials, or polymers.

Additionally, Cu's high boiling point makes it compatible with high-temperature and -pressure chemical reactions, including continuous flow reactions, microwave-assisted reactions, vaporphase reactions, and various organic transformations.[119–123] Such unique properties, conducive for the development of reactive and selective catalytic systems, have made Cu and its alloys among the most valuable metals in the past, and will ensure that they remain important in the future.

Figure 2-7 Applications of Cu-based nanocatalysts.

2.6 Design and Application of Foams for Electrocatalysis

Developing low cost and efficient anode and cathode materials toward electrocatalysis are regarded as one of the most desirable yet challenging research directions, which are intimately related to the pressing energy, environmental and human health issues. Currently, 3D foam (such as Ni foam, Cu foam, and graphene foam) based heterogeneous catalysts have been intensively explored for actively catalyzing the electrode reactions.

Their inherent characteristics of stereo-network structure, high specific area and large pore volume not only provide better mass transport of reactants to electrode surfaces, but also pave 3D electron transport pathways. Herein, recent significant progress and rational design of foam-based electrocatalysts are reviewed. In addition, some insights into current challenges and future directions of foams for efficient electrocatalysis are proposed and discussed.

The pioneering work by Bowden and Riddeal (1928) [123] is believed to be the first to utilize various electrode materials to drive the hydrogen evolution reaction (HER). The nomenclature of “electrocatalysis” arose rather recently (1963) after the advent of research into fuel cells as an effective means of energy conversion.[124] Earlier development of electrocatalysis was mainly focused on the HER, and in the subsequent decades its expansion in both the range of electrode reactions and electrode materials can be witnessed.

The developed electrode reactions such as HER, oxygen evolution reaction (OER), oxygen reduction reaction (ORR), carbon dioxide reduction, electrocatalytic oxidation or reduction of small molecules (such as methanol, urea, glucose and H_2O_2), etc., is in correlation with our energy, environmental and human health issues (such as fossil fuel depletion, CO_2 emissions and diagnosis of diabetes).

To complete these anodic or cathodic reactions and make the whole process more energy-efficient, stable and highly active electrode materials are required to lower the large overpotential, increase the current density, and facilitate the reaction rates. To date, noble metals (Pt, Pd, Ru, Ir, Au, and Ag) and alloys remain the most efficient for almost all the electrode reactions.[125–131] However, these noble metals are not sustainable resources due to their low abundance and consequently highcost, which hinder their long-term viability. Over the years, the search for cheap and abundant catalyst materials with high activities as a substitute for the traditional noble metal catalysts has been growing intensively and great progress has been made in developing efficient transition metal-, and carbonbased alternatives.[132–135] However, notably, the catalytic activities of these electrode materials remain significantly inferior to that of traditional ones, which will no doubt limit their largescale application.

To improve the activities of these catalysts to match and even exceed that of noble metal-based catalysts, some effective strategies have been developed, such as engineering porous nanostructures,[136] doping non-metal elements (O, S, Se, B, P or N) or metal elements (Ni, Co, or Fe) in their structures,[137-140] constructing nanohybrids,[141-143]

and designing three-dimensional (3D) integrated electrodes,[144] etc. Among these favorable methods, fabricating a 3D porous nanostructure is an attractive way to dramatically improve the electrocatalytic performances of catalysts with two main advantages.

Firstly, without using any polymer binder such as Nafion, the integrated 3D catalysts can be directly employed as a working electrode by forming free-standing films or monoliths on current collectors, offering a large surface area, high-speed multidimensional electron transport pathways and good mechanical strength. [145, 146] The second advantage is its porous structure. On account of the pore sizes, they can be rationally classified into three different categories; macropores >50 nm, micropores <2 nm and mesopores 2–50 nm.[147] Various effective means have been developed to fabricate porous nanostructures, such as the sacrificial template method,[148-150] thermal decomposition of precursor materials (such as metal hydroxides and fluorides),[151,152] thermal carbonization of corresponding metalorganic– framework grown on current collectors,[153] sulfuration/selenation/phosphidation/nitridation of a corresponding metal oxide or hydroxide nanoarrays, [153-155] and selective etching layered double hydroxide nanoplate precursors containing amphoteric metal,[124] and so on. These methods allow for the introduction of mesopores or macropores into their 3D structures, further enlarging the surface area, increasing the number of catalytic active sites and shortening mass and ion diffusion length.[155]

The use of commercial 3D macroporous materials, foams such as Ni foam, FeNi foam, Cu foam, carbon foam, graphene foam, etc., have been brought to the forefront in heterogeneous catalysis in recent years for their flexible uses (Scheme 1). They can be used as 3D substrates, or current collectors, to grow or load catalytic active substances and even directly used as catalysts. Compared with other 2D and 3D supports such as carbon paper, carbon cloth, Ti mesh and Ti plate, foam has a highly macroporous structure, providing a larger surface area, more active sites and enhanced electrolyte penetration and gas diffusion. Its conductive and continuous 3D framework enables excellent mechanical strength and 3D fast electron-transfer pathways.

Figure 2-8. Schematic diagram of foam-based catalytic electrodes for HER, ORR, OER, and MOR.

Water Splitting

The urgent demand of establishing a clean energy economy, has increased efforts devoted to the search for renewable clean energy alternatives in the past several years.[155,156] Hydrogen (H_2), with its zero carbon content, has been recognized as one of the most promising energy carriers to cater for our need in future fuel applications.[157] The traditional steam reforming method for industrial H_2 production still consumes fossil fuels and the produced H_2 suffers from low-purity.[158] By contrast, electrochemical water splitting is considered as an effective and clean approach to produce H_2 with high-purity.[160] It involves two electrode reactions: the cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER). Actually, the production of H_2 from electrochemical water splitting is highly limited because it is a steep uphill reaction with a large overpotential (commercial electrolyzers operate at $\geq +1.8V$ whereas the theoretical ΔE^0 is $1.23V$ vs.

NHE).[161] Highly active HER and OER electrocatalysts are thus essential to be implemented to overcome the large water-splitting overpotential and thereby make this process more energy-efficient.[162]

Hydrogen evolution reaction

If a strong external voltage is imposed onto the cathode, water molecules will be decomposed and reduced into H₂, which can be stored for fuels. This half reaction can be expressed by the following Equation 1 and Equation 2

Under acidic conditions, HER undergoes three possible reaction steps (Equation 3, Equation 4 and Equation 5). On transfer of an electron to the cathode, it will capture a proton from the electrolyte to produce an intermediate state of an adsorbed hydrogen atom (H_{ads}) on the electrode surface:

If the H_{ads} coverage is relatively low, the H_{ads} prefers to couple with another electron a new proton to produce H₂:

If the H_{ads} coverage goes up beyond a certain point, the adjacent H_{ads} tends to recombine with each other, and with the further increase of H_{ads} coverage, the following reaction will become dominant:

No matter for which route, HER always involves the initial proton adsorption process.

Therefore, the free energy of hydrogen adsorption (DGH) is commonly used to theoretically evaluate the HER activities of catalytic materials.[163] The larger the absolute value of DGH is, the slower the overall turnover rate is. Pt, with a ΔH value of approximately zero, is the most active single-metal catalyst known for HER.

As is the case in acid, HER in base also experiences three reaction steps.[164] First, a water molecule couples with an electron to produce H_{ads} on the cathode surface: $H_2O + e^- \rightarrow H_{ads} + OH^-$ (Step 1 Volmer reaction). At the start, the H_{ads} tends to couple with another electron and catch a new water molecule to produce H_2 : $H_{ads} + H_2O + e^- \rightarrow H_2(g) + OH^-$ (Step 2 Heyrovsky reaction). Subsequently, if the amount of H_{ads} coverage increases, adjacent H_{ads} begins to couple with each other: $H_{ads} + H_{ads} \rightarrow H_2(g)$ (Step 3 Tafel reaction).

Open-cell metallic foams, such as Ni foam, FeNi foam and Cu foam, are the most commonly used 3D porous metal current collectors and have been widely applied in hosting catalytic active species due to their large surface area, high conductivity and good mass-transport properties.[165] Due to the inherent catalytic activities of Ni, Fe and Cu elements toward a variety of electrocatalytic reactions such as HER, these foams can perform well both as electrocatalysts and electrode support materials.

Therefore, in comparison to other substrates such as Ti mesh, Ti plate and carbon cloth, catalysts assembled on metallic foams will improve the catalytic performances of corresponding monolithic electrodes by synergistic effects. For noble metal catalysts, methods commonly implemented to load on metallic foams are electrochemical, spontaneous and chemical depositions, [166-168] forming free-standing particles or films on the surface of foams. Jerkiewicz et al. reported a 3D nanoscopic Pt electrocatalyst by chemical deposition of Pt on an open-cell Ni foam with low loading.[169] The resulting Pt-modified Ni foam (Pt/Ni foam) shows excellent catalytic activity towards the HER, which can even keep pace with the Pt

polycrystalline Pt (Pt (poly)) in a basic medium. Some explanations of this improvement in catalytic activity are given as follows. 1) The enhanced activity of Pt is due to electronic interactions between Pt and Ni. 2) The underlying Ni foam also has HER activity. 3) The 3D mass transport path to and from the surface of Pt nanoparticles on Ni foam improves the diffusion of reactants and products, contributing to a more efficient catalytic turnover. This unique 3D macroporous structure of Pt/Ni foam effectively decreases the use of noble metals to a minimal level, and facilitates the homogeneous distribution of electrodeposited metal particles, fully exposing Pt active sites and thus increasing the electrochemically active surface area.

Compared to noble metal loaded foam catalysts, transition metals (such as Ni, Co, Fe, Mo, W, and Cu) oxides and their derivatives grown or loaded on metallic foams have attracted great attention in heterocatalysis on account of their abundance, remarkable catalytic activity and high stability. In the past several years, a great number of reports on this topic have been published, which can be divided into two categories. The first category uses the metallic foam as electrode support material. Shen and co-workers synthesized a nanoflower like metallic conductive MoO_2 on Ni foam through a facile hydrothermal treatment followed by annealing treatments.[170] MoO_2 , similar to WO_2 with excellent activity toward HER reported by Zhang and co-workers,[171] has a distorted rutile crystal structure with complex bonding involving delocalization of some of Mo electrons in the conduction band,[172] that defines its metallic conductivity and thus potential application in electrocatalysis. When used as an integrated cathode toward HER, this MoO_2/Ni foam electrode shows ultra-high activity with an onset overpotential of near 0 V and a small overpotential of 55 mV to achieve 10 mA cm^{-2} as well as acceptable stability in basic conditions. The exchange current density of this catalyst was calculated to be up to about 1.8 mA cm^{-2} almost the same as that of Pt/C, thus again demonstrating its superior HER performance. Different from the metallic transition metal oxides such as MoO_2 and WO_2 , other transition metal oxides such as nickel oxide and cobalt oxide suffer from poor HER activities.

However, recent works revealed that metal-metal oxide hybrids such as Ni–NiO/CNTs, Ni–NiO/Cr₂O₃, Co–CoO/N-C, Co–CoO_x/Co-N-C have excellent catalytic activities toward HER,[173-175] which has triggered great attention on designing such catalysts. Chen and co-workers designed a 3D crystalline/ amorphous Co/Co₃O₄ core/shell nanosheets composed of a metallic Co core and an amorphous Co₃O₄ shell on Ni foam by combining a highly scalable solution growth method and a low-temperature hydrogen reduction treatment.[175]

This 3D foam supported Co/Co₃O₄ nanosheets catalyst enables a small overpotential of 90 mV to support a HER current density of 10 mAcm⁻² in 1.0M KOH. It can be explained as follows: the metallic Co core enhances the electrical conductivity and acts as an electron reservoir to ensure high current density and a hydroxyl-enriched amorphous Co₃O₄ shell (with some possible oxygen vacancies) favours the adsorption of water molecules and lowers the HER energy barrier. In addition, considering the increased conductivity of metal sulfides compared with metal oxides,[176] our group has demonstrated the feasibility of a one-step hydrothermal synthesis of Ni₃S₂ nanosheets array structure on Ni foam and using this monolithic electrode to actively catalyze the HER in both neutral and basic conditions.[177]

It only needs overpotentials of 123 and 220 mV to afford 10 mAcm⁻² in basic and neutral conditions, respectively. Zou and co-workers recently reported a cobalt acetate-assisted hydrothermal synthesis of single-crystalline g-Cu₂S nanoplates on Cu foam to efficiently catalyze HER at a neutral pH.[178] Besides these hydrothermally grown catalysts on metal foams can be used to actively catalyze the HER, electrodeposition of catalyst films on metal foams is also attractive to fabricate effective HER cathodes. Sun and co-workers developed a 3D nanoporous Ni-Mo alloy film on Cu foam by a facile electrodeposition method.[179] It exhibits ultra-high activity and stability toward HER with a negligible overpotential of 34 mV to drive 20 mAcm⁻² in 1.0M KOH, achieved through its well-controlled composition, desired surface roughness and Nano porosity.

Although all the above foam catalysts show high catalytic activity and good stability towards the HER in basic or neutral conditions, their catalytic activities toward HER in acid remain challenging because of their instability under these conditions.

This may be attributed to the inevitable dissolution of Ni from the catalysts or incomplete coverage of Ni skeleton in acid. To solve this problem, graphene-protected metal foams were explored to serve as robust collectors to load catalysts. Chang et al. developed a 3D graphene/Ni foam structure through the chemical vapor deposition (CVD) method and formulated MoS_x ($x+2$) catalysts on this substrate to form a rigid electrocatalytic architecture, in which the MoS_x materials were grown by the thermolysis of ammonium thiomolybdates at different temperatures in a H_2/Ar environment in a CVD chamber.[180] With effective improvement of the stability in acid, the normalized HER current density of this 3D $\text{MoS}_x/\text{graphene}/\text{Ni}$ foam catalyst is higher than that of MoS_x on other various planar carbon electrodes such as carbon paper and carbon cloth. The graphene sheets not only provide robust protection against acid but also effectively increase loading of the catalysts and enhance electrocatalytic efficiency towards HER. In other similar work done by Du and co-workers, graphene/Ni foam was first prepared by the CVD process in the presence of methane at high temperatures and Ni_2P nanoflakes were synthesized on graphene/Ni foam by sprinkling a thick layer of red phosphorous over the surface of graphene/Ni foam followed by annealing at 750°C under an Ar atmosphere.[181] When served as a cathode material, compared with $\text{Ni}_2\text{P}/\text{Ni}$ foam, the Ni_2P -graphene/Ni foam catalyst shows more efficient and robust HER activities in all pH values with very small onset overpotentials. The enhanced HER performance of this Ni_2P -graphene/Ni foam cathode can be rationally explained as follows: 1) graphene layers on Ni foam could prevent it from being oxidized in air and provides good electrical contact between the active catalyst and current collector; 2) the coated graphene sheet film provides a larger surface area and thus more active sites for this catalyst. These works demonstrate that the graphene-covering CVD process could highly improve both the catalytic activity and stability of Ni foam-based catalysts in acid. However, this process is energy intensive and time

consuming and the use of red phosphorus at high temperatures make it laborious and precarious. Cai et al. designed a facile multi-step electrodeposition and followed a low-temperature phosphidation synthetic method to fabricate a 3D Ni₂P-graphene/Ni foam structure (Figure 1a).[182] First, graphene nanosheets were electrodeposited on Ni foam and Ni₂P nanosheets were then fabricated on the graphene-Ni foam by low-temperature phosphidation conversion of the corresponding Ni(OH)₂ precursor. When used as an integrated cathode in acid, the Ni₂P-graphene/Ni foam exhibits promising catalytic activity toward HER with the need of a small overpotential of 75 mV to afford a current density of 10 mAcm⁻². Long-term stability test shows that, in contrast to Ni₂P/Ni foam, Ni₂P-graphene/Ni foam has a better stability with negligible decay after 5000 cycles and could well maintain a large current density at a overpotential of 100 mV for 60000 s (Figure 1b,c). In this system the electrodeposited graphene layer could also protect Ni foam from being oxidized in air and etched in acid and improve the conductivity of this electrode.

Figure 2-0-9 a) Schematic illustration of the synthesis procedure for the 3D architecture of Ni_2P -graphene/Ni foam. b) Polarization curves of Ni_2P -graphene/ Ni foam and Ni_2P /Ni foam before and after 5000 cycles. c) The timedependent current density curves for Ni_2P -graphene/Ni foam and Ni_2P /NF with static overpotentials of 100 mV for 60000 s.

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Chapter 3

Experimental Methodology

This section introduces the methods and materials used for the pollution degradation especially for the glycerol. Copper is one of the major metal materials that also possesses good catalytic properties in numerous fields. One of the advantages for Copper is the lower price which will decrease the cost of industrial application. Hence the Copper application in industrials becomes one of the hottest topics of nowadays. CGDE is one of the new technologies in wastewater degradation field. How to combine these materials and technology together in order to decrease the cost as well as increase the degradation rate. Herein, focus on how to combine these materials and technology together in order to decrease the cost as well as increase the degradation rate; HPLC and FTIR will be the main methods to analyze the major products and calculate the conversion rate. Detailed processes and essential equipment settings are elaborated. Advanced materials characterizations and electrochemical property testing techniques are also described.

3.1 Experiment Setting for glycerol degradation

The experimental setup adopted a two-electrode system shown in **Figure 3-1**. Pt foil (99.9% purity) is used as anode and Cu wire (99.9% purity) of 1 mm diameter as cathode in the 1 M NaCl electrolyte solution. The anode and cathode is connected to a low voltage 70 V DC power supply. 5 mL or 8mL glycerol was added with magnetic stirring for 2 min; 2 mL mixture solution was withdrawn at an interval of 10 min during the plasma discharge process. After centrifuging at 9600 rpm for 3 min, those samples were stored in the microtubes covered with aluminum foil to avoid light exposure.

Figure 3-1 Schematic diagram of the experimental setup

3.2 Experiment procedure for glycerol degradation

The voltage was slowly increased to 70 V at a ramping rate of 5 V/s. When the voltage exceeds the threshold value 55 V, bubbles started to appear on the surface of cathode. With voltage increasing, obvious plasma discharge region could be spotted surround the cathode, and large amount of oxygen bubbled out near anode as well. The products in liquid phases were analyzed with high performance liquid chromatography (HPLC, Agilent, USA) coupled with ultraviolet (UV) and refractive index (RI) detectors (**Figure**

3-2). The liquid analytes were separated using an Alltech OA-1000 organic acid column (300 mm × 6.5 mm, ID = 9 m), and eluted with 4 mM H₂SO₄ aqueous solution at 80 °C.

Figure 3-2 HPLC mythology

3.3 Characterization methods for glycerol degradation

Figure 3-3 FTIR spectrometer

The functional groups of the degradation products were analyzed by Fourier transform infrared (FTIR) spectrometer (Frontier, Perkin Elmer, USA), which was operated under the transmission mode with wave number ranging from 4000 to 400 cm^{-1} (**Figure 3-3**). A thin pellet of potassium bromide (KBr, specific for FTIR analyst) was prepared in a die (10 mm diameter, 2 mm thickness) set and used for baseline collection. A force is applied under a vacuum of 10 kPa for several minutes form transparent pellets. Degassing is performed to eliminate air and moisture from the KBr powder.

1 mL of each degradation product was made into a homogeneous mixture and drop-coated onto the surface of the same pellet. After 2 min, the sample was uniformly coated and dried for FTIR analyses with automatic baseline subtraction. A new KBr pellet was used for each sample and these steps were repeated when measuring the samples at 0, 10, 20, 30 and 40 min of discharging time.

The crystallinity and phases of the samples were characterized using a thin film X-ray diffractometer (XRD, XRD-6000, Shimadzu, Japan), which employs Cu K α radiation under 2 θ mode with X-ray grazing angle of 1.5°. The morphology and internal structure of the nanocomposites were further examined by using field emission scanning electron microscope (FE-SEM, JEOL JSM-7600F). X-ray photoelectron spectroscopy (XPS) for elemental analysis was conducted on a Kratos Axis Ultra DLD X-ray photoelectron spectrometer.

3.4 Experiment setting for Rh B

Three parallel metal foils (i.e. tantalum Ta, copper Cu, Ti foil and gold coated titanium Ti/Au) were chosen and used as cathode in the two-electrode system to compare with the combination method of adding the commercial P25 TiO₂ powders (Sigma, 99% purity) in terms of their degradable performance to rhodamine B. The cathode and anode are connected to a low voltage DC power supply. When the voltage exceeds the threshold value, a large number of gas bubbles are produced over the surface of the cathode forming a gaseous film that insulates the electrolyte

solution leading to the generation of liquid plasma discharge at the gas-solid interface in the solution. The value of threshold voltage is dependent on the electrolyte. In the present study, NaCl mixed with Rh B solution was used. During the degradation process, water bath was employed to control the temperature of electrolyte. Magnetic stirring at 300 rpm was also maintained to ensure the uniform concentration of Rh B (Sigma) in the solution.

Figure 3-4 Schematic diagram of the two electrode system

3.5 Characterization methods for Rh B degradation

Upon the completion of liquid plasma process, the obtained products were collected with the help of centrifugation followed by washing for several times with deionized water to remove the NaCl salt. After drying for 10 h in oven, the crystallinity and phases of the samples were characterized using a thin film X-ray diffractometer (XRD, XRD-6000, Shimadzu, Japan), which employs Cu Ka radiation ($1 \frac{1}{4} 0.154059$ nm) under 2θ mode with X-ray grazing angle of 1.5° .

All samples were placed at the stage height of 7.3 mm and scanned at the rate of 1° min^{-1} within the range $20^\circ \leq 2\theta \leq 80^\circ$. The morphology and internal structure of the nanocomposites were further examined by using field emission scanning electron microscope (FESEM, JEOL JSM-7600F) and high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2100F) at an accelerating voltage of 200 kV, respectively. Raman spectra were conducted on a Horiba Micro Raman HR Evolution System.

X-ray photoelectron spectroscopy (XPS) for elemental analysis was conducted on a Kratos Axis Ultra DLD X-ray photoelectron spectrometer. Concentration of Rh B present in the electrolyte as a function of liquid plasma discharge time was monitored in every 10 min. Each time, a sample with 3 ml solution was retrieved from the electrolyte and subsequently centrifuged at 8000 rpm for 2 min. The Rh B concentration of the sample was then measured using the UV-visible spectrophotometer (UV-2700, Shimadzu) with the wavelength ranging from 400 to 700 nm at a medium scanning speed and in an auto mode of the sampling interval.

Figure 3-5 LC-MS setting

The LC-MS and GC-MS were used to illustrate the degradation mechanism of this combined degradation method. The obtained supernatant in different time intervals was centrifuged at 9000 rpm for 3 min and the clear supernatant was diluted ten times in volume ratio of 9:1 with methanol. The clear solutions were detected by LC-MS (Thermo Scientific, Accela Autosampler, 1250 Pump, USA) equipped with an electrospray ionization (ESI) positive ion mode. The test samples were infused at the rate of 5 mL min⁻¹, whereas the other parameters were kept as follows: capillary temperature 350 °C, source voltage 5 kV and the electron multiplier voltage 1350 V. The peak patterns were recorded in the m/z range of 90-450. The clear solutions were also conducted by a GC-MS (Thermo Fisher Scientific DSQ, USA) with positive ion 70 eV EI mode. The measure temperature was set in the range from 80 °C to 300 °C and the running time 18 min with the sample of 0.5 mL

Figure 3-6 The UV-visible spectrophotometer

Chapter 4

Results and Discussion

This section summaries the experimental data. According to the experiment procedure, some of the phenomena need to be further analyzed and discussed. In the meantime, based on the characterizations and testing, the results are analyzed, trend lines are established and the reasons contributing to the properties are thoroughly discussed. According to the literature review, different experimental process of degradation have been introduced and discussed. Different figures corresponding to different chemicals characteristic performance in FTIR as well as HPLC helped to get results more obvious and convenient to compare with other research.

4.1 Results

● Results of glycerol degradation

On completion of plasma discharge, the obtained CuO particles were collected by centrifugation then washed for several times with deionized water to remove the recrystallized NaCl salt. After drying for 24 h in oven, the morphology and internal structure were characterized by FESEM, as shown Fig4-1. The particles are uniform with the size about 40 nm. The XRD patterns of CuO nanoparticles were illustrated in Fig. 4-1b). Fig. 4-1c) and 4-1 d) showed the X-ray photoelectron spectroscopy (XPS) was performed to further clarify the phase structures of CuO. As usual, the calibration was made by using the C 1s peak (284.6 eV). The binding energy of O 1s can be fitted well by two peaks located at 529.8 and 531.6 eV, which can be ascribed to the respective O²⁻ from CuO, in agreement with the XRD results. And the peak 531.6 eV was associated with O²⁻ species in the lattice and oxygen defects [36,37]. In the Cu 2p spectra, typical Cu 2p_{3/2} peaks were observed with binding energies of 933.8 eV, whilst their associated shakeup peaks at 941.2 and 963.8 eV were also visible. These Cu 2p peaks were consistent with previous studies of CuO [38]

Figure 4-1 CuO nanoparticles generated in the LPD process. (a) the SEM image, (b) the XRD image, (c) the high-resolution XPS spectra of O 1s and (d) Cu 2p.

Based on the HPLC mythology, **Figure 4-2** shows the chemical concentration for different degradation time. As the different retention time, the chemicals could be indicated as well as calculated by the related area. Hence, a series of figures will display the results of 5ml glycerol added.

Figure 4-2 Degradation products of 1 M NaCl solution with addition of 5 mL glycerol (0 min CGDE)

The major peak shown in **Figure 4-2** can be the base line to indicate the retention time of glycerol and conversion rate without CGDE. As the glycerol added into the solution, without CGDE, the degradation still could occur.

After 10 min reaction (**Figure 4-3**), the concentration of glycerol decreased as other chemicals' concentration increased. Hence, the CGDE played a critical role in the catalytic degradation process.

Figure 4-3 Degradation products of 1 M NaCl solution with addition of 5 mL glycerol (10 min CGDE)

Figure 4-4 Degradation products of 1 M NaCl solution with addition of 5 mL glycerol (20 min CGDE)

Figure 4-5 Degradation products of 1 M NaCl solution with addition of 5 mL glycerol (30 min CGDE)

Figure 4-6 Degradation products of 1 M NaCl solution with addition of 5 mL glycerol (40 min CGDE)

As degradation time increased, **Figure 4-4** to **Figure 4-6** show that the concentration of glycerol keeps decreasing with other chemicals increasing at the meantime. Hence, the catalytic degradation effect of CGDE is obvious.

Figure 4-7 Degradation products of 1 M NaCl solution with addition of 5 mL and 8 mL glycerol

In order to express the results more obvious and convenience, the data of retention time and relevant area have been plotted in **Figure 4-7** for both 5ml and 8ml glycerol added in, which illustrates the degradation products of 1 M NaCl solution with addition of 5 mL and 8 mL glycerol. Five main peaks are shown for different retention time of 11.54, 12.26, 12.93, 14.14 and 14.56 s. With the plasma discharging time increasing, the peak area increases for the peaks at retention time of 11.54, 12.26, 12.93, 14.14 s while decreases for the peak at retention time of 14.56 s. It can be predicted that the four increasing peaks represent the oxidation products while the decreasing one is the reactant (glycerol). The peaks are indexed to their representing chemicals according to the FTIR spectrum obtained and matched with relevant literatures; the four main degradation products

might be glyoxylic acid, glyceric acid and so on, and are proved with standard HPLC solutions (results are shown in **Figure 4-8**).

Figure 4-8 HPLC graphs of standard solutions (glyoxylic acid, glyceric acid, glyceraldehyde and glycolic acid)

In the experiment, glycerol was added into 50 mL 1 M NaCl solution; according to the density and molecular weight of glycerol, 0.068 mol of glycerol was added in. For the calculation convenience, 0.168 mol of glycerol per 10 mL 1 M NaCl solution was set as the standard for the first four oxidation products; then 0.168 mol of the oxidation products were dispersed into 10 mL 1 M NaCl solution to form the standard HPLC solution

while 0.1 mL of glycerol per 1 mL NaCl solution was set as the standard for glycerol. 1.5 mL of each standard HPLC solution was transferred into a test bottle and measured by HPLC to get standard retention time and peak area for these chemicals (**Figure 4-8**). Therefore, the peaks at retention time of 10.26, 11.54, 12.26 and 12.93 s are glyoxylic acid, glyceric acid, glyceraldehyde and glycolic acid respectively; while for the peak at retention time of 14.14 s, it is named as Product 4; meanwhile, it is obvious that the amount of glyceraldehyde is more than others.

In addition, oxidation products: glyceraldehyde, glycolic acid and glyceric acid are the dominating chemicals which can be directly used as or transformed into important industrial chemicals of food, pharmacy and so on [11]. Hence, by the CGDE, glycerol can be used as the raw material for industrial production of many useful chemicals.

The real concentration of each product and reactant is calculated based on the HPLC results of the standard chemical solutions. Based on the principle of HPLC, the ratio of chemical's concentration to peak area is a constant; hence, for the standard solution, the concentration and peak area (from HPCL results) are known, therefore, the ratio can be calculated according to Equation 6:

Equation 6 Calculation of conversion rate

$$K_n = \frac{C_0}{A_0} \quad (6a)$$

$$C_t = A_t K_n \quad (6b)$$

$$Conversionrate = \frac{C_0 - C_t}{C_0} \times 100\% \quad (6c)$$

Where K_n is the ratio of the concentration and area, C_0 is the concentration of standard solution, A_0 is the peak area of standard solution in HPLC figure. C_t and A_t are the concentration and peak area of sample solutions after specific durations of discharging.

As shown in **Figure 4-8**, at retention time of 14.56 s, the standard peak area is measured as 112.6 units for 1.36 mM glycerol, and the concentration/area ratio is 0.01215 mM per unit area. Based on the equations and results above, the real concentration of glycerol in

the production solutions and conversion rates are calculated and summarized in **Table 4-1**.

Table 4-1 Concentrations and conversion rates with different durations of discharging

Time(min)	5 mL glycerol		8 mL glycerol	
	Concentration (mM)	Conversion rate(%)	Concentration (mM)	Conversion rate(%)
10	0.3475	39.40	0.3584	64.73
20	0.2843	50.40	0.3305	71.15
30	0.2127	62.90	0.3005	78.40
40	0.1846	67.80	0.2588	81.27

Table 4-1 shows that the conversion rate rapidly increases in the first 20 min and especially in the first 10 min, during which it reaches almost 40% with 5 mL glycerol added and exceeds 60% for 8 mL glycerol; with the time increasing, the conversion rate increased more slowly and after 40 min of discharging time, it reaches 67.8% and 81.27% with 5 mL and 8 mL glycerol added, respectively. This phenomenon might be due to the increase of the amount of reactant (concentration of glycerol is increased). For enough plasma energy supplied, the increasing concentration of glycerol will enhance the effective utilization rate of the energy produced by plasma. In addition, part of the input energy is transformed into solution by thermal conduction, after the experiment, the solution temperature increase to 60 °C from room temperature. According to the previous research, high temperature might accelerate the oxidation of glycerol. When increasing the amount of the glycerol under certain limited value, more glycerol will be oxidized and with the discharge time increasing, the amount of the glycerol is reduced, so the conversion rate will increase more slowly.

According to **Figure 4-9** and the literatures [1], the different functional groups present in

the samples can be indexed and matched by FTIR spectroscopy. For example, the peak at the wave number of $\sim 3469\text{ cm}^{-1}$ represents the -OH group, it might be the -CH- group at 2888 and 2956 cm^{-1} , and it could be C=O, C=C or mixture of them at $\sim 1650\text{ cm}^{-1}$. Hence according to the FTIR analysis and relevant literature, the composition of the products could be verified.

Figure 4-9 FTIR spectrum of degradation product

Figure 4-10 Voltage-current characteristic curve

Both the ionization and excitation of H_2O molecules by solution plasma rapidly produce $\cdot\text{OH}$, which is necessary for the degradation of glycerol. Many researchers detected the radicals generated during glow discharge to verify the model by optical emission spectroscopy method [25, 30, 33], which found the outstanding hydroxyl radical $\cdot\text{OH}$ at 309 nm with the high peak intensity [30]. It is indicated that the generated hydroxyl radicals $\cdot\text{OH}$ played a crucial role to degrade the glycerol in the solution plasma with a low voltage.

Based on the research done previously on oxidation of glycerol [4, 11], with consideration of the degradation products, the plausible degradation mechanism of CGDE was suggested as shown in **Figure 4-11**, in which there are two possible degradation ways in this experiment. First of all, the high energy of the plasma might break the C-C chain of the glycerol, hence it will be converted into several smaller fragments; the second is the

oxidation reaction.

● Results of the degradation of Rh B

In the degradation process, the discharge voltage was set to be 80 V with the output power of approximately 60 W. 5.85 mg of NaCl was dispersed as electrolytic irons in 100 mL of 0.6 mM Rh B solution (initial pH 7–8). The cathode with the area of 0.8 cm² was immersed into the electrolyte. **Figure 4-11** shows the concentration ratio of Rh B as a function of the discharge time for four different cathodes (i.e. Ti, Ti—Au, Cu, Ta). The results show that Ti—Au electrode offers the most rapid degradation to Rh B. Cu electrode degrades the Rh B faster at the beginning but becomes lower than Ti electrode after around 45 min. Rh B is degraded at the lowest speed in Ta electrode system with some amount that is still remained in the electrolyte after 50 min. In contrast, all Rh B in the electrolyte is almost removed by the other three electrodes. An additional experiment was carried out by using Ta foil electrode with TiO₂ mixed in the electrolyte, which was found to degrade the Rh B faster than Ta electrode. This result verifies the additional photocatalysis performed by plasma-irradiated TiO₂ in the solution that accelerates the degradation of Rh B.

Figure 4-12 Degradation of Rh B (concentration of 0.6 mM) with four different cathode materials. a, degradation efficiency curves and b, degradation rate curves with Ti foil, Ti—Au foil, Cu foil, Ta foil and Ta foil– P25 TiO₂ powders. The inset of b, absorption spectra of Rh B after different discharge time with Ti foil cathode.

Among the four metal electrodes, Au coated Ti has the highest electrical conductivity over the rest three metals. Cu comes to the second and is more electrically conductive than Ti followed by Ta. It is the electrical conductivity that plays an important role in the plasma discharge efficiency. As proved by **Figure 4-11** the degradation rates of different cathodes (apart from Ti based foil) are linear with the discharge time. Therefore, rate constant k_a is actually a measure of the slope gradient of the straight line which is also called as the apparent reaction rate constant for the degradation. Thus, Fig. 2b is a plot transformed from Fig. 2a. It can be used to figure out the degradation rate and evaluate the degradation rate by plasma-induced process. The inset image of Fig. 2b is the UV-vis absorption spectra images collected at different times of the Ti foil cathode discharge. It is observed from the UV-vis studies that the absorbance maxima of Rh B solution remain relatively constant at 554 ± 3 nm.

Based on **Figure 4-11**, the $k_{40\text{min}}$ values of the foil electrodes in the order of Ti, Ti—Au, Cu, Ta — TiO_2 and Ta were measured to be 52.5×10^{-3} , 73.7×10^{-3} , 62.8×10^{-3} , 37.5×10^{-3} and $20.9 \times 10^{-3} \text{ min}^{-1}$, respectively. Apparently, Ti—Au foil offers the highest degradation rate, whilst Ta foil electrode performs the weakest in the degradation of Rh B. Cu foil electrode starts with the larger degradation rate but turns out to be smaller than Ti foil electrode after ~ 40 min discharge. This is due to the Ti foil that produces TiO_2 particles during the discharge process. The presence of TiO_2 particles in the electrolyte increases the degradation of Rh B as the plasma was generated with a wider range of waves. This catalysis-assisted plasma degradation process is shown in **Figure 4-11** marked as Part II if the plasma-induced process is denoted as Part I. However, the Cu and Ta oxide particles produced from their respective electrodes during plasma discharge have no photocatalytic performance. As a result, the fast degradation achieved by Ti foil is benefited from its bifunctional processes, i.e. cathode plasma degradation and photocatalysis. Therefore, it is reasonable that the apparent reaction rate constants k_a is significantly improved and much higher (up to one order of magnitude) than the degradation rate induced by the pure photocatalysis of TiO_2 based materials as reported in the reference (Rasalingam et al., 2015).

This cathodic LPD can be classified into partial electrical discharge, in which the electric fields for initiation of such plasma discharge are on the order of 10^8 V m^{-1} . So the conductivity of cathode plays an important role in parameters of the generated plasmas. Higher electric conductivity of cathodes causes a larger discharge current and stronger intensity of plasma, which benefit the photocatalytic process and generate more chemically various active species, such as $\bullet\text{OH}$ radicals, $\bullet\text{H}$ radicals, H_2O_2 , and hydrated electrons. In this work, it is obvious that the electric conductivity of Ti—Au and Cu is higher than pure Ti and Ta. Therefore, in Part I process, the degradation rates of Ti—Au is the fastest compared with other material electrode. In Part II process, the photocatalysis play dominant degradation mechanism. Among the Au coated Ti foil (Ti—Au), Ti foil, and Ta foil added with P25 TiO_2 powder, Ti—Au has the best electric conductivity and therefore generates strongest intensity of plasma to improve the photocatalysis. It has been demonstrated that the TiO_2 -Au nanocomposites exhibit strong absorption of visible light owing to the presence of Au NPs on the surface of TiO_2 forming a schottky barrier at the interface resulting in a shift of Fermi level to lower potential. A detailed explanation of fast degradation rates of Ti—Au is that the Au thin film coating on the Ti foil improve the electric conductivity to generate stronger intensity of plasma and the gold NPs generated by the plasma discharge restrain the recombination of conduction band (e^-) and valence band hole (h^+) to enhance the TiO_2 photocatalytic activity.

Dependence of the degradation on the initial concentration of Rh B for Ti foil electrode was investigated with the results presented in Fig. 3. Three different initial concentrations of Rh B were selected, which were 0.6, 0.2 and 0.05 mM. The plasma generated from Ti foil electrode rapidly destroys almost the all 0.05 mM Rh B molecules in the electrolyte within approximately 30 min in Part I and therefore the degradation rate dramatically falls down in Part II. At a higher Rh B concentration of 0.2 mM, the degradation rate slows down in Part I but goes up quickly in Part II. The complete removal of Rh B in the electrolyte requires 50 min. Although the initial Rh B concentration increases three times higher than 0.2 up to 0.6 mM, the full decomposition of Rh B molecule still needs about

50 min. It is the relatively higher degradation power offered in Part II that satisfies this which compensates the degradation rate drop in Part I.

Figure 4-13. Degradation of different concentration Rh B with Ti cathode materials. a, degradation efficiency curves and b degradation rate curves of concentration 0.6, 0.2 and 0.05 mM.

Subsequently, the particles formed after LPD with Ti based metal foil were further characterized by XRD, SEM, TEM, Raman and XPS **Figure 4-12** and **Figure 4-13** show the X-ray diffraction (XRD) patterns of different particles that are formed by the pure Ti foil and Au coated Ti foil (Ti—Au) after plasma discharge, commercial TiO_2 after and before plasma discharge, and marked as sample 1 to 4, respectively. Two compositional phases (i.e. TiO_2 and Ti_9O_{17}) are identified from samples 1(Ti foil) and 2 (Ti—Au) from **Figure 4-12**. It is worth noting that Au is determined from sample 2. It is reasonable that samples 1 and 2 appear grey, which are different from the colour of white commercial TiO_2 (**Fig. SM 1**). The oxygen defects of $\text{Ti}_n\text{O}_{2n-1}$ are responsible for the colour change of particles. The Au film coated on the Ti foil improves the electrical conductivity in the plasma discharge process, but also produces many Au NPs attached in the Ti oxide particles, affecting the morphology of products (**Fig. SM. 2**) shows the spherical Ti oxide particles that are formed after the liquid plasma discharge 50 min. Due to the Joule heat, partial melting and gasification may take place around the surface and tip of Ti cathode. The applied electric field allows the cations in the plasma to bombard the cathode leading to the occurrence of a sputtering event. When the molten metal from the cathode dissolves into the solution at ambient condition, spherical particles are then formed as a result of the reduc-

tion of the surface free energy based on the effect of surface tension and cohesion. **Fig. SM.3** is a bright-field TEM image showing a single Ti oxide particle, which appears a solid sphere. The in-set FFT (fast Fourier transform) pattern, a reciprocal image of the high-resolution TEM image (Fig. SM.3b) taken from the square marked area in Fig. SM.3a is generated from TiO_2 at the zone axis of $[1\ 1\ 1]$ by indexing.

Figure 4-14. Plasma discharge product after discharge 50 min. (a) The XRD image of particles formed after plasma discharge with Ti foil and Au coated Ti foil (Ti -Au), (b), (c) and (d) the SEM image, the TEM and HRTEM images of particles formed after discharge of Ti foil-Au, and FFT images (inset).

Fig. 4-12b shows some spherical particles (TiO_2) along with flower-like particles decorated on the sample 2 that are identified to be Au NPs from the high-resolution TEM im-

age (Fig. 4c). The in-set FFT patterns, corresponding reciprocal images of the high-resolution TEM image taken from the respective square marked areas in **Figure 4-12**, are generated from TiO_2 at the zone axis of $[0\ 0\ 1]$ and Au at the zone axis of $[1\ 0\ 1]$ by indexing. The Au particles are very small in size (less than 10 nm) and are believed to produce very active catalytic performance (Ayati et al., 2014). The presence of Au nanoparticles was further proven by EDS, XPS and Raman analysis below. It is worth noting that many Au NPs are distributed around the Ti oxide particles in **Figure 4-12**. The Au NPs are evident as small dark spots, while the Ti oxide substrate is brighter and larger. **Figure 4-12** clearly shows a gold nanoparticle less than 5 nm in size that is well dispersed on the TiO_2 particle. **Fig. SM.4** obviously shows a peak around 1590 cm^{-1} , which indicate the presence of Au nanoparticles. The EDS mapping images (**Figure 4-14**.) was performed to further clarify the Au nanoparticles distributing on the TiO_2 particles. The presence of Au nanoparticles on the surface of TiO_2 creates schottky contact at the interface allows a shift of Fermi level to negative potential leading to the increase of the interfacial charge transfer process and the decrease of the recombination rate of electron/hole pairs in TiO_2 nanoparticles. As a result, a high quantum efficiency and enhanced photocatalytic activity are achieved. During the liquid plasma discharge, the annealing process at the low temperature solution improves the formation of the close Au— TiO_2 schottky contact (Ding et al., 2014). In addition of the small Au NPs supported by the TiO_2 particles that provide a high surface to volume ratio and strong quantum-size effect (Kim et al., 2013), the synergy of Au with Au—Ti cathode renders remarkably improvement on the catalytic performance. It is believed that in this hybrid process of plasma discharge, the TiO_2 base supported Au NPs is attributed to effectively remove organic pollutants.

Figure 4-15. The EDS mapping of particles formed after plasma discharge with Au coated Ti foil.

These results were further verified from the high-resolution XPS spectra of Ti 2p, O 1s and Au 4f (**Figure 4-14 and Fig. SM5**). In the Ti 2p spectra (**Figure 4-14**), typical Ti 2p_{3/2} and Ti 2p_{1/2} peaks are observed with binding energies of 458.4 and 464.3 eV (Karbalaee et al., 2018). **Figure 4-14** shows the Ti 2p peaks of sample 1 (Ti foil) and 2 (Ti - Au) shift to lower bonding energies compared with the commercial TiO₂ (sample 4), attributed to the oxygen defects after plasma discharge. The binding energy values at 530 and 531.4 eV are associated with O²⁻ species in the lattice and oxygen vacancies or defects (Cui et al., 2016). **Figure 15 d** shows that the binding energy of Au 4f can be fitted well by two peaks located at 83.8 and 87.5 eV, indicating the formation of gold NPs on TiO₂-Au nano-composite (Guo et al., 2018).

Figure 4-16. XPS analysis of TiO₂/Au particles. a, high-resolution XPS spectra of Ti 2p, c, O 1s, d, Au 4f and b, the Ti 2p of four particles (Au coated Ti foil after plasma discharge, Ti foil after plasma discharge, commercial TiO₂ after and before plasma discharge).

4.2 Plausible degradation mechanism of CGDE

Figure 4-10 showed the typical voltage-current curve in the liquid plasma discharge process [40]. When the voltage E is below 1.8 V (the theoretical electrolysis voltage of water is 1.229 V), the current i is zero because the water cannot be electrolysed, and the solution resistance is large. With increasing voltage E from point, A to point B, the current i also show an increasing trend. Owing to the Joule heating during the oxidation reaction, the solution around the cathode gets gasified and generates gas bubbles that coalesce to form a continuous pulsating thin vapor sheath around the whole copper electrode and isolate the cathode surface from the electrolyte solution. When the voltage is sufficiently high (point B), the plasma discharges are initiated. The color changing is observed

on the surface of electrode in the solution, and the current i sharply drops to mA level. In addition, there is physical action through the Joule heating to bombard the copper cathode, where the temperature of discharge point in the plasma region is approximately 10000 K. Then the bombarded Cu particles were oxidized by the strong oxidizing agents of plasma. The major component in this system is H_2O molecules, contains two states: vapor H_2O molecules in the plasma reaction zone around the cathode electrode and liquid H_2O molecules in the liquid phase reaction zone near the plasma-catholyte solution interface [28], [41].

In the plasma reaction zone (Equation 7), due to the plasma, the water molecules mainly produce large number of free radicals ($\cdot OH$, $\cdot O$), which are strong oxidizing agents [42], [43].

On the other hand, in the liquid-phase reaction zone (Equation 7), each electron e_{plasma} emerging from the plasma reaction zone can break up liquid H_2O molecules and becoming bound to form hydrated electrons e_{aq}^- :

Under cation bombardment on the copper cathode(), the free Cu particles would be oxidized by the $\cdot OH$ free radicals and H_2O_2 , as shown in the following chemical reactions (Equation 8 and Equation 9):

The H_2O_2 which were generated around the cathode plasma discharge zone was the preferred oxidizing agent for the reaction and CuO doesn't supply oxygen for the reaction, like that in the Mars van Krevelen type mechanism [19]. In addition, the generation of the

CuO catalysts in the presence of H_2O_2 was required for the transformation of glycerol to other fragments.

Both the ionization and excitation of H_2O molecules by solution plasma rapidly continuously produce abundant $\bullet\text{OH}$ and other free radicals to degrade glycerol. Many researchers detected the radicals generated during glow discharge to verify the model by optical emission spectroscopy method [40], [44], [45], which found the outstanding hydroxyl radical $\bullet\text{OH}$ at 309 nm with the high peak intensity [40].

The oxidational potential (2.8 V) of hydroxyl species $\bullet\text{OH}$ was only lower than that of F_2 (3.03 V), which has very stronger oxidation action. Although the hydroxyl species has short lifetime (few hundreds μs), their reaction rate constants with organic pollutions was much faster ($10^7 \sim 10^9 \text{M}^{-1}\text{s}^{-1}$) than ozone. And the highly activated species $\bullet\text{OH}$ generated by LPD in water can easily diffuse into the solution to oxidize the organics in close proximity to plasma discharge zone in water. Due to the temperature near the cathode electrode was higher than average temperature of electrolyte, which make temperature gradient to cause the electrolyte convection, improving the oxidation of glycerol. In addition, due to the high voltage, the anode region would generate O_2 bubbles and small amount of ClO^- , which could improve the degrade efficiency. Therefore, the NaCl solution not only provides the conductive pathway for plasma discharge but also generate strong oxidizing ion ClO^- , which could improve the degrade efficiency. A comparison Table S1 (in appendix) of this bifunctional cathode glow discharge with other plasma discharge technologies is provided and shows the larger energy yield of bifunctional cathode glow discharge with the degradation efficiency of 10.02 g/(kW h).

Based on the research done previously on oxidation of glycerol [9], [46], with consideration of the degradation products, the plausible degradation mechanism of LPD was suggested in Fig. 6, in which there were two plausible oxidation ways for this experiment. First of all, due to the high intensity electric field in water, the high energy of the plasma might break the C-C chain of the glycerol, hence it will be converted into several smaller

fragments and the high active species in the plasma region result in the glycerol oxidation; the second way was the dehydration reaction around the cathode with the CuO catalysts. In addition, for this experiment design, the cathode generated large volume of hydrogen due to the water splitting, which improved the copper-based catalysts hydrogenation reaction with the glycerol [47].

Figure 4-17 Plausible process of degradation for glycerol

In this hybrid method of LPD with the tantalum foil as cathode, the primary chemical reactions produce species ($\cdot OH, \cdot H, H_3O^+$) which then either recombine to form stable by-products (hydrogen peroxide H_2O_2 and hydrogen H_2), or return to a lower energetic state and emit UV light (Equation 10)

The main radical species in plasma generated by the electrical discharge plasma in water include $\cdot\text{OH}$ (294 and 308 nm), H (656 nm Ha and 486 nm Hb), and $\cdot\text{O}$ (777 and 845 nm) as determined by optical emission spectroscopy (OES). Among these free radicals, hydroxyl radical ($\cdot\text{OH}$) which has a highest redox potential of 2.8 V attacks the organic pollutants molecules with a rate constant in the order of $10^6\text{--}10^9\text{ M}^{-1}\text{ s}^{-1}$, approximately 10⁹ times faster than ozone. Although hydroxyl radicals $\cdot\text{OH}$ are short lived and decay quickly, they can diffuse into the solution to break up organic pollutants through hydrogen abstraction, electron transfer, and formation of a double bond with the organic compounds in close proximity to plasma discharge zone. On the other hand, in the liquid-phase reaction zone, $\cdot\text{OH}$ itself could combine to form H_2O_2 which subsequently attacks the organic compounds in aqueous solutions. The TiO_2 particles generated in the plasma discharge zone diffuse into liquid-phase reaction zone, resulting in photocatalytic process stimulated by the plasma, in particular, in the form of ultraviolet radiation. The main reaction pathway of plasma induced photocatalysis may proceed as follows (Equation 11, Equation 12, Equation 13 and Equation 14)

Therefore, both the hydroxyl radicals $\cdot\text{OH}$ and hydrogen peroxide H_2O_2 play an important role in the destruction of organic compounds. Based on the LC-MS and GC-MS identification, the possible photocatalytic degradation pathway of Rh B in this combined degradation technique was proposed and illustrated in Fig. SM.6. As shown in Fig. 7, the peak of m/z 443, attributed from the pure Rh B disappears in 30 min, in agreement with the experiment above. Those other peaks at m/z 431, 415, 362 and 304 are likely generated by N-de-ethylation process of pure Rh B.

However, several other small peaks (at different m/z values of 226, 199, 130 and 94) are also observed after different discharge times. In particular, two peaks at m/z 431 and

226 are visible, which Fig. 6. XPS analysis of TiO₂/Au particles. a, high-resolution XPS spectra of Ti 2p, c, O 1s, d, Au 4f and b, the Ti 2p of four particles (Au coated Ti foil after plasma discharge, Ti foil after plasma discharge, commercial TiO₂ after and before plasma discharge). 346 C. Li et al. / Chemosphere 214 (2019) 341-348 indicate the replacement of hydrogen by hydroxyl to m/z of 415 and 210, respectively. N-de-ethylation, de-alkylation, de-amination, de-carboxylation, de-hydration, cleavage of chromophore, and the breakage of ring structure are reported to be ways of the degradation of Rh B. Based on the GC-MS data, in this hybrid degradation process, the fragmented peaks of m/z of 74, 83, 90, and 192 may be the results of the occurrence of N-de-ethylation, cleavage chromophore and hydroxyl replacement, owing to the $\cdot\text{OH}$ and H_2O_2 generated by the plasma and photocatalysis that break up organic pollutants. The destruction of the chromophore structure of Rh B causes the production of some organic acidic molecules by opening-ring process, which can be mineralized to water and carbon dioxide.

Figure 4-18. The mass spectra of the degradation products in the different time intervals.

Titanium-based metal foil is discovered to play bifunctional roles in the rapid degradation of organic pollutants for the in-situ hybrid induced photocatalytic method proposed in this work.

The Au film coated on the Ti foil improves the electrical conductivity in the plasma discharge process, and also produces many gold NPs to enhance the photocatalytic performance. The generation of the plasma discharge from the cathode allows the organic pollution molecules to be attached through hydrogen abstraction, electron transfer, and formation of a double bond with the organic compounds in the plasma discharge zone. On the other hand, the TiO_2 particles produced during the plasma discharge process from Ti-based metals act as catalyst in the electrolyte and perform the photocatalytic process that significantly enhances the degradation of organic pollution. Along with the plasma discharge process, the degradation rate improves up to one order of magnitude over the traditional TiO_2 -based particles photocatalytic technique. This study opens a possible way to modify the TiO_2 particles with noble metal and to improve water treatment efficiency in hybrid method of discharge plasma.

Fig. SM.1, The XRD patterns of commercial TiO_2 powder before (red line) and after (blue line) plasma discharge.

Fig. SM.2, The SEM image of particles formed after plasma discharge with Ti foil

Fig. SM.3, the particle formed after plasma discharge with Ti foil, a, TEM image of spherical Ti oxide particles b, HRTEM image taken from the area marked with a red rectangle in a).

Fig. SM.4, the Raman spectra of Au coated Ti foil after plasma discharge and Ti foil after plasma discharge.

Fig. SM.5, the XPS survey of four different particles (Au coated Ti foil after plasma discharge, Ti foil after plasma discharge, commercial P25 TiO₂ after and before plasma discharge), and the lower binding energy range (55-115 eV) (inset).

Fig. SM.6, Plausible process of Rh B degradation

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Unfinished experiment results:

Retention time	Sample A	Sample B	Sample C	Sample D	Sample E
2.379	--	--	--	133.18	--
2.657	--	682.60	--	--	--
2.982	--	--	--	--	1002.78
3.015	--	--	--	55.74	--
3.117	2338.21	1576.26	2067.68	--	883.89
3.762	--	--	--	--	461.14
4.526	336.55	298.16	--	--	--
4.692	--	--	479.19	--	124.35

HPLC results of Sample(0min)

HPLC results of Sample(10min)

HPLC results of Sample(20min)

HPLC results of Sample(30min)

By analyzing the figure and hplc results above, there is table which will present the result more obviously. As the table shown that, the chemical which retention time is 2.67 and 3.717 will decrease at first and as experiment keep going on, the peak area will increase. It is not similar to the glycerol and Rh B, which might due to the complex structure and components. The reactant used in this experiment was the mixture of several different chemicals. In addition, the sulfonated resin has a complex structure hence while the high energy applied on it, the chemical bond might be broken and intermediates would be produced. The chemicals at retention time 2.670 and 3.717 might be the intermediates. When the reaction just happened, there is a large amount of reactant the rate of intermediates generated will faster than the rate of it degraded. As time kept going on, the reactant has been degraded hence there was limited reactant which lead to decrease the generating rate. Then amount of the intermediate will decreased.

The HPLC results of Sulfonated resin by using Cu wire:

The HPLC Result of Sulfonated resin by using Cu Wire:

Retention time (min)	Sample A	Sample B	Sample C
2.670	1290.22	1006.33	1285.89
3.717	438.66	299.74	877.88
3.851	214.55	186.96	--
4.175	85.58	46.79	--
4.304	104.14	65.19	186.77
4.512	94.71	--	156.69

As changed the electrode materials to Cu wire, it is obvious that the HPLC results different from the previous one. Which might due to the different elements emitted during the discharging period. By comparing the wire and foam, it is obvious that by using the Ni and Ni alloy's foam, there are faster degradation rate than the Cu wire. According to the literature review, the materials in foam structure will offer reaction area and more bubbles would be generated during the experiment period.

Chapter 5

● Conclusions and Future Work

Among the whole experiment, in order to find out the new efficient methods that can improve the existing water pollution degradation system, different types and forms of materials have been tried out. This experiment combined different methods and materials and has made a great improvement in the water pollution degradation rate. Following conclusions were obtained.

Conclusions

1. A low voltage CGDE was obtained to degrade the glycerol in the solution. Subjected to CGDE, glycerol was firstly oxidized and then transferred to glyceric acid and glyceraldehyde which are not toxic and safe chemicals and are recyclable. On the other hand, an ideal conversion rate within short experiment time was achieved. After 40 min, the conversion rate would increase from 67.8% to 81.27% while the amount of glycerol added from 5mL to 8mL. To certain extent, increasing amount of glycerol within a limit value would induce to high conversion rate of the energy produced by glow plasma in the solution.
2. The Au film coated on the Ti foil improves the electrical conductivity in the plasma discharge process and thus enhances degradation of the Rh B whilst producing many gold NPs. Therefore, CGDE is a potential method for the synthesis of nanostructured materials
3. Titanium-based metal foil is discovered to play bifunctional roles in the rapid degradation of Rh B. The generation of the plasma discharge from the cathode carries high energy to break organic bonds of Rh B molecules rendering them degradation. On the other hand, the TiO₂ particles produced during the plasma discharge process from Ti-based metals act as catalyst in the electrolyte and perform the photocatalytic process that significantly improves the degradation of Rh B. Thus, the degradation rate increases one order of magnitude over the traditional TiO₂-based particles.

Future work

More work will need to be carried out for this research in the future, which is listed here:

First, the voltage applied in this experiment is still higher than the safety number; therefore, for the industry application it is quite dangerous for handling. It might cause a lot of safety issues; hence to bring the operating voltage further down should be one of targets in the future research. More work will be set to investigate the operating voltage required in response to different shapes and diameters of electrodes as well as various electrolyte and their corresponding concentrations.

Second, after the experiment, the pollutants could be transferred to small molecular chemicals which should be recyclable for the sake of eco-green environment. This also will help to save the resource. However, how to collect and separate different products is also an issue that needs to be solved. On the one hand, different boiling point and solubility of different chemicals might help for separation. On the other hand, the pollutants that are fully transferred to final products that should be non-toxic, safe and do not harm to human beings and environments. Apparently, there should be a lot of work that requires to be carried out in this area.

In addition, how to apply the methods developed in this thesis into the real industrial applications is an issue that needs to be solved in the future work. Industrial applications are different from the lab-based experiment; all the devices are larger and more complex than the ones used in lab.

Appendix

Table S1. Comparison of different plasma discharge for waste treatment.

R e f .	No	Types of discharge	Conditions	Treatment time (min)	Removal efficiency (%)	Energy yield g/(kW h)	Refs
1		DC glow discharge	Phenol, 100 ppm, V:500V, I:100mA,	30	61	0.34	2
2		Dielectric barrier discharge	Phenol, 7 mL, V: 16.5–18 KV, 50 Hz,	180	97	0.56	3
3		Dielectric barrier discharge	Methylene blue (20 mg/L), V: 20kV 20 kHz	5	100	0.68	4
4		DC pulseless corona discharge	Phenol, 0.5 L, 28 ppm, V: 14 kV; I: 0.5 mA,	90	82	1.09	5
5		Pulsed electrical discharge	Phenol, 0.2 L, C: 94 ppm, V: 38 kV, F: 10 Hz,	5	38	2.97	6
6		DC arc plasma	Phenol, C: 1 mol%, V: 150 V, I: 8 A	10	100	8.12	7
7		Bifunctional cathode glow discharge	Glycerol (5mg/L) V:70V, I:0.8A,	40	81.3	10.02	<i>This work</i>

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