

Catalytic Conversion of Waste Plastics into Value-Added Chemicals

by

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A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Applied Science
in
Mechanical and Mechatronics Engineering (Nanotechnology)

Waterloo, Ontario, Canada, 2022

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Plastics are indispensable in many industries (such as packaging and transportation) owing to its durability, diversity and versatilities. However, the decomposition rate of plastic is far from generation speed. The plastic waste problems are becoming increasingly serious all over the world. In order to address this crisis, a sustainable and feasible method is hoped to be proposed. This thesis aims to transfer plastic waste into highly valuable chemicals in a mild environment.

The first part of this thesis focuses on upcycling plastic waste via photocatalytic reaction. There are two catalysts synthesized, that is, graphitic carbon nitride (written as C_3N_4) catalysts and C_3N_4 doped with iron single atoms (written as Fe- C_3N_4 SAC). It has been found that the introduction of Fe single atoms could enhance the photoreaction's efficiency, which was explained by the yield of acetic acid. It is evaluated that the yield of acetic acid is around $3.43 \text{ mg h}^{-1} \text{ gcat}^{-1}$ when using Fe- C_3N_4 SAC, while the yield of acetic acid is reduced to a third when using C_3N_4 . To explore the mechanism, Electron spin resonance (ESR) was also employed to capture hydroxyl radicals.

The second part of this thesis is to convert plastic materials into glycolic acid. A combination of hydrolysis and electrochemical oxidation was applied in this study. Firstly, the polyethylene terephthalate was decomposed into ethylene glycol in a base solution. Then ethylene glycol was applied to a certain voltage for upcycling.

Keywords:

plastic waste, upcycling, catalytic reaction

Acknowledgements

I would like to express my sincerest gratitude to my supervisor Professor Yimin Wu for his guidance, passion and endless patience throughout my graduate studies. Without his invaluable guidance, none of my studies would be possible.

A sincere thanks to Professor Xiaoyu Wu and Professor Peng Peng for reviewing my thesis, providing valuable suggestions and comments.

I also would like to wholeheartedly thank my colleagues in Materials Interface Foundry (MIF), especially Dr. Cheng Du and Dr. Zuolong Chen for their help during the research.

My sincere gratitude also goes to Janet Venne who taught me to test the NMR of samples. My appreciation also extends to Peter Sprenger, Dmitry Akhmetzyanov and Fatemeh Fani Sani, for their help with ESR test.

Finally, I would like to show great thankfulness to my parents for their love and support. To my dog, Dou Dou, for her constant love.

Dedication

To my parents

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List of Abbreviations

PET: Polyethylene terephthalate

PE: Polyethylene

HDPE: High-density polyethylene

LDPE: Low-density polyethylene

LLDPE: Linear low-density polyethylene

PP: Polypropylene

PPE: Personal protection equipment

AOPs: Advanced oxidation processes

$\cdot\text{OH}$: Hydroxyl radicals

$\text{SO}_4^{\cdot-}$: Sulfate radicals

$\text{O}_2^{\cdot-}$: Super oxygen radicals

$^1\text{O}_2$: Singlet oxygen

$\cdot\text{O}_2\text{H}$: Hydroperoxyl radicals

EDTA: Ethylene diamine tetraacetic acid

PCA: Protocatechuic acid

AA: Ascorbic acid

SE: Secondary electrons

BSE: Backscattered electrons

Chapter 1

Introduction

1.1 Overview

Over the past decades, polymeric materials, such as plastics, have received intensive attention owing to adverse environmental problems and pollution they caused in modern society. [1] As is shown in Fig. 1.1, there will be over 25,000 plastic wastes generated while only one third of them will be recycled in 2050. Noted that this conclusion is derived based on simply extrapolating the past trends. The usage of traditional petroleum-based plastics is limited by fossil fuels, while dependence on such energy sources may be not sustainable.

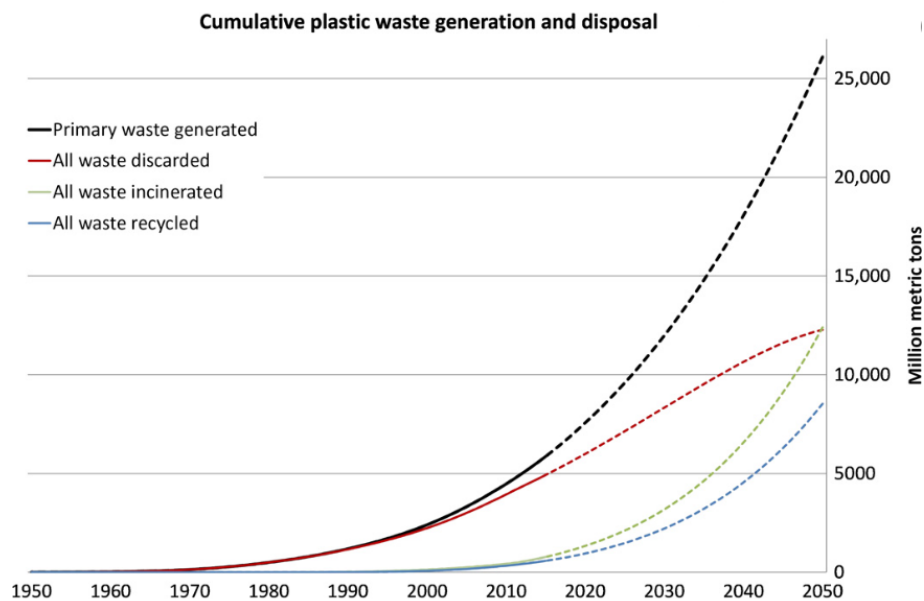


Fig. 1.1 Cumulative plastic waste generation and disposal (in million metric tons).

Solid lines show historical data from 1950 to 2015; dashed lines show projections of historical trends to 2050. [2]

Moreover, a large amount of discarded plastics will finally enter the ocean due to mismanagement. [3] It was first reported in the early 1970s. Usually speaking, the plastics

appeared in the ocean have small sizes and are likely to appear on coastlines, sea surface and sea floor, which partially explains why they are not traceable for their source and not easy to remove. Based on the current waste management, it is estimated that there will be an increase for the cumulative quantity of microplastics by 2025 (Fig. 1.2). [3]

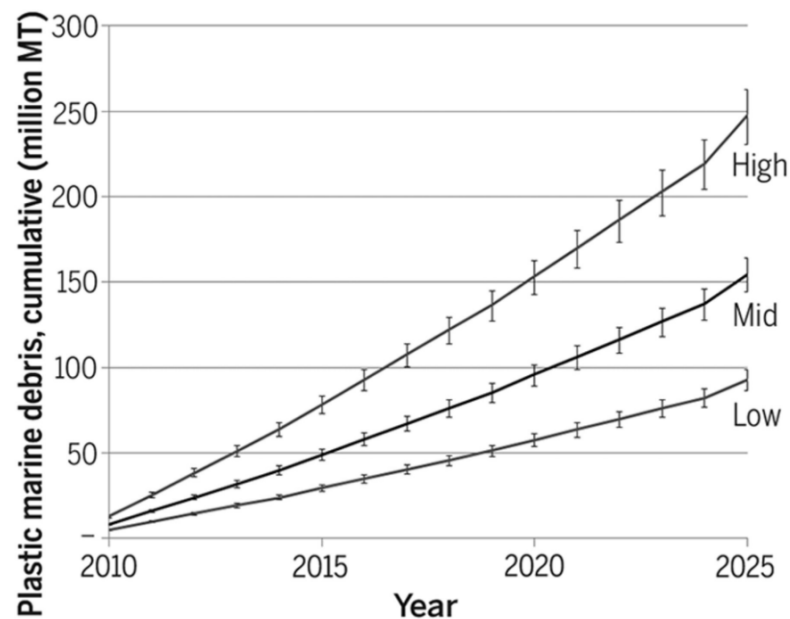


Fig. 1.2 Estimated mass of mismanaged plastic waste (millions of metric tons) input to the ocean by populations living within 50 km of a coast in 192 countries, plotted as a cumulative sum from 2010 to 2025. Estimates reflect assumed conversion rates of mismanaged plastic waste to marine debris (high, 40%; mid, 25%; low, 15%). Error bars were generated using mean and standard error from the predictive models for mismanaged waste fraction and percent plastic in the waste stream. [3]

Many researchers have endeavored to solve these problems. Considering the low recycling rate of plastic wastes, one alternative solution is to reclaim these plastics. [4] It is estimated that there would be equivalent to save 3.5 billion barrels of oil if human could recycle all plastic. [5]

1.2 Objectives and Scopes of Research Project

The aims of the research are listed below:

(1) To propose two feasible strategies to upcycling commonly used plastics into value-added chemicals.

In order to do this, some mild methods (such as appropriately increasing the temperature and changing the pH of the solution) were introduced in the experiment. Besides, different kinds of plastics were tested in this process.

(2) To compare several materials about their ability to oxide plastic and generate new chemicals.

For both catalysis, nuclear magnetic resonance (NMR) was used to determine the yield of product.

1.3 Outline of the Thesis

This thesis is organized in six chapters and the layout of my master's research could be summarized below:

- **Chapter 1** briefly introduces the motivation, objectives and overall structure of this project.
- **Chapter 2** presents a literature review of relevant background. Different types of plastic, their environmental hazards and current recycling techniques are presented in this chapter.

It also focuses on the different types of advanced oxidation processes and their main mechanisms.

- **Chapter 3** contains the general characterization methods and techniques used in this thesis.
- **Chapter 4** will focus on photooxidation process. The fabrication of catalysts and results about this catalyst are reported and discussed in this chapter.
- **Chapter 5** will give information on electrocatalytic processes. In particular, this chapter will describe the synthesis of catalysts and their electrochemical performance in the upcycling of ethylene glycol.
- **Chapter 6** summarizes the main conclusions gotten in my master's studies and also includes outlooks for future work.

Chapter 2

Literature Review

In this chapter, several commonly used plastics, their environmental hazard, and current recycling methods will be presented. It aimed to highlight the importance of the plastic recycling and the need for conversion of waste into valuable matters via upcycling.

The background information about advanced oxidation processes (AOPs) will also be provided in this chapter. Different types of AOPs and their catalytic mechanisms will be summarized. Besides, this chapter will also include a brief overview of recent development pertaining to the cocatalysts used in the Fenton reaction.

2.1 Introduction to plastics

2.1.1 Commonly Used Plastics

2.1.1.1 Polyethylene Terephthalate (PET)

Polyethylene terephthalate (PET), which is a typical petroleum-based plastic, is commonly used in textiles and packaging. [6] It is reported that there is around 70 million tons PET generated per annum. [4] Moreover, the demand for PET is significantly increasing during the coronavirus disease 2019 (COVID-19) pandemic. [7] However, according to a report from the US Environmental Protection Agency (EPA), the recovery rate of PET is only 19.5%, indicating its recycling potential. [8] Thermal methods are main recycling approaches for PET, resulting in the recovery of monomers. Fig. 2.1.1 shows some common monomers derived from the thermal decomposition of PET. [8]

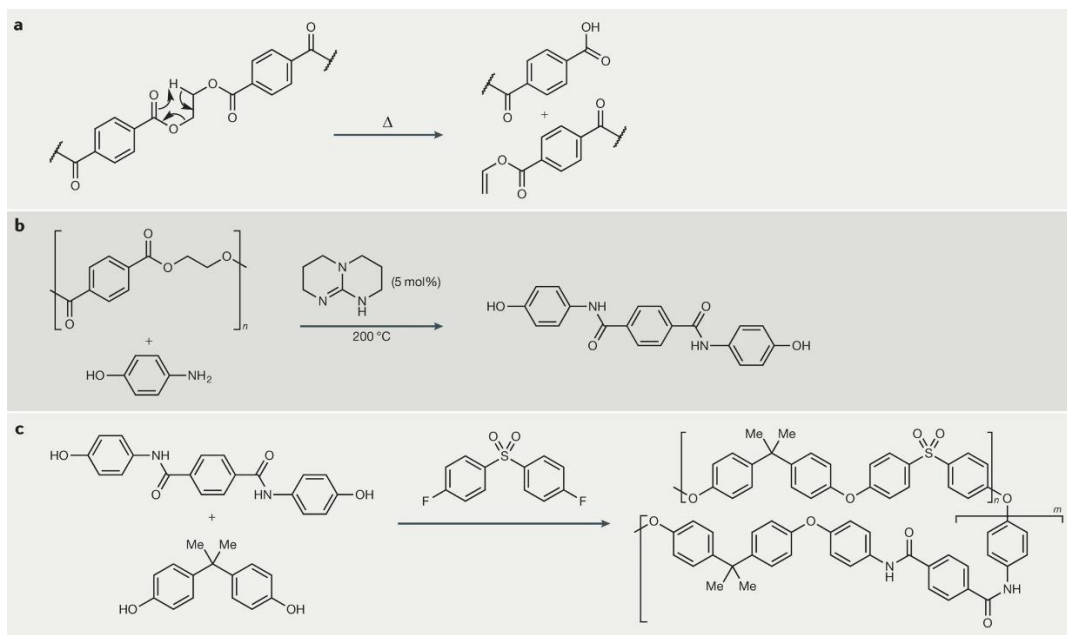


Fig. 2.1.1 Depolymerization of waste PET can afford a range of useful monomers.

(a) Thermolysis of polyethylene terephthalate affords carboxylic acid- and vinyl-terminated fragments. [9] The reaction can be conducted in the absence or presence of an acid catalyst.

(b) A guanidine base catalyses depolymerization to ethylene glycol and N,N'-bis(4-hydroxyphenyl)terephthalamide. [10] (c) The N,N'-bis(4-hydroxyphenyl)terephthalamide product can be copolymerized with bisphenol A and bis(4-fluorophenyl) sulfone to afford poly(aryl ether sulfone amide)s. [11]

2.1.1.2 Polyethylene (PE)

Polyethylene (PE) is one of the highest demand plastics in the world. [12] A large variety of products are very common in day-to-day life, such as carry bags used in supermarkets and milk jugs. There are three main types of PE, which are high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE) as presented in Fig. 2.1.2. [12]

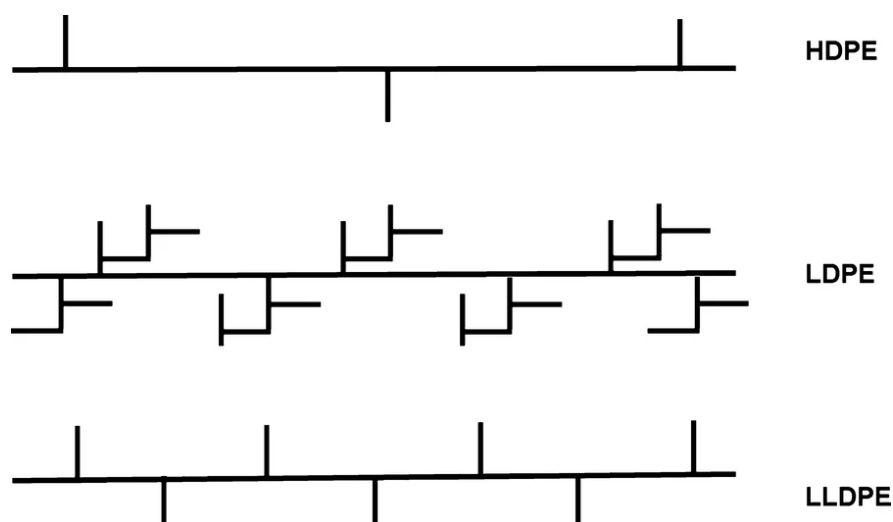


Fig. 2.1.2 Structures of different types of polyethylene. [13]

2.1.1.3 Polypropylene (PP)

Polypropylene (PP) was born in the 1950s. [14] It is reported that personal protection equipment (PPE) is mainly made of PP because this material could protect humans from bacterial infections. [15] As a result, the production of PP is booming due to the COVID-19 pandemic.

Table 2.1 Raw materials of PPE components. [16]

PPE components	Raw materials
Facemasks	Polypropylene
Normal surgical masks	Polypropylene
Single use isolation gowns	Mainly polypropylene
Goggles	High quality polycarbonates
Coveralls	High density polyethylene
Hair nets	Polypropylene
Shoe covers	Polypropylene

2.1.2 The Effects on the Environment

2.1.2.1 Ecological Impacts

Evidence to date, predominantly on the wide existence of plastics, has shown the high possibility for both invertebrates and vertebrates to encounter and ingest plastic particles. [17] The fact is that such ingestion is widely present in many marine organisms. Typically speaking, some marine species are observed of the reduction of feeding, which is the detrimental result of ingestion of plastics. [18]-[21] It was investigated that the mortality was enhanced when *Lumbricus terrestris* earthworms were exposed to more amount of PE. [22] And the similar found is also consistent with the studies for marine species.

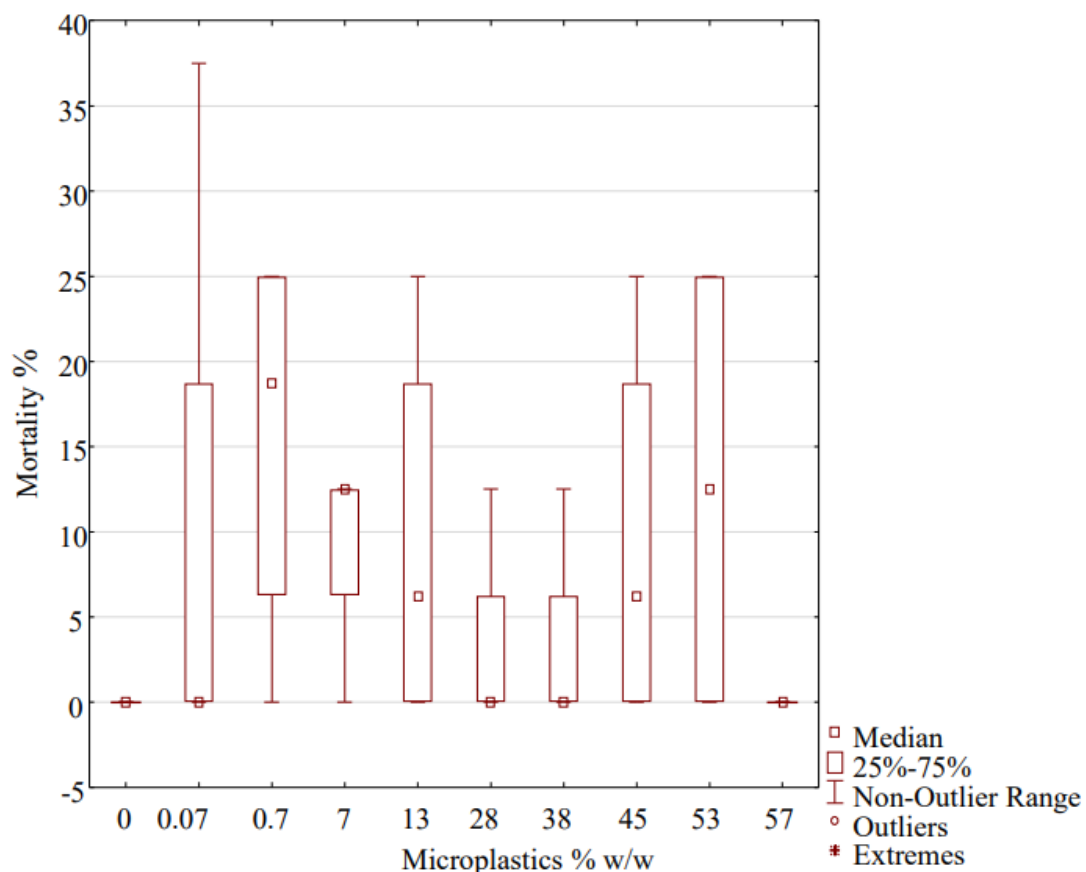


Fig. 2.1.3 Preliminary *Lumbricus terrestris* Mortality study. Ten treatments with 4 replicas per each, following OECD procedures. No significant differences were observed. [22]

2.1.2.2 Chemical Hazard

In order to get specific physical properties, a variety of toxic chemicals are added when manufacturing plastic. These additive chemicals, such as phthalates, have weak interaction with the polymer molecule, which are easily released into the environment. [23]-[24] It was analyzed that the toxicity in solution would be increased after the plastic product leached out at most cases. The extent of the increase varied from polymer to polymer. [25]

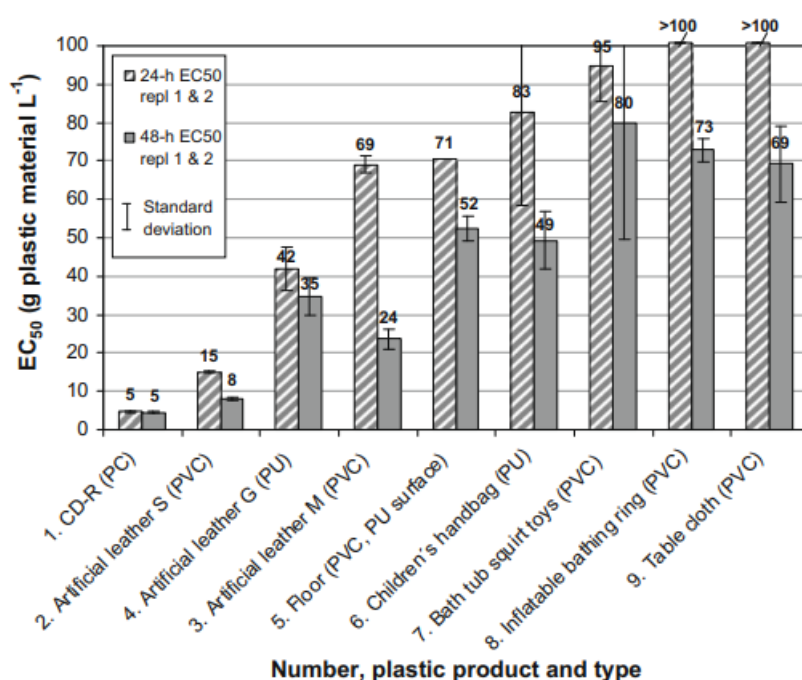


Fig. 2.1.4 EC₅₀s for *Daphnia magna* for plastic product leachates. The presented EC₅₀ concentrations refer to the plastic concentrations that occurred in the water during the batch leaching tests, before the plastic pieces were removed and the water phase was tested for toxicity. The mean and standard deviation of two replicates is presented. [25]

2.1.3 Current Recycling Methods

2.1.3.1 Primary Recycling

Primary recycling, which is also called closed-loop recycling, is the repossession of original plastic. There are few differences for their purpose between the recycled plastic and the virgin one. [8] The merits of this method are obvious, such as low energy consumption and simplicity. Nevertheless, it has a high purity require for the plastic. [26] Further, a few recycling circles limits the widespread use of primary recycling. [27]-[28]

2.1.3.2 Secondary (Mechanical) Recycling

Secondary (mechanical) recycling refers to recycling the virgin materials while producing new purposed materials. It is always regarded as ‘downcycling’ because this process typically deteriorates the properties of materials. [8]



Fig. 2.1.5 Common fates for current plastic waste. [Color figure can be viewed at wileyonlinelibrary.com] [29]

2.1.3.3 Tertiary (Chemical) Recycling

This recycling method is a sustainable way, involved in many chemical processes (e.g., pyrolysis, methanolysis and aminolysis). [30]-[33] This process could generate more monomers while consuming less time. [34]

2.1.3.4 Quaternary (energy) recovery

This term usually refers to incineration. The energy of plastic will be collected as heat and electricity. It is an appropriate method for collecting harmful and toxic wastes. [26] However, the pollutants produced in the process will damage human health. [35]

2.2 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) have been widely investigated for the removal of many organic pollutants since it was proposed in the 1980s. In these processes, some reactive species, such as hydroxyl radicals ($\cdot\text{OH}$) will be produced, which play powerful roles in the treatment of recalcitrant organic chemicals. Nowadays, apart from hydroxyl $\cdot\text{OH}$ radicals, there will also be other strong oxidation agents formed in experiments, such as sulfate radicals ($\text{SO}_4^{\cdot-}$), super oxygen radicals ($\text{O}_2^{\cdot-}$) and singlet oxygen ($^1\text{O}_2$). Fig. 2.2.1 displays some powerful transitory species with excellent AOPs results.

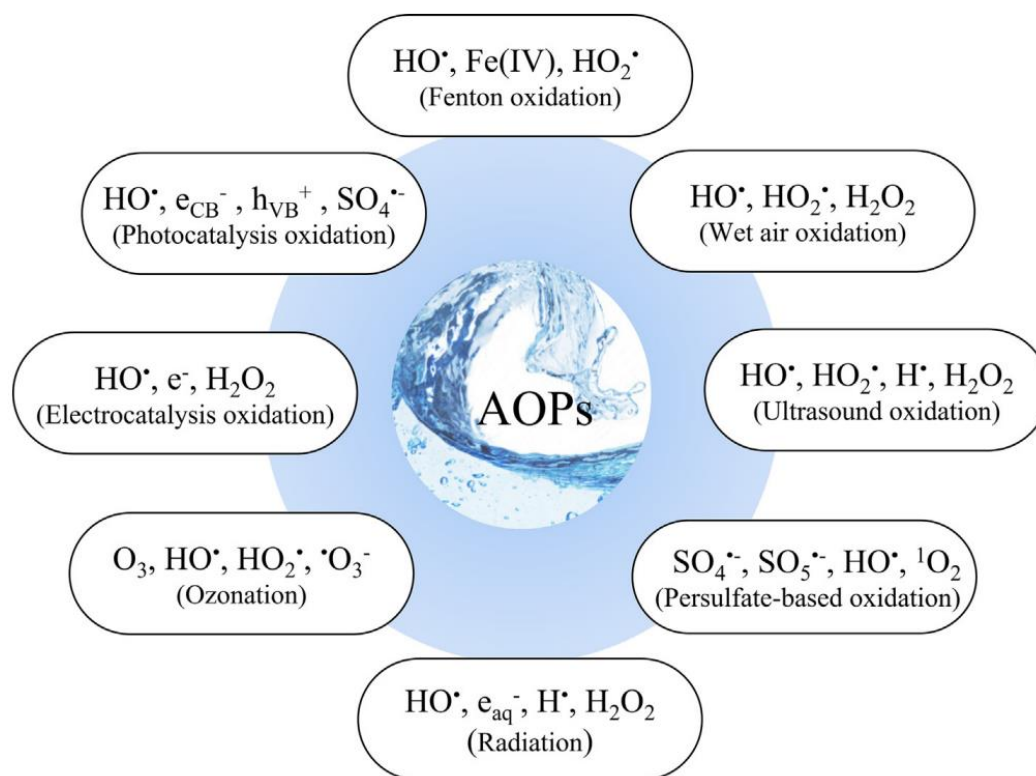


Fig. 2.2.1 Possible reactive species produced in different AOPs. [36]

2.2.1 Fenton Process

The Fenton process is an important and typical class of AOPs. This method was first proposed

by Henry J. Fenton in 1894. By mixing soluble iron (II) salt (Fe^{2+}) and H_2O_2 , he found the oxidation of tartaric acid. [37] The classical mechanisms behind it are expressed by Equations 1-4. [38]-[40]



Hence, $\cdot\text{OH}$ radicals are obtained via the photo decomposition of H_2O_2 by sufficient Fe^{2+} , which preferably oxidize many organic molecules (Equation 4). Subsequently, Fe^{2+} can be formed during the reduction of Fe^{3+} . Based on Table 2.2, $\cdot\text{OH}$ radicals play an irreplaceable role due to their strong oxidation ability.

Table 2.2 Redox potentials of common oxidants referred to normal hydrogen electrode (NHE). [41]

Redox potentials of some oxidants	Species $E_0(\text{V}, 25^\circ\text{C})$
Fluorine	3.03
Hydroxyl radical	2.80
Sulphate radical	2.5–3.1
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
Permanganate	1.68
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Chlorine	1.36
Bromine	1.09
Iodine	0.54

However, Equation 2 is a time-consuming step, which limits the efficiency for entire Fenton reaction. Given that Equation 1 has higher efficiency than Equation 2, there will be excessive Fe^{3+} produced, leading to iron cement and catalyst poisoning. [42] In addition, Equation 2 tends to produce hydroperoxyl radicals ($\cdot\text{O}_2\text{H}$). As intermediate radicals, $\cdot\text{O}_2\text{H}$ radicals will also be

involved in many complex reactions: [43]



It is worth noting that Fe^{2+} can not only help to produce $\cdot\text{OH}$ radicals, but also prevent the reactions of certain radicals ($\cdot\text{O}_2\text{H}$).

Furthermore, the pH range will also influence the activity of Fe species. The optimal pH value is in a range 2-3, where Fe has excellent catalytic activity. [44] Iron hydroxide precipitation will be formed once pH increases above 3.5. Additionally, H_2O_2 tends to decompose under the same conditions. [45]

Owing to these obvious drawbacks, a large number of investigations have been published. Among them, the emergence of cocatalysts provides with a novel perspective for their practical applications. According to previous studies, suitable cocatalysts are pivotal to improving some properties (e.g., activity, selectivity, antitoxicity or stability) of the original catalysts. Here are some typical types of these cocatalytic Fenton reactions:

(1) Organic acids cocatalysts.

Organic acids can not only possess chelation ability but also function as reductants. It is known that the induction of chelating agents will promote Fenton agents dissolving in the solution, therefore accelerating the reaction and improve the efficiency. Ethylene diamine tetraacetic acid (EDTA), a common chelating agent, was introduced to prevent the generation of iron sludge in previous studies. [46]-[47] Note that EDTA is hard to be decomposed, resulting in unfavourable environmental consequences. [48]

There are other eco-friendly and degradable organic acids, such as protocatechuic acid (PCA) [49]-[50], cysteine [51]-[52] and ascorbic acid (AA) [53]-[57]. Qin and coworkers [49]-[50] found that PAC could significantly increase the decomposition of target pollutants (e.g., alachlor and rhodamine B). During the reaction, stable complexes could also be produced by regarding PAC as a chelating agent. Meanwhile, Fe(III) tends to be reduced into Fe(II) while PAC is going through the oxidation reaction. This process prevents precipitation of irons, guaranteeing the concentration of $\cdot\text{OH}$ radicals and enhancing Fe(III)/Fe(II) cycle.

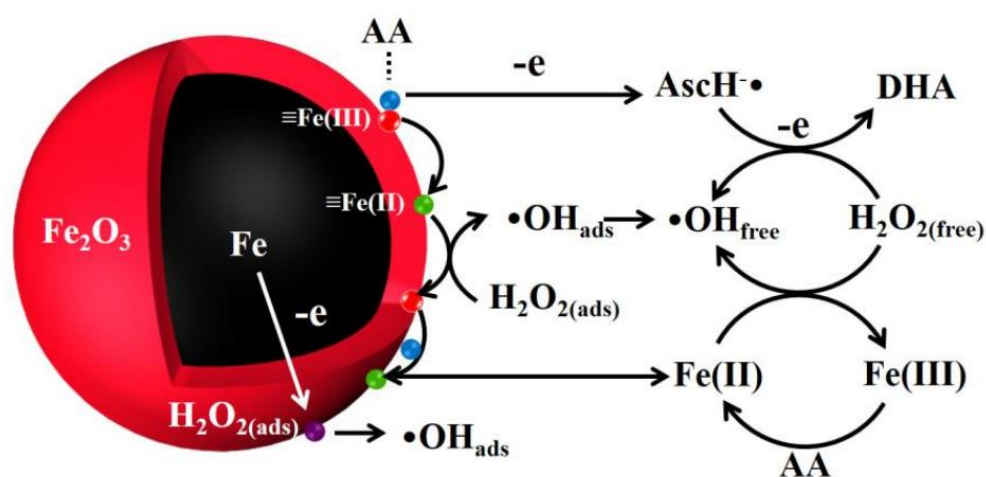


Fig. 2.2.2 Schematic illustration of the possible hydroxyl radical generation mechanism during alachlor degradation in the AA/Fe@Fe₂O₃/H₂O₂ system (where DHA and AscH $\cdot$ represent dehydroascorbic acid and ascorbate free radical, respectively). [54]

Hou et al. [54] demonstrated that AA cocatalytic Fenton had a higher reaction rate than those in the traditional system. AA, which is commonly found in fruits and vegetables, is considered to be an efficient chelating agent and coexists with iron species. At the same time, AA is indispensable as a reductant. Similar to PAC, AA will also promote Fe(III)/Fe(II) cycle and enhance the accumulation of $\cdot\text{OH}$ radicals, as is illustrated in Fig. 2.2.2.

There is no doubt that organic acids play an indispensable role in promoting reaction performance. However, the industrial application of this method is limited by the easy reaction

with reactive oxygen species. Thus, too many organic acids are required, making lots of costs and low efficiency.

(2) Zero-valent metals (ZVMs) cocatalysts.

ZVMs cocatalytic Fenton system has shown great potential for the acceleration of Fe^{2+} and interruption of iron sludge. Zero-valent iron (ZVI) [58]-[64], which has a strong reduction ability, is a typical category in ZVMs. The mechanisms are shown by Equations 9-12.



In general, Fe^{2+} is generated during the reaction between Fe^0 and H^+ . $\cdot\text{OH}$ radicals is formed during the reaction between Fe^0 and H_2O_2 . It is noted that ZVI could reduce Fe^{3+} into Fe^{2+} . Meanwhile, Fe^{2+} can also be recovered from ZVI, which is presented in Equation 12.

Although there are many advantages such as the price of raw materials is acceptable, and pH has a wide controllable range, it is still a challenge to improve the reproduction of ZVMs cocatalysts. In other words, the shortcoming of this method is obvious, such as ZVMs can be easily deactivated, and the processing system is not stable after several cycles.

(3) Single atom cocatalysts.

A single atom cocatalytic system is a novel reaction due to its uniform distribution of active sites. Qiao and coworkers [65] successfully fabricated the first single atom catalyst. Their results demonstrated that this new catalyst exhibits excellent activity and stability, thus leading to high atom efficiency. Based on this, Zhang *et al.* [66] studied further its synthesis,

characterization, properties and catalytic performance.

It has been well proved that the efficiency of Fenton reactions could be enhanced by some supporting materials (e.g., nitrogen-rich materials). The nitrogen atoms that existed in such materials could coordinate with single metal atoms, maximizing the atom-utilization efficiency. [67]-[68] An and coworkers fabricated a catalyst by doping ultra-small clusters and single atom Fe sites on graphitic carbon nitride (g-C₃N₄) as shown in Fig. 2.2.3. [69] This catalyst showed promising potential in decomposing various organics (i.e., methyl orange, rhodamine B, phenol, and methylene blue), while exhibiting low iron leaching.

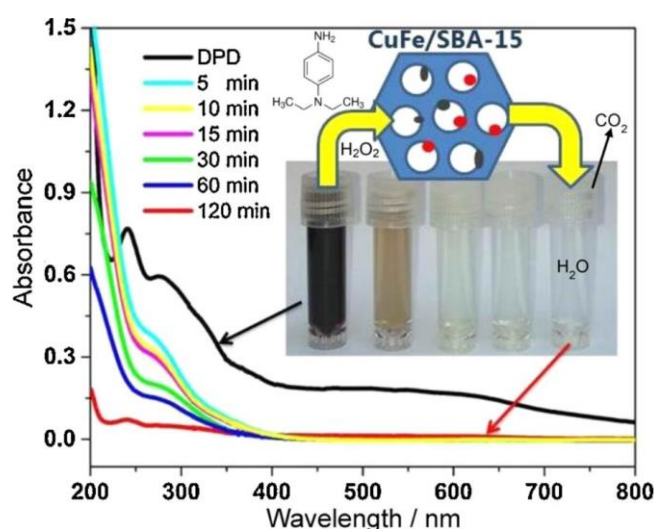


Fig. 2.2.3 CuFe/SBA-15 catalyzed DPD mineralization. [70]

The mesoporous silicon oxide also emerges as promising support due to its high surface area, ordered structure and tunable pore size. A Cu and Fe bimetallic oxidation catalyst was prepared by Karthikeyan *et al.* [70] Subsequently, they used this catalyst for the removal of N, N-diethyl-p-phenyl diamine (DPD).

Nevertheless, single atom catalysts show great potential in practical application owing to their uniform distribution of active sites and stability. Currently, finding easy synthesis methods, enhancing catalytic yield, and finding appropriate support materials are keys to realizing their broad application in industrial settings.

(4) Metal sulfide cocatalysts.

Metal sulfides as cocatalysts were firstly discovered by Xing and coworkers. [42] Metallic active sites (such as Mo^{4+}), which are surrounded by unsaturated S existing in the Fenton system, could enhance the $\text{Fe}^{3+}/\text{Fe}^{2+}$ conversion rate, therefore accelerating the entire Fenton process. This process could be summarized by Equation 13. For the S atoms, they could react with protons, forming an acidic environment for the reaction mentioned in Equation 14.



Moreover, a 3-dimensional (3D) MoS_2 sponge has been employed to broaden industrial applications. By loading MoS_2 nanospheres and graphene oxide (GO) on a melamine sponge, Zhu and coworkers realized a great enhancement in removing pollutants. [71] The advantages of such catalysts are obvious. Compared with classic AOPs, the 3D- MoS_2 sponge system could hamper the production of iron sludge, which guarantees entire efficiency. In addition, the operating cost is low, showing its huge potential in the industry.

2.2.2 Electrochemical AOPs

Electrochemical AOPs are innovations on the traditional AOPs, which are inexpensive and effective for purifying wastewaters. [72]-[74] The electric current will be applied between two electrodes, which will also generate hydroxyl $\cdot\text{OH}$ radicals and hydrogen peroxide. The reaction is shown as Equations 15 & 16:



The total reaction is shown as Equation 17:



As a result, the $\cdot\text{OH}$ radicals, which attack and oxidize the organic contaminants easily, are considered as the product on the anode surface. And hydrogen peroxide can be formed in the cathode by oxygen. [75]

The electrochemical oxidation of organic pollutants is mainly achieved in the following ways:

(a) Direct oxidation.

Direct oxidation involves electron transfer only within recalcitrant organics and electrodes, which is regarded as an unselective reaction. Besides, some compounds with smaller molecules would be generated by destroying the pollutants. [76]-[78]

(b) Indirect oxidation.

Indirect oxidation is also called mediated oxidation. During this oxidation process, there would be some intermediate species generated, such as $\cdot\text{OH}$ radicals and “active oxygen”. These products have high oxidizing power, which could further degrade organic pollutants. [79]-[80]

The detailed mechanisms of this process are shown in Fig. 2.2.4.

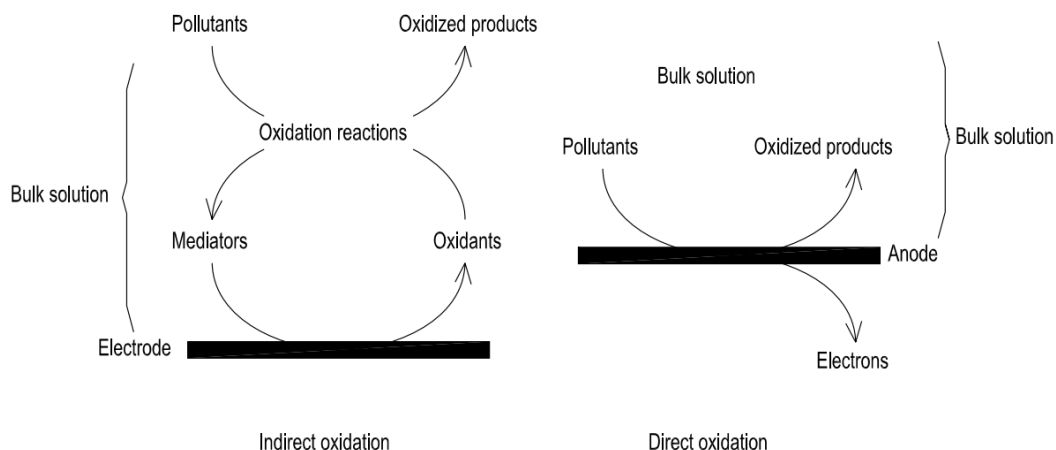


Fig. 2.2.4 Pollutant removal pathways in electrochemical oxidation (indirect and direct oxidation). [81]

2.2.3 Ozone-Based AOPs

Ozone, a powerful oxidant, can react with a variety of organic matters. Similar to electrochemical oxidation, ozonation mainly follows two pathways: direct and indirect reactions. [82] Ozone is highly likely to have an electrophilic attack on functional groups during the direct reaction, especially for double bonds, amines, and activated aromatic rings. [83] As for the indirect processes, three different kinds of radicals (i.e., $\cdot\text{OH}$ radicals, superoxide radicals and hydroperoxide radicals) can be produced by the decomposition of ozone, according to Equations 18-22. [84]



Hence, $\cdot\text{OH}$ radicals are the most responsible species during the decomposition of organic matter. And hydroperoxide radicals are important to sustain and initiate the chain reaction.

However, it is hard for ozone alone to oxidize contaminants completely. In order to enhance its efficiency, the ozone-based AOPs are coupled with some catalysts (e.g., metal oxides, supported metal oxides and some porous materials) or other methods (such as ultraviolet light and ultrasonic). Fig. 2.2.5 describes the possible catalytic process between ozone and metal oxides.

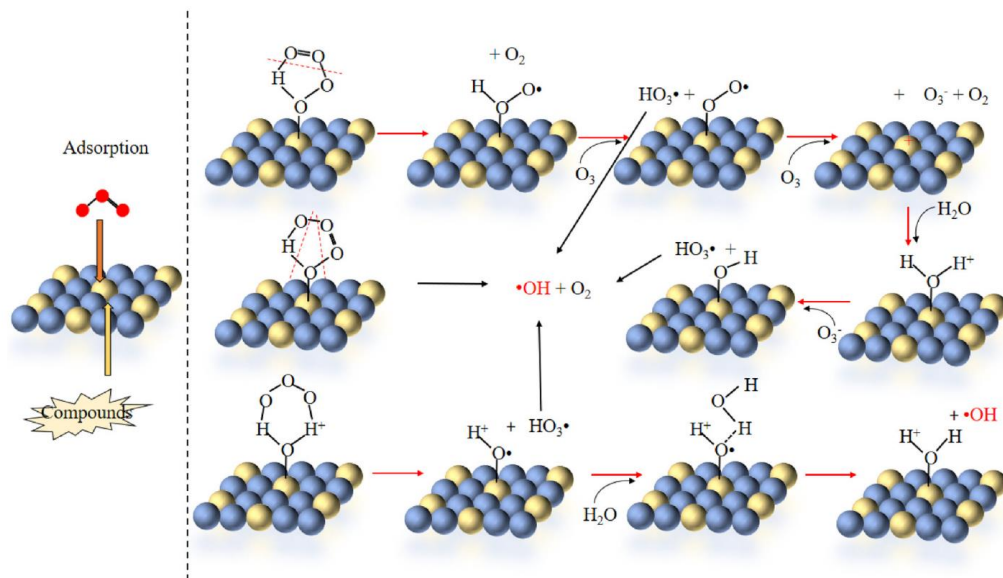


Fig. 2.2.5 Catalytic mechanism of ozone (based on Wang and Chen. [85]). [36]

2.2.4 Other AOPs

2.2.4.1 Ionizing Radiation

The ionizing radiation is considered as a promising method for decomposing many recalcitrant pollutants from aqueous solution, as is shown in Fig. 2.2.6. Two options are widely discussed for this process: gamma ray and electron beam.

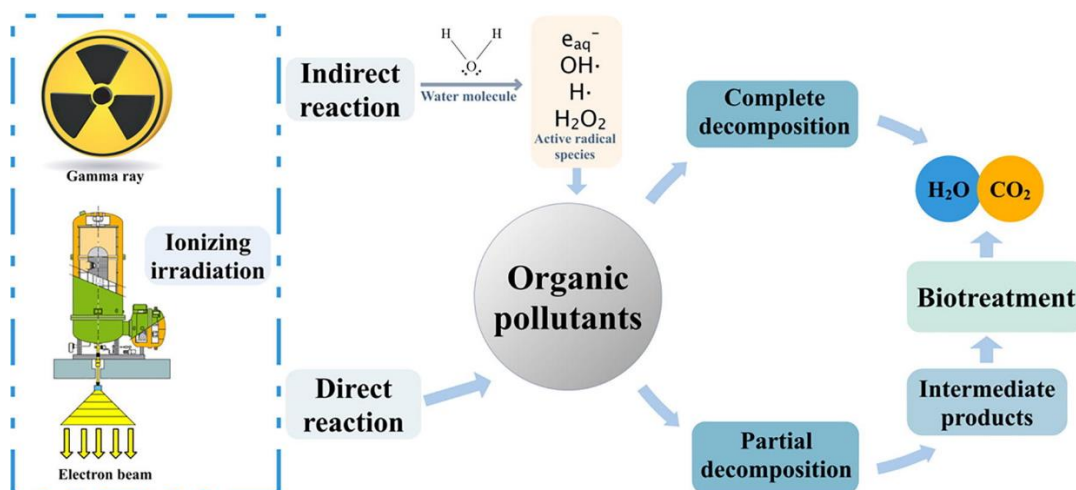


Fig. 2.2.6 Principles of ionizing radiation for the decomposition of organic pollutants. [43]

Many active species involved in radiolytic reaction follow the Equation 23 [86]:



It is interesting to note that $\cdot\text{OH}$ radicals and hydrated electrons are effective transient species in the degradation process. [87]-[88]

2.2.4.2 Persulfate-Based Oxidation

AOPs based on sulphate radicals ($\text{SO}_4^{\cdot-}$) have attracted interest since sulphate radicals have greater oxidation potential than $\cdot\text{OH}$ radicals and other radicals. [89] Compared with $\cdot\text{OH}$ radicals, sulphate radicals have higher selectivity and a longer half-life period, which enables them better to react with the target matters. The reaction patterns for these radicals are quite different. As is mentioned in the previous chapter, $\cdot\text{OH}$ radicals are prone to have addition reactions with unsaturated chemical bonds (e.g., $\text{C}=\text{C}$ bonds). [90] It would be noted that sulphate radicals preferably remove the electrons within organic matters. [91]

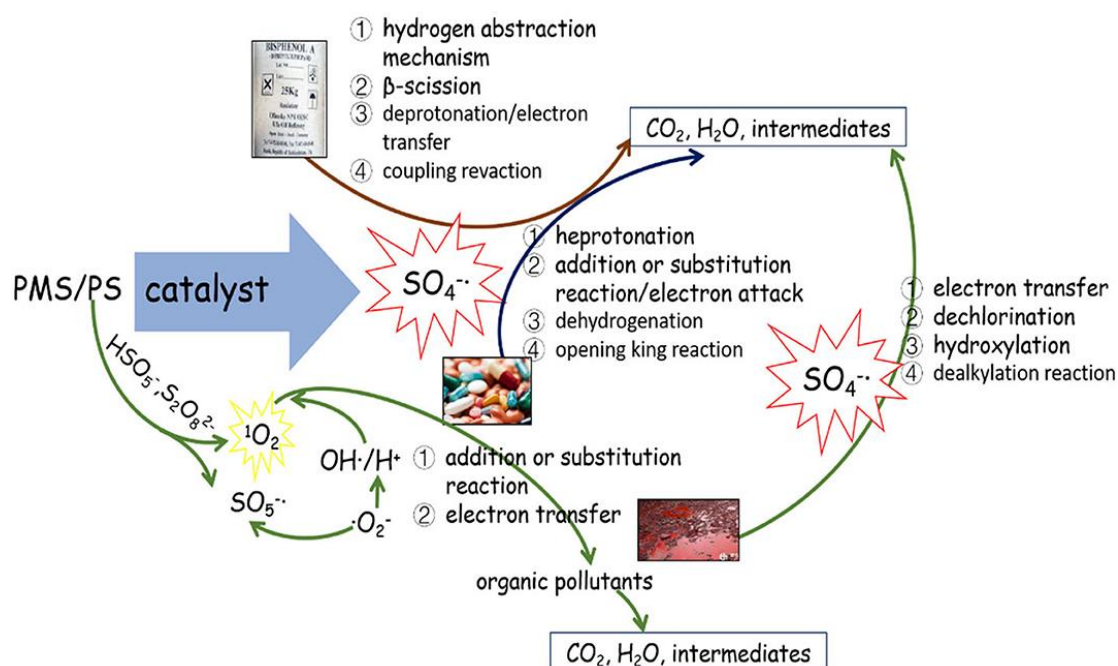


Fig. 2.2.7 The possible mechanism of persulfate/peroxymonosulfate (PS/PMS) activation.

[92]

There is a variety of research about generating sulphate radicals. It has been reported that peroxymonosulfate (PMS, $\text{HSO}_5^\bullet$) and peroxydisulfate (PDS, $\text{S}_2\text{O}_8^{2-}$) have shown great potential for the oxidation processes due to the existence of O-O bonds. [92]-[93] However, these chemicals ($\text{HSO}_5^\bullet$ and $\text{S}_2\text{O}_8^{2-}$) are stable and have low efficiency, which limits their practical application. [94] Therefore, various activation approaches such as heating, UV energy, the addition of alkaline, and metal ion reactions can be used with promising results. [95]-[100]

Chapter 3

Characterization Methods and Techniques

This chapter gives general descriptions of the characterization methods and techniques used in our study. It consists of physical and electrochemical characterization. More details (such as the preparation procedures of catalysts and specific electrochemical parameters) about each study are provided in the corresponding chapter.

3.1 Physical Characterization

3.1.1 Scanning Electron Microscopy (SEM)

SEM is one of the most routinely used techniques, which is designed to measure the size and the topography of materials. Typically speaking, the working principle of SEM is based on the interaction between electrons and sample. Firstly, the surfaces of sample will be scanned by electron beams. The beams of electrons are fired by the electron gun, then accelerated and focused through a series of apertures and condenser lenses. After this process, a variety of signals can be generated from the interaction between electrons and different depths within the matter. Secondary electrons (SE), backscattered electrons (BSE) and characteristic x-rays are the common signals formed in the process. Subsequently, these detected signals are collected and utilized, allowing to produce image of the sample. The layout of this technique is shown in Fig. 3.1.

It is known that SEM has the ability to have a high magnification range, enabling them to image the micro or nano structures. The resolution of SEM can be affected by many factors, such as probe current, incident angle, beam brightness and electron source. In order to have a higher resolution, longer acquisition time, more aberration and larger electron-matter interaction

volume are applied to SEM system.

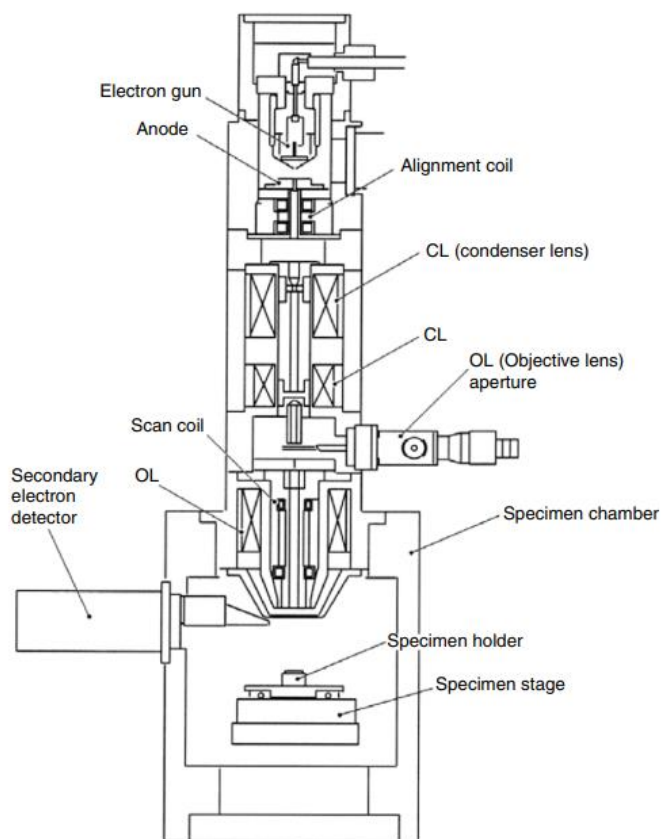


Fig. 3.1 Schematic diagram of a scanning electron microscope
(JSM-5410, courtesy of JEOL, USA). [101]

In our studies, SEM images for were tested by a Hitachi S4800 equipped with 10 kV (working accelerating voltage).

3.1.2 Transmission Electron Microscopy (TEM)

TEM is the instrument that provides detailed morphology and other information (such as particle size distribution, atomic structure, elemental distribution) of materials. It can also focus on a single nanoparticle, meaning that it has the ability to reveal a sample's information at 1 nm or better resolution (sub-nanometer).

Fig. 3.2 a displays a layout of a TEM system. Similar to SEM, TEM also employs a high-energy electron beam generated from an electron gun. Then these emitted electrons will travel through the vacuum tube, be accelerated by a large voltage, and be focused into a fine beam. Afterwards, the smaller beam will strike the sample. As is stated in SEM, some of the electrons will scatter, then being collected by SEM's detector. However, there are still a majority of electrons which pass through the sample and interact with the sample. These electrons will finally hit a fluorescent screen to generate the image of TEM. Noted that TEM specimen is placed in the middle of the layout, while SEM sample stage is put at the bottom. It is because these electrons, which have transmitted through the thin sample, need to be further magnified by subsequent electromagnetic lenses considering TEM's working principle.

As is displayed in Fig. 3.2 a & b, there are two operation modes for TEM, that is, imaging mode (real space) and diffraction mode (reciprocal space). And it is possible to generate both of these patterns by adjusting an aperture in the selected area.

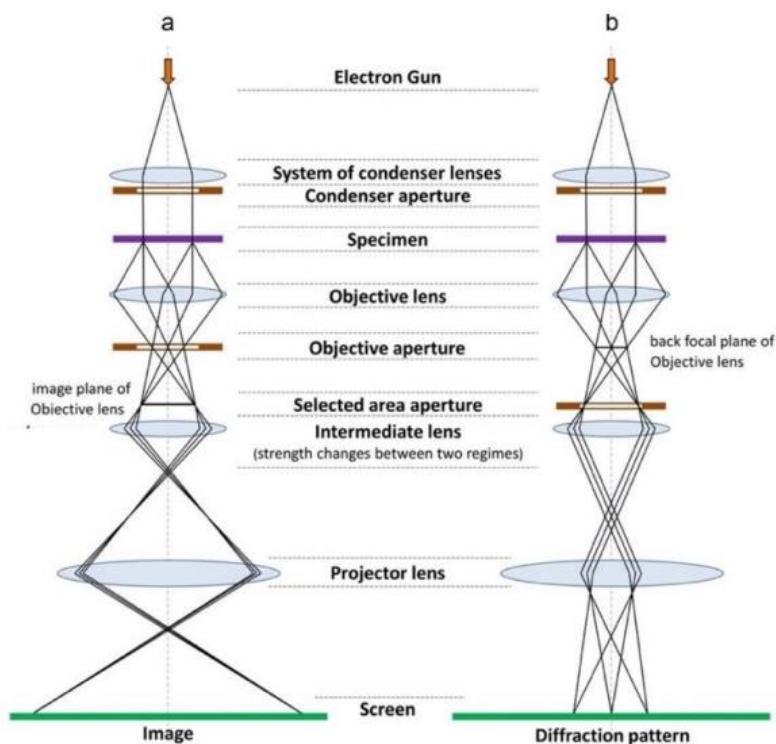


Fig. 3.2 Schemes illustrating the imaging (a) and diffraction (b) modes to operate a TEM. In each case, the intermediate lens selects either the image plane (a) or the back focal plane (b) of the objective lens as its object. [102]

For the photocatalytic studies, double aberration-corrected scanning transmission electron microscope (AC-STEM) tests were carried out on an FEI Titan 80-300 HB TEM with energy-dispersive X-ray spectroscopy (EDS) at 200 kV. The HAADF-STEM images were recorded by FEI Titan 80-300 HB TEM/STEM with a double aberration corrector operating at 300 kV.

3.1.3 X-Ray Diffraction (XRD)

XRD is a powerful and rapid analytical tool, employed to identify the crystal structure of materials (e.g., minerals, inorganic chemicals) without any destruction. Some other information, such as atomic spacing, bulk composition, and purity could be also provided via this technique. An x-ray tube, a sample holder, and an x-ray detector are basic components for an XRD system, as is shown in Fig. 3.3. Typically, the electrons are produced, accelerated, and bombarded within the x-ray tube. The x-ray will form when these electrons bring sufficient energy to the target material. Then the radiation will be filtered, collimated, and focused on the sample.

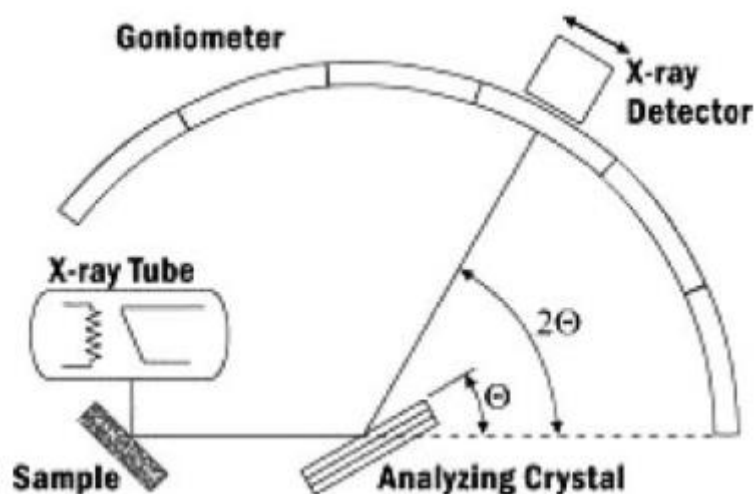


Fig. 3.3 Schematic diagram of a diffractometer system. [103]

The XRD is the result of the constructive interference between an x-ray and a crystalline substrate. To be specific, there is a set of planes existed in a crystalline sample. The path difference between the interplanar distance (d) could lead to constructive interference at Bragg

condition. Fig. 3.4 presents this situation.

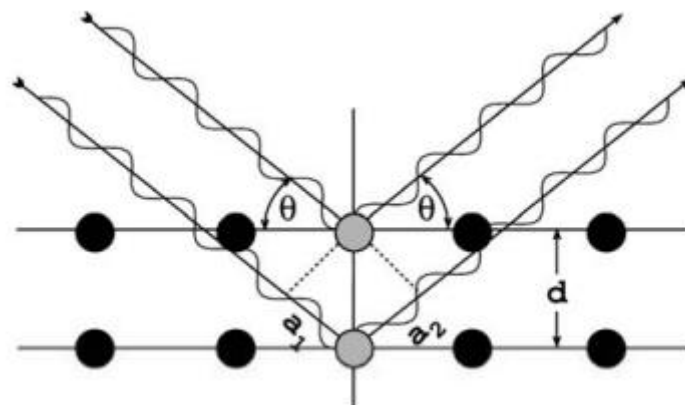


Fig. 3.4 Geometric derivation of Bragg's law: Constructive interference occurs when the delay between waves scattered from adjacent lattice planes given by $a_1 + a_2$ is an integer multiple of the wavelength λ . [104]

Based on Bragg's law, the lattice spacing, diffraction angle and wavelength of x-ray could be related. The constructive interference only happens when:

$$2d \sin \theta = n \lambda$$

Equation 24

where θ is the angle between incident beam and lattice planes, n represents the order of the spectrum, and λ is the wavelength of the beam. By altering diffracted angle, all the possible diffraction directions of the sample could be obtained. The diffraction peaks are then converted into lattice spacing, which is unique for different samples and could help to identify crystal structure and crystal phase. That is, using the obtained XRD pattern compares with standard patterns in the database.

In our studies, glancing-incidence X-ray diffraction (GIXRD) result was collected using a PANalytical X'Pert Pro MRD diffractometer with Cu K α radiation (1.54 Å) at an incidence angle of 1°.

3.1.4 X-Ray Photoelectron Spectroscopy (XPS)

XPS is a powerful device technique which normally used to analyze the elemental composition in the sample surface or within the material, as well as the chemical state. Typically, an XPS instrument mainly includes the source of X-rays, an ultra-high vacuum chamber, retarding lenses, collection lenses, analyzer, detector, and sample stage, as is shown in Fig. 3.5. X-ray source is used to provide irradiation to the sample, making the inner electrons ready to be excited and emitted.

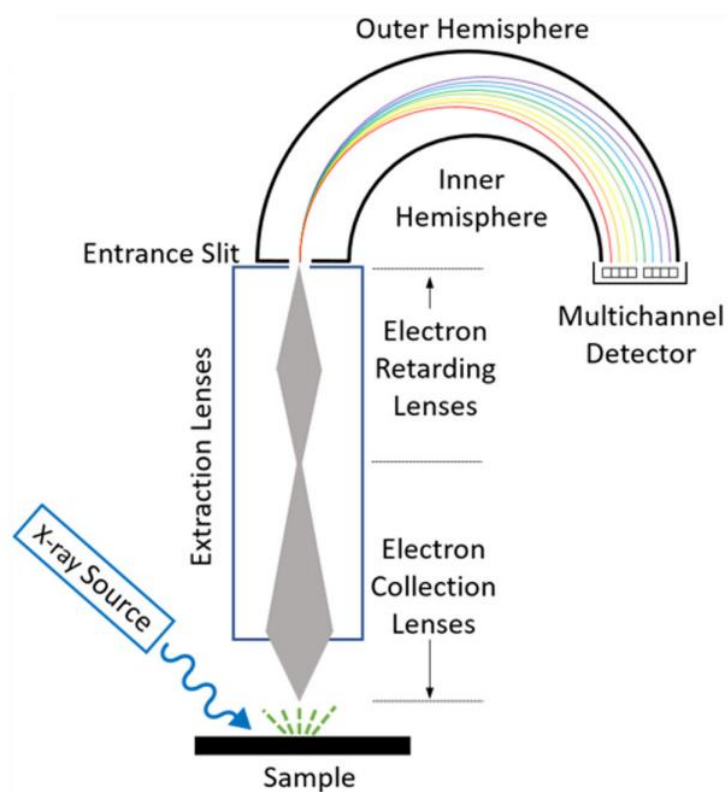


Fig. 3.5 Schematic diagrams show the major components of an XPS instrument. [105]

XPS works based on the photoelectric effect, which was discovered by Heinrich Rudolf Hertz in 1887. As for a typical XPS test, the sample is firstly irradiated by x-rays and the photos could be absorbed by the electrons on the atomic orbital of a certain element in the sample. These electrons are then freed and emitted from the interior of the atom with a certain kinetic energy. The kinetic energy of the emitted photoelectrons is further measured. According to Equation

25, the binding energy of these emitted electrons could be determined mathematically.

$$BE = h\nu - KE - \Phi_{\text{spec}}$$

Equation 25

where BE represents the binding energy on a specific orbital of an atom, $h\nu$ refers to the energy of the x-ray source photon, KE is the kinetic energy of the electron and Φ_{spec} is a constant work function term. It is also illustrated diagrammatically in Fig. 3.6. It is noted that Φ_{spec} is listed in the formula as the binding energy is detected with respect to the Fermi level. Besides, it is also interesting that the binding energy is an intrinsic property of materials. In other words, the binding energy of different atomic orbitals is different. It will never change when using other x-ray sources to carry out the experiment. Once the x-ray source is fixed, the energy of photoelectron is only dependent on the element type and its atomic orbital. Therefore, the peaks in XPS results can help us analyze the element and orbital involved. For instance, the electrons ejected from the 1s orbital of a carbon atom can be written as “C 1s”.

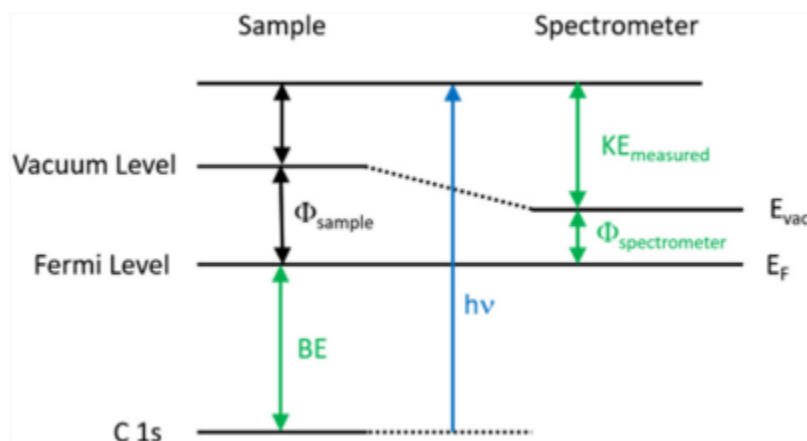


Fig. 3.6 Energy level diagram illustrates schematically the basic XPS equation, including the x-ray source energy ($h\nu$), the binding energy of the electron (BE), the measured kinetic energy of the electron (KE_{measured}), and the work function of the spectrometer ($\Phi_{\text{spectrometer}}$).

[105]

XPS can not only provide us with information about elemental composition, but also determine the chemical states and molecular structures of elements. The binding energy of the inner shell

will change due to different chemical environments (such as the atoms they bound to, and different valence states). Moreover, the difference will be shown as the chemical shift on the spectrum.

For photocatalytic and electrocatalytic upcycling studies, x-ray photoelectron spectroscopy (XPS) measurements were acquired from a Thermo-VG Scientific ESCALab 250 microprobes with a monochromatic Al K α X-ray source. The obtained spectra were calibrated using C 1s line.

3.1.5 Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance (NMR) is an important method for the characterization of material structure. Especially in organic chemistry, NMR can be used to determine the type and number of groups in a sample. ¹H-NMR is the most commonly used type of nuclear magnetic resonance spectroscopy in organic chemistry. ¹H-NMR identifies groups according to chemical shifts, determines the group connection relationship by the number of split peaks, etc., and obtains the proton ratio of each group based on the integral surface of each proton peak. Nuclear magnetic resonance spectroscopy can be used in a variety of organic/structural chemistry studies.

The principle of NMR was discovered and proposed by the famous physicist Pauli in 1924. In simple terms, when an atom or molecule is placed in a strong magnetic field, the atomic nucleus will have an absorption effect on radio waves, which will cause the energy level of the nucleus to jump, spin-flips from lower energy levels to higher energy levels. Nuclei at higher energy levels are usually unstable, and this part of the absorbed energy is eventually released by the nucleus in the form of light or other forms, and the nucleus is related to a lower energy state.

Furthermore, there are quite a few determinants for electromagnetic wave absorption, such as atomic species, electron cloud around the nucleus, etc. However, for the same atom, the frequency of the electromagnetic wave absorbed by the atom itself is affected by the

environment in which the atom itself is located in the molecule, which can be used to judge:

1. The position of the atom in the molecule
2. The distance and number of adjacent atoms of the same kind
3. Number of target atoms

Proton nuclear magnetic resonance (H-NMR) was measured on Bruker Avance III 300 MHz in our studies.

3.1.6 Electron Spin Resonance (ESR)

Electron spin resonance (ESR), which is also called electron paramagnetic resonance (EPR) spectroscopy is a powerful tool for characterizing molecular radicals. The mechanism of ESR is analogous to the one of NMR, while ESR excites the electrons' spins. Two M_s quantum states ($M_s = +1/2$ and $M_s = -1/2$) present in every electron. Both of them are degenerated and have the same energy when there is no external magnetic field applied. However, these two states would be changed with the existence of a magnetic field as depicted in Fig. 3.7. Typically, the energy of the $-1/2$ state will drop, and the energy of another state will enhance. Therefore, the separation of energy between the two spin states is $g\beta_e B_0$, where g is the Landé g -factor (usually equals to 2.0023 for the free electrons), β_e refers to the Bohr magneton, and B_0 is the strength of the applied magnetic field.

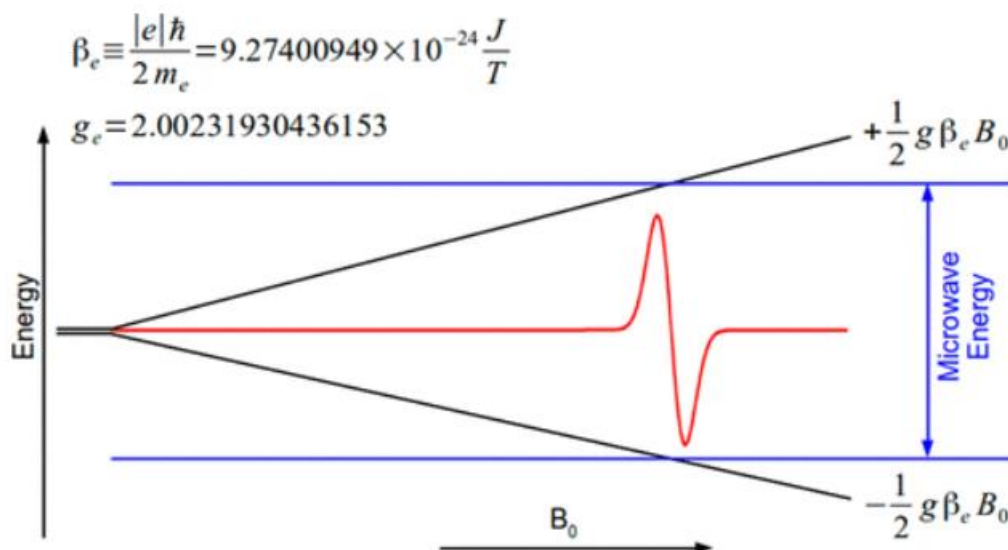


Fig. 3.7 EPR transitions occur when the energy contained in the microwave photons matches the splitting between two electron spin states. In the simplest system, this splitting as a function of the magnetic field is $g\beta_e B_0$. [106]

Electron paramagnetic resonance (EPR or ESR) spectra were measured on an ESR spectrometer (JEOL JES-FA200) at room temperature. This measurement was applied into the photocatalysis in order to confirm the generation of $\cdot\text{OH}$ radicals.

3.1.7 Ultraviolet and Visible (UV-Vis) Absorption Spectroscopy

UV-Vis spectrophotometer is an important analytical instrument, which has a long history. Generally, a UV-Vis spectrophotometer is mainly composed of a light source system, a monochromator, a sample chamber, and a detection system, as shown in Fig. 3.8. The main components of a light source are deuterium arc (190-330 nm) and tungsten filament lamp (330-800 nm), which could emit continuous and stable spectra in the ultraviolet and visible regions, respectively. The spectra are decomposed into monochromatic light by the monochromator and then pass through the sample chamber. After being partially absorbed, the light will reach the detector and will be analyzed.

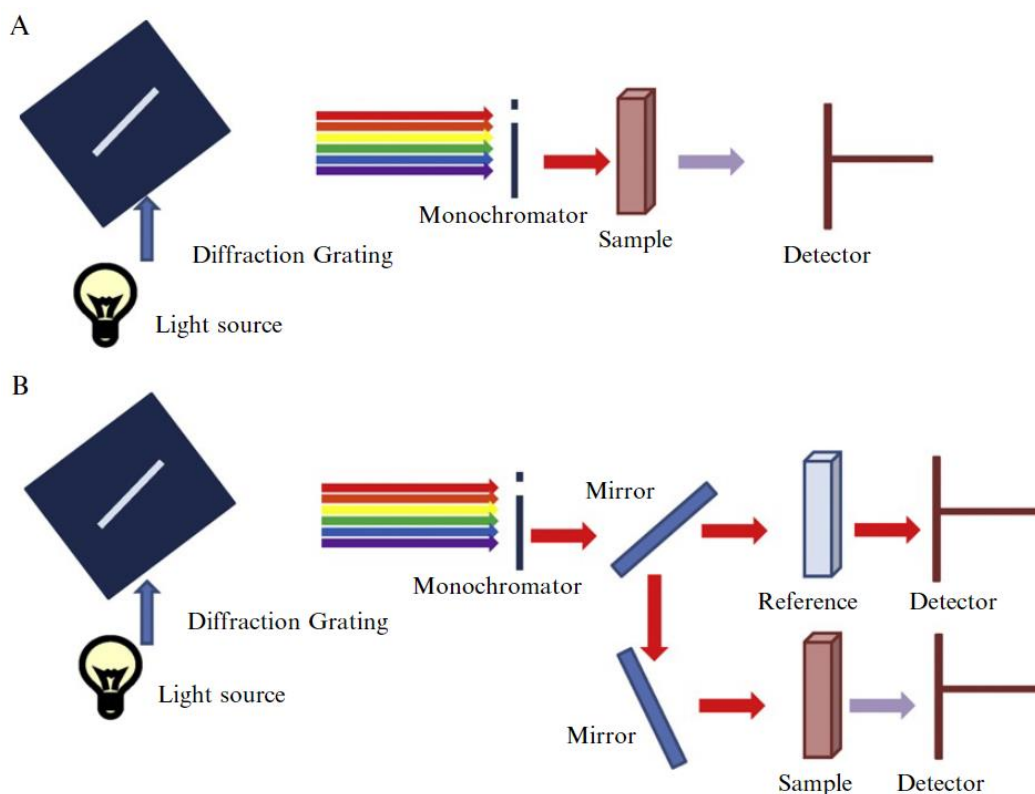


Fig. 3.8 Typical optical layout of an absorption spectrophotometer. (A) Single beam spectrophotometer and (B) double beam spectrophotometer. [107]

Essentially, the UV-Vis absorption spectrum is the result that molecules (or ions) absorb the light energy of certain wavelengths (usually 200-800 nm), and therefore have the transition of valence electrons. Generally speaking, these energy level transitions are always accompanied by transitions between vibrational and rotational energy levels, eventually causing a broad band presented in the UV-Vis spectrum. Noted that different substances have their characteristic absorption spectrum curves, given that they have different molecule & atom types and different molecule spatial structures.

The quantitatively analytical basis of UV-Vis spectrophotometry is the Beer–Lambert law. That is, the absorbance or extinction (A) of the radiation is proportional to the thickness (also refers to path length, l) of its absorbing medium and the concentration (c) of absorbing species, and its mathematical expression is as follows:

$$A = \varepsilon cl = -\lg \left(\frac{I}{I_0} \right) = -\lg T \quad \text{Equation 26}$$

where ε is the molar absorption coefficient of the material, I and I_0 are intensities of reflective and incident light, respectively. The $\left(\frac{I}{I_0} \right)$ term is also called transmittance (T), indicating the fraction of light which passes through the sample.

It was carried out in the photocatalytic studies to confirm the generation of $\cdot\text{OH}$ radicals.

3.2 Electrochemical Characterization

3.2.1 Cyclic Voltammetry (CV)

CV, a potentiodynamic electrochemical measurement tool, involves cycling sweeping the electrode potential between specific upper and lower limits at a constant scanning rate. CV measurement is normally carried out in a three-electrode system including a working electrode (WE), a counter electrode (CE) and a reference electrode (RE). During the measurement, the potential of WE is controlled with respect to the RE, and is scanned within the chosen limits. Saturated calomel electrode (SCE) or silver/silver chloride electrode (Ag/AgCl) is commonly used as the RE. In the meanwhile, the current at the WE is measured, which is regarded as the response signal. It could be adjusted by changing the potential scan rate, the materials of WE and the composition of the electrolyte. As one of the most powerful tools in electrochemistry, it is usually used to study the redox properties of catalysts.

Fig. 3.9 illustrates a conventional CV obtained in a model system, where solution-phase species P is reversibly reduced into species Q. Two distinct peaks existed in this figure means charging and discharging. To be specific, the upward peak indicates the oxidation of active species, while another peak illustrates the reduction.

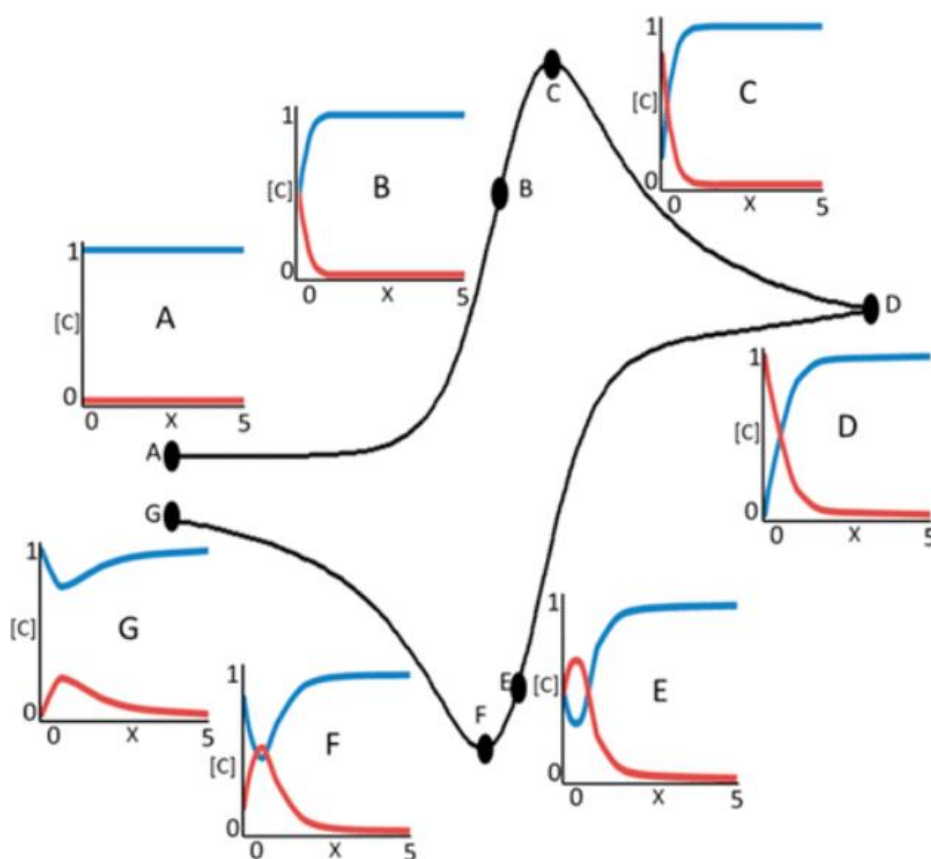


Fig. 3.9 Concentration ($[C]$, mM) versus distance from the electrode (x , $\text{cm} \cdot 10^{-2}$) at various points during a reversible CV wave: C_P (blue); C_Q (red).

Scan rate = 100 mV s^{-1} . [108]

In a typical measurement of the alcohol oxidation reactions (AOR) activity, the electrode potential is swept from -0.6 V to 0.7 V vs. Ag/AgCl in an argon-saturated 2 M KOH and 0.5 M EG electrolyte cell at a certain rotation speed. Then the electrode potential was calibrated with respect to an Ag/AgCl , for unified evaluation of catalytic activity, according to Equation 27.

$$E_{\text{RHE}} = E_{\text{Ag}/\text{AgCl}} + 0.197 \text{ V} + 0.0591 \times \text{pH}$$

Equation 27

Chapter 4

Upcycling of Plastic Waste via Photocatalysis

4.1 Introduction

The pollution of plastic litter has aroused a great concern given that the annual production of plastic waste has been booming since 1970. Due to their low cost, high durability, corrosion-resistance and biosafety, plastics are commonly used in our daily life. [109] It seems that there is no excellent constitute for them from the plant and biomass. [110] Consequently, it is estimated that there are over 8300 million metric tons (Mt) of plastic generated. [2] Apart from this, it would be a long time for them to spontaneous degrade.

Previously, it had been reported that a single atom photocatalyst could enhance the efficiency of solid containment removal. [111]-[112] Inspired by this, we speculated that a universal photocatalyst doped Fe single atom would have a similar effect.

4.2 Synthesis of Photocatalysts

4.2.1 C₃N₄

A certain amount of melamine was directly heated to 550°C for 4h in argon to obtain the final graphitic carbon nitride (denoted as C₃N₄) photocatalysts.

4.2.2 Fe-C₃N₄ SAC

Fe-C₃N₄ catalysts were prepared in a typical procedure from a previous study [111]. A

homogeneous solution of 2 g melamine and 20 mg $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dispersed separately in ultrapure water and then mixed together. After continuous magnetic stirring at 100 °C, the water in the resulting mixture was completely evaporated. Afterwards, the obtained sample was calcined in a tube furnace at 550 °C for 4 h under an argon atmosphere. The as-prepared sample was then collected and labelled as Fe- C_3N_4 SAC.

4.3 Material Characterization

Inductively coupled plasma-atomic emission spectrometry (ICP-MS) tests were obtained an Agilent 8800 triple quadrupole, using He as a collision cell gas. The details related to other used methods have been listed in Chapter 3.

4.4 Photocatalytic Measurements

4.4.1 Apparatus

The photocatalytic activities of catalysts were mainly evaluated by the degradation of different plastics (i.e., polyethylene terephthalate (PET), polypropylene (PP) and polyethylene (PE)) under the simulated natural environment. In a typical experiment, a certain amount of catalyst was dispersed in deionized water. After well stirring for several hours, the sediment was removed by centrifugation. Then 30 mL solution (10 mg catalysts in 30 mL solution) was added to the reactor and H_2SO_4 was also used to adjust the pH value until pH=3. Afterwards, the well-dispersed solution was transferred into the reactor and 2 mL of H_2O_2 (30 wt. %) was added. Before light irradiation, the reactor was shielded to the light, ensuring that the adsorption equilibrium was established. During the photoreaction processes, the reaction system was under continuous magnetic stirring, while the temperatures of the reactor were controlled at 298 ± 0.2 K by recirculating cooling water system during irradiation. The light source for the

photocatalysis was a 300 W Xe lamp (PLS-SXE300DUV, Beijing PerfectLight Technology Co., Ltd, China) with a standard AM 1.5G filter, which could provide the one-sun irradiation.



Fig. 4.1 Experimental setup.

4.4.2 Analytical Methods

Acetic acid, as the main liquid product, was determined by H-NMR method. Specially speaking, standard curve of acetic acid was firstly built using pure chemicals with known concentrations. NMR tubes were prepared by combining 80 μL of aqueous 0.5mg/mL maleic acid internal standard with 600 μL sample. After photocatalytic reaction, the solution was collected and mixed with the NMR detecting solution (as above). The Fig. 4.2 a shows the standard curve for our project. When setting maleic acid area into 1, the concentration of liquid products is determined via:

$$\text{Area ratio to maleic acid} = 0.05 + 3.81 * \text{Concentration}$$

Obviously, this relation could provide us with the actual yield and the trend of product production.

For H-NMR tests, 128 scans were performed, with excitation sculpting used to suppress the water peak. As presented in Fig. 4.2 b, acetic acid and maleic acid can be ascribed to the peaks located at 1.80 ppm (triplet), and 6.07 ppm, respectively.

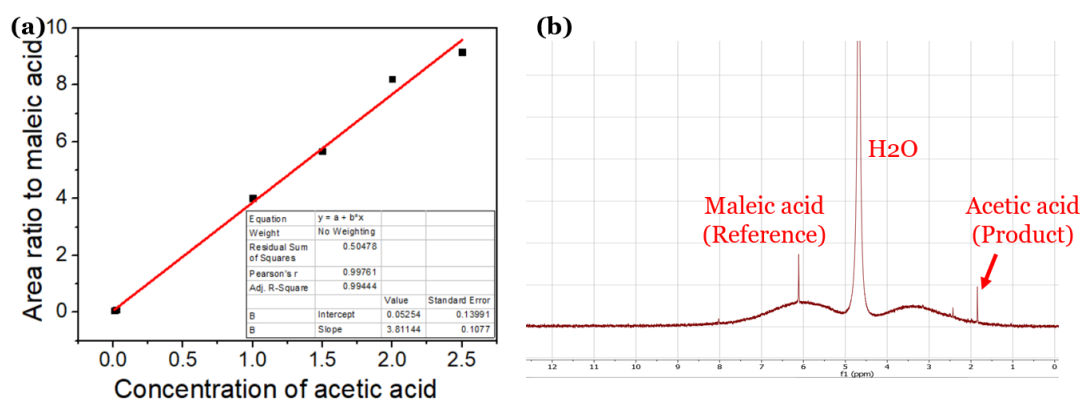


Fig. 4.2 (a) The calculation of liquid products. (b) An example of H-NMR results.

4.4.3 ESR Detection of Hydroxyl Radical ($\cdot\text{OH}$)

$\cdot\text{OH}$ was captured using 5, 5-dimethyl-1-pyrroline N-oxide (DMPO). In typical measurements, a well-dispersed catalysts solution was prepared followed by the addition of DMPO. The concentration of DMPO is 0.14M in the final solution. ESR spectra were obtained before the irradiation. After 10 min irradiation on the solution under simulated natural environments, the solution was analyzed in a second time.

4.4.4 UV-Vis Detection of Hydroxyl Radical ($\cdot\text{OH}$)

Irradiation of well-dispersed catalysts solution and salicylic acid (SA) mixtures was performed in reactor. The solution was collected at certain minutes and was determined the $\cdot\text{OH}$ concentration from UV–Vis spectra acquired between 200 nm and 800 nm.

4.4.5 Synchrotron Based X-ray Absorption Spectroscopy

XAS measurements were carried out at the 20-BM and 20-ID-C beamline of Advanced Photon Source (APS), Argonne National Laboratory. The measurements at the Fe K-edge were performed in fluorescence mode using a Lytle detector. The XAS data were analyzed using the software package Athena.

4.5 Results and Discussions

4.5.1 Characterization of Catalyst

The SEM images of the catalyst are shown in Fig. 4.3 a-b, which shows the nanosheet morphology of C_3N_4 and $\text{Fe-C}_3\text{N}_4$ SAC and the iron clusters or nanostructures cannot be observed. In order to reveal the distribution of iron atoms in the catalyst, double aberration-corrected high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was carried out. As presented in Fig. 4.3 c, according to the z-contrast, the bright spots representing iron single atoms uniformly dispersed indicating iron single atoms were homogeneously introduced. Moreover, it can be further confirmed by the element mapping results (Fig. 4.3 d-g). Besides, inductively coupled plasma-atomic emission spectrometry (ICP-MS) was also employed to observe the mass ratio of iron, which is 0.5 wt % in the $\text{Fe-C}_3\text{N}_4$

SAC.

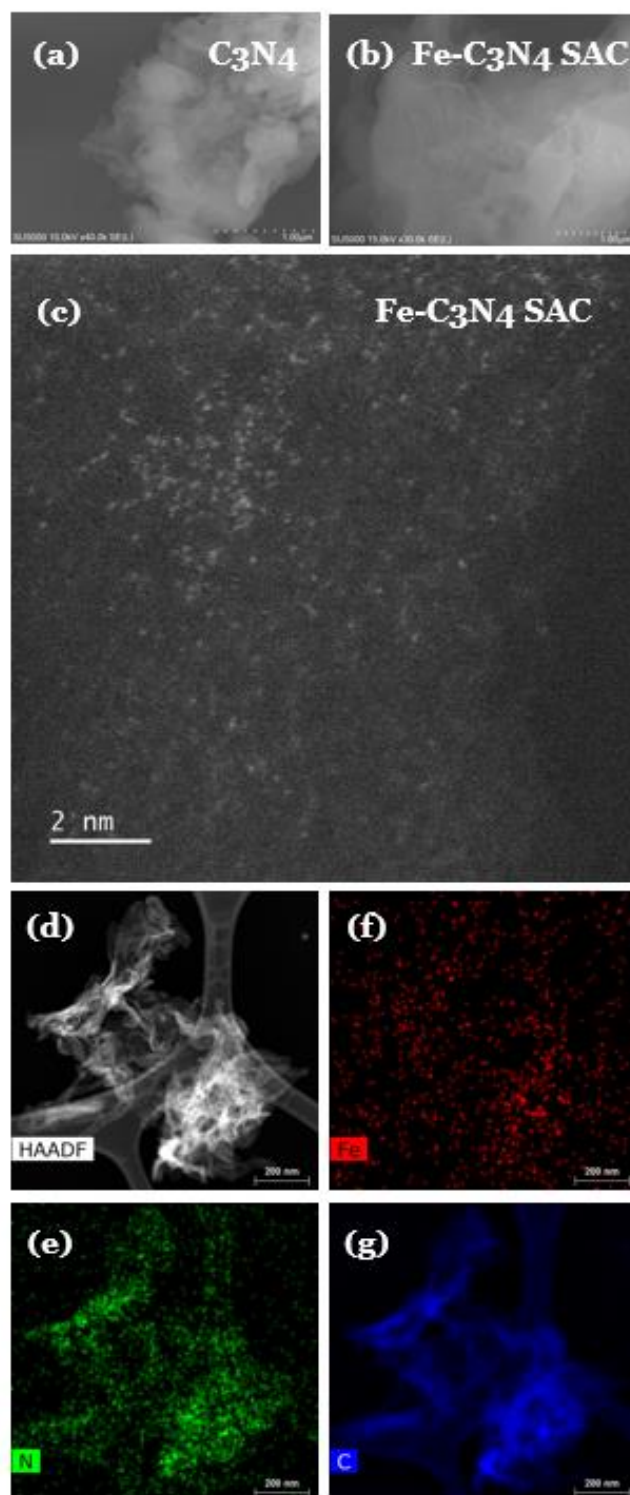


Fig. 4.3 (a) SEM image of C₃N₄. (b) SEM image of Fe-C₃N₄ SAC.

(c) HAADF-STEM image of Fe-C₃N₄ SAC. (d)-(g) Element mapping images of Fe-C₃N₄

SAC.

Furthermore, the X-ray powder diffraction (XRD) analysis of C_3N_4 and $Fe-C_3N_4$ SAC could be observed in Fig. 4.4 a. There are two diffraction peaks at 13.3° and 27.4° in C_3N_4 , which are referred to as the standard card (JCPDS 87-1526). The sharp peaks at $2\theta \approx 27^\circ$ were formed by the π - π interlayer stacking reflection and the broad peaks located at 13.3° were generated due to the in-plane structural packing motif. [113] Compared to C_3N_4 , $Fe-C_3N_4$ SAC shows a decreased intensity of diffraction peaks due to the addition of Fe single atoms. The results indicated Fe species was doped into C_3N_4 lattice. Besides, there is no new signal related to crystalline Fe species, further showing a homogeneous distribution of Fe species.

The chemical valence states were studied by X-ray photoelectron spectroscopy (XPS). Fig. 4.4 b depicts Fe 2p spectra recorded with $Fe-C_3N_4$ SAC. As observed, there are two main broad peaks at about 710 and 724 eV. It is also clear that three major components (i.e., Fe(II), Fe(III), and metallic Fe) could be detected by deconvolution in each peak. The characteristic C 1s and N 1s peaks could be clearly observed in both samples (Fig. 4.4 c-f). As for C_3N_4 , there are three typical N 1s core levels located at 398.60 eV, 399.81 eV and 401.11 eV, as displayed in Fig. 4.4 e. These peaks correspond to sp^2 C-N=C, sp^3 N-C₃ and C-N-H, and the ratio of these bonds are 0.28, 0.55 and 0.17, respectively. While for $Fe-C_3N_4$ SAC, the ratio of sp^2 C-N=C, sp^3 N-C₃ and C-N-H are 0.37, 0.48 and 0.15. The C 1s peaks present C-C, C-N-C and C-O bonds, which are located at 285.1 eV, 288.2 eV and 289.2 eV, respectively. Given that it is easy for carbon peaks to be contaminated, the nitrogen spectra are key when considering the bonding structure. [114]

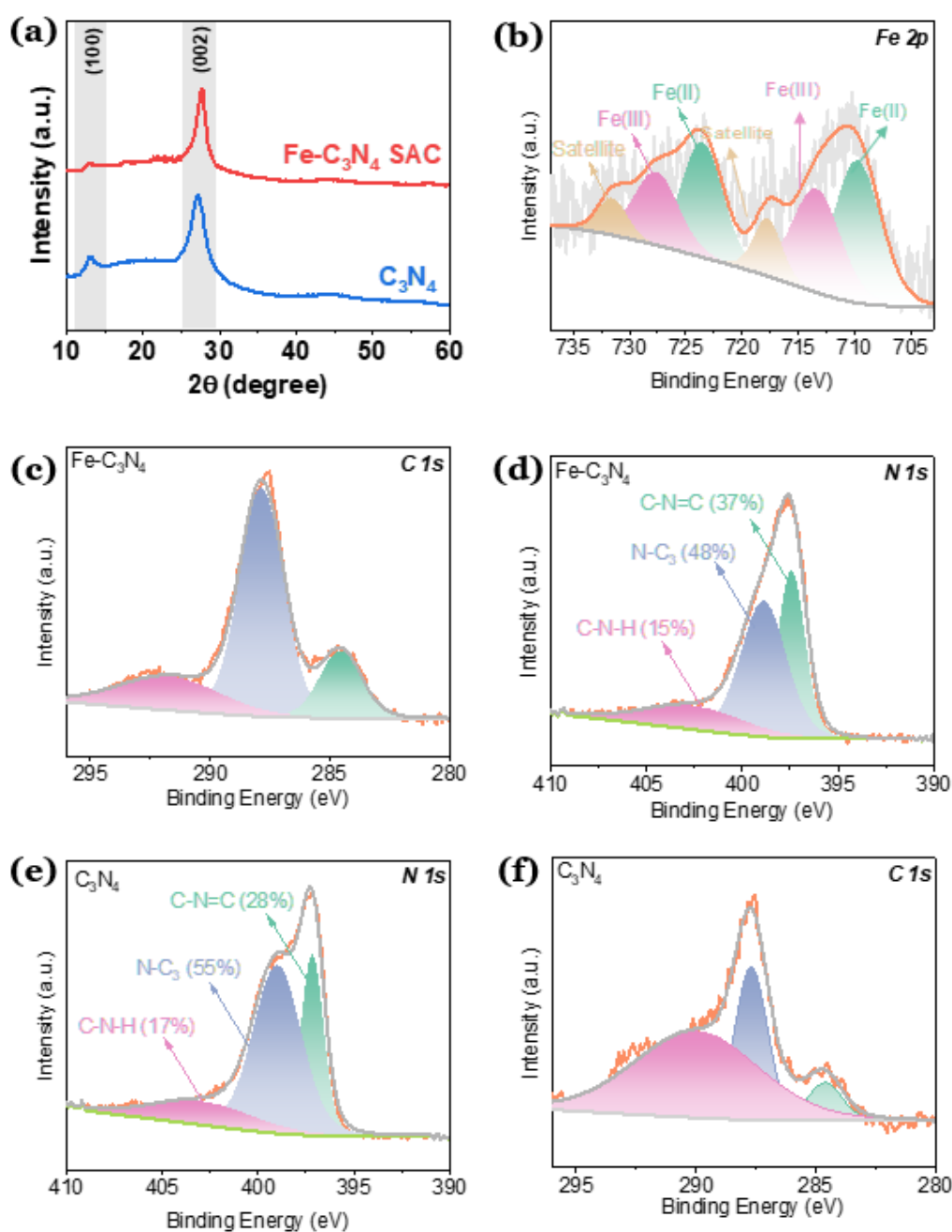


Fig. 4.4 (a) X-ray diffraction (XRD) patterns of C₃N₄ and Fe-C₃N₄ SAC.

(b-d) The high-resolution Fe 2p, C 1s, and N1s XPS spectra of Fe-C₃N₄ SAC.

(e-f) The high-resolution C 1s, and N1s XPS spectra of C₃N₄.

In order to better understand the coordination environment of Fe atoms, the X-ray absorption spectroscopies were measured at Advanced Photon Source, Argonne National Laboratory. Fig. 4.5 a presents the X-ray absorption fine structure spectroscopy (XAFS). The k³-weighted

Fourier transformation of Fe K-edge from extended X-ray absorption fine structure (EXAFS) spectra for Fe-C₃N₄ SAC and Fe foil were further summarized as shown in Fig. 4.5 b. The Fe-C₃N₄ SAC shows a peak at ~ 1.5 Å, which can be assigned to Fe-N bonds. [115] The Fe existed in Fe-C₃N₄ SAC are single atoms, which is confirmed by the evidence that there is no peak displayed at around 2.2 Å (Fe-Fe bond) in Fig. 4.5 b. The corresponding fitting results were studied in Fig. 4.5 c-f. Besides, wavelet transform (WT) analysis of Fe-C₃N₄ SAC presents one maximum intensity at 6 Å^{-1} , corresponding to Fe-N bond (Fig. 4.5 g). Compared with the WT plots of Fe foil in Fig. 3.5 h, there is no Fe-Fe signal ($\approx 8 \text{ Å}^{-1}$) detected, confirming the coordination of Fe single atoms and N atoms. [116]

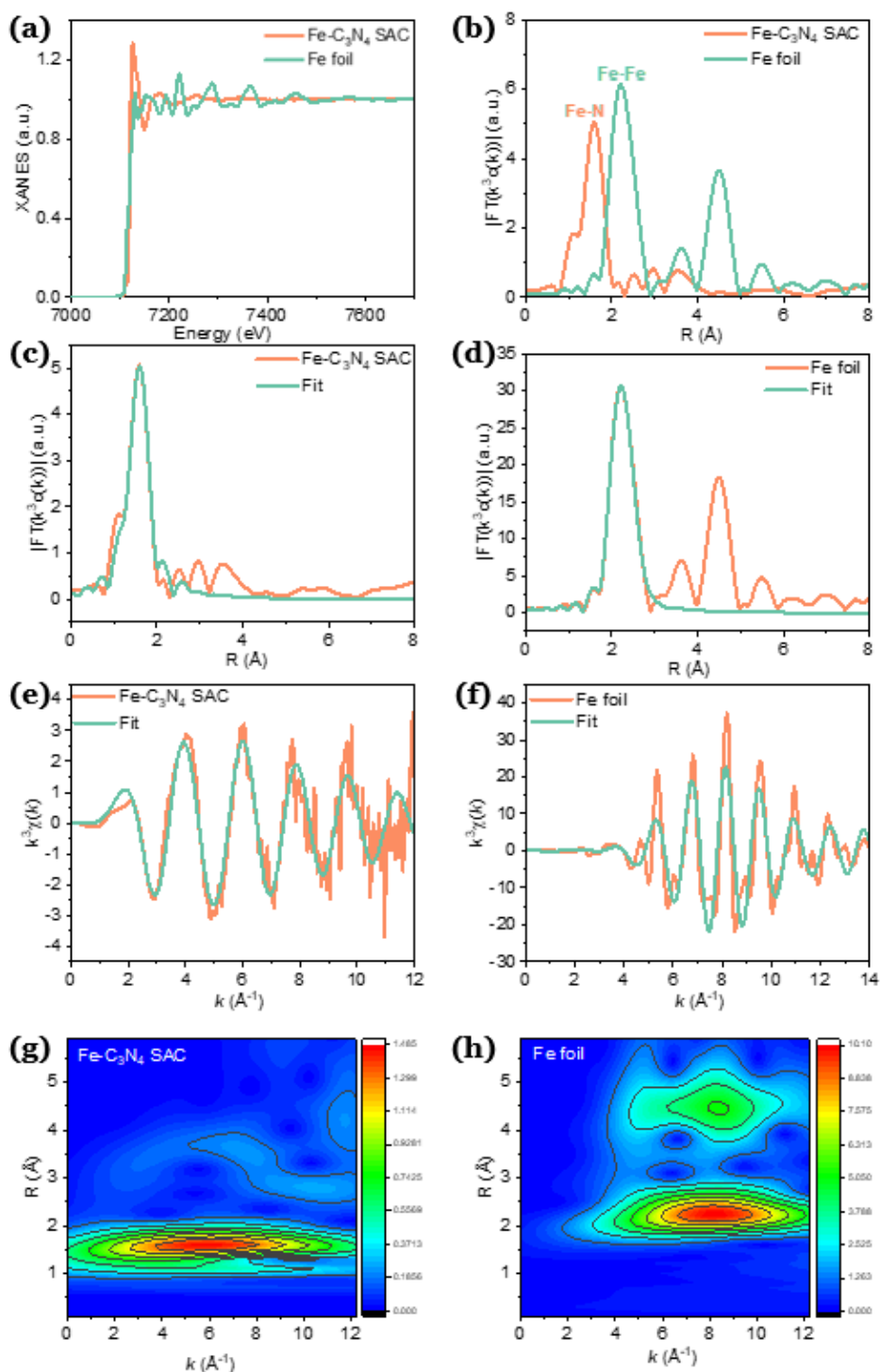


Fig. 4.5 (a) Fe K-edge XANES spectra of Fe-C₃N₄ SAC and Fe foil.

(b) Fourier-transformed (FT) curves at R space for Fe-C₃N₄ SAC and Fe foil.

(c-d) The corresponding EXAFS R space fitting result for Fe-C₃N₄ SAC and Fe foil.

(e-f) The corresponding EXAFS k₃-weighted k-space fitting result for Fe-C₃N₄ SAC and Fe

foil. (g-h) WT-EXAFS of Fe K-edge for Fe-C₃N₄ SAC and Fe foil.

4.5.2 Photocatalytic Characterization

The Fenton-like activity of Fe-C₃N₄ SAC and C₃N₄ was evaluated by the degradation of PET. All the experiments were carried out under a simulated natural environment. As depicted in Fig. 4.6 a, Fe-C₃N₄ SAC shows a great improvement in the production of acetic acid, indicating the existence of active sites. It is also calculated that the yield using Fe-C₃N₄ SAC is around 3.43 mg h⁻¹ g_{cat}⁻¹, while the yield of acetic acid is reduced to a third when using C₃N₄. Additionally, several conditions which could affect the photocatalytic activity were studied in Fig. 3.6 b. The combination of H₂O₂, catalysts and light are essential for the degradation of PET. This process is also involved in the generation of some reactive oxygen species (ROS). In order to find the main ROS and their influence on degradation, four scavengers (Tert-butanol (TBA), p-benzoquinone (p-BQ), EDTA-2Na, and silver nitrate (AgNO₃)) were applied for trapping, which would trap ·OH, superoxide radicals (O₂⁻), hole (h⁺) and electron, respectively. As is manifested, the degradation process is drastically restrained by ·OH, confirming that ·OH is the main functional free radical.

To further identify the ·OH formed during the PET degradation processes, ultraviolet-visible (UV-Vis) absorption spectra were obtained in Fig. 4.6 c-d. It is known that ·OH radicals could be directly detected by UV-Vis by adding salicylic acid (SA). [117]-[118] According to the results, Fe-C₃N₄ SAC has a higher ·OH generation ability compared with C₃N₄. Furthermore, electron paramagnetic resonance (ESR) spectra were employed to explore the behind mechanism. Apparently, there are characteristic signals of 1:2:2:1 existed in all systems, which could be assigned to DMPO-OH·.[119] It is implied that the H₂O₂ is decomposed and ·OH is formed during the photocatalytic processes. Although the signals were at the same positions, the signals involved in Fe-C₃N₄ SAC were more obvious and stronger than those in C₃N₄, which is the same conclusion as the previous analysis. Therefore, all the analysis above reveal that the efficiency of plastic decomposition is enhanced by the introduction of iron single sites.

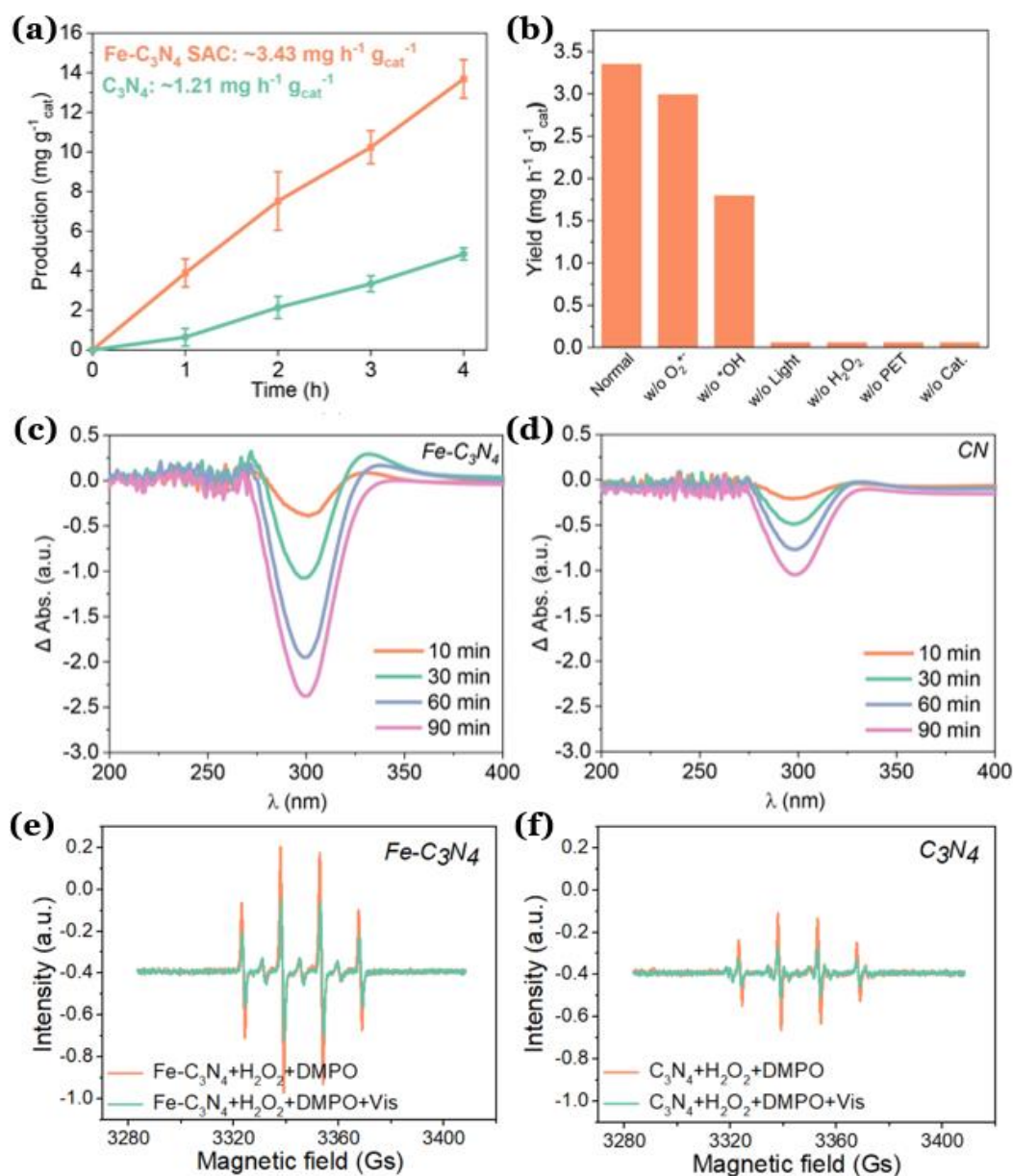


Fig. 4.6 (a) The yield of acetic acid during the photocatalytic of pure PET over different catalysts. The error bars in (a) represent the standard deviations of three independent measurements of the same sample. In the photocatalytic tests, the usage amount of all chemicals is the same at the first hour. Afterwards, H₂O₂ was added to the reaction systems at a rate of 2 mL/hour. (b) Photocatalytic activation of Fe-C₃N₄ SAC for PET degradation in the presence of different scavengers. (c-d) The UV-Vis spectra of Fe-C₃N₄ SAC and C₃N₄. (e-f) DMPO spin-trapping EPR spectra for •OH in Fe-C₃N₄ SAC and C₃N₄ solutions under different conditions.

As for the H_2O_2 excess experiments, all chemicals were used in the same amount in the first hour as before. Then there were no additional H_2O_2 in the system due to checking whether the H_2O_2 amount was enough. As revealed in Fig. 4.7 a, there would still be acetic acid formed in the following two hours, meaning that the H_2O_2 was excess. Besides, diverse plastic wastes (i.e., PET, PP and PE) were also degraded by our system (Fig. 4.7 b). According to Fig. 4.7 b, a higher yield of acetic acid was observed in PE. It is possibly because PE has a smaller plastic particle size which has more specific surface areas to contact with the solution.

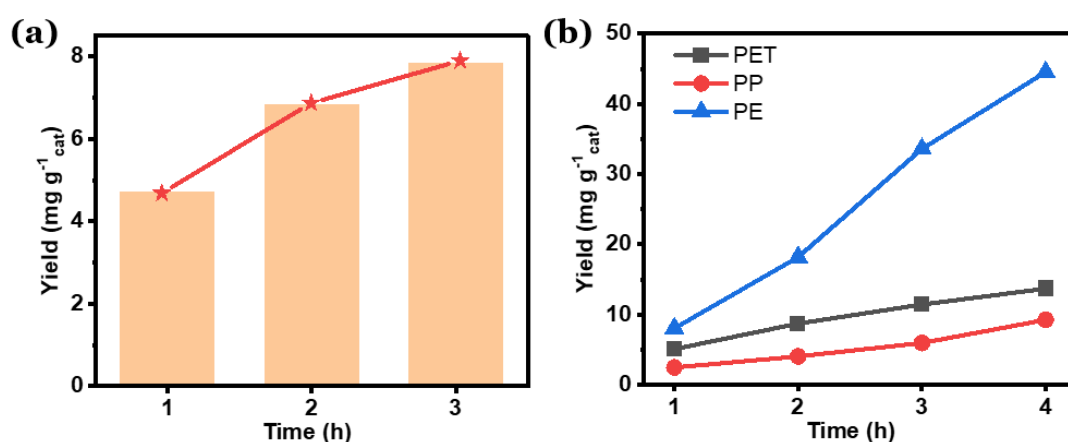


Fig. 4.7 (a) The Evidence for excess H_2O_2 with the increasing yield of acetic acid.

(b) Degradation of diverse plastic wastes (PE, PET, PP) in the $\text{Fe-C}_3\text{N}_4$ SAC/ H_2O_2 /Vis system with the production of acetic acid.

4.6 Summary

In this work, a promising strategy to upcycling plastics has been proposed. The excellent catalyst (Fe-C₃N₄ SAC) was prepared by magnetic stirring and calcining. Through introducing Fe single atoms into graphitic carbon nitride, a dramatic improvement could be seen in the catalytic activity. Characterizations have been carried out to investigate the mechanism. The main conclusions of this study are as follows:

1. Both C₃N₄ and Fe-C₃N₄ SAC have effects on plastic decomposition. Typically, the introduction of iron could significantly improve the reaction efficiency.
2. STEM analysis showed the existence of Fe single atoms uniformly distributed in the Fe-C₃N₄ SAC. This conclusion has been further proved by XRD, XPS and XAFS results.
3. UV and ESR results revealed that there are ·OH radicals formed during the degradation process. It is noted that ·OH radicals play important role in the Fenton-like system.
4. Considering the size of different plastics, those plastics with large specific surface areas have higher degradation rates.

Chapter 5

Electrocatalytic Upcycling of Polyethylene Terephthalate

5.1 Introduction

Electrocatalysis provides a promising strategy to form high-value organic oxygenates. [4] In the electrochemical oxidation process, it could be carried out in a mild condition with high selectivity by tuning the electrode potential. [120] It is reported that abundant value-added chemicals, such as formate [121]-[122] and acetate [123]-[124], could be generated during the electrocatalytic reforming processes. The techno-economic analysis (TEA) has been studied as shown in Fig. 5.1, which exhibits the economic possibility of this upcycling.

However, it still needs to explore how to transfer PET into high-value matters via this method. Here, we focus more on the combination of electrochemical oxidation and PET upcycling.

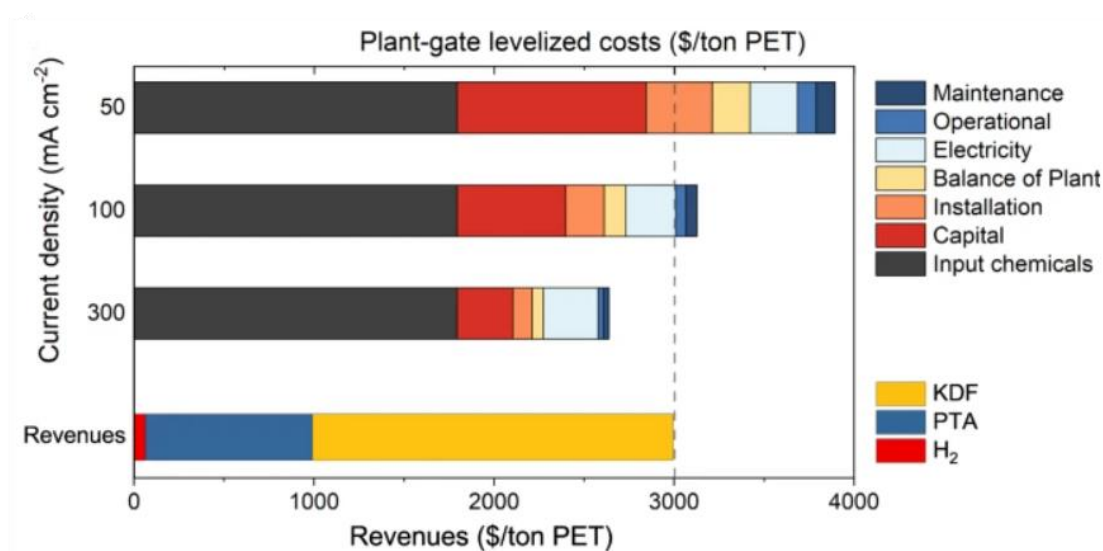


Fig. 5.1 Techno-economic analysis (TEA) of Route I at different current density.

Route I: the conversion of PET waste into functional commodity chemicals (i.e., potassium diformate and terephthalic acid) and clean fuel (H₂). [4]

5.2 Synthesis of Catalysts

5.2.1 Ni(OH)₂

The Ni(OH)₂ was fabricated by a facile hydrothermal method. Initially, small pieces of nickel foam (3cm * 4cm) was sequentially washed with acetone, 0.5M H₂SO₄ solution, deionized water, and absolute ethanol, each for 10 min in order to clean its surface. Afterwards, the pre-treated nickel foam was dried in air and then transferred into a 100mL Teflon-lined stainless steel autoclave with 80mL deionized water. The autoclave was sealed and then maintained in an oven at 180°C for 5 h. After cooling to room temperature naturally, the nickel foam was collected and rinsed three times with absolute ethanol and deionized water. It was then oven-dried at 50°C to purify.

5.2.2 NiO

The as-prepared Ni(OH)₂ was heated in a tube furnace at 300°C and 500°C in air for 2h.

5.2.3 NiO@Au

Au nanoparticles supported NiO were synthesized through electrochemical deposition in a three-electrode system, using a saturated calomel electrode (SCE) and a platinum (Pt) foil as reference and counter electrodes respectively. The as-prepared NiO was used as the working electrode. Typically, the NiO@Au was prepared in an aqueous solution with 0.1 M NaCl and 5 mM HAuCl₄. The Au nanoparticles were first deposited on NiO by stepping the potential to -0.6 V vs. SCE for 10 s, followed by stepping back to -0.2 V vs. SCE for 10 s for three cycles. [125]-[126]

5.3 Experimental Measurements

5.3.1 Apparatus

As for thermal degradation of PET, 100 mL 2 M KOH aqueous solution was firstly prepared and put into a 250 mL of round-bottom flask. Then 12.6 g PET and a stir bar were put into the same flask. The flask was sealed and heated on a hotplate at 80 °C with stirring. During the thermal reactions, solution was taken at different times (1, 2, 4, 6, 22, and 28 hour). Afterwards, the yields of ethylene glycol (EG) were analyzed by H-NMR (The specific analytical methods will be discussed later).

All electrochemical experiments were carried out in an H-cell on an electrochemical workstation (CHI). As is shown below in Fig. 5.2, the solutions were separated by anion exchange membrane. The active area of NiO@Au electrode is 1 cm × 1 cm for all experiments. The tests were performed in a three-electrode system, equipped with saturated Ag/AgCl and platinum foil as reference and counter electrodes, respectively. All potentials measured against Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale using $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.0591 \text{ pH}$. The electrocatalytic reactions were carried out at potentiostatic mode with iR compensation.

After reactions, the concentration of products (glycolic acid and formate) was quantified by H-NMR. The Faradaic efficiency (FE) was calculated through the following Equation [4]:

$$\text{FE}(\%) = 100\% \times \frac{\text{mole of produced product}}{\text{total charge passed}/(n \times 96485 \text{ C mol}^{-1})}$$

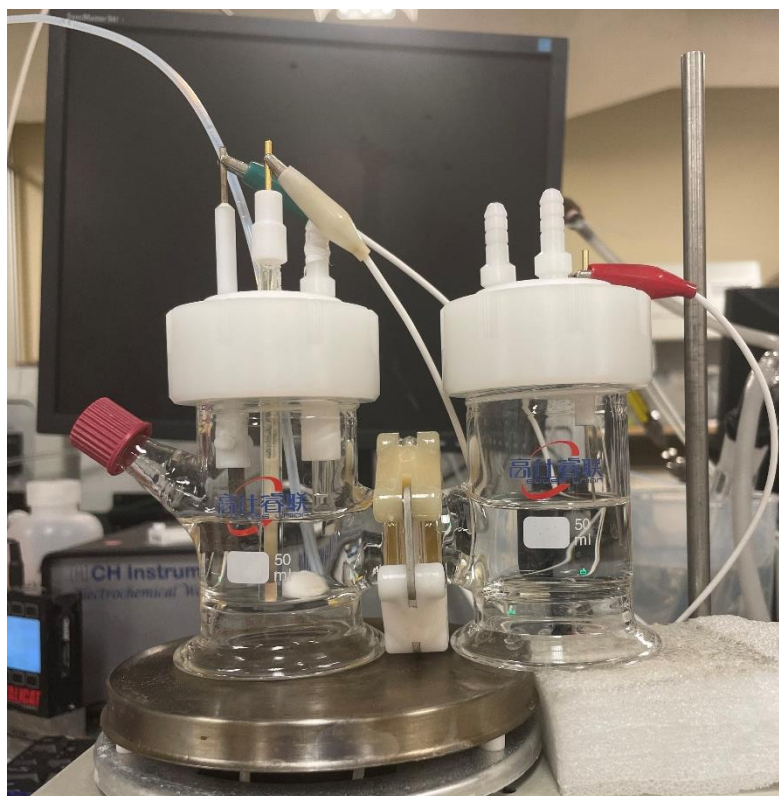


Fig. 5.2 Experimental setup.

5.3.2 Analytical Methods

The concentration of thermal product was analyzed by H-NMR. Firstly, several different ethylene glycol (EG) solutions of known concentration were prepared and mixed with the internal solution in order to obtain the standard curve. The ratio of the mixture solution is 100 μ L of internal standard solution and 630 μ L sample. The internal standard solution is made of 10 mL H₂O, 3.9 μ L DMSO and 22.25 mL D₂O.

Fig. 5.3 a shows the standard curve for our project. When setting DMSO area into 1, the concentration of liquid products is determined via the fitted linear relationship in Fig. 5. 3 a:

$$\text{Area ratio to DMSO} = 0.01 + 0.46 * \text{Concentration}$$

128 scans were used in order to suppress the water peak. From this curve, the actual concentration of EG could be estimated. As presented in Fig. 5.3 b, EG and DMSO can be ascribed to the peaks located at 3.58 ppm, and 2.63 ppm, respectively.

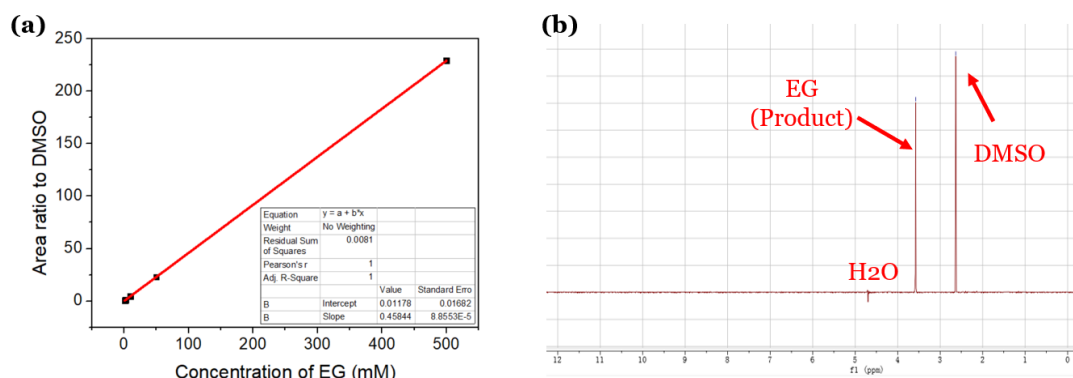


Fig. 5.3 (a) The standard curve of EG. (b) An example of H-NMR results.

Glycolic acid, as the main liquid product of the electrochemical oxidation of EG, was determined by H-NMR method. Specially speaking, the standard curve of glycolic acid was firstly built using pure chemicals with known concentrations. After the electrocatalytic reaction, the solution was collected and mixed with the NMR detecting solution (as above). The Fig. 5.4 a shows the standard curve for our project. When setting the area of DMSO into 1, the concentration of liquid products is determined via the fitted linear relationship in Fig. 5.4 a:

$$\text{Area ratio to DMSO} = -0.15 + 0.32 * \text{Concentration}$$

Obviously, this relation could provide us with the actual yield and the trend of product production. As presented in Fig. 5.4 b, glycolic acid and DMSO can be described to the peaks located at 3.83 ppm, and 2.63 ppm, respectively.

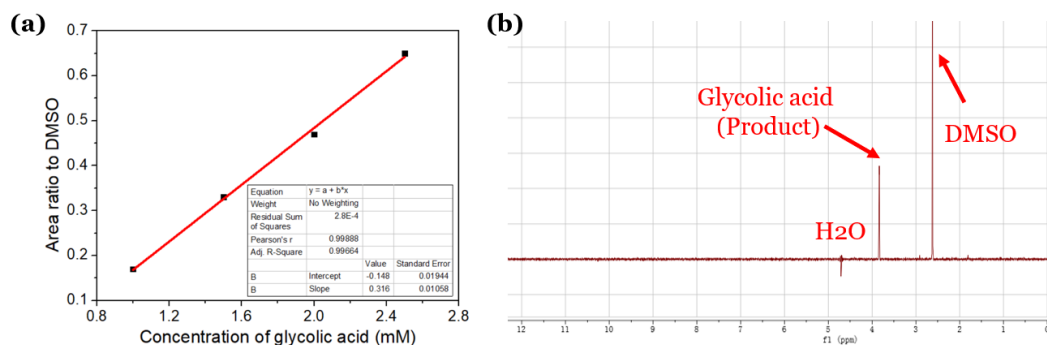


Fig. 5.4 (a) The standard curve of liquid products. (b) An example of H-NMR results.

5.4 Results and Discussions

5.4.1 Characterization of Catalyst

Morphological characteristics of the $\text{Ni}(\text{OH})_2$, NiO , NiO@Au , NiO@Au after 1 hour i-t test (under -0.2V), and NiO@Au after 200 hours i-t test (under -0.2V) samples were characterized by scanning electron microscope (SEM) as shown in Fig. 5.5 a-e. Fig. 5.5 a illustrates a hydrotalcite-like structure of $\text{Ni}(\text{OH})_2$. This has similar structure as reported in the literature. [127] These $\text{Ni}(\text{OH})_2$ nanosheets overlay over nickel foam substrate, spatially interconnecting with each other. Moreover, there are hexagonal architectures randomly appeared in Fig. 5.5 b. This gives evidence of the conversion between $\text{Ni}(\text{OH})_2$ and NiO , close to the previous study. [128] As clearly displayed in Fig. 5.5 c-e, gold nanoparticles are uniformly dispersed on the surface of NiO .

Fig. 5.5 f elaborates the X-ray powder diffraction (XRD) patterns of the NiO , NiO@Au , NiO@Au after 1 hour i-t test (under -0.2V), and NiO@Au after 200 hours i-t test (under -0.2V). It is detected that the major peaks at 44.5° , 51.7° , and 76.3° match well with the diffractions from (111), (200) and (220) planes of metallic nickel. [129]-[130] These peaks are strong due

to the nickel foam substrates. Similarly, the peaks located at 37.0° , 43.2° and 62.8° belong to the diffractions from (111), (002) and (220) planes of NiO, respectively (JCPDS no.: 89-5881). [131]-[133] After electrodeposition of gold nanoparticles, the new diffraction peaks demonstrated in the XRD patterns are $2\theta = 38.1^\circ$ and 64.5° . These peaks can be indexed to the (111) and (220) planes of face centered cubic (fcc) phase Au (JCPDS File No. 04-0784). [134] Noted that the (200) planes of Au should have a peak at 44.3° , which is completely overlapped with the peak of nickel foam substrates. This result confirmed the existence of Au nanoparticles and the structure of materials.

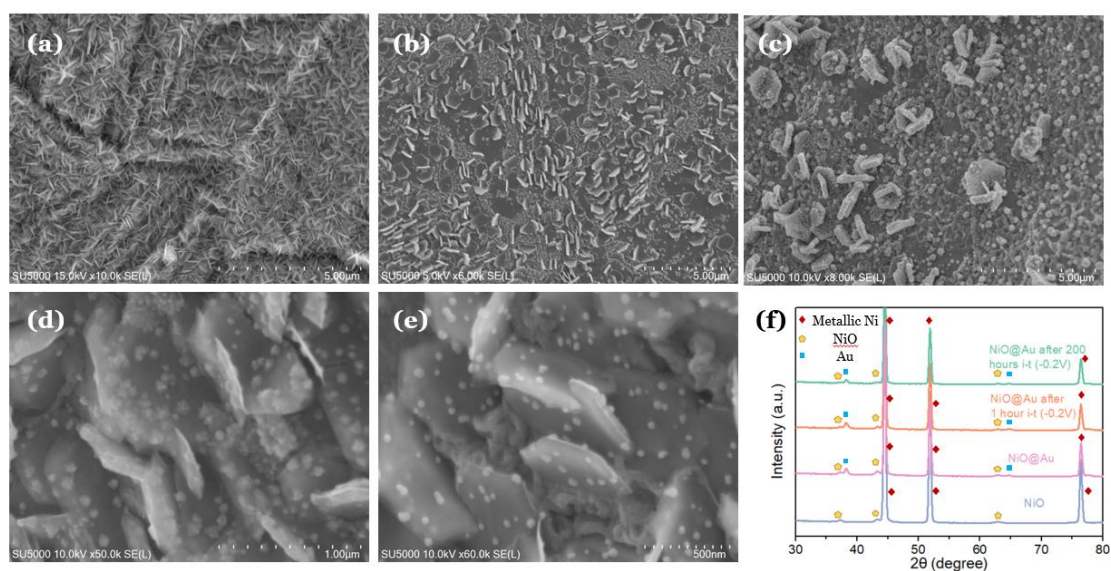


Fig. 5.5 The SEM images of (a) Ni(OH)₂; (b) NiO; (c) NiO@Au; (d) NiO@Au after 1 hour i-t test (under -0.2V); (e) NiO@Au after 200 hours i-t test (under -0.2V). (f) The XRD patterns of NiO, NiO@Au, NiO@Au after 1 hour i-t test (under -0.2V), and NiO@Au after 200 hours i-t test (under -0.2V).

The surface compositions and valence states of the catalysts were verified by X-ray photoelectron spectroscopy (XPS) spectra, as demonstrated in Fig. 5.6. The spectra indicated the existence of Ni, O and Au elements (Fig. 5.6 a & e), which is in agreement with the XRD results. From the survey spectra, the C 1s peak could be observed due to the carbon contamination. [135]-[136] Fig. 5.6 b & f show the characteristic spectrum of O 1s. The peak situated at 529.6 eV could be assigned to the Ni-O bond. The intensity of Ni-O peak decreases

after the reaction. This indicates the decrease of oxygen concentration on the surface of the material. This may be due to the lattice oxygen participating in the electrochemical oxidation of EG to Glycolic acid. The peak located at 531.9 eV in Fig. 5.6 b & f reveals the presence of O-H group. [137] In the Ni 2p spectrum (Fig. 5.6 c & g), two characteristic peaks at 856.5 eV (Ni 2p_{3/2}) and 873.8 eV (Ni 2p_{1/2}), which could be explained by β -Ni(OH)₂ phase. [138]-[140] In addition, there are broad peaks situated at 861.4 and 880.5 eV, which can be assigned to Ni 2p_{3/2} and Ni 2p_{1/2} satellite peaks. [141] The weak peak at 853.8 eV illustrates the existence of NiO, which is consistent with the previous reports. [142] Fig. 5.6 d & h show the Au 4f XPS spectrum. The two peaks at binding energies of 84.2 eV and 87.8 eV, corresponding to the metallic Au 4f_{7/2} and Au 4f_{5/2} peaks, respectively. [143]-[144]

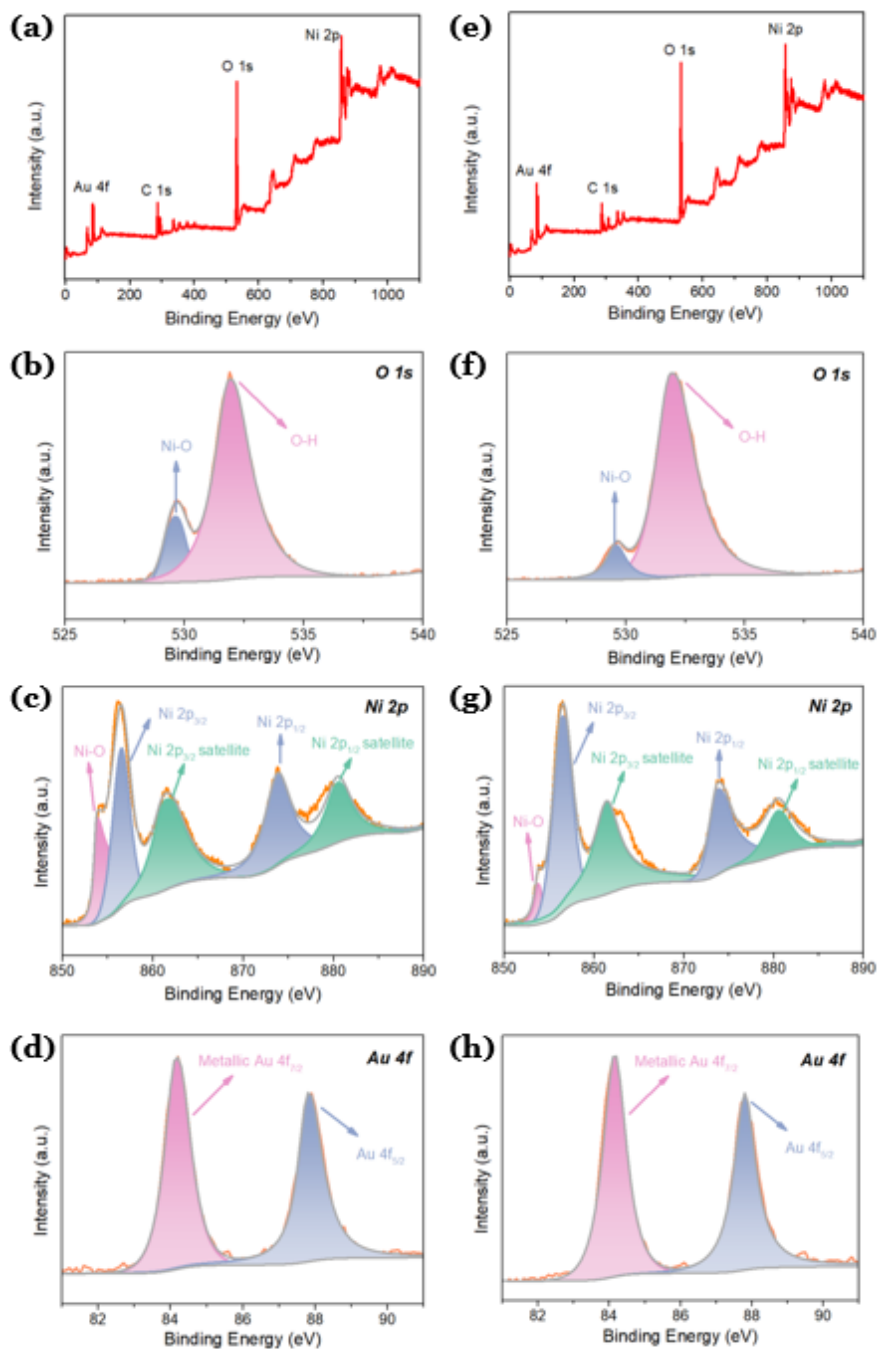


Fig. 5.6 The XPS spectra of NiO@Au: (a) full spectrum, (b) O 1s, (c) Ni 2p, and (d) Au 4f; the XPS spectra of NiO@Au after 200 hours i-t test (under -0.2V): (e) full spectrum, (f) O 1s, (g) Ni 2p, and (h) Au 4f.

5.4.2 Hydrolysis of PET

It is known that two monomers (i.e., terephthalic acid (PTA) and EG) could be obtained from the thermal reaction due to the nature of PET. However, both of these chemicals are relatively cheap. As one of the oxidation products of EG, glycolic acid has increasing application scope in the cosmetics and textile industries, and its market value is predicted to achieve USD 415.0 million in the following two years. [145]

The aim of our project is to upcycle the PET plastic into value-added chemicals. Initially, the 12.6 g PET was easily hydrolyzed into EG in the presence of 2 M KOH solution at 60 °C. In the 28th hour, the yield of EG is near 0.5 M (Fig. 5.7). The solution (2 M KOH and 0.5 M EG) was then used for electrolysis, in which EG was selectively oxidized to glycolic acid, which has a higher economic value than EG (The results will discuss in 5.5.3).

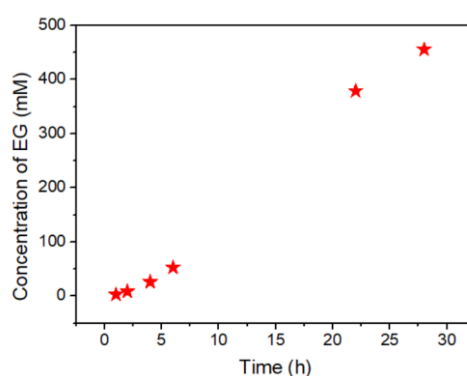


Fig. 5.7 The EG productivity of PET hydrolysis as the function of time in 2 M KOH at 60 °C.

5.4.3 Electrocatalytic Oxidation

Cyclic voltammetry (CV) was applied to study the electrooxidation of EG. Fig. 5.8 a illustrates the CV curves of NiO@Au electrodes in the absence and presence of 0.5 mol L⁻¹ EG in a 2.0 mol L⁻¹ KOH solution at a scan rate of 100 mV s⁻¹. There is a reduction peak shown in the

backward scan at 0.08 V in Fig. 5.8 a, which is related to the reduction of the formed product. [146] The oxidation peak at 0.22 V in Fig. 5.8 a is related to the oxidation of EG to glycolic acid. The EG oxidation over electrode was evaluated in a three-electrode H-cell system separated by an anion exchange membrane (AEM). As shown in Fig. 5.8 b, glycolic acid is the main product in the processes. It could be obtained between -0.2 V and 0.1 V vs. Ag/AgCl on NiO@Au. It is worth to mention that the highest FE for generating it is over 50 %, which is under -0.2 V vs. Ag/AgCl. And the maximum yield of glycolic acid on NiO@Au could be obtained at 0.1 V vs. Ag/AgCl. As for NiO, the glycolic acid would only be gotten under 0 V and 0.1 V vs. Ag/AgCl. Furthermore, the excellent catalyst stability of NiO@Au was evaluated at a constant potential of -0.2 V vs. Ag/AgCl for 200 hours, as shown in Fig. 5.8 c.

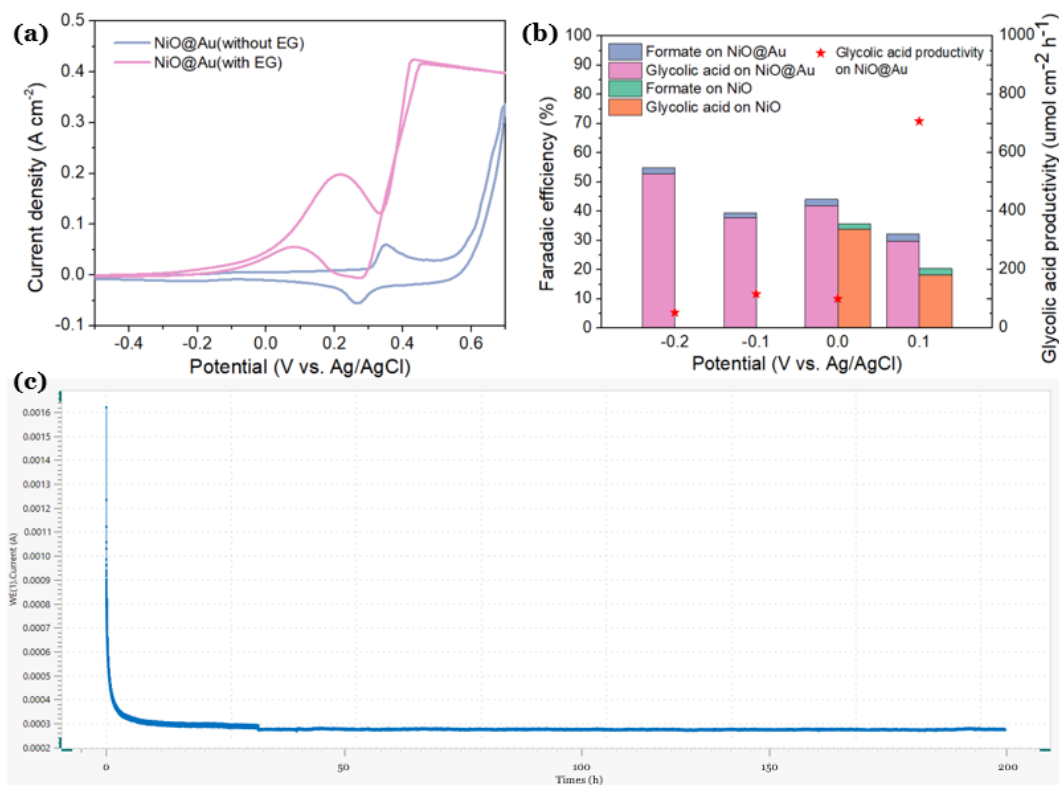


Fig.5.8 (a) CV curves of the NiO@Au electrodes for EG oxidation. Electrolyte: 2.0 M KOH and 0.5 M EG (optional). Scan rate: 100 mV s⁻¹. (b) FE and productivity of glycolic acid on NiO and NiO@Au at different potentials. (c) Chronoamperometric stability test for EG oxidation at -0.2 V vs. Ag/AgCl on NiO@Au.

5.5 Summary

An upcycling method for plastic waste with the combination of hydrolysis and electrocatalytic oxidation was demonstrated in this project. The reason why we use PET in this study is that ester links exist in PET main chain and these bonds are easily attacked during pyrolysis. Firstly, the PET was decomposed into monomers (EG and terephthalic acid) in a mild environment. EG was then electrocatalytic converted into glycolic acid by NiO@Au with high stability and FE (~53%).

Chapter 6

Conclusion, Limitations and Future Studies

To conclude, this thesis demonstrates two possible strategies for the catalytic upcycling of plastic waste. In the first part of the thesis, two photocatalysts are prepared and their catalytic efficiency has been studied. Fe-C₃N₄ SAC shows a great yield of acetic acid, which could generate approximately triple product after one hour's reaction. In addition, the presence of ·OH formed in photocatalysis is also proved by UV-Vis and ESR. For the second studies, PET is thermally degraded into ethylene glycol, then converted into glycolic acid by electrochemical reaction. It is investigated that high stability and FE (~53%) could be obtained in the electroconversion process by the NiO@Au electrode materials.

However, there are still some limitations. For the first results chapter, density-functional theory (DFT) calculations are still expected to be employed to explore the undergoing pathways. In addition, the photoconversion of plastic products could also be evaluated. As for the second result chapter, the FE could be further enhanced by the optimization of NiO@Au electrode.

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