

Design and Synthesis of Metal-Organic Framework-Based Photocatalysts and Their Application in Upcycling of Plastic

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Design and Synthesis of Metal-Organic Framework-Based Photocatalysts and Their Application in Upcycling of Plastic

Jibo Qin

PhD Thesis December 2023

DTU Sustain Department of Environmental and Resource Engineering Technical University of Denmark

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The synopsis part of this thesis is available as a PDF file for download from the DTU research database ORBIT: http://www.orbit.dtu.dk

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Preface

This PhD thesis, entitled "Design and Synthesis of Metal-organic Frameworkbased Photocatalysts and Their Application in Upcycling of Plastic," summarises research conducted at the Department of Environmental and Resource Engineering, Technical University of Denmark, from November 2020 to October 2023. The author was supported by the Novo Nordisk Foundation (NNF18OC0034918), the Innovation Fund Denmark Grand Solution (Grant No. 2079-00012B) and the Chinese Scholarship Council for his stay at the Technical University of Denmark. Under the primary guidance of Associate Professor Wenjing Zhang (DTU Sustain) and the collaborative cosupervision of Associate Professor Yibo Dou (Beijing University of Chemical Technology) and Associate Professor Henrik Rasmus Andersen (DTU Sustain), the research endeavours were diligently carried out.

The thesis is organised in two parts: the first puts into context the findings of the PhD in an introductive review; the second part consists of the papers listed below. These will be referred to in the text by their paper number, written with the Roman numerals **I-III**.

- I Qin, J., Dou, Y., Wu, F., Yao, Y., Andersen, H. R., Hélix-Nielsen, C., Lim, S. Y., and Zhang, W. (2022) In-Situ Formation of Ag₂O in Metal-Organic Framework for Light-Driven Upcycling of Microplastics Coupled with Hydrogen Production. *Applied Catalysis B: Environmental.* 319, 121940.
- II Qin, J., Dou, Y., Zhou, J., Candelario, W. M., Andersen, H. R., Hélix-Nielsen, C., and Zhang, W. (2023) Photocatalytic Valorization of Plastic Waste over Zinc Oxide Encapsulated in a Metal–Organic Framework. *Advanced Functional Materials*, 33, 2214839.
- III Qin, J., Dou, Y., Zhou, J., Zhao, D., Orlander, T., Andersen, H. R., Hélix-Nielsen, C., and Zhang, W. (2024) Encapsulation of Carbon-Nanodots into Metal-Organic Frameworks for Boosting Photocatalytic Upcycling of Polyvinyl Chloride Plastic. *Applied Catalysis B: Environmental*, 341, 123355.

Furthermore, the following publications were not included in this thesis:

- I Qin, J., Dou, Y., Hélix-Nielsen, C., and Zhang, W. Functionalized Advanced Materials for Waste Plastic Management. Manuscript in preparation.
- Wu, F., Dou, Y., Zhou, J., Qin, J., Jiang, T., Yao, Y., Hélix-Nielsen, C., and Zhang, Y. (2023). High-Entropy (FeCoNiCuZn)WO₄
 Photocatalysts-Based Fibrous Membrane for Efficient Capturing and Upcycling of Plastic. *Chemical Engineering Journal*, 470, 144134.
- III Yao, Y., Lim, S. Y., Frandsen, C., Li, Z., Dou, Y., Wu, F., Jiang, T., Qin, J., Zou, J., Stamate, E and Zhang, W. (2023). Universal Synthesis of Half-Metallic Diatomic Catalysts for Efficient Oxygen Reduction Electrocatalysis. *Small*, accepted.
- IV Wang, H., Chen, N., Feng, C., Deng, Y., Qin, J. Interaction Mechanisms of Agricultural Waste-Driven Denitrification and V (V) Reduction: Internal Electron Competition, Sequential Transfer and Activation of Vanadium. *Chemical Engineering Journal (Manuscript submitted)*.

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Summary

Plastic is a widely used product in our daily lives due to its light weight, chemical resistance and excellent electrical insulation properties. Since the 1950s, more than 8.3 billion tons of plastic have been produced, approximately 80% of which becomes plastic waste in the natural environment. Due to the strong chemical inertness of plastic waste, its spontaneous degradation process takes centuries, resulting in a severe global environmental problem known as "white pollution."

In recent years, photocatalysis, as an environmentally friendly and energysaving technology that can upcycle plastic waste into valuable fuels, has received increasing attention. However, the vast majority of existing photocatalysts have low activity in relation to plastic upcycling, which can be ascribed to their high carrier recombination rate and low quantum efficiency. Metal-organic frameworks (MOFs) have attracted the attention of researchers recently due to their high surface area, modifiable functional groups and tuneable structure. These unique characteristics enable MOFs materials to exhibit excellent performance in the fields of photocatalytically splitting H₂O, degrading organic pollutants and reducing gas. To the best of our knowledge, there have been no reports of MOFs as photocatalysts being used for plastic upcycling.

The main objective of this thesis is to introduce innovative methodologies employed in designing and constructing heterojunction photocatalysts for converting plastics. Diverse plastics, such as polyethylene glycol (PEG), polylactic acid (PLA) and polyvinyl chloride (PVC), are utilised to evaluate the catalytic efficacy of synthesised photocatalysts. A detailed explanation of the correlation between the structural characteristics of MOF-based composite photocatalysts and their photocatalytic activity is provided. Furthermore, this project also involves conducting an in-depth study of the pathways and mechanisms for photocatalytic plastic upcycling.

We first evaluate the feasibility of MOF-based composite materials for the photocatalytic conversion of PEG. Specifically, we propose a photochemical synthesis approach to embed Ag₂O within the MIL(Fe)-101 to fabricate Ag₂O/MIL(Fe)-101. During the synthesis of photocatalysts, the maintained MOF structure of Ag₂O/MIL(Fe)-101 can effectively regulate Ag₂O particle size (~6 nm). The presence of a heterojunction between Ag₂O and MIL(Fe)-101 ensures that Ag₂O/MIL(Fe)-101 has an efficient electron-hole separation

rate. As a result, the resulting $Ag_2O/MIL(Fe)$ -101 heterojunction can convert 27.5 mg PEG into acetic acid within 3 h, coupled with H₂ production. Hence, this work preliminarily verifies the possibility of MOFs photocatalysts in plastic upcycling.

Inspired by previous work, a strategy involving partial calcination is developed herein to convert Zn sites in Zn-UiO66-NH₂ into ZnO semiconductors that are encapsulated in UiO66-NH₂ pores. The intricate interplay between ZnO and UiO66-NH₂ at the interfacial level creates a pathway for efficient charge transfer while also ensuring the structural stability of ZnO/UiO66-NH₂. A biodegradable plastic-PLA is used to evaluate the catalytic performance of the ZnO/UiO66-NH₂. As a result, the ZnO/UiO66-NH₂ shows remarkable selectivity for acetic acid production during the PLA upcycling process, coupled with efficient H₂ production. Therefore, this work presents a novel approach to designing and constructing heterojunction photocatalysts for plastic upcycling.

To improve the light absorption performance of MOF-based photocatalysts, a mild pyrolysis strategy is developed to encapsulate carbon nanodots (CDs) into UiO66 pores to fabricate CDs/UiO66. The introduction of CDs enhances the solar light absorption capacity and promotes the carrier separation rate of CDs/UiO66. In this work, a non-biodegradable plastics-PVC is used as the target plastic. As a result, the as-prepared CDs/UiO66 exhibits high catalytic activity when converting PVC into acetic acid. Overall, this work provides a novel method to enhance the plastic conversion capability of MOF-based photocatalysts.

Dansk sammenfatning

Plastik er et bredt anvendt produkt i vores daglige liv på grund af dets lette vægt, kemiske resistens og fremragende elektriske isoleringsegenskaber. Siden 1950'erne er der blevet produceret mere end 8,3 milliarder tons plastik, hvoraf cirka 80% bliver til plastikaffald i den naturlige omgivelse. På grund af plastikaffaldets stærke kemiske inertness tager dets spontane nedbrydningsproces århundreder og resulterer i et alvorligt globalt miljøproblem kendt som "hvid forurening."

I de senere år har fotokatalyse som en miljøvenlig og energibesparende teknologi, der kan omskabe plastikaffald til værdifulde brændstoffer, modtaget stigende opmærksomhed. Ikke desto mindre har flertallet af eksisterende fotokatalysatorer lav aktivitet i forhold til omskabelse af plastik, hvilket kan tilskrives deres høje bærerrekombinationshastighed og lave kvanteffektivitet. Metal-organic frameworks (MOFs) har for nylig tiltrukket forskernes opmærksomhed på grund af deres store overfladeareal, modificerbare funktionelle grupper og justerbar struktur. Disse unikke karakteristika gør det muligt for MOF-materialer at opvise fremragende præstationer inden for områder som fotokatalytisk spaltning af H₂O, nedbrydning af organiske forurenende stoffer og reduktion af gas. Efter vores bedste viden er der dog ikke rapporteret om anvendelse af MOFs som fotokatalysatorer til omskabelse af plastik.

Hovedmålet med denne afhandling er at introducere innovative metoder, der anvendes til at designe og konstruere heterojunktionelle fotokatalysatorer til omdannelse af plastmaterialer. Forskellige plastmaterialer, såsom polyethylen glycol (PEG), polymælkesyre (PLA) og polyvinylchlorid (PVC), anvendes til at vurdere den katalytiske effektivitet af de syntetiserede fotokatalysatorer. Der gives en detaljeret forklaring på korrelationen mellem de strukturelle karakteristika af MOF-derivater og deres fotokatalytiske aktivitet. Desuden involverer dette projekt også en dybtgående undersøgelse af fotokatalytiske ruter og mekanismer for omskabelse af plastmaterialer.

Vi vurderer først muligheden for MOF-baserede kompositmaterialer til fotokatalytisk omdannelse af PEG. Konkret foreslår vi en foto-kemisk syntesemetode til at indlejre Ag_2O i MIL(Fe)-101 for at fremstille $Ag_2O/MIL(Fe)$ -101. Under syntesen af fotokatalysatorer kan den opretholdte struktur af et MOFs effektivt regulere Ag_2O -partikelstørrelsen (ca. 6 nm). Tilstedeværelsen af en heterojunktion mellem Ag_2O og MIL(Fe)-101 sikrer, at

 $Ag_2O/MIL(Fe)$ -101 har en effektiv adskillelsesrate for elektron-huller. Som resultat heraf kan den resulterende heterojunktion $Ag_2O/MIL(Fe)$ -101 omdanne 27,5 mg PEG til eddikesyre inden for 3 timer, sammen med produktion af H₂. Dette arbejde bekræfter således foreløbigt muligheden for MOF-fotokatalysatorer i omskabelse af plastmaterialer.

Inspiret af tidligere arbejde er der udviklet en strategi, der involverer delvis kalcinering, for at omdanne Zn-steder i Zn-UiO66-NH₂ til ZnO halvledere, der er indkapslet i UiO66-NH₂-porerne. Det komplekse samspil mellem ZnO og UiO66-NH₂ på grænsefladen skaber en vej for effektiv overførsel af ladning ved lysexcitation samtidig med at det sikrer strukturel stabilitet for fotokatalysatorerne. En nedbrydelig plastik, PLA, bruges som målplastik for at evaluere den katalytiske præstation af de syntetiserede fotokatalysatorer. Som et resultat viser ZnO/UiO66-NH₂ bemærkelsesværdig selektivitet for produktion af eddikesyre under PLA-omskabelsesprocessen, sammen med effektiv produktion af H₂. Derfor præsenterer dette arbejde en ny tilgang til design og konstruktion af heterojunktionelle fotokatalysatorer til omskabelse af plastmaterialer.

For at forbedre lysoptagelsespræstationen af MOF-baserede fotokatalysatorer er der udviklet en mild pyrolysestrategi til at indkapsle kulstofnanoprikker (CDs) i UiO66-porerne for at producere CDs/UiO66. Introduktionen af CDs forbedrer kapaciteten til at absorbere sollys og fremmer adskillelseshastigheden af bærere for CD/UiO66. I dette arbejde bruges en ikke-nedbrydelig plastik, PVC, som målplastik. Som resultat viser de forberedte CDs/UiO66 en bemærkelsesværdig katalytisk aktivitet og stabilitet ved omdannelse af PVC til eddikesyre. Samlet set giver dette arbejde en at forbedre plastikomdannelsesevnen for MOF-baserede metode til fotokatalysatorer.

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List of Abbreviations

PVC	Polyvinyl chloride
PEG	Polyethylene glycol
PLA	Polylactic acid
CB	Conduction band
VB	Valence band
XRD	X-ray diffraction
DMF	N, N-Dimethylformamide
CDs	Carbon nanodots
MOFs	Metal-organic-frameworks
SEM	Scanning electron microscopy
TEM	Transmission electron microscope
TISSA	Teflon-lined stainless steel autoclave
ΔG^0	Gibbs free energy
EDX	Energy-dispersive X-ray spectroscopy
XPS	X-ray photoelectron spectroscopy
ESR	Electron spin resonance
DMPO	5,5-dimethyl-1-pyrroline-N-oxide
PL	Photoluminescence spectra
DRS	UV-vis diffuse reflectance spectra
G	Glucose

1 Introduction

1.1 Plastic waste pollution

Since Leo Baekeland introduced the first synthetic polymer in 1907, a variety of plastics have been developed over the ensuing decades [1]. The exceptional qualities of plastics, such as affordability, high elasticity and lightweight properties, guarantee their widespread utilisation in various aspects of our daily lives [2]. The global production of plastic has witnessed an exponential surge, escalating from a mere 2 million tons in 1950 to an astounding 380 million tons in 2015 (**Figure 1.1**), with projections pointing towards a further increase to over 500 million tons by 2050 [3,4].

The excessive use of plastics leads to a significant amount of plastic waste entering the natural environment, causing serious resource wastage and environmental pollution [5–7]. Therefore, plastic pollution is a global issue that has far-reaching consequences for both the environment and human wellbeing. In addition, the spontaneous degradation of plastic products in natural conditions can produce numerous fragments, including microplastics and nanoplastics, which can continue to absorb heavy metals and organic pollutants [8–10]. When they are eaten by fish, birds and marine mammals, the toxicity of the adsorbed toxic substances is continuously concentrated through the food chain, thereby having adverse effects on human health [11–13].

Overall, the discharge of plastic waste is not only a great waste of resources, but it also causes catastrophic pollution of the natural environment – a subject attracting the attention of increasingly more researchers [14-16].



Figure 1.1 Global mismanaged plastic waste (MPW) generation in 2015 [17]. Reprinted under the Creative Commons CC BY licence.

1.2 The technologies for plastic waste management

Currently, four traditional methods are used to deal with plastic waste worldwide, namely landfill, incineration, mechanical recycling and pyrolysis [18–22]. Incineration and landfill are two commonly used approaches in this regard, and because of their advantages in terms of simple operating processes and high processing efficiency for different types of plastic waste [23]. Up to now, incineration and landfill have been practically applied in large-scale plastic waste treatment [24]. However, these conventional approaches suffer from several limitations. For example, landfill sites take up a large amount of land resources. Meanwhile, incinerating plastic waste will release a large amount of pernicious gases and particulate matter, both of which can have a negative impact on air quality and the atmospheric environment [2].

Mechanical recycling is another common plastic waste disposal strategy. However, due to the large variety of plastics in mixed municipal solid waste, mechanical recycling requires a lot of manual work and complicated operating procedures to screen targeted plastics [25]. Additionally, the mechanical recycling of plastics requires repeated washing, crushing and melting processes, which can lead to a degradation of the mechanical properties of plastic products [26,27].

In recent years, some chemical recycling methods, including hydrogenolysis and solvolysis, have also been used to treat waste plastics [28–31]. However, these methods are still in the early stages of research and generally face problems of poor processing efficiency and product selectivity.

Overall, the methods mentioned above face challenges in effectively dealing with plastic waste. To address these issues, a large number of chemical catalysis methods have been developed to convert plastic waste into valuable chemicals [32–34].

1.3 Chemical catalysis technologies

In recent years, in order to control plastic pollution effectively, researchers have developed many chemical catalysis technologies, mainly including thermal catalysis, enzyme catalysis, electrocatalysis and photocatalysis [35– 37]. From a catalytic perspective, plastic waste can be seen as an energy storage medium for C and H elements [38]. Transforming plastics into high-valueadded chemicals through appropriate catalytic methods will be beneficial for solving plastic pollution and future energy crises. Therefore, chemical catalysis is an energy-saving plastic treatment technology compared with traditional pyrolysis technology. The following section provides an overview of advanced catalytic technologies for chemical upcycling plastic waste.

1.3.1 Thermal catalysis technology

Thermal catalysis is a process in which waste plastics are pyrolyzed at high temperatures under anaerobic conditions with the assistance of a catalyst [39]. Thermal catalysis methods can break down long-chain polymer plastics into valuable hydrocarbon products, which can be utilized as energy sources or chemical feedstocks [40]. This innovative approach offers a promising solution to the problem of "white pollution" [41]. However, the thermal catalysis of plastic requires high-temperature treatment, which leads to the consumption of large amounts of fuel energy.

1.3.2 Enzyme catalysis technology

Enzyme catalysis refers to using biological enzymes as catalysts to convert plastic substrates into desired products [42]. Specifically, through the action of enzymes produced by microorganisms, chemical bonds within polymers can be cleaved, thereby converting plastic molecules into shorter-chain plastic fragments or small molecular organic compounds [43]. It should be emphasised that short-chain organic molecules derived from the breakdown of plastic molecules can be utilised by microorganisms as carbon sources. Therefore, compared with the traditional pyrolysis method, the biocatalytic method can be carried out with low pollution and low energy consumption [44]. However, enzyme catalysis technology still faces challenges, such as low reaction rates and high operating costs.

1.3.3 Electrocatalysis technology

Recently, electrocatalysis technology has been used in the chemical upcycling of waste plastics [45,46]. Compared to the traditional pyrolysis method, electrocatalysis has the following advantages: 1) Electrocatalytic reactions commonly occur in ambient temperatures and pressures, thus reducing energy consumption, and 2) adjusting electrode potential can effectively control the reaction rate [44]. Therefore, electrocatalysis is an ideal solution to solve the problem of plastic pollution. However, electricity consumption associated with the conversion of plastics may increase operating costs.

1.3.4 Photocatalytic technology

Photocatalysis is considered an environmentally friendly technology to control plastic waste pollution because it can utilize solar energy to produce active species for the upcycling of plastics under mild conditions [47,48]. In general,

the photocatalytic process consists of three main stages: i) The generation of electron-hole pairs through solar energy excitation, ii) the subsequent migration and separation of carriers and iii) the conversion of pollutants by carriers or active radicals on the surface of the photocatalyst [49]. Up to now, photocatalysis has been employed not only in the realm of energy, where it converts solar energy into high-density clean energy but also in the environmental domain, where it uses light energy to degrade and mineralize organic pollutants [50–53]. Therefore, photocatalysis is a green technology with significant potential for applications in both energy storage and environmental protection.

1.4 Photocatalytic plastic upcycling

Based on the above analysis, photocatalysis is an effective technology that can be applied to upcycle waste plastics. Given the advantages of photocatalysis, My PhD project is dedicated to the upcycling of various plastics into valuable organics by photocatalytic technology.

1.4.1 The mechanism of plastic upcycling

Currently, photocatalytic reaction systems used to convert plastics can be classified into photodegradation and photoreforming [23,54]. In the case of photodegradation, waste plastics are treated as waste materials that can be degraded or mineralized into CO_2 by photocatalysts during the photodegradation process [55]. In the case of photoreforming, plastic waste is considered a hydrocarbon-rich energy source, and plastic waste can be converted into valuable chemicals or materials [56]. According to the different transfer pathways of carriers, the mechanism behind photoreforming of plastics has two main aspects:

i) Photocatalysts directly upcycle plastics into chemicals, coupled with H_2 generation [57].

The reaction system is usually in an anoxic condition. When the photocatalyst is excited by sunlight, holes generated by photocatalysts can directly oxidise plastics to generate high-value-added chemicals, while electrons are used to split H_2O to produce H_2 . The reaction is as follows:

Photocatalyst +
$$hv \rightarrow h^+ + e^-$$
 (1)

$$2 e^{-} + 2 H^{+} \rightarrow H_{2} \tag{2}$$

Plastics + h^+ , \rightarrow high-value-added organics (3)

ii) Upcycling waste plastics into high-value-added chemicals via active radicals [58].

In this reaction system, the photocatalyst does not have direct contact with the plastic. During photocatalytic plastic conversion, photogenerated holes are used to convert H_2O into hydroxyl radicals and protons. And, the O_2 in this reaction system can be reduced to superoxide radicals via photo-generated electrons. These generated active radicals then participate in converting plastic waste into high-value-added chemicals. It should be emphasized that in the above process, C-C bonds in the plastic waste are first broken by active free radicals, subsequently producing long-chain plastic fragments. Then, the corresponding plastic fragments are further converted into oxygen-containing small organic compounds under aerobic reaction conditions. Meanwhile, the generated photo-generated electrons can also be used to reduce the protons in the reaction system to produce H_2 . The reaction is as follows:

Photocatalyst +
$$hv \rightarrow h^+ + e^-$$
 (4)

$$e^- + O_2 \to \bullet O_2^- \tag{5}$$

$$h^{+} + H_2 O \rightarrow \bullet OH + H^{+}$$
(6)

$$2e^{-} + 2H^{+} \rightarrow H_{2} \tag{7}$$

Plastics + •OH and •O₂⁻ \rightarrow high-value-added organics (8)

Overall, photoreforming can not only solve the plastic pollution problem but also produce valuable chemicals. In addition, the photoreforming method offers significant economic value and advantages in energy conservation and environmental protection when compared to photodegradation, aligning with the principles of sustainable development.

1.4.2 The challenge in photocatalytic plastic upcycling

Although there has been some progress in using photocatalytic technology to convert plastics into high-value-added chemicals, there are still certain challenges in researching the subject.

i) Strong chemical bonds: Most plastics contain a large number of strong C=O, C-C, C-H and C-O bonds with high bond energy, which makes it difficult for existing photocatalysts to convert plastics efficiently.

ii) Complex mechanism: The current research on photocatalytic plastic conversion is still in the early stages, and so the mechanism behind the photocatalytic conversion of plastics is still unclear.

iii) Low efficiency and product selectivity: The photocatalytic conversion of plastics faces the challenges of low reaction efficiency and poor product selectivity.

iv) Limited catalyst type: There are a few types of photocatalysts that can be used for plastic conversion. Meanwhile, the existing photocatalysts have some shortcomings, such as low quantum efficiency and high toxicity.

1.4.3 Design and construction of photocatalysts

The design and development of efficient catalysts is considered a feasible solution to solve the challenges faced in the photocatalytic conversion of plastic waste. In the catalytic process, the use of catalysts has a dual purpose: to improve catalytic efficiency and to adjust product selectivity [59,60]. This can be attributed to the fact that the reaction rate, product distribution and yield can be effectively controlled by adjusting the structural features of the catalysts [61].

Therefore, the development of novel photocatalysts with high catalytic activity will be the key focus of my research. I plan to improve the efficiency of plastic upcycling reactions by designing and synthesizing novel catalysts, and tuning their crystal structure, surface active sites, and light-absorbing properties.

1.5 Metal-organic frameworks (MOFs) photocatalyst

In recent years, MOFs materials have been widely used in gas storage, separation and catalysis [62–64]. In contrast to conventional semiconductor photocatalysts, MOFs have obvious advantages, such as tuneable pore sizes and high specific surface area [65]. In recent years, various MOFs have been used as photocatalysts to degrade organic pollutants or reduce NO_x gases [66]. However, MOFs photocatalysts suffer from the fast recombination of carriers and poor light absorption capacity, which limits their photocatalytic activity [67]. To date, various methods have been used to enhance the catalytic activity of MOF-based photocatalysts, including heterostructure construction, defective engineering and structural regulation.

1.5.1 Modification methods

i) Heterojunction construction

catalytic activity of MOFs photocatalysts Improving the through heterostructure construction has attracted more and more attention in recent years [68]. This strategy combines MOFs materials with other semiconductor materials to create heterojunctions, which increase the carrier separation rate of photocatalysts and enhance their photocatalytic performance [69]. Take the Type-II carrier separation mechanism as an example [70,71]. Under light irradiation conditions, electrons and holes tend to move to lower-energy band positions. Differences in the electron energy levels of different semiconductors in the heterojunction cause electrons and holes in the composite photocatalyst to accumulate in the conduction band (CB) and valence band (VB) of different semiconductors, respectively. These results prevent these electrons and holes from recombining, which in turn prolongs the lifetime of these electron-hole pairs. It should be emphasized that the specific bandgap of MOFs is intricately influenced by organic linkers and metal clusters. It should be emphasised that the specific bandgap of MOFs is intricately influenced by organic linkers and metal clusters. Specifically, MOFs possess a broad spectrum of band gaps, which typically range from 1.0 eV to 5.5 eV [72]. Therefore, it is crucial to design and screen semiconductors that are suitable for coupling with MOFs.

ii) Defective engineering

Structural defect engineering is a common method for modifying MOF photocatalysts [73–75]. It can be achieved by introducing metal defects and ligand defects to increase the specific surface area, expose more catalytic sites, improve light absorption, and enhance the electron transfer performance of MOFs, thereby significantly improving the catalytic efficiency of MOFs [76–78]. It needs to be emphasized that in order to ensure the structural stability of MOFs, the introduction of these defects should not destroy the original skeleton structure of MOFs.

iii) Structural regulation

Structural regulation is another common modification method to improve the photocatalytic activity of MOFs [79,80]. Structural regulation mainly includes the organic linker regulation and metal nodes regulation. For organic linker regulation, changing the organic ligands during the synthesis process of MOFs will lead to changes in the light absorption properties of MOFs, thereby affecting their photocatalytic activity [81,82]. For example, García et al. use 2-amino terephthalic acid as the organic linker to synthesize UiO66-NH₂, which exhibits a light absorption range of 300~440 nm, superior to UiO66 synthesized using terephthalic acid as the organic linker, with a light absorption

range of 270~300 nm [83]. As for the regulation of metal nodes, by introducing new metal nodes into the MOFs framework, the band gap of the MOFs can be narrowed and the photogenerated carrier separation efficiency can be improved, which is beneficial to promote the catalytic activity of the MOFs [84]. For example, Sun et al. prepare a Ti-substituted UiO66-NH₂ (Zr/Ti), which exhibits enhanced CO₂ reduction activity (5.8 mmol mol⁻¹) within 10 h compared to UiO66-NH₂ (3.4 mmol mol⁻¹) [85].

1.5.2 Construction of heterojunction MOFs photocatalyst

Based on the strategies discussed above, heterojunction construction represents an effective approach to augmenting the photocatalytic activity of MOFs. Therefore, this work considers using heterojunction construction strategies to modify MOFs materials, thereby enhancing their catalytic activity.

Currently, the most common method used to construct heterojunction-modified MOFs involves loading different semiconductors onto the surface of MOFs [86]. However, these approaches often involve certain challenges, including limited interfacial contact and weak integration forces between MOFs and semiconductors, both of which hamper the separation efficiency of carriers [87]. In addition, during long-term use, the supported semiconductors may detach from the surface of the MOFs, leading to reduced structural stability of composite MOFs photocatalysts. As a result, new strategies need to be explored to address these limitations and enhance the photocatalytic performance of MOFs.

Inspired by a number of studies on the embedding of single-atom nanoparticles in MOFs [88], we decided to encapsulate semiconductors inside MOFs to construct a composite photocatalyst, aiming to improve carrier separation efficiency and light absorption performance of MOFs. In this way, the limited space of MOFs pores can adjust the particle size of embedded materials and ensure the establishment of tight interfacial connections between MOFs and embedded semiconductors. It should be emphasised that when semiconductors are encapsulated into MOFs pores, the problem of semiconductor particles falling off the composite photocatalyst can be avoided, which in turn improves the structural stability of the composite photocatalyst.

Considering the function of MOF-based photocatalysts, candidate MOFs materials should have the following characteristics:

- i) A suitable energy band structure, which ensures the MOF-based materials can be used to construct heterojunctions with embedded semiconductor particles.
- ii) Abundant pore structures, which can provide space for embedded semiconductors.
- iii) Stable physical and chemical structures, which ensure long-term stable photocatalytic activity of MOF-based materials.

Among various MOFs, Fe-MOF (MIL(Fe)-101) and Zr-MOF (UiO66-NH₂ and UiO66), as novel photocatalysts, have attracted the attention of researchers due to their high thermal stability, good photoresponsive features and controllable pore sizes [79,89–93]. Therefore, Fe-MOF and Zr-MOF have the potential to act as photocatalysts for plastic pollution remediation. Based on the above considerations, we selected MIL(Fe)-101, UiO66-NH₂ and UiO66 as MOFs templates to synthesise MOF-based photocatalysts for upcycling plastics.

It should be emphasized that due to the size of most semiconductor particles far exceeding the size of the pores of MOFs, embedding them within the pores of MOFs presents a challenge. Therefore, it is imperative to explore new strategies to effectively embed semiconductors into the pores of MOFs to enhance the photocatalytic activity of MOF-based composites.

1.6 Thesis objectives

This work aims to investigate novel methods to synthesize MOFs-based photocatalysts embedded in semiconductor particles and evaluate their applicability in plastic upcycling. The specific aims are listed below:

Aim 1 Screening suitable MOFs templates and exploring appropriate methods to embed semiconductors inside MOFs pores.

Aim 2 A preliminary evaluation of the feasibility of MOF-based photocatalysts for upcycling plastics.

Aim 3 Optimising the photocatalyst preparation method and tuning the energy band structure of MOF-based photocatalysts to improve their catalytic activity and product selectivity.

Aim 4 Revealing the pathways and mechanisms of plastic upcycling.

1.7 Outline and structure of the thesis

The content of this thesis is based on three works presented in **Papers I-III**. It is written to provide research background, essential experimental details and discussions in each chapter, ensuring that readers can easily follow the content.

Chapter 1 Introduces the current situation regarding plastic waste pollution, outlines different strategies that can be used to deal with plastic and highlights the unique advantages of photocatalytic technology in the field of plastic upcycling. It then moves on to describe the structure of MOFs photocatalysts, modification techniques and the selection of MOFs materials for embedding semiconductors.

Chapter 2 Elucidates the experimental work and characteristic techniques employed in **Papers I-III** to help comprehend the results presented in the subsequent chapters.

Chapter 3 Discusses the feasibility of embedding Ag_2O within MIL(Fe)-101 and evaluates its photocatalytic activity for the conversion of polymers (**Paper I**). Specifically, the structural features and catalytic activity of $Ag_2O/MIL(Fe)$ -101 are discussed. We also evaluate the performance of $Ag_2O/MIL(Fe)$ -101 in the catalytic conversion of polyethylene glycol (PEG). Experimental results show that $Ag_2O/MIL(Fe)$ -101 can convert PEG into high-value-added acetic acid. This work preliminarily confirms the potential of MOF-based photocatalysts in the upcycling of plastics.

Chapter 4 To further broaden the application of MOFs photocatalysts in the field of plastic conversion, we choose Zr-based MOF-UiO66-NH₂ with high structural stability as a template to synthesise composite photocatalysts. Specifically, we develop a ZnO/UiO66-NH₂ heterojunction, wherein ZnO is enclosed within the framework of UiO66-NH₂. In this chapter, a biodegradable plastic-polylactic acid (PLA) is selected as the target plastic. Consequently, ZnO/UiO66-NH₂ shows high catalytic activity when upcycling PLA, as outlined in **Paper II**. In addition, the analysis of intermediate products provides evidence for revealing the mechanism of PLA conversion.

Chapter 5 To improve the visible light absorption performance of MOFs photocatalysts, a novel carbon nanodots (CDs)-embedded UiO66 heterojunction photocatalyst is fabricated, as described in **Paper III**. The tight combination between CDs and UiO66 improves the visible light absorption of CDs/UiO66. When the non-biodegradable plastic-polyvinyl chloride (PVC) is selected as the target plastic, the resultant CDs/UiO66 exhibit excellent

catalytic performance in the conversion of PVC to acetic acid. This work develops novel method for the synthesis and construction of MOF-based photocatalysts and offers a solution to the problem of plastic waste pollution.

Chapter 6 Summarizes the main findings and conclusions of this PhD thesis.

Chapter 7 Outlines future prospects for photocatalytic plastic conversion.

2 Methodology

The main experimental work and characteristic techniques are explained to enhance the understanding of the thesis. This chapter includes material synthesis, material characterisation and the evaluation of photocatalytic performance.

2.1 Material Characterisation

The morphology, element composition, crystal structure and light absorption properties of photocatalysts have a crucial impact on their catalytic performance. In this work, the size and morphology of photocatalysts are analysed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Sample composition is determined through energy-dispersive X-ray spectroscopy (EDX), while X-ray photoelectron spectroscopy (XPS) is employed to investigate the surface electronic states of photocatalysts. Optical absorption properties of photocatalysts is assessed using UV-vis diffuse reflectance spectroscopy (DRS). Electron spin resonance (ESR) is used to analyze the types of active free radicals with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin-trapping agent. The photoluminescence (PL) spectra of photocatalysts is tested by steady-state/transient fluorescence spectrometer.

2.2 Experimental Design

2.2.1 Preparation of Ag₂O/MIL(Fe)-101.

The MIL(Fe)-101 can be obtained by following a hydrothermal strategy [94]. Specifically, MIL(Fe)-101 is synthesised through the following steps: 2.7 g of FeCl₃•6H₂O and 1.6 g of 1,4-dicarboxybenzene are accurately weighed and dissolved into 100 mL of N, N-Dimethylformamide (DMF), following which the prepared solution is introduced into a Teflon-lined stainless steel autoclave (TISSA) for the hydrothermal reaction at 110 °C for 24 h.

Subsequently, the synthesis of MIL(Fe, Ag)-101 involves the following procedure: 2.0 g MIL(Fe)-101 is evenly dispersed into 10 mL of AgNO₃ solution in an ultrasonic water bath, and then the above mixture is continuously magnetically stirred for 30 min to obtain MIL(Fe, Ag)-101.

Finally, $Ag_2O/MIL(Fe)$ -101 is synthesised using a photochemistry method (**Figure 2.1**): initially, 0.1 g of MIL(Fe, Ag)-101 is evenly dispersed into 30 mL of deionised water. Then, the suspension is exposed to xenon lamp

irradiation for 15 min under continuous magnetic stirring to obtain Ag₂O/Fe-MOFs. Finally, the obtained Ag₂O/Fe-MOFs are dried at 65° C for 24 h.



Figure 2.1 The preparation of MIL(Fe, Ag)-101 and Ag₂O/MIL(Fe)-101 with a post-synthetic strategy and a photochemical strategy, respectively.

2.2.2 Preparation of ZnO/UiO66-NH₂

The porous ZnO/UiO66-NH₂ is fabricated by partial calcination (**Figure 2.2**). Initially, UiO66-NH₂ is synthesised using a previously reported procedure [95]: 150 mL of DMF solution and 0.11 g of 2-amino-1,4-benzenedicarboxylic acid are thoroughly mixed in a 500 mL beaker to form a transparent solution by an ultrasonic water bath. Subsequently, 10 μ L of triethylamine and 20 mL of acetic acid are introduced to the above solution. Then, 100 mL of DMF solution containing 0.14 g ZrCl₄ is added to the above mixture solution. Afterwards, the suspension is placed into a TISSA and held at 120 °C for 20 h.

Subsequently, 0.6 g Zn (NO₃)₂ $6H_2O$ and 100 mg UiO66-NH₂ are uniformly dispersed into 50 mL deionized water by ultrasonic water bath. After that, the suspension is stirred for 24 h to obtain Zn-UiO66-NH₂. Finally, ZnO/UiO66-NH₂ can be obtained by calcinating Zn-UiO66-NH₂ at 350 °C for 4 h.



Figure 2.2 The preparation of Zn-UiO66-NH₂ and ZnO/UiO66-NH₂ through a post-synthetic strategy and a partial calcination strategy, respectively.

2.2.3 Preparation of CDs/UiO66

The CDs/UiO66 photocatalyst is fabricated via mild pyrolysis (**Figure 2.3**). First, the UiO66 is synthesised by the method reported in **Chapter 2.2.2**, except that 2-amino-1,4-benzenedicarboxylic acid is replaced by terephthalic acid.

Subsequently, the G/UiO66 is synthesised via the following steps: 0.3 g of UiO66 is dissolved in 20 mL of glucose (G) solution to obtain G/UiO66. Finally, the G/UiO66 precursor is pyrolysed to 240 °C for 4 h under an N_2 stream to obtain CDs/UiO66.



Figure 2.3 The preparation of G/UiO66 and CDs/UiO66 photocatalyst via a post-synthetic strategy and a mild pyrolysis strategy, respectively.

2.2.4 Photocatalytic conversion of plastic

The photocatalytic reaction is carried out in a quartz reactor under atmospheric pressure. A 300 W Xenon lamp is employed as a simulated solar light source. The distance between the photocatalytic reactor and the lamp is controlled at 5 cm. The reaction temperature is maintained at 25 °C, which is achieved through the circulation of cooling water. Typically, 0.1~1.0 g of the photocatalyst and 0.2~1.0 g of plastic are dispersed in 50 mL of deionised water. Afterwards, the xenon lamp is switched on, and the photocatalytic reaction begins. During photocatalysis, gas and liquid products are analysed by high-performance liquid chromatography and gas chromatography-mass spectrometry, respectively.

3 Preliminary evaluation of the catalytic activity of Ag₂O/MIL(Fe)-101 for plastic upcycling

Chapter 3 preliminarily evaluates the possibility of MOFs photocatalysts in converting PEG plastic. This chapter is related to **Paper I**.

3.1 Introduction and Motivation

In the field of photocatalysis, MOFs are widely used as photocatalysts or lightabsorbing materials, as they can absorb light energy and convert it into chemical energy through catalytic processes. These properties mean that MOFs are a promising material for energy conservation and environmental protection [96-98]. However, their catalytic activity is still limited due to the fast recombination efficiency of carriers [99,100]. To overcome this limitation, numerous studies have been dedicated to coupling different semiconductors and MOFs materials to construct heterostructures. For example, Xu et al. employed the in-situ growth strategy to construct a series of CdS/Ni-MOF [101]. Among them, the 20% CdS/Ni-MOFs exhibited excellent CO₂ reduction performance, surpassing Ni-MOF by 16 times and CdS by 7 times in terms of CO yield. Ma et al. reported that the Ni-MOF@BiOBr composites can be synthesised by the solvothermal method [102]. The methylene blue degradation rates over the optimal catalyst reached 82.8% within 120 min. Up to now, MOF-based photocatalysts have primarily found applications in the fields of H₂ generation through H₂O splitting, the degradation of organic pollutants and the oxidation of nitric oxide. However, most MOF-based heterojunctions photocatalyst are constructed mainly by loading semiconductors onto MOFs surfaces, which leads to poor structural stability.

Herein, we develop a novel photochemical strategy to synthesise heterojunction photocatalysts with semiconductors embedded within the MOFs framework. For this purpose, MIL(Fe)-101, with its excellent structural stability and high surface area, is selected as the template. First, Ag sites are introduced into the MIL(Fe)-101 framework to obtain MIL(Fe, Ag)-101 through post-synthesis. Subsequently, we prepare the Ag₂O/MIL(Fe)-101 heterojunction photocatalyst by converting the Ag sites of MIL(Fe, Ag)-101 into Ag₂O via a photochemical strategy. In this work, the photocatalytic activity of photocatalysts is evaluated using PEG as a target plastic (**Scheme** **3.1**), aiming to preliminarily evaluate the feasibility of MOF-based photocatalysts in the field of plastics conversion.



Scheme 3.1 Schematic illustration of the Ag₂O/MIL(Fe)-101 heterojunction photocatalyst upcycling polymer into high-value-added chemicals.

3.2 Structural Characterisation

The SEM technique is employed to characterise the morphology of photocatalysts. **Figure 3.2 a** shows that the MIL(Fe)-101 has a smooth surface and a regular octahedral morphology with a size of 1 μ m. After post-synthesis treatment, although some of the Fe sites on the MIL(Fe)-101 framework are replaced by Ag sites, the morphology of MIL(Fe, Ag)-101 does not change compared to that of pure MIL(Fe)-101 (**Figure 3.2 b**). The corresponding EDX spectrum of MIL(Fe, Ag)-101 shows that the MIL(Fe, Ag)-101 sample contains uniformly dispersed Ag elements (**Figure 3.2 c**).



Figure 3.2 SEM images of (a) MIL(Fe)-101 and (b) MIL(Fe, Ag)-101. (c) The EDX mapping of MIL(Fe, Ag)-101.

As shown in **Figure 3.3 a** that the $Ag_2O/MIL(Fe)-101$ have similar morphology structure to that of MIL(Fe)-101. To observe the $Ag_2O/MIL(Fe)-101$

microstructure, and to prove that Ag_2O is embedded inside MIL(Fe)-101, scanning STM (STEM) characterisation analysis is carried out. Compared with pure MIL(Fe)-101, abundant Ag_2O particles (~6 nm) are clearly observed inside $Ag_2O/MIL(Fe)$ -101 (**Figure 3.3 b-c**), indicating that the Ag sites of MIL(Fe, Ag)-101 can be in-situ converted to Ag_2O and embedded within the MOFs framework. In addition, the EDX analysis results also indicate that $Ag_2O/MIL(Fe)$ -101 has a uniform distribution of Ag, O, Fe and C elements (**Figure 3.3 d**).

Moreover, high-resolution TEM (HRTEM) is also employed to provide additional evidence that the ultra-small-sized Ag₂O particles can be embedded in the MIL(Fe)-101 framework. **Figure 3.3 e** suggests that the fringes with a lattice spacing of about 0.27 nm are indexed to the (111) planes of the Ag₂O phase [103], which again indicates that the ultra-small particles inside the MOFs are Ag₂O.



Figure 3.3 (a) SEM, (b-c) STEM images, (d) EDX mapping and (e) HRTEM image of Ag₂O/MIL(Fe)-101.

Next, the obtained photocatalysts are investigated by XRD analysis (**Figure 3.4 a**). The results show that the XRD peaks of the synthesised MIL(Fe)-101 are consistent with previously reported data [104]. After post-synthesis and photochemical treatment, MIL(Fe, Ag)-101 and Ag₂O/MIL(Fe)-101 exhibit similar XRD peaks to pure MIL(Fe)-101, which indicates that the crystal structure of MIL(Fe)-101 is maintained in MIL(Fe, Ag)-101 and

Ag₂O/MIL(Fe)-101. Following this, XPS is employed to elucidate the electronic interactions present within the obtained samples. In comparison to the pristine MIL(Fe)-101 (**Figure 3.4 b**), noteworthy deviations are observed in the MIL(Fe, Ag)-101 spectrum. Specifically, the Fe $2p_{3/2}$ peak and the Fe $2p_{1/2}$ peak of MIL(Fe, Ag)-101 display negative shifts of 0.8 and 0.7 eV, respectively, which are attributed to the introduction of Ag sites. Additionally, the Fe 2p peaks of Ag₂O/MIL(Fe)-101 also exhibit negative shifts in binding energies, measuring 711.8 and 725.6 eV, respectively (**Figure 3.4 c**). These observed deviations in the electronic structure of Fe within Ag₂O/MIL(Fe)-101 confirm the good integration between Ag₂O and MIL(Fe)-101 [105].



Figure 3.4 (a) XRD patterns of Ag₂O, MIL(Fe)-101, MIL(Fe, Ag)-101 and Ag₂O/MIL(Fe)-101. (b) XPS spectra of MIL(Fe)-101 and MIL(Fe, Ag)-101. (c) XPS spectra of MIL(Fe)-101 and Ag₂O/MIL(Fe)-101.

Then, N₂ adsorption-desorption isotherm measurements for MIL(Fe)-101, MIL(Fe, Ag)-101 and Ag₂O/MIL(Fe)-101 are carried out (**Figure 3.5 a**). Specifically, the specific surface area of MIL(Fe)-101 is 1402 m² g⁻¹. After photochemical treatment, the specific surface area of Ag₂O/MIL(Fe)-101 decreases significantly to 110 m² g⁻¹, which is mainly caused by the introduction of Ag₂O into the MOFs pores. This observed phenomenon provides evidence supporting that the photochemical strategy developed in this work enables the embedding of Ag₂O within the MOFs framework.

As illustrated in **Figure 3.5 b**, MIL(Fe)-101 can only absorb solar light with a wavelength of less than 420nm. Notably, when Ag_2O is integrated into the MIL(Fe)-101 framework, the resulting $Ag_2O/MIL(Fe)$ -101 reveals a significantly expanded light absorption range. These findings indicate that the introduction of Ag_2O into the MIL(Fe)-101 pores can enhance its light absorption performance, which is beneficial in terms of improving the catalytic activity of $Ag_2O/MIL(Fe)$ -101.

To evaluate the charge separation and transfer efficiency of Ag₂O, MIL(Fe)-101 and Ag₂O/MIL(Fe)-101, their photocurrent density is measured under light irradiation (**Figure 3.5 c**). Current densities in this case follow the sequence Ag₂O < MIL(Fe)-101 < Ag₂O/MIL(Fe)-101. These results indicate that introducing Ag₂O into MIL(Fe)-101 can enhance the carrier separation rate of Ag₂O/MIL(Fe)-101.



Figure 3.5 (a) N_2 adsorption-desorption isotherm curves of MIL(Fe)-101, MIL(Fe, Ag)-101 and Ag₂O/MIL(Fe)-101 photocatalysts. (b) DRS spectra and (c) photocurrent density spectra of Ag₂O, MIL(Fe)-101 and Ag₂O/MIL(Fe)-101 photocatalysts.

3.3 Photocatalytic Conversion of PEG: A Performance Evaluation

The catalytic performance of photocatalysts is evaluated for PEG upcycling under light illumination. As depicted in Figure 3.6 a-b, both Ag₂O and MIL(Fe)-101 exhibit limited PEG conversion capabilities due to their wide bandgap and rapid carrier recombination rates. Notably, Ag₂O is unable to split H₂O to generate H₂. In contrast, Ag₂O/MIL(Fe)-101 demonstrates enhanced catalytic activity. Particularly, with the increase of the Ag₂O weight fraction within Ag₂O/MIL(Fe)-101 from 0.05 wt% to 0.2 wt%, there is a corresponding rise in PEG weight loss from 14.7 mg to 27.5 mg. The results show that the introduction of Ag₂O is beneficial for enhancing the catalytic activity of Ag₂O/MIL(Fe)-101. When the weight fraction of Ag₂O is increased to 1 wt%, both the weight loss and H₂ production of Ag₂O/MIL(Fe)-101 decrease to 10.2 mg and 1.6 mmol g^{-1} h⁻¹, respectively. This decline can be attributed to the structural defects of the MOFs structure, caused by the excessive introduction of Ag₂O into MIL(Fe)-101 [87]. In addition, the physical mixture sample (Ag₂O@MIL(Fe)-101) exhibits a low PEG conversion capacity of 6.1 mg and H₂ production of 0.9 mmol g^{-1} h⁻¹. Meanwhile, the Ag₂O-MIL(Fe)-101 catalyst, wherein Ag₂O is supported by MIL(Fe)-101, also demonstrates low plastic conversion capability, yielding 8.0 mg, along with a H₂ generation rate

of 1.4 mmol g⁻¹ h⁻¹. The results further confirm that the photochemical strategy developed in this work generates a strong heterostructure between Ag₂O and MIL(Fe)-101, which can facilitate interfacial charge transfer and enhance photocatalytic activity. By analyzing intermediate products during the photocatalytic reaction, it is observed that the concentration of acetic acid increases to 57.5 mg l⁻¹ within 30 h (**Figure 3.6 c**), which highlights the remarkable ability of Ag₂O/MIL(Fe)-101 to convert PEG into valuable fuels.



Figure 3.6 (a) PEG weight loss and (b) H_2 evolution rate over Ag_2O and $xAg_2O/MIL(Fe)$ -101 photocatalysts. (c) Alteration in acetic acid concentration as a function of time during photocatalysis.

A possible mechanism for $Ag_2O/MIL(Fe)$ -101 catalytic conversion of PEG is proposed in **Figure 3.7 a**. During the photocatalytic process, electrons in the CB of Ag_2O can migrate to the CB of MIL(Fe)-101, thereby contributing to the formation of H_2 and $\bullet O_2^-$. Simultaneously, holes in the VB of MIL(Fe)-101 can transfer to the VB of Ag_2O , hence facilitating the production of $\bullet OH$ radicals. Ultimately, these generated radicals can be used to convert PEG into acetic acid. Based on the results of this work and previous reports [106], we propose a possible pathway for PEG conversion (**Figure 3.7 b**). During the photocatalytic process, PEG is first cleaved into plastic fragments. Subsequently, these plastic fragments are converted into high-value-added chemicals.



Figure 3.7 (a) The mechanism and (b) pathway of PEG conversion over Ag₂O/MIL(Fe)-101.

3.4 Conclusions

Herein, we present a novel photochemical strategy aimed at in-situ creating Ag_2O particles within MIL(Fe)-101 pores for converting plastics and efficiently producing H₂. The heterojunction between Ag_2O and MIL(Fe)-101 broadens the light absorption range and improves the photogenerated carriers transfer rate of $Ag_2O/MIL(Fe)$ -101. As a result, $Ag_2O/MIL(Fe)$ -101 exhibits high photocatalytic activity in the conversion of PEG into acetic acid and the generation of H₂. This work preliminarily confirms the feasibility of MOF-based photocatalysts in the upcycling of plastics.

3.5 Shortcomings and Plans for Chapter 4

During the photocatalytic process, some disadvantages of the Ag₂O/MIL(Fe)-101 photocatalyst are also observed, as shown below:

i) Although Ag₂O/MIL(Fe)-101 can convert PEG into high-value-added organic chemicals, its catalytic efficiency is low.

ii) This photocatalyst contains the heavy metal Ag, which poses potential environmental pollution risks.

Therefore, further research should be done to develop novel photocatalysts that can upcycle plastics with high catalytic efficiency. In addition, the presence of heavy metals should be avoided in future synthesized photocatalysts. To solve the above question raised in **Chapter 3**, we carry out a series of works, which are presented in **Chapter 4**.

4 Construction of ZnO/UiO66-NH₂ for upcycling of biodegradable plastics

This chapter will develop a novel MOF-based photocatalyst with high catalytic activity in the upcycling of biodegradable plastic. The chapter is related to **Paper II**.

4.1 Introduction and Motivation

To further promote the application of MOF-based composite photocatalysts in upcycling of plastic, it is necessary to develop novel catalysts with high catalytic activity. In recent years, UiO66-NH₂ has been regarded as a promising photocatalyst due to its excellent thermal and chemical stability and high surface area [107,108]. However, it also has some disadvantages, such as limited catalytic sites and wide band gap, which limits its photocatalytic activity [109,110]. As a result, there is an urgent need to investigate new strategies to enhance the catalytic activity of UiO66-NH₂.

Herein, we develop a partial calcination strategy to embed ZnO particles in UiO66-NH₂ frameworks for the upcycling of plastics (Scheme 4.1). Specifically, Zn-UiO66-NH₂ is chosen as the template, in which the amine group (-NH₂) has a strong coordination effect on Zn²⁺. During the calcination process, Zn sites in Zn-UiO66-NH₂ can be transformed into ZnO embedded in the UiO66-NH₂ pores. It is worth emphasizing that the MOFs framework of UiO66-NH₂ is well preserved during the calcination process. As a result, the maintained MOFs structure in UiO66-NH₂ can tune the size and dispersion of encapsulated ZnO, which is beneficial to enriching the active sites of ZnO/UiO66-NH₂. In this work, PLA is selected as the target plastic to evaluate the catalytic activity of ZnO/UiO66-NH₂. The objective of this chapter is to develop novel MOF-based composite photocatalysts and evaluate their activity in upcycling of plastics.



Scheme 4.1 Schematic illustration of the $ZnO/UiO66-NH_2$ heterojunction photocatalyst upcycling PLA into acetic acid coupled with H_2 production.

4.2 Structural Characterisation

Figure 4.2 a and Figure 4.2 d illustrate that UiO66-NH₂ and ZnO/UiO66-NH₂ have a similar rhombohedral morphology and smooth surfaces, suggesting that the MOFs structure of ZnO/UiO66-NH₂ is well preserved during the photocatalyst synthesis process. Subsequently, the obtained ZnO/UiO66-NH₂ is characterised by TEM. Figure 4.2 b-c and Figure 4.2 e demonstrate that UiO66-NH₂ and ZnO/UiO66-NH₂ exhibit an average size of 200 nm. Moreover, the analysis from EDX mapping confirms the homogeneous dispersion of Zr, O and Zn elements within ZnO/UiO66-NH₂ (Figure 4.2 f), which indicates the existence of ZnO inside the MOFs framework. By comparing UiO66-NH₂ and ZnO/UiO66-NH₂, it is found that there is abundant $ZnO - about 2 \sim 7$ nm in size - in the ZnO/UiO66-NH₂, which confirms the MOFs framework of ZnO/UiO66-NH₂ can ensure that ZnO has an ultra-small size (Figure 4.2 g-h). Additionally, the HRTEM results reveal an obvious lattice fringe measuring 0.248 nm, which can be attributed to the (1 0 1) plane of ZnO (Figure 4.2 i) [111]. This finding further confirms the successful embedding of ZnO into the UiO66-NH₂ framework during the partial calcination process.



Figure 4.2 (a) SEM and (b-c) TEM images of UiO66-NH₂, respectively. (d) SEM image (e) TEM image, (f) EDX mapping and (g-i) HRTEM images of ZnO/UiO66-NH₂, respectively.

Thermogravimetric analysis (TGA) is employed to investigate the calcination conversion process and the thermal stability of obtained photocatalysts. Remarkably, a weight loss in Zn-UiO66-NH₂ occurs at 346 °C (**Figure 4.3 a-b**). The generation of ZnO is responsible for causing this phenomenon [112], which suggests that Zn sites within Zn-UiO66-NH₂ can be converted to ZnO during partial calcination.



Figure 4.3 (a) TGA curves of UiO66-NH₂ and Zn-UiO66-NH₂. (b) The thermal stability analysis of UiO66-NH₂, Zn-UiO66-NH₂ and ZnO/UiO66-NH₂ respectively.

The results of the XRD analysis indicate that both Zn-UiO66-NH₂ and ZnO/UiO66-NH₂ maintain the diffraction peaks of UiO66-NH₂ (**Figure 4.4 a**). This result shows that the crystal structure of UiO66-NH₂ is not destroyed during the photocatalysts synthesis process. The XRD pattern of ZnO/UiO66-NH₂ does not contain any peaks belonging to ZnO, which may be attributable to the relatively low amount of ZnO. Furthermore, pure UiO66-NH₂ can only absorb UV light (**Figure 4.4 b**). Notably, the ZnO/UiO66-NH₂ sample exhibits a broadened light absorption range, from 200-450 nm, suggesting that the encapsulation of ZnO into UiO66-NH₂ enhances its light absorption capacity.



Figure 4.4 (a) XRD patterns of UiO66-NH₂, Zn-UiO66-NH₂ and ZnO/UiO66-NH₂. (b) DRS spectra of ZnO, UiO66-NH₂ and ZnO/UiO66-NH₂, respectively.

To explore the ability of different photocatalysts to separate charge carriers, their transient photocurrent responses are examined. As depicted in **Figure 4.5 a**, ZnO/UiO66-NH₂ demonstrates the highest photocurrent intensity, indicating its superior ability to separate electron-hole pairs compared to ZnO and UiO66-NH₂. Furthermore, in contrast to ZnO and UiO66-NH₂, ZnO/UiO66-NH₂ exhibits the lowest photoluminescence (PL) spectral intensity (**Figure 4.5 b**). This result suggests that the heterojunction structure present in ZnO/UiO66-NH₂ can effectively avoid the recombination of electron-hole pairs.



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Figure 4.5 (a) Photocurrent density spectra and (b) PL spectra of ZnO, UiO66-NH₂ and ZnO/UiO66-NH₂ photocatalysts.

ESR technology was used to analyze the active free radicals generated during the photocatalytic process. As shown in Figure 4.6, six characteristic peaks belonging to DMPO- \cdot O₂⁻ (**Figure 4.6 a**) and four characteristic peaks belonging to DMPO- \cdot OH (**Figure 4.6 b**) can be clearly observed in all photocatalysts, indicating that \cdot O₂⁻ and \cdot OH radicals can be generated in this work. It is worth noting that ZnO/UiO66-NH₂ has a stronger \cdot O₂⁻ and \cdot OH signal intensity compared with ZnO and UiO66-NH₂. This result indicates that during the photocatalytic process, the carriers generated by the ZnO/UiO66-NH₂ photocatalyst can be used to generate \cdot OH and \cdot O₂⁻ radicals, which is beneficial to the enhancement of the catalytic performance of the ZnO/UiO66-NH₂.



Figure 4.6 ESR spectra of (a) DMPO- \cdot O₂⁻ and (b) DMPO- \cdot OH for ZnO/UiO66-NH₂, ZnO and UiO66-NH₂.

4.3 Photocatalytic Conversion of PLA: A Performance Evaluation

As depicted in **Figure 4.7 a**, both UiO66-NH₂ and ZnO exhibit poor ability to convert PLA into acetic acid, yielding only 4.7% and 3.3%, respectively. In contrast, ZnO/UiO66-NH₂ shows an enhanced yield of 14.4%, and the PLA conversion rate is 57.10 mg g_{cat}^{-1} h⁻¹, indicating that the heterojunction inside of ZnO/UiO66-NH₂ is important in terms of improving catalytic activity. Besides, it is evident that ZnO/UiO66-NH₂ can also split H₂O to generate H₂ in the catalytic process (**Figure 4.7 b**). Specifically, the ZnO/UiO66-NH₂ composite demonstrates significantly improved performance in H₂ generation with a turnover number (TON) of 26.36 and a turnover frequency (TOF) of

0.75 h⁻¹, which confirms again that embedding ZnO into UiO66-NH₂ to construct a heterojunction can improve the catalytic ability of ZnO/UiO66-NH₂. Furthermore, the capability of ZnO/UiO66-NH₂ to convert PVC is also evaluated. **Figure 4.7 c** illustrates the PVC conversion rate of ZnO/UiO66-NH₂ is 21.40 mg g_{cat}^{-1} h⁻¹ and the acetic acid yield is 9.2%. It is obvious that compared with PLA, ZnO/UiO66-NH₂ has lower catalytic activity on PVC plastics.

Based on characterisation and experimental results, it can be inferred that the charge transfer mechanism observed in ZnO/UiO66-NH₂ corresponds to the Z-scheme mechanism (**Figure 4.7 d**). Under light irradiation, ZnO and UiO66-NH₂ are excited to generate electrons and holes. Guided by the internal electric field, electrons in the CB of ZnO can recombine with holes in the VB of UiO66-NH₂, which then lead to the electron of UiO66-NH₂ is kept at the CB of UiO66-NH₂ and the hole of ZnO is kept in the VB of ZnO. In this way, electrons in the CB of UiO66-NH₂ contribute to the generation of \cdot O₂⁻ through trapped O₂, while holes in VB of ZnO can react with H₂O to produce \cdot OH. Finally, active radicals can be used to convert plastics into acetic acid, while electrons can also be used to split H₂O and thus generate H₂.



Figure 4.7 (a) Acetic acid yield and (b) H_2 generation during the conversion of PLA by ZnO/UiO66-NH₂, respectively. (c) Acetic acid yield during the conversion of PVC by ZnO/UiO66-NH₂. (d) The mechanism of plastics conversion in this work.

4.4 Conclusions

This work introduces a partial calcination method to convert Zn sites to ultrasmall ZnO particles enclosed within UiO66-NH₂ pores, leading to the fabrication of a ZnO/UiO66-NH₂ heterojunction. Consequently, ZnO/UiO66-NH₂ demonstrates remarkable efficiency in converting PLA into acetic acid, accompanied by efficient H₂ production. The excellent photocatalytic performance of ZnO/UiO66-NH₂ is attributed to the matching energy band structure between ZnO and UiO66-NH₂ promotes the separation and migration of photogenerated carriers. Compared with Ag₂O/MIL(Fe)-101 synthesized in **Chapter 3**, the ZnO/UiO66-NH₂ has the following advantages:

i) There is no heavy metal in ZnO/UiO66-NH₂, so it is a more green and environmentally friendly material compared with Ag₂O/MIL(Fe)-101.

iii) ZnO/UiO66-NH₂ has high photocatalytic activity and can upcycle polyester plastic molecules instead of PEG polymers with a simple molecular structure.

Overall, this work addresses the scientific question posed in **Chapter 3**. In addition, it presents an effective approach to fabricating MOF-based heterojunction photocatalysts for plastic upcycling.

4.5 Shortcomings and Plans for Chapter 5

Based on the results obtained in the experiments above, $ZnO/UiO66-NH_2$ has some obvious disadvantages:

i) The solar light absorption performance of $ZnO/UiO66-NH_2$ is poor, especially in terms of absorbing visible light. This shortcoming hinders its overall efficiency in absorbing and utilizing solar energy.

ii) Although ZnO/UiO66-NH₂ can efficiently convert polyester plastics, its photocatalytic activity for non-biodegradable plastics such as PVC is poor.

To address these challenges, it is essential to develop novel photocatalysts with excellent light absorption properties and catalytic activity, especially for nonbiodegradable plastics. Based on these considerations, we carry out a series of works, as presented in **Chapter 5**.

5 Fabrication of CDs/UiO66 for upcycling of non-biodegradable plastics

This chapter develops a novel MOF-based photocatalyst with excellent visible light absorption properties and high catalytic activity, namely CDs/UiO66, for upcycling non-biodegradable plastics. The chapter is related to **Paper III**.

5.1 Introduction and Motivation

As discussed in **Chapter 3** and **Chapter 4**, MOF-based photocatalysts can be used for upcycling plastic. However, MOF-based photocatalysts still face the challenge of a narrow light absorption range, which results in MOF-based photocatalysts demonstrating poor catalytic activity when converting polyolefin plastics. As a result, there is an urgent requirement to investigate new methods to enhance the light absorption capacity of MOF-based photocatalysts.

In recent years, CDs have been considered innovative photosensitive materials with great application potential in catalysis [113–115]. Various studies have been conducted to improve the light absorption capacity of MOFs materials by coupling MOFs photocatalysts with CDs. For instance, Wei et al. synthesised a novel MOF-based photocatalyst by incorporating CDs into ZIF-8, which greatly improved the visible light absorption performance of CDs/ZIF-8 [116]. He et al. ingeniously incorporated CDs into the NH₂-MIL-125 (Ti). This approach aimed at promoting the H₂ evolution of CDs/NH₂-MIL-125 (Ti) by capitalising on the up-conversion effect of CDs [117]. Based on the above analysis, in this work, CDs are regarded as an excellent photosensitive material that can be used to expand the range of light absorption for UiO66 photocatalysts. To the best of my knowledge, the photocatalytic conversion of PVC over CDs/UiO66, prepared by embedding CDs into UiO66, has not been reported.

In this chapter, a mild pyrolysis strategy is developed to embed CDs into UiO66 pores to convert PVC (**Scheme 5.1**). It should be emphasised here that embedding CDs into UiO66 pores greatly broadens the visible light absorption performance of CDs/UiO66, which is beneficial to enhance its catalytic activity. This research highlights how the structural properties of MOFs derivatives influence their photocatalytic performance.



Scheme 5.1 Schematic illustration for fabricating a CDs/UiO66 photocatalyst via mild pyrolysis.

5.2 Structural Characterisation

The SEM image shows the sample size of CDs/UiO66 is about 0.5 μ m and the shape is octahedral, which is similar to UiO66 (**Figure 5.2 a**). As illustrated in **Figure 5.2 b-d**, after pyrolysis, a number of CDs begin to appear and evenly distribute throughout the UiO66 pore. Additionally, EDX mapping (**Figure 5.2 e**) illustrates the uniform distribution of O, C and Zr throughout the entire CDs/UiO66 framework.



Figure 5.2 (a) SEM, (b-d) TEM images and (e) EDX mapping of CDs/UiO66 photocatalyst, respectively.

The TGA analysis results indicate that the UiO66 framework is stable up to 650 °C in an N₂ atmosphere (**Figure 5.3 a**), and the G can be decomposed to product CDs at 210 °C [118]. Therefore, we selected a pyrolysis temperature of 240°C to transform G/UiO66 into CDs/UiO66. The above results indicate that the choice of pyrolysis temperature is crucial for synthesising CDs/UiO66 photocatalysts.

To investigate further the influence of pyrolysis temperature on a crystalline structure, XRD patterns of the UiO66 and their derivatives are measured (**Figure 5.3 b**). The peaks of G/UiO66 and CDs/UiO66, with reduced intensity, are similar to those in pristine UiO66, which indicates that the porous structure of UiO66 is not affected by loading G and the CDs.

Following the compositional and structural analyses, the light-absorbing capabilities of UiO66 and CDs/UiO66 are evaluated using DRS spectra (**Figure 5.3 c**). Optical absorption analysis results for CDs/UiO66 show a noticeable increase in absorption intensity within the range of 200-535 nm, compared to pure UiO66. These findings highlight the excellent optical responsiveness of CDs, contributing to enhanced solar energy utilization efficiency of CDs/UiO66.



Figure 5.3 (a) TGA curves of UiO66 and CDs/UiO66. (b) XRD patterns of UiO66, G/UiO66 and CDs/UiO66. (c) DRS spectra of UiO66 and CDs/UiO66, respectively.

5.3 Photocatalytic Conversion of PVC: A Performance Evaluation

Encouraged by the above characterisations, the catalytic performance of different photocatalysts is evaluated with PVC as a target plastic. The PVC conversion of UiO66 is about 41.5% (**Figure 5.4 a**). Notably, when the quality fraction (X) of CD in CDs/UiO66 increases to 10%, PVC conversion increases to 76.5%. However, the PVC conversion of CDs/UiO66 (20%) is ~53.0%,

indicating that excess CDs are not conducive to enhancing photocatalytic performance. Therefore, we selected CDs/UiO 66 (10%) as the target photocatalyst to conduct further research.

To investigate the effect of temperature on the catalytic activity of photocatalysts in this work, the C/ZrO₂ catalysts are prepared by pyrolyzing CDs/UiO66 at 470 °C under N₂ atmosphere. The performance of CDs/UiO66, UiO66 and C/ZrO₂ in converting PVC into valuable chemicals is also evaluated. **Figure 5.4 b** illustrates that among these catalysts, CDs/UiO66 exhibits the highest acetic acid yield of 0.17 mg g_{cat}^{-1} h⁻¹, which indicates that the CDs/UiO66 photocatalyst can efficiently convert PVC into high-value-added acetic acid. It should be emphasized that C/ZrO₂ cannot convert PVC into acetic acid, which indicates that an excessively high pyrolysis temperature will cause the MOFs structure of CDs/UiO66 to collapse and generate C/ZrO₂, which will inhibit its photocatalytic activity.

To explore the electron-hole pair separation efficiency of obtained photocatalysts, their photocurrent densities are analysed. **Figure 5.4 c** shows the CDs/UiO66 photocatalyst exhibiting the highest photocurrent intensity. These results reveal that embedding CDs into MOFs can effectively separate the photogenerated carriers under light irradiation, which is beneficial for generating more active radicals for the conversion of PVC. Based on the analysis provided above, we can conclude that CDs/UiO66 effectively address the shortcomings of poor light absorption performance and low catalytic activity in MOF-based photocatalysts.



Figure 5.4 (a) Conversion of PVC, (b) acetic acid yield and (c) photocurrent density spectra of obtained photocatalysts.

To investigate the mechanism of plastics conversion, ESR technology is used to analyze the active radicals in the reaction system. As presented in **Figure 5.5 a-b**, among these photocatalysts, the CDs/UiO66 photocatalyst showed the

strongest DMPO-·OH and DMPO-·O₂⁻ signal intensity, indicating that the photogenerated electrons and holes of the CDs/UiO66 photocatalyst can be used to interact with O₂ and H₂O to generate ·OH and ·O₂⁻. In addition, the above analysis results also indicate that ·O₂⁻ and ·OH are the main active radicals in this reaction system.



Figure 5.5 ESR spectra of (a) DMPO- \cdot OH and (b) DMPO- \cdot O₂⁻ for CDs/UiO66, UiO66 and C/ZrO₂.

Then, the mechanism of plastics conversion over the CDs/UiO66 photocatalyst is investigated. A potential electron and hole transfer mechanism at the interface of CDs/UiO66 is illustrated in **Figure 5.6 a-b**. In this work, electrons are transferred from the CB of UiO66 to CDs, Subsequently, the electrons accumulated in CDs can react with O₂, leading to the formation of $\cdot O_2^{-}$. Additionally, holes in the VB of UiO66 can be used to react with H₂O to generate \cdot OH. In this way, electrons and holes of CDs/UiO66 are effectively separated. Finally, the generated active radicals will participate in converting PVC into acetic acid. In this work, the pathway for the plastic conversion is proposed as follows:

$$CDs/UiO66 + hv \rightarrow CDs/UiO66 (h^+ + e^-)$$
(1)

$$e^{-} + O_2 \rightarrow \bullet O_2^{-} \tag{2}$$

$$H_2O + h^+ \rightarrow \bullet OH + H^+ \tag{3}$$

Plastics + •OH and •O₂⁻
$$\rightarrow$$
 high-value-added organics (acetic acid) (4)



Figure 5.6 (a) The mechanism and (b) pathway for PVC conversion over CDs/UiO66.

5.4 Conclusions

To improve the light absorption performance of MOF-based photocatalysts, a mild pyrolysis strategy is developed to embed CDs nanoparticles into the UiO66 framework to fabricate CDs/UiO66 composite photocatalysts. As photosensitizer and electron traps, CDs can improve the light absorption properties and promote carrier separation efficiency of CDs/UiO66. As a result, the CDs/UiO66 exhibits high activity in the conversion of PVC into a high value-added chemical (acetic acid), superior to that of pristine UiO66. Compared with Ag₂O/MIL(Fe)-101 synthesised in **Chapter 3** and ZnO/UiO66-NH₂ synthesised in **Chapter 4**, CDs/UiO66 exhibits excellent visible light absorption properties, which ensures that it has high solar energy utilization efficiency. This work presents a promising method for designing and synthesising MOF-based catalysts for converting plastics.

6 Conclusion

Based on Papers **I-III**, the research focus of this thesis is on the creation of new MOF-based composite materials by embedding different ultra-small nanoparticles into MOFs frameworks and investigating their catalytic activity in upcycling of plastics. The main findings are summarised below:

- A facile photochemistry strategy is developed to embed Ag₂O into the pores of MIL(Fe)-101. Due to the well-matched band structures between Ag₂O and MIL(Fe)-101, the Ag₂O/MIL(Fe)-101 photocatalyst can rapidly separate electrons and holes, enhancing its catalytic activity. The resultant Ag₂O/MIL(Fe)-101 heterojunction can efficiently convert PEG into acetic acid, accompanied by H₂ generation. This work not only proposes a novel method for fabricating heterojunction photocatalysts but also preliminarily verifies the feasibility of MOF-based photocatalysts for upcycling plastics.
- A partial calcination method is developed to embed ZnO into UiO66-NH₂ • for fabrication of ZnO/UiO66-NH₂. The size and dispersion of the encapsulated ZnO particles can be controlled by the MOFs framework in ZnO/UiO66-NH₂. Meanwhile, the retained porous structure of ZnO/UiO66-NH₂ not only provides abundant catalytic sites but also promotes the effective diffusion of plastic fragments. In addition, the formation of heterojunction in ZnO/UiO 66-NH₂ is beneficial to improve its carrier promoting separation efficiency, thereby its catalytic activity. Consequently, ZnO/UiO66-NH₂ show a high activity for PLA conversion coupled with H₂ production. This work demonstrates the feasibility of MOF-based composite photocatalysts for the upcycling of biodegradable plastic.
- To enhance further the light absorption capacity of MOF-based photocatalysts, CDs are embedded into the pores of UiO66 through a mild pyrolysis strategy. As an electron trap center and photosensitizer, CDs effectively broaden the solar light absorption range of CDs/UiO66 and achieves rapid photogenerated carrier separation, which is favourable for promoting the plastic conversion rate. As a result, the obtained CDs/UiO66 exhibits high catalytic activity when converting PVC plastics into high-value-added chemicals. The work not only offers an effective method for synthesizing MOF-based composite photocatalysts but also promotes the application of MOF-based photocatalysts in the field of upcycling non-biodegradable plastics.

Overall, this work not only provides some novel methods for the synthesis of MOF-based composite photocatalysts, but it also offers new insights into understanding the mechanisms and pathways of plastic upcycling.

7 Future Perspectives

The content of this thesis will help promote the application of MOFs materials in the field of photocatalysis, especially in waste plastic upcycling. Given the current research progress, future research should focus on the following content:

- Up to now, the performance evaluation of MOF-based photocatalysts in plastic upcycling is still mainly in the laboratory research stage. Further research should consider conducting pilot experiments to verify the feasibility of MOFs materials in plastic upcycling. Meanwhile, this work only considers the catalytic activity of MOF-based photocatalysts for a single plastic. However, plastic waste in real life is often mixed with multiple types of plastics. Therefore, further studies should employ plastic samples mixed with different kinds of plastics to evaluate the catalytic activity of MOF-based photocatalysts.
- For the photocatalytic upcycling of plastics, the product selectivity is difficult to control, mainly due to the fact that the upcycling of plastics is a complex reaction process and the products vary in line with different reaction states (reaction time, temperature, pressure, etc.). Further research should be devoted to improving the selectivity of the desired product by optimizing the catalyst structure, adjusting reaction conditions and developing product separation and purification technologies.
- At present, research on photocatalytic waste plastic upcycling is still in its initial stages, and so there is no unified understanding of the plastic conversion pathway and mechanisms, which further hinders the development of photocatalytic technology in the field of plastic conversion. Therefore, it is necessary to explore continuously the mechanisms and pathways for plastic upcycling in future research. Theoretical calculations and advanced characterization techniques are considered effective methods for analyzing the mechanisms of plastic conversion.
- In terms of upcycling waste plastics, although photocatalytic technology is an environmentally friendly strategy for solving the "white pollution" problem, its overall efficiency is lower compared to traditional pyrolysis technologies. To promote the application of photocatalytic technology for converting plastic, further research should be devoted to integrating photocatalysis technology with other technologies (such as electrocatalysis and thermo-catalysis) to improve reaction efficiency.

In conclusion, while photocatalytic technology is an effective method for addressing plastic pollution, it still faces certain challenges and limitations that need to be overcome in the future.

8 References

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9 Papers

- Qin, J., Dou, Y., Wu, F., Yao, Y., Andersen, H. R., Hélix-Nielsen, C., Lim, S. Y., and Zhang, W. (2022) In-Situ Formation of Ag₂O in Metal-Organic Framework for Light-Driven Upcycling of Microplastics Coupled with Hydrogen Production. *Applied Catalysis B: Environmental.* 319, 121940.
- II Qin, J., Dou, Y., Zhou, J., Candelario, W. M., Andersen, H. R., Hélix-Nielsen, C., and Zhang, W. (2023) Photocatalytic Valorization of Plastic Waste over Zinc Oxide Encapsulated in a Metal–Organic Framework. *Advanced Functional Materials*, 33, 2214839.
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- **IV Qin, J.,** Dou, Y., Hélix-Nielsen, C., and Zhang, W. Functionalized Advanced Materials for Waste Plastic Management. *Manuscript in preparation*.

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