Photocatalytic and photoelectrochemical systems for oxidation of aromatic compounds in an aqueous environment

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**PHOTOCATALYTIC AND PHOTOELECTROCHEMICAL
SYSTEMS FOR OXIDATION OF AROMATIC COMPOUNDS
IN AN AQUEOUS ENVIRONMENT**

NG YUN RU

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2020

**Photocatalytic and photoelectrochemical systems for oxidation of
aromatic compounds in an aqueous environment**

Ng Yun Ru

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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

2020

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Chapter 5 was published as Ho, Xian Liang; Das, Siva Prasad; Ng, Leonard Kai-Sheun; Ng, Andrew Yun Ru; Ganguly, Rakesh; Soo, Han Sen, "**Cobalt complex of a tetraamido macrocyclic ligand as a precursor for electrocatalytic hydrogen evolution**" *Organometallics* **2019**, 38, 1397-1406.

The contributions of the co-authors are as follows:

- Dr. Soo Han Sen provided the initial project direction and edited the manuscript drafts.
- Ho Xian Liang prepared the manuscript drafts. The manuscript was revised by both Xian Liang and Dr Soo Han Sen.
- I ran the XPS experiments, interpreted and analysed the data, as well as wrote the section about the XPS data.
- Dr. Siva Prasad Das did the initial synthesis of the Co-TAML and preliminary hydrogen evolution experiments.
- Dr. Leonard Ng Kai-Sheun did the FESEM-EDX and TEM characterisation for the complex.
- Dr. Rakesh Ganguly conducted the single crystal X-ray diffraction pattern acquisition and analysis of the data.

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The contributions of the co-authors are as follows:

- Dr. Soo Han Sen and Dr. Hong Zonghan conceived the initial idea and research direction.
- Dr. Hong Zonghan did the synthesis of the materials and most of the material characterisations, as well as designed and ran the photocatalytic reactions. He also wrote the drafts of the manuscript. The manuscript was revised together with Dr. Soo Han Sen and Prof. Sum Tze Chien
- Dr. Chong Wee Kiang collected the VTPL and VR-TRPL data and analysed the results. Dr. Li Mingjie and Prof. Sum Tze Chien also helped in the data analysis.
- I performed the AFM and PESA measurements, data processing, and analysis.
- Dr. Rakesh Ganguly conducted the single crystal XRD measurements, data processing, and analysis.

06th March 2020

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Abstract

As the demand for chemical products increases, alongside a rising problem of pollution due to chemical wastes, there is great interest in developing systems that can resolve either or both issues in a sustainable way. Inspired by nature, the development of photocatalytic and photoelectrochemical (PEC) systems had been pursued as a possible solution. In this work, both a PEC system involving nanoporous bismuth vanadate (BiVO_4) with tetraamidomacrocyclic ligand iron complexes (Fe-TAML) as co-catalysts and a photocatalytic system involving modified graphitic carbon nitrides ($\text{g-C}_3\text{N}_4$) were investigated. Both systems were also applied to the oxidation of bisphenol compounds, as well as the oxidation of lignin in lignocellulose. In addition, a hydrophobic metal halide perovskite photocatalytic system was explored for C-C bond cleavage and dehydrogenation reactions, while tetraamidomacrocyclic ligand cobalt complexes (Co-TAML) were investigated for hydrogen evolution reaction.

In Chapter 2, I present a literature review of the components of the photosystems we had worked on. These include reviews of lignocellulose and bisphenols as the substrates of interest, as well as the materials BiVO_4 , $\text{g-C}_3\text{N}_4$, and metal halide perovskites as viable semiconductors. The possible modifications and applications of the materials in various reactions were also investigated in this chapter. In addition, this chapter will also offer a look into the Fe-TAML co-catalysts and other TAML complexes, their origins and applications, before ending with a summary about how the proposed systems would be like.

Chapter 3 follows on by describing the syntheses and characterisations of the nanoporous BiVO_4 plates and the addition of Fe-TAML as co-catalysts (from hereon known as $\text{BiVO}_4/\text{Fe-TAML}$). The PEC activities of the resulting system were shown to be promising in oxidising a selection of substrates, namely bisphenol F (BPF), bisphenol S (BPS), and lignin.

Chapter 4 then describes a photocatalytic system involving a modified $\text{g-C}_3\text{N}_4$ that has both an improved surface area, as well as pyromellitic diimide (PDI) incorporated within the $\text{g-C}_3\text{N}_4$. The improvement to the photocatalytic ability of the resulting $\text{g-C}_3\text{N}_4$ was then discussed and examined, with subsequent application to the degradation of BPF.

Chapter 5 summarises the collaborative projects done in exploring metal halide perovskites as a photocatalysts and Co-TAML as an electrocatalyst, with further discussions into some characterisations of the materials and catalysts involved. The thesis concludes with Chapter 6 looking into possible future work.

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List of abbreviations

ACN	–	Acetonitrile
AM	–	Air mass
AFM	–	Atomic force microscopy
BPS	–	Bisphenol S
BPF	–	Bisphenol F
BPA	–	Bisphenol A
BiVO ₄	–	Bismuth vanadate
BiOI	–	Bismuth iodide oxide
BET	–	Brunauer-Emmett-Teller
CO ₂	–	Carbon dioxide
Co-TAML	–	Cobalt complex with tetraamidomacrocyclic ligand
CA	–	Chronoamperometry
CBM	–	Conduction band minima
DMF	–	Dimethylformamide
DRS	–	Diffused reflectance spectroscopy
DMSO	–	Dimethylsulfoxide
Et ₃ N	–	Triethylamine
Et ₂ O	–	Diethyl ether
EtOH	–	Ethanol
EA	–	Ethyl acetate
EDX	–	Energy-dispersive X-ray
FTO	–	Fluorine-doped tin oxide
Fe-TAML	–	Iron complex with tetraamidomacrocyclic ligand
G-C ₃ N ₄	–	Graphitic carbon nitride
H ₂	–	Hydrogen gas
HPLC	–	High performance liquid chromatography
IT	–	Current-time
IR	–	Infra-red chromatography
LSV	–	Linear sweep voltammetry
MeOH	–	Methanol
Na ₂ SO ₃	–	Sodium sulfite
Na ₂ SO ₄	–	Sodium sulphate
N ₂	–	Nitrogen gas
PDI	–	Pyromellitic diimide
PDMA	–	Pyromellitic dianhydride
PXRD	–	Powder X-ray diffraction
PL	–	Photoluminescence
PEC	–	Photoelectrochemical
PESA	–	Photoelectron spectroscopy in air
RHE	–	Relative hydrogen electrode
ROS	–	Reactive oxygen species

SEM	–	Scanning electron microscopy
THF	–	Tetrahydrofuran
TAML	–	Tetraamidomacrocyclic ligand
UV-Vis	–	Ultraviolet-visible light spectroscopy
VBM	–	Valence band maxima
XRD	–	X-ray diffraction
XPS	–	X-ray photoelectron spectroscopy

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Chapter 1

Introduction

1.1. Hypothesis/problem statement

The continuous increase of human population, coupled with the rising affluence in many parts of the world, had resulted in the growth of consumerism. What this entails for the chemical industry is a greater demand for chemical products ranging from pharmaceuticals, such as antibiotics, to everyday products including plastics, agricultural chemicals, and even nanomaterials. However, to meet these rising demands, more resources and chemical precursors will be needed, while the production and consumption of these products result in generation of large amounts of waste materials.¹

In recent studies, trace amounts of chemicals have been detected in the environment worldwide, particularly in our water sources. Water samples collected from streams and rivers of the United States were reported to contain pollutants such as pharmaceuticals and other chemicals.² In Singapore, this was similarly observed in a study conducted regarding the presence of bisphenol A (BPA) in our reservoirs, despite currently employed water treatment methods.³ Such chemicals are neither environmentally benign nor passive, but can bioaccumulate and are persistent and toxic to both wildlife and humans.⁴ Therefore, there is a need for novel, improved, and sustainable methods that could be utilised to remove such chemical pollutants.

Furthermore, as the demand for polymeric materials and pharmaceutical products increases due to the rising consumption, there is an ever-pressing need for a more sustainable source of aromatic precursors, which are presently obtained from non-renewable fossil fuels. One such source could be the naturally abundant lignin. Lignin is one of three main components of lignocellulose, commonly found in plants,

and contain large number of aromatic groups in its polymeric framework.⁵ However, current usage or treatment of lignocellulose has been mainly for producing biofuel, namely bioethanol, and heat by combustion.⁶ The biorefineries focus on converting cellulose and hemicellulose without utilising the lignin component. Hence, there has been much research effort in developing methods that could potentially increase the efficiency of lignin utilisation via direct and selective conversion to aromatic precursors.

1.2. Objectives and scope

Therefore, the objectives of this research are to design sustainable photoelectrochemical (PEC) system and photocatalytic system, with applications for the degradation of aromatic compounds in water supplies or the conversion of lignin to aromatic precursors. One of the key features of our systems is the sustainable and eco-friendly design of our photocatalysts and photoanodes, thus excluding many common semiconductors and doping methodologies that rely on elements of known toxicity to both the environment and humans. To that end, the focus of this thesis will be on two specific systems. The first would be a PEC system that consists of a nanoporous bismuth vanadate (BiVO_4) photoanode, which is subsequently doped with iron complexes with tetraamidomacrocyclic ligand (Fe-TAML) as co-catalysts, known from here on as $\text{BiVO}_4/\text{Fe-TAML}$. Depicted in Figure 1.2.1. is the system, along with the hypothetical reaction pathway by which substrates such as bisphenol or lignin can be oxidised at the photoanode. The second design approach would be a photocatalytic system that uses modified graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) as the photocatalyst for the degradation of pollutants as shown in Figure 1.2.2.

Figure 1.2.1. Proposed scheme for the oxidation of lignocellulose or bisphenol using $\text{BiVO}_4/\text{Fe-TAML}$ electrodes in a PEC system.

Figure 1.2.2. Proposed scheme for the degradation of pollutants using $\text{g-C}_3\text{N}_4$ as a photocatalyst.

Furthermore, additional objectives of this research would be in exploring other possible photocatalytic systems, such as hydrophobic metal halide perovskites for photoredox reactions, or electrocatalytic systems, such as cobalt complexes with a tetraamidomacrocyclic ligand (Co-TAML) in hydrogen (H_2) evolution reactions (HER), that could be coupled with the above described systems. These coupled systems could function as tandem PEC systems, in which there is no need for an application of an external bias, while allowing for different reactions to occur at the photocathode and photoanode. Requiring only the light illumination to run the tandem PEC systems in a multi-functional role would add value to the individual parts and the system as a whole.

1.3. Dissertation overview

Chapter 1 will introduce the context and premise of the thesis. It gives a general overview of the objectives of this thesis and the findings from the work done in fulfilling these objectives.

Chapter 2 explores the most recent advances regarding the concepts of PEC and photocatalytic systems, lignocellulose oxidation, bisphenol degradation, BiVO_4 , and $\text{g-C}_3\text{N}_4$.

Chapter 3 contains the description and discussion of the $\text{BiVO}_4/\text{Fe-TAML}$ photoanode synthesis. It includes the characterisation of the resulting BiVO_4 semiconductor, as well as the analysis of the successful loading of the Fe-TAML onto BiVO_4 . It also highlights the utilisation of the resulting BiVO_4 in a PEC cell system for the simultaneous generation of useful lignin-derived products. Bisphenol degradation was also explored as a possible application of the system.

Chapter 4 covers the simultaneous modifications of bulk $\text{g-C}_3\text{N}_4$ to obtain $\text{g-C}_3\text{N}_4$ with a larger surface area that is also doped with pyromellitic diimides (PDI). It also contains the discussion of the improvement in the rate of bisphenol oxidation reaction as a result of these modifications.

Chapter 5 summarises the collaborative works done in exploring metal halide perovskites as potential photocatalysts and Co-TAML as a possible electrocatalyst. It contains the photoelectron spectroscopy in air (PESA) data of the synthesised lead-

based perovskites which was used to determined their valence band minima (VBM) value, as well as atomic force microscopy (AFM) images of the recovered lead based perovskite after reactions. It would also discuss the X-ray photoelectron spectroscopy (XPS) data acquired in determining the active species of Co-TAML in H₂ evolution reactions.

Chapter 6 concludes the thesis with a summary of the prior chapters, while also providing insights into the future work regarding both projects, specifically their subsequent directions and plausible outcomes.

1.4. Findings and originality

1. A BiVO_4 PEC system incorporating Fe-TAML as a potential co-catalyst
2. A PEC system that is able to oxidise cellulose acetate, lignin, bisphenol F (BPF), bisphenol S (BPS), as well as polymers such as polyethylene glycol (PEG) and polyethylene terephthalate (PET) at ambient conditions.
3. The two-part simultaneous modification of $\text{g-C}_3\text{N}_4$ that would be inexpensive and simple in application. The resulting $\text{g-C}_3\text{N}_4$ was shown to have a higher conduction band and greater surface area, which increased the rate of reaction for $\text{g-C}_3\text{N}_4$ in degrading BPF.
4. XPS conducted of the Co sample after reaction indicates the presence of Co^{II} , which could indicate the oxidation of the electrodeposited Co^0 nanoparticulate film in the presence of air.
5. PESA data indicates the novel hydrophobic lead halide perovskite to have a VBM value close to other reported lead halide perovskites.⁷ AFM images also indicate fragmentation of the perovskite after one cycle of photoredox reaction.

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Chapter 2

Literature review

2.1. Introduction

In the previous chapter, it briefly described the efforts to develop a PEC system for biomass reformation or pollutant degradation. In the following section, a more in-depth investigation and review of the reasons behind the development of the system, as well as the most recent works regarding such systems will be presented. First, the objectives will be discussed, namely the reformation of lignocellulose and degradation of bisphenol, their values, and contemporary work related to them. Next, general descriptions of PEC and photocatalytic systems are explored, along with their uses and the most recent works in the field. Lastly, it will showcase the semiconductors of interest to the thesis, namely BiVO_4 and $\text{g-C}_3\text{N}_4$, as well as the co-catalyst Fe-TAML. In the first section, it will examine two types of substrates for the purpose of potential applications in a PEC or photocatalytic system.

2.2. Substrates of interests

2.2.1. Lignocellulose – a potential source of fuel and aromatic precursors

Lignocellulose is a cheap and abundant resource that can be found in the plant mass in forests and in agriculture.¹ It comprises lignin, cellulose, and hemicellulose (Figure 2.2.1.), and has been investigated for its potential in the production of 2nd generation biofuels.² However, lignocellulose has a high resistance toward being selectively deconstructed, requiring harsh conditions to pre-treat the lignocellulose.³⁻⁵ Subsequently, simple sugars produced from hemicellulose would be fermented directly to ethanol (EtOH), while treatment of the lignocellulose with cellulase would see cellulose hydrolyse to glucose before it is finally converted into EtOH.⁶ Lignin, on the other hand, has the potential to be further utilised as a source of biodiesel and chemical precursors.³ However, current refining methods of lignocellulose produce a great stream of lignin as a waste product and thus, lignin is underutilised as a source of liquid fuels or biomaterials.⁷

Figure 2.2.1. Components of lignocellulose.

Therefore, one possible way of increasing the sustainability and efficiency of a biorefinery toward fully utilising lignocellulose would be to convert lignin into renewable aromatics.⁸ Although much research has been done in producing aromatics from lignin model compounds and Organosolv lignin (pretreated lignin for solubility in organic solvents),⁹⁻¹¹ the challenge of fractionalising lignocellulose still remains.¹² Current methods of fractionalisation, such as the Kraft or Organosolv processes, would alter the lignin structure so that the vulnerable β-O-4 bonds become less available, thus making the resulting lignin less susceptible to transformations or reactions to produce aromatic products.¹³ In this regard, the lignin-first concept, where lignin is first catalytically valorised from biomass, gives an interesting way to fully utilise lignocellulose.¹⁴ There are currently three differing pathways that have been explored within this concept, with the first being the use of a multi-purpose catalyst under extreme reaction conditions in a single pot. In this

approach, there is a lack of control over the products evolved from the concurrent conversions of lignin, cellulose, and hemicellulose, often generating a wide-variety of aliphatic alcohols, alkanes, or phenolic compounds.¹⁵⁻¹⁶

Figure 2.2.2. The general reaction step and products generated in the presence of the catalyst (Ni-W₂C/AC) under harsh conditions.¹⁶

The second approach involves two steps, by first hydrogenolysis to aromatics at high temperature,¹⁷ followed by the conversion of cellulose/ hemicellulose to aliphatic alcohols or sugar alcohols under harsh conditions or with an acid catalyst.¹⁸ Further processes would then be needed to re-functionalise the resulting products into commercially valuable chemicals, incurring a greater energy cost and lowering the atomic efficiency.

Figure 2.2.3. Reaction scheme and products of the hydrogenolysis of lignin at high temperature.¹⁷

Recently, progress was made in developing a solar-powered catalytic transformation method as a third approach for the lignin-first concept. In this approach, biomass can be depolymerised in a process similar to reverse photosynthesis, due to the cleavage of β -O-4 ether bonds.¹⁹⁻²⁰ Metal complexes and semiconductors have been shown to activate and reductively cleave β -O-4 bonds via first oxidising the C_α -OH to a ketone.²¹⁻²⁴ In addition, CdS quantum dots were shown to selectively and photocatalytically cleave β -O-4 bonds, and were even applied to native lignin to obtain a variety of aromatic monomers at room temperature (Figure 2.2.4).¹³ In brief, upon the photogeneration of an electron-hole pair in CdS, the hole would proceed to undergo oxidative dehydrogenation along the β -O-4 bonds. The resulting radical would then interact with the photogenerated electron, undergoing reductive bond cleavage to produce the monomers. Although this example demonstrates the

plausibility of such a system, the toxicity of CdS would pose a serious issue, if such methods were to be employed on a larger scale.

Figure 2.2.4. Some of the key products from the photocatalytic cleavage of β -O-4 bonds in lignin from Birch woodmeal by CdS quantum dots.¹³ The major product is highlighted in red with yield at 14.0%.

2.2.2. Bisphenol – commonly occurring endocrine disruptors

As the increasing population results in a corresponding rise in the consumption of chemical products, there is a growing concern regarding the chemical pollution generated during the production of useful chemicals and the effects it has on the environment and humans. One category of significant chemical pollutants is bisphenols and their analogues. Although bisphenols have been reported to be endocrine disruptors,²⁵ they are still used in the industrial production of polycarbonate plastics and epoxy resins (Figure 2.2.5)²⁶ in order to meet the global annual demand of about 7.7 million metric tons.²⁷

Figure 2.2.5. Bisphenol used in a) polycarbonate plastics and b) epoxy resin.

Studies have shown that BPA exhibits adverse gender-specific outcomes since they are endocrine-disrupting chemicals, which affects many human physiological functions, ranging from effects on the brain²⁸ and metabolic processes to the reproductive and immune systems.²⁹⁻³⁰ In addition, other analogues of bisphenols that are used as substituents for BPA, such as BPF and BPS, have shown genotoxicity and cytotoxicity towards human cell lines.³¹ Reviews of many *in vivo* and

in vitro studies of BPF and BPS have also shown that both analogues possess similar endocrine-disrupting properties as BPA.³²

Figure 2.2.6. Bisphenol and its analogues.

Although bisphenols are easily biotransformed in the environment and do not bioaccumulate along the food chains,³³⁻³⁴ the large volume production and their subsequent disposal result in a pseudo-persistence in the environment.³⁵ Research regarding human exposure to these harmful chemicals has shown that bisphenols are present and ubiquitous among the human population,³⁶ even among American.³⁷ Even though the lifetime of bisphenol, such as BPA, was reported to be short and is being metabolised and excreted from the body,³⁸ the pseudo-persistence of bisphenols has raised concerns regarding potential adverse health effects.³⁹ Hence, there is a need to not just look for alternatives, but also find ways to sustainably remove and reduce the occurrence of bisphenols in the environment.

2.3. A sustainable treatment methodology - PEC system and photocatalytic system

In recent times, many research groups have turned to nature for inspiration in emulating and designing possible solutions to some of the problems of the modern society. The nature-inspired system's main objectives are to both sustainably treat chemical pollutants, such as bisphenols, and to efficiently utilise lignocellulose to meet the rising global demands for chemical products. Looking to nature, plants can convert CO_2 and water to glucose and oxygen. The photosynthetic system found in the green leaves can perform such biochemical conversions via a process known as a Z-scheme. As shown in Figure 2.3.1., the Z-scheme includes the presence of two photosystems (P680 and P700) in which sunlight is harvested, and a series of other bioorganic intermediates help to channel the resulting electron from one photosystem to the other and eventually to the catalytic active site where the chemical conversion can take place.⁴⁰ This allows for an eco-friendly and sustainable way of converting chemical compounds.

Figure 2.3.1. Z-scheme of photosynthesis, showing the reduction of CO_2 and H^+ to HCOOH , CH_3OH and H_2 , while oxidising H_2O to oxygen and H^+ . Adapted with

permission from *Acc. Chem. Res.* **2013**, 46, 2355-2364. Copyright 2019 American Chemical Society.⁴⁰

Keeping in mind the process of natural photosynthesis, the artificial photosynthetic system shown in Figure 2.3.2. was designed to emulate similar oxidation and reduction reactions via two different co-catalysts anchored to a semiconductor. In addition, by using a semiconductor of an appropriate bandgap, the hybrid photocatalyst can possibly increase the catalytic efficiency of the system. Furthermore, the conduction band and valence band edges in a semiconductor can be selected or adjusted to activate different co-catalysts. By such modifications, a wider range of chemical pollutants can be oxidised or reduced by the artificial photosynthetic system in the presence of light.

Figure 2.3.2. Hybrid photocatalyst for the oxidation of water and reduction of CO_2 . Adapted with permission from *Acc. Chem. Res.* **2013**, 46, 2355-2364. Copyright 2019 American Chemical Society.⁴⁰

In recent years, there has been extensive research regarding different types of dye-sensitised photoelectrosynthetic cells (DSPECs) with various semiconductors. Most of these studies describe the usage of a semiconductor, which upon illumination, can perform water splitting reactions⁴¹ or a H_2 evolution reaction,⁴² both of which would

produce H_2 gas as a possible source of green energy. Amongst them, TiO_2 and ZnO , have been identified as potential photocatalysts for the degradation of organic pollutants in various media.⁴³ For example, the generation of hydroxyl radicals produced by the interaction of water with photogenerated holes in TiO_2 has been found to be a key component for the subsequent degradation of organic pollutants.⁴⁴ However, most of such photocatalysts require high-energy ultra-violet light for the generation of the electron and hole pairs, leading to the need for the anchoring of dyes in order to increase the range of wavelength of light that the semiconductor can adsorb.⁴⁵ In addition, some of them are not stable in aqueous environments during multiple catalytic cycles, requiring morphological or other extensive modifications to improve their performance and stability.⁴⁶

Figure 2.3.3. Photocatalytic pollutant degradation system. Reprinted (adapted) with permission from *Chem. Soc. Rev.* **2014**, 43, 7520-7535. Copyright 2019 Royal Society of Chemistry.⁴⁷

PEC water splitting has garnered much attention over the years as a viable system for the generation of a sustainable fuel in the form of H_2 .⁴⁸ Recent developments into PECs had mainly been focused on improving the solar-to-hydrogen efficiency.⁴⁷ However, the applications of such systems on industrial scale are still at early

stages.⁴⁹ As previously described, in a typical photocatalytic system, the semiconductor would first absorb photons. This would lead to the generation of holes (h^+) in the valence band and electrons (e^-) in the conduction band. The difference between a PEC and a photocatalytic system is that while both h^+ and e^- are present on the photocatalyst, the h^+ and e^- are localised on the photoanode and photocathode of the PEC, respectively. The charge carriers would then transfer from the bulk material towards the surface of the photoanode or photocathode where reactions would take place.⁵⁰

However, a typical PEC setup would require the application of an external potential bias in order to drive the reaction. Thus, further research into improving the PEC cell system has led to the idea of a tandem PEC cell. In a tandem PEC cell, photovoltage is generated at either electrode and is adequate to be utilised to carry out reactions, such as water-splitting.⁵¹ A tandem PEC cell could potentially exist in three different configurations. The first configuration is a two-electrode system in which both electrodes are photosensitive, whereas in the second and third configuration only a photoanode or a photocathode is used.⁵² Alternatively, the tandem PEC could contain a dye-sensitised solar cell connected to the system to act as a source of photoelectrons.⁵³

Figure 2.3.4. PEC water splitting system a) with a photoanode, b) with a photocathode, and c) with both a photoanode and photocathode for a tandem PEC setup. Reprinted (adapted) with permission from *Chem. Soc. Rev.* **2014**, 43, 7520-7535. Copyright 2019 Royal Society of Chemistry.⁴⁷

Commonly used semiconductors for PEC systems, such as TiO_2 ⁵⁴ and WO_3 (Figure 2.3.5.),⁵⁵ have wide band gaps that only allow for the absorption of the ultraviolet region of the solar spectrum. Therefore, there has been an increase of studies related to using materials of smaller band gaps, such as BiVO_4 . In addition, photocathodes such as NiO with Co H_2 evolution catalyst have also been investigated for applications in a tandem PEC cell, as potential alternatives to the expensive platinum (Pt).

2.3.1. BiVO₄ as a potential photocatalyst or PEC system

BiVO₄ was initially explored as a non-toxic alternative to other inorganic compounds containing lead, chromium, and cadmium in pigments for plastic coatings.⁵⁷ It was soon discovered that BiVO₄ was ferroelastic, acousto-optical, exhibited ionic conductivity, and most interestingly, it showed photocatalytic ability in water oxidation.⁵⁸ Researchers have shown the correlation between BiVO₄ and its crystal structure, and shown how its differing electronic structures affect its photocatalytic activity. In addition, the upward shift of the valence band of monoclinic BiVO₄ due to the hybridisation of its Bi 6s and O 2p orbitals not only results in a lower potential with a small band gap of 2.4-2.6 eV, but also provides enough potential for the oxidation of water and other organic compounds. As such, BiVO₄ has been utilised in both photocatalytic and PEC setups. However, the efficiency of BiVO₄ suffers from poor charge separation, leading to other issues, such as poor electron transport,⁵⁹ slow kinetics in water oxidation,⁶⁰ and a low carrier mobility.⁶¹ Therefore, much research has been conducted in altering the surface and bulk properties of BiVO₄ as possible solutions to increase the efficiency of BiVO₄. Generally, the approaches can be categorised into four distinct types of modifications, namely crystal facet engineering, coupling with graphitic carbon materials, annealing treatment, and nanoscaling.⁵⁷

BiVO₄ is known to be an n-type semiconductor and was found to have great potential as a photoanode.⁶² Its small band gap allows for the absorption of light in the visible region, while the conduction band edge is slightly lower than the redox potential of H⁺/H₂. Since a higher conduction band position would allow for a more negative

photocurrent onset potential at the anode, this would enable a lower external potential bias to be applied in a PEC cell. Consequently, this would increase the efficiency of the resulting PEC cell.⁶³ In addition, as the charge separation is facilitated by the application of the external potential bias,⁶⁴ diminished efficiency due to the recombination of charge carriers at the surface of BiVO₄ photoanode would no longer be a problem. On the other hand, volume recombination is a key parameter that affects the efficiency of a BiVO₄ photoanode. This is because of the interparticle transportation of the charges as the photogenerated hole-electron pairs diffuse to their respective ends of the BiVO₄ particle film (holes toward the electrolyte-semiconductor interface, electrons to the back of substrate such as fluorine tin oxide).⁶⁵ This would eventually result in the recombination of charges at the grain boundaries between BiVO₄ particles in the film.

Therefore, nanostructuring and nanoscaling methodologies are highly desirable in optimising the BiVO₄ photoanodes. Nanostructuring and nanoscaling methodologies have been known to overcome the limitations of many oxide photocatalysts,⁵⁷ and have been widely adopted as an approach to increase the efficiency of BiVO₄ as a photoanode in PEC cells.⁶² As evident from the work of Kim *et al.*, BiVO₄ with a small particle size of about 76 nm is able to achieve a high percentage of charge separation.⁶⁶ As a result, the reduction of particle size would increase the amount of BiVO₄ on the photoanode surface, allowing for a thinner film that could minimise the volume recombination at the grain boundaries.

Although BiVO₄ has generally been reported as a photoanode for water oxidation, it is known to be able to degrade organic compounds as well. In such experiments,

organic compounds, such as methylene blue or nonylphenol,⁶⁷⁻⁶⁸ are degraded either because of the direct interaction with holes generated from BiVO₄ upon irradiation by visible light, or by the ROS, such as superoxide and hydroxyl radicals.⁶⁹ In the second pathway, ROS are generated either by the interaction of water with photogenerated holes, or by the reduction of oxygen, which yields superoxide anions. Regarding the reaction mechanism, most research groups proposed the *in situ* generated hydroxyl radical to be the active intermediate in the process.⁷⁰ However, in the application of oxidising terephthalic acid to 2-hydroxyterephthalic acids, the generation of hydroxyl radicals was observed to be minimal and not significant, indicating that the hydroxyl generation reaction may be thermodynamically unfavourable.⁷¹ Therefore, I could potentially utilise the photogenerated holes directly to activate the oxidation co-catalyst for the transformations of other organic compounds.

2.3.2. G-C₃N₄ – an organic semiconductor for more sustainable applications

The material g-C₃N₄ was recently found to be a suitable, metal-free, polymeric semiconductor for oxidising pollutants, such as BPA and trichlorophenol. The g-C₃N₄ materials have band gaps of approximately 2.70 V and were found to be capable of splitting water.⁷² In addition, g-C₃N₄ was found to have an optical absorption edge of 460 nm,⁷³ which makes it a potential photocatalyst for the oxidation of pollutants in aqueous environments, with visible light as the energy source.

In g-C₃N₄, the valence band is made up of nitrogen p_z orbitals with a potential of +1.40 V, while the conduction band consists of carbon p_z orbitals with a potential of -1.30 V.⁷⁴ This results in a spatial separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), allowing for oxidation and reduction reactions to occur independently at nitrogen and carbon atoms, respectively.⁷⁵ The separation of the HOMO and LUMO allows g-C₃N₄ to catalytically generate H₂O₂ for the degradation of pollutants, and may likewise be able to directly oxidise pollutants upon visible-light irradiation.

Lately, g-C₃N₄ has been reported in various applications, including water oxidation, CO₂ reduction, and H₂ evolution due to the favourable valence and conduction band edges. At present, the photocatalytic efficiency of g-C₃N₄ is still comparatively lower than those of other inorganic semiconductors. The small specific surface area, rapid rate of charge recombination, marginal optical absorption of visible light, and generally low electric conductivity are the main factors limiting the photocatalytic

performance of g-C₃N₄.⁷⁶ However, subsequent studies have shown that modifying the electronic structure, nanostructure, crystal structure, or heterostructure of the g-C₃N₄ material could improve its photocatalytic abilities.⁷⁷

Changing the nanostructure of the g-C₃N₄ would improve the photocatalytic efficiency by enhancing its optical and electrical properties. This is achieved by increasing the rate of mass transfer during catalysis, as well as the rate of accumulating and separating electron-hole pairs for catalytic reaction.⁷⁸ Liquid exfoliation, thermal exfoliation, and liquid ammonia assisted lithiation are some of the top-down approaches used to obtain g-C₃N₄ nanosheets from bulk g-C₃N₄.⁷⁹ By such methods, g-C₃N₄ nanosheets of 2.0 to 2.5 nm in thickness can be obtained, with their thickness corresponding to approximately six to seven atomic layers of g-C₃N₄. In contrast to the bulk material, a thinner layer of g-C₃N₄ showed a significant increase in the light absorption and photocatalytic activity.⁸⁰ Hence, I aim to synthesise and obtain single atomic layers of g-C₃N₄ that are structurally similar to graphene sheets, which would theoretically have even greater electrical conductivity and better charge separation upon optical irradiation.⁸⁰

Furthermore, higher photocatalytic activities in g-C₃N₄ can be achieved by the modification of its heterostructure. To this end, inorganic compounds, such as BiPO₄⁸¹ and TaON⁸² can be added to g-C₃N₄ either as effective dopants or for the purpose of generating heterojunctions. Similarly, by introducing other organic compounds as co-monomers, or minute amounts of other elements, such as phosphorus and sulphur, during the polymerisation of g-C₃N₄, the π electrons on the aromatic carbon nitride rings can be modulated to alter the electronic structure of g-

C₃N₄.⁸³ The subsequent changes of the energy levels of the valence and conduction bands, as well as the optical absorption of g-C₃N₄, would thus improve the photocatalytic activity.⁸⁴

Due to its photocatalytic ability, g-C₃N₄ has been successfully employed for the degradation of various chemical compounds. It has been used to degrade many different types of organic compounds including: dyes such as Rhodamine B⁸⁵ and methylene blue,⁸⁶ pharmaceutical products like tetracycline⁸⁷ and carbamazepine,⁸⁸ chlorinated organic compounds like trichlorophenol,⁸⁹ and even phenolic pollutants such as bisphenol.⁹⁰ Such photocatalytic reactivity of g-C₃N₄ has been credited to the catalytic production of various ROS, including endoperoxide, hydrogen peroxide, superoxide anion and hydroxyl radical, which participate in the degradation reaction as seen in Figure 2.2.6.

Figure 2.3.6. Proposed photocatalytic H₂O₂ production for degradation of organic pollutants. Adapted with permission from *Angew. Chem. Int. Ed. Engl.* **2014**, 53, 13454-13459. Copyright 2019 John Wiley and Sons.⁹¹

2.3.3. Hybrid metal halide perovskites for photoredox reactions

Metal halide organic-inorganic perovskites are generally defined as a wide range of materials that have the crystal structure with the formula of ABX_3 , where A denotes an organic cation, B as an inorganic cation and X denotes a halide anion.⁹² Further exploration into the properties of 3D metal halide organic-inorganic perovskites shows such perovskites to have a narrow band gap of about 1.55 eV to 1.60 eV, which allows for absorption of a wide range of the visible light spectrum, and was thus initially utilised in the production of perovskite-based solar cells.⁹³ Recent developments in perovskites have improved their efficiency in converting light to electrical power (more than 23 %) and made them competitive against other single crystal silicon devices.⁹³ In addition, studies have demonstrated their use beyond the fields of photovoltaics and solar cells, including optoelectronic devices, such as LEDs, X-Ray detectors, and lasers.⁹⁴

Figure 2.3.7. a) Structure of organo metal halide perovskite crystal. b) Bandstructure of lead-based perovskite. Adapted with permission from Jena, A. K.; Kulkarni, A.; Miyasaka, T., *Chem. Rev.* **2019**, 119, 3036-3103. Copyright 2019 American Chemical Society.⁹³

The adaptability of metal halide perovskites has made it a topic of many research studies. The alteration of the electronic properties of metal halide perovskite has been explored in numerous recent studies as a way to tune the perovskites' light absorbing capabilities.⁹⁵ Concurrently, these modifications have also led to studies on the defect resistance, where nonradiative recombinations were minimised, while a balance of electron and hole effective mass was obtained.⁹⁶

Another unique trait of the metal halide perovskite semiconductor is the independent tuning of its organic and inorganic components. This can be seen in studies from groups such as Stupp et. al., who reported the usage of aromatic moieties for improved conductivity and light absorption capability of (R-NH₃)PbI₄ perovskites.⁹⁷ Alternatively, the employed halide (chloride, bromide, iodide) and metal components (tin, lead) can also be varied as measures to tune and control the carrier states in the perovskites.⁹⁸

The myriad methods available for the synthesis of perovskite films of high quality has also been an important factor for the potential device integration. Methods of synthesising such thin films of perovskite range from simultaneous or sequential growth of perovskites on substrates, to various deposition methods. These have resulted in a variety of halide perovskite thin films with distinct properties and performances, depending on the method used.⁹² In addition, the adaptability of the perovskite material has also allowed for various substrate/surfaces to be used in layering the perovskite, as seen in the Figure 2.3.8.

Figure 2.3.8. Energy levels (vs vacuum) of lead halide perovskites and various electron or hole transport materials that are often employed in solar cell devices. MA and FA denote methylammonium and formamidinium, respectively. PCBM refers to [6,6]-phenyl-C 61-butyric acid methyl ester, while PTAA, P3HT, and PEDOT:PSS refer to poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine], poly(3-hexylthiophene-2,5-diyl), and poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate respectively. Adapted with permission from Jena, A. K.; Kulkarni, A.; Miyasaka, T., *Chem. Rev.* **2019**, *119*, 3036-3103. Copyright 2019 American Chemical Society.⁹³

Having great optoelectronic properties and adaptability, metal halide perovskites have been applied to tandem cell setups. For example, McGehee *et al.* designed perovskite/silicon tandem solar cells exhibiting efficiencies of 23.6%, and were stable under ambient conditions.⁹⁹ These instances demonstrate the possibility of using perovskites in tandem cell systems, but perovskites could theoretically be coupled with other systems (such as PEC) to allow for a wider range of applications, including photoredox catalysis.

2.3.4. TAML complexes – Co-catalysts for pollutant treatment and other applications.

Heme enzymes are essential for many biological processes, such as the transport and storage of oxygen for aerobic respiration, as well as the catalysis of various metabolic biochemical reactions. Particularly of interest to this project is the enzyme cytochrome P450. As seen in Figure 2.3.9., it uses oxygen and peroxide radicals to activate an iron centre(Steps 3-5) and subsequently generating the high-valent iron-oxo motifs(Steps 6), which are responsible for the oxidation of many biological molecules.¹⁰⁰⁻¹⁰¹

Figure 2.3.9. General catalytic cycle for cytochrome P450-mediated reactions. The numbers represent the steps in the catalytic cycle. Reprinted (adapted) with permission from *ACS Catal.* **2018**, 8, 10964-10976. Copyright 2019 American Chemical Society.¹⁰¹

Drawing inspiration from the naturally occurring cytochrome P450, many research groups attempted to design and develop non-heme synthetic catalysts in order to achieve similar reactivities, while circumventing the need for huge protein scaffolds that stabilise the iron centre found in cytochrome P450. Some representative examples include Fe(BDDP), a high spin mononuclear iron-superoxo complex that can abstract the protons of dihydroanthrazene,¹⁰² and Fe(PyBisulidine) (Figure 2.3.13.a.) which can perform the direct α -oxygenation of ethers (Figure 2.3.10.).¹⁰³ However, the abovementioned catalysts have only been reported in non-aqueous environments or at very low temperatures, which would not be suitable for degradation of chemical waste in the natural environment.

Figure 2.3.10. Reaction scheme for the direct α -oxygenation of ethers by Fe (PyBisulidine).¹⁰³

Recently, Collins *et al.* reported the successful development of Fe-TAMLs that can catalytically mineralise persistent pollutants in an aqueous environment (Figure 2.3.11.). The stability and high catalytic activity of Fe-TAMLs can be attributed firstly to its rigid macrocyclic ligand, which minimises the structural changes upon oxidation.¹⁰⁴ Secondly, the ligand possesses electron-rich deprotonated amido moieties, which stabilise the high-valent iron-oxo species such as Fe(V).¹⁰⁵ This

allows the high valent iron complexes to proceed with the oxidation of sulfides, alcohols and sp^3 C-H bonds upon activation of Fe(III)-TAML by *m*-chloroperoxybenzoic acid (*m*CPBA), NaOCl, photochemical oxidation¹⁰⁶, oxygen gas,¹⁰⁷ or by other peroxides (Figure 2.3.12).¹⁰⁸

Figure 2.3.11. Catalytic oxidative degradation of 2,4,6-trichlorophenol by Fe-TAML.¹⁰⁴

Figure 2.3.12. Catalytic activation of benzoyl peroxide with Fe-TAML. Adapted with permission from *Green Chem.* **2007**, 9, 49-57. Copyright 2020 Royal Society of Chemistry¹⁰⁸

Over the years, multiple variations and generations of the TAML ligands had been made and utilised as seen in Figure 2.3.13.b., with much attention focused on the application of the 1st generation TAML ligand system with an iron centre or other metal centres. However, the 4th generation TAML ligand with an iron centre was the catalyst reported to perform the best among the Fe-TAML compounds for degrading methyl orange dye at neutral pH.¹⁰⁹ As such, 4th generation TAML ligand-based iron complexes could potentially be applied to photoelectrochemical or photocatalytic reactions in solvents of neutral pH such as water.

Figure 2.3.13. a) Structure of [Fe(PyBisulidine)]. b) Some of the current generations of (TAML)Fe complexes reported for water treatment. The axial ligand Y is commonly H₂O, while further details on the different X₁ and X₂ can be found in the report by Denardo et. al.¹⁰⁹

Although Fe-TAML complexes are commonly activated by chemical oxidants such as hydrogen peroxide and *m*CPBA, a recent development by Das *et al.* has shown the electrochemical activation of the 1st generation TAML ligand Fe complex to catalyze C-H oxygenation and alcohol dehydrogenation reactions.¹¹⁰ The authors reported that the application of two different potentials of 1.25 V and 0.80 V vs Ag/AgCl to a solution of water and acetonitrile (1:1) containing 10 mol% Fe-TAML led to the conversion of ethylbenzene and 1-phenylethanol to acetophenone (Figure 2.3.14.). From Figure 2.3.15., the active species at 0.80 V was the oxo-bridged Fe^{IV}-TAML dimer, while at the higher potential of 1.25 V Fe^V-TAML(O) could be generated, resulting in faster reactivity.¹¹⁰ This recent development, therefore, expands the applicability of Fe-TAML catalysts and indicates that Fe-TAML complexes can

potentially be activated either by the photogenerated holes directly or by the ROS produced in situ by the semiconductor upon light irradiation, which could eliminate the need to use excessive amounts of hydrogen peroxide in future applications. As such, the incorporation of Fe-TAML complexes onto BiVO₄ or g-C₃N₄ as the co-catalysts would be a viable enhancement to the oxidative abilities of the photocatalytic or PEC systems.

Figure 2.3.14. Reaction schemes for the electrochemical activation of Fe-TAML for C-H oxygenation and alcohol hydrogenation.¹¹⁰

Figure 2.3.15. Activation of Fe-TAML at applied potentials of a) 0.80 V and b) 1.25 V.¹¹⁰

Furthermore, recent studies have shown the application of TAML complexes with various metal centres in other catalytic reactions. Nam *et al.* reported Co-TAML and Mn-TAML for the oxidative activation of C-H bonds, and for oxygen atom transfer reactions.¹¹¹⁻¹¹² These examples illustrate that TAML systems have great potential to be explored and utilised in a wider range of reactions. Therefore, it would be interesting to explore the capability of Co-TAML complexes for their potential as reduction electrocatalysts, as viable alternatives to reactions at the photocathode of a PEC setup.

2.4. Ph. D in context of the literature

Based on the literature review, the following gaps can be identified:

1. The selective valorisation of lignin to other value-added aromatic compounds is one that could potentially increase the efficiency and utilisation of lignocellulose. However, such methods should also be environmentally sustainable and eco-friendly.
2. Although the use of BPA has been restricted in some countries as a result of its endocrine disrupting properties, its substitutes (BPF and BPS) were found to have similar properties. This thus raises a need for more sustainable ways in removing or breaking down such chemicals in the environment.

Therefore, it would be interesting to design two sustainable systems, a PEC system using BiVO_4 with Fe-TAML and a photocatalytic system with $\text{g-C}_3\text{N}_4(\text{urea})/\text{PDI}$, for the application of lignocellulose oxidation and/or bisphenol oxidation.

In the PEC system, nanoporous BiVO_4 was examined and modification made to it with the addition of Fe-TAML for the two applications mentioned above. Nanoporous BiVO_4 has been reported to not just catalyse water splitting reactions,⁶⁶ but also the upgrading of hydroxymethylfurfural to furandicarboxylic acid with the assistance of TEMPO.¹¹³ Thus, Fe-TAML could replace TEMPO as a co-catalyst for reactions with lignin or bisphenols. In addition, the PEC system could be further improved so that it can function as a tandem PEC system.

Regarding the further development of the photocatalytic system, the synthesis of g-C₃N₄ with a larger surface area was investigated for their potentially better charge separation upon optical irradiation.⁸⁰ Additional to the nanostructure alteration, the simultaneously modify the electronic structure of g-C₃N₄ via the addition of PDMA to form g-C₃N₄/PDI was proposed.⁹¹ The incorporated PDI group would then cause a positive shift of valence band of g-C₃N₄ due to this group's high electron affinity, thus increasing the catalytic ability of g-C₃N₄ to favour oxidation.¹¹⁴

In addition, Co-TAML and hydrophobic metal halide perovskites are explored and developed for their potential to be applied and combined with the prior two systems in a tandem PEC setup.

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Chapter 3

BiVO₄/Fe-TAML – a PEC system for lignin and bisphenol oxidation

3.1. Introduction

BiVO₄ has been used in a PEC cell for the purpose of water splitting.¹ This is due to its small band gap of approximately 2.40 eV, which corresponds to a wavelength of about 520 nm corresponding to visible light photons.² In addition, BiVO₄ has the added advantages of its conduction band being close to 0 V vs RHE, making it thermodynamically close to the redox potential of H⁺/H₂.³ This advantage, along with the inexpensive precursors and non-toxic nature of BiVO₄, increase its viability as a photoanode for possible large-scale production and application.

Recent developments of BiVO₄ PEC cells have shown that nanoporous BiVO₄ is not only able to effect water splitting reactions, but also convert hydroxymethylfurfural to furandicarboxylic acid with the assistance of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl(TEMPO).⁴ The BiVO₄ PEC has also been reported for the oxidation of glycerol to dihydroxyacetone.⁵ These examples illustrate the potential of BiVO₄ to be utilised for oxidations of bioorganic compounds to other industrially useful organic compounds. One such possible application could be the oxidation of lignin or lignocellulose to platform chemicals. The recent rise in interest for the oxidation of lignocellulose, a waste product of agriculture, to more useful chemical products has seen a surge in the design of new photocatalytic systems to achieve greater efficiency in fully utilising lignocellulose. For example, Reisner *et al.* has shown that the use of a photocatalytic system with CdS or carbon nitride is able to oxidise lignin and produce H₂ gas.⁶⁻⁷ However, there is still a need for an improved photocatalytic or a PEC system that could be used to convert lignin into its aromatic monomers or

even simpler aromatic precursors that can be utilised in subsequent syntheses of high-value compounds.⁸⁻⁹

In 2014, Kim *et al.* reported that they had made a BiVO₄/FeOOH/NiOOH material that exhibits high photocurrent with little modification, for the purposes of water oxidation.¹⁰ This indicates the possibility of adding other inorganic or organometallic compounds as co-catalysts to improve the oxidative catalytic capability of BiVO₄ by improving the charge transfer and hindering the charge recombination rates. One possible co-catalyst for BiVO₄ are the Fe-TAML complexes, which has previously been reported to efficiently degrade toxic pollutants¹¹ as well as estrogenic compounds.¹²

Although such transformations are often performed only with the activation of the Fe-TAML catalysts by chemical oxidants, recent work done by Das *et al.* had shown that electrochemically activated Fe-TAML in aqueous media was able to catalyse C-H oxygenations and alcohol dehydrogenations.¹³ In addition, Lim *et al.* had previously reported the cyclic voltammograms of a similar 4th generation TAML ligand Fe-complex, showing three oxidation peaks of +0.10 V, +0.39 V, and +0.63 V vs ferrocenium/ferrocene(Fc⁺/Fc). These indicate that the 4th generation TAML ligand Fe complexes could be similarly activated upon the application of an electrical potential to generate high-valent Fe-oxo complexes.¹⁴ These are alternatives to the well-established chemical activation of Fe-TAML, where photogenerated holes from a semiconductor material in PEC cells can be used activate Fe-TAMLs to high valent Fe-oxo complexes. Thus, the synthesis of a nanoporous BiVO₄/Fe-TAML photoanode(Figure 3.1.1.) was proposed in this chapter for the oxidation of lignin as our main substrate. The oxidations of BPF and BPS are included as preliminary

studies to examine the effects of this photoanode on the oxidations of aromatic compounds.

Figure 3.1.1. Proposed illustration of a nanoporous $\text{BiVO}_4/\text{Fe-TAML}$ photoanode.

3.2. Materials characterisations

Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) experiments were conducted to investigate the morphologies and elemental compositions of the nanoporous BiVO_4 and $\text{BiVO}_4/\text{Fe-TAML}$. In Figure 3.2.1.a., BiVO_4 formed from the electrodeposition method was observed to be dense columnar particles, which is similar to what was reported in the literature.¹⁵ When Fe-TAML was dissolved in methanol (MeOH) and dropcasted onto the BiVO_4 photoanode, similar defined columnar particles morphology were observed as seen in Figure 3.2.1.b.

Figure 3.2.1. SEM Images of a) BiVO_4 and b) $\text{BiVO}_4/\text{Fe-TAML}$.

The EDX spectra shown in Figure 3.2.2. indicates that even after washing of the $\text{BiVO}_4/\text{Fe-TAML}$ with MeOH, there are still significant amounts of iron on the $\text{BiVO}_4/\text{Fe-TAML}$. These would suggest that the Fe-TAML co-catalyst was successfully added onto the BiVO_4 photoanodes, with a resulting bismuth(Bi):vanadium(V):iron(Fe) ratio by atomic percentage of 1.00:1.26:0.57. Before adding Fe-TAML, BiVO_4 was shown to have a Bi:V ratio by atomic

percentage of 1.00:1.16, which is higher than the reported Bi:V ratio of 1:1.02 by Choi *et al.* obtained through inductively coupled plasma optical emission spectroscopy (ICP-OES).¹⁰ The slight difference in the ratio of V with respect to Bi is most likely because the synthesis included the use of excess VO(acac)₂ in the preparation of the BiVO₄ plates from BiIO. Although most of the excess, unreacted V would be dissolved in the presence of 1.0 M NaOH, there would likely still be some V that remains even after 30 min according to the reported synthetic procedure.⁴

Figure 3.2.2. EDX spectra of a) BiVO₄ and b) BiVO₄/Fe-TAML.

From the X-ray powder diffraction (pXRD) pattern shown in Figure 3.2.3, both the synthesised BiVO₄ and BiVO₄/Fe-TAML photoanode contains peaks which correspond to that of a monoclinic scheelite structure.¹⁰ By obtaining the monoclinic structure, the photoanode is ensured to be the most photocatalytically active.¹⁶ On the other hand, the pXRD pattern obtained of the pure Fe-TAML sample showed that not only was the intensity of the pXRD pattern of Fe-TAML relatively lower when compared to BiVO₄ samples (the comparatively high signal to noise ratio), but the Fe-TAML pXRD pattern was also found to have peaks that are in the same region as

that of BiVO_4 . As such, the peaks corresponding to Fe-TAML could have overlapped with the peaks of BiVO_4 in the $\text{BiVO}_4/\text{Fe-TAML}$ photoanode, such that the signals are not significant enough to be differentiated from the noise.

Figure 3.2.3. pXRD patterns of BiVO_4 (red pattern), $\text{BiVO}_4/\text{Fe-TAML}$ (black pattern), and Fe-TAML (blue pattern). The blue circles denote peaks that correspond to the pXRD pattern of FTO plates.

Using XPS, the presence of Fe-TAML on the BiVO_4 photoanode can be further verified. From Figure 3.2.4., the binding energies of $\text{Bi } 4f_{5/2}$ and $\text{Bi } 4f_{7/2}$ were observed to be at 164.3 and 159.0 eV. The binding energies for $\text{V } 2p_{1/2}$ and $\text{V } 2p_{3/2}$ were observed to be at 523.2 and 516.0 eV respectively, with an additional binding energy value of 520.8 eV corresponding to the O 1s residual signal. For $\text{BiVO}_4/\text{Fe-TAML}$, the binding energies of $\text{Bi } 4f_{5/2}$ and $\text{Bi } 4f_{7/2}$ were observed to be at 164.8 and 158.8 eV. The binding energies for $\text{V } 2p_{1/2}$ and $\text{V } 2p_{3/2}$ were observed to be at 523.0 and 515.8 eV respectively, with a similar additional binding energy value of 520.8 eV

corresponding to O 1s residual signal. In addition, there are slight shifts to the binding energies of Bi and V when comparing BiVO₄ and BiVO₄/Fe-TAML (a -0.20 eV shift for V 2p and an approximate +0.50 eV shift for Bi 4f of BiVO₄/Fe-TAML), which suggests possible minute interactions of the Fe-TAML co-catalyst with BiVO₄ photoanode upon dropcasting.

Figure 3.2.4. XPS spectra of a) BiVO₄: Bi 4f, b) BiVO₄/Fe-TAML: Bi 4f, c) BiVO₄: V 2p, d) BiVO₄/Fe-TAML: V 2p, and e) BiVO₄/Fe-TAML: Fe 2p.

In addition, binding energies of 709.8 eV and 723.4 eV were observed only in BiVO₄/Fe-TAML and were found to correspond to Fe 2p_{1/2} and Fe 2p_{3/2}. These would further support the EDX analysis of the presence of Fe-TAML on the BiVO₄ photoanode after the dropcasting and washing. The binding energies also indicate that the oxidation state of iron was about +3, which would be the expected oxidation state of iron in Fe-TAML.¹⁷

Furthermore, X-ray absorption spectroscopy (XAS) experiments were conducted to further investigate the possible interactions between the Fe-TAML complexes and BiVO₄. Firstly, XAS measurements were conducted on both BiVO₄ and BiVO₄/Fe-TAML plates to observe the oxidation states of Fe and its coordination environment. Since Fe-TAML complexes were dropcasted onto the BiVO₄ plates, the oxidation states or the coordination environments of Fe-TAML were not expected to change significantly. From Figure 3.2.5, it can be observed that the X-ray absorption near edge spectra (XANES) of Fe₂O₃, Fe-TAML powders, and Fe-TAML on BiVO₄/Fe-

TAML showed relatively similar edges which would suggest that they are all of the same oxidation state of +3.

Figure 3.2.5. Fe K-edge XANES spectra of Fe_2O_3 (blue line), Fe-TAML powder (black line) and $\text{BiVO}_4/\text{Fe-TAML}$ (red line).

However, the comparison of the R-space extended X-ray absorption fine structure (EXAFS) data of the Fe-TAML powder and $\text{BiVO}_4/\text{Fe-TAML}$ suggests a slight difference in the coordination environment of Fe in both samples. From Figure 3.2.6., the Fe-TAML was observed to have peaks at apparent radial distances of 1.4, 2.2, and 2.6 Å, which could represent the Fe-N/Fe-O bonds (first coordination), the Fe-N-C bonds, and the Fe-N-C-C/O bonds respectively. In contrasting, the Fe-TAML in the $\text{BiVO}_4/\text{Fe-TAML}$ sample appeared to have significant peaks at apparent radial distances of 1.4 and 2.6 Å, with the first peak at 1.4 Å to be due to Fe-N/Fe-O bonds. A shoulder at 2.2 Å could be observed overlapping with the peak at a radial distance of 2.6 Å. Interestingly, the peak at radial distance of 2.6 Å was observed to be of higher intensity than what was expected for second or third coordination sphere interactions with the Fe centre, as observed previously in Fe-TAML powder. This suggests that for $\text{BiVO}_4/\text{Fe-TAML}$, an atom of a high molecular mass may be in the

second coordination sphere of Fe, suggesting the possibility of Fe-O-Bi, Fe-O-V, or Fe-O-Fe bonds (Figure 3.2.7.)

Figure 3.2.6. Fourier transforms of the Fe K-edge k^2 -weighted EXAFS data for Fe-TAML powder and BiVO₄/Fe-TAML.

Figure 3.2.7. Possible coordination structures of Fe-TAML in BiVO₄/Fe-TAML.

To narrow down the most probable coordination environment, the Fourier transforms of the Fe K-edge k^2 -weighted EXAFS data of BiVO₄/Fe-TAML was compared to Fe₂O₃ to determine if the second peak in the R-space EXAFS data of BiVO₄/Fe-TAML could be similar to the Fe-O-Fe of Fe₂O₃. From Figure 3.2.8., it can be observed that Fe₂O₃ has a second significant peak at a radial distance of 2.5 Å, which is shorter than the second peak of BiVO₄/Fe-TAML at 2.6 Å. This thus reduces

the plausibility of Fe-TAML having an O-bridged bond with another Fe-TAML as seen in Figure 3.2.7. Furthermore, examination of the R-space EXAFS V K-edge data for BiVO₄ and BiVO₄/Fe-TAML showed that they have similar values of 1.2 Å. This would indicate a low possibility of a Fe-O-V coordination structure (Figure 3.2.9.), where a second peak at a longer radial distance was expected if there is Fe-O-V bonds. Lastly, oxygen bridged Fe-O-Bi bond might be possible upon dropcasting of Fe-TAML onto BiVO₄ plates, with such interactions reported previously in the literature with other Fe compounds.¹⁸ It would therefore be interesting to measure the L₃-edge of Bi to compare the EXAFS data as a way to confirm the interactions between the Fe and Bi centre.

Figure 3.2.8. Fourier transforms of the Fe K-edge k²-weighted EXAFS data for Fe₂O₃ and BiVO₄/Fe-TAML.

Figure 3.2.9. Fourier transforms of the V K-edge k^2 -weighted EXAFS data for BiVO_4 and $\text{BiVO}_4/\text{Fe-TAML}$.

Furthermore, the diffused-reflectance spectroscopy (DRS) spectra obtained from $\text{BiVO}_4/\text{Fe-TAML}$ also supported the presence of Fe-TAML on the photoanode. From Figure 3.2.10., BiVO_4 showed an optical absorption edge of about 520 nm,² thus indicating that the desired BiVO_4 was obtained as our synthesised photoanode. In $\text{BiVO}_4/\text{Fe-TAML}$, we observed an additional absorption band from about 520 to 650 nm. These bands are similar to the UV-visible light absorption (UV-Vis) spectra of similar Fe-TAML complexes that were reported to have an optical absorption edge at about 650 nm,¹⁴ as well as the UV-Vis spectrum of the Fe-TAML used in the synthesis of $\text{BiVO}_4/\text{Fe-TAML}$ (Figure 3.2.10.)

Figure 3.2.10. a) DRS of BiVO₄ and BiVO₄/Fe-TAML and b) UV-Vis spectrum of 0.40 mM of Fe-TAML in acetonitrile(ACN).

Lastly, the effects on the photophysical properties of BiVO₄ upon the addition of the Fe-TAML co-catalyst were investigated using the Tauc plots and PESA spectra. The band gap of the synthesised BiVO₄ photoanode is slightly greater than the reported theoretical value of approximately 2.50 eV (Figure 3.2.11.).¹⁹ However, there are other researches that showed BiVO₄ of similar band gap as a result of variations in morphology.²⁰ Interestingly, the addition of Fe-TAML as a co-catalyst on BiVO₄ resulted in a narrowing of the band gap from 2.64 eV to 2.56 eV. This indicates that the doping of Fe-TAML has resulted in impurity states within BiVO₄, similar to the effect when TiO₂ is doped with Fe.²¹

Figure 3.2.11. Tauc plots of a) BiVO_4 , and b) $\text{BiVO}_4/\text{Fe-TAML}$.

The narrowing of the band gap is further supported by the PESA spectra, which give us the work function of the BiVO_4 and $\text{BiVO}_4/\text{Fe-TAML}$. PESA had been used previously to measure the photoemission threshold energies of TiO_2 and the VBM of p-type Fe_2O_3 .²²⁻²³ The work function is generally defined as the minimum energy required to remove an electron from a semiconductor's Fermi-level to a point in vacuum,²⁴ where the Fermi level is generally near the conduction band maximum (CBM) of most n-type semiconductors.²⁵ As seen in Figure 3.2.12., there is an increase in the work function of 0.44 eV for BiVO_4 . This would suggest that the Fermi-level or the CBM had shifted to a more negative potential (vs vacuum).

Figure 3.2.12. PESA spectra of a) BiVO_4 and b) $\text{BiVO}_4/\text{Fe-TAML}$.

In addition, the VBM values could be calculated based on the subtraction of the CBM values from the values of the respective band gaps obtained with the Tauc plots. Figure 3.2.13. is a visualisation of the BiVO_4 and $\text{BiVO}_4/\text{Fe-TAML}$ CBM, VBM and band gap. The shift of the VBM was observed to be smaller in magnitude when compared to the shift of the conduction band, thus resulting in a narrowing of the band gap. These suggest that the VBM could be at a more negative potential (vs vacuum). (Figure 3.2.13.)

Figure 3.2.13. Illustration of the approximate CBM based on values acquired from PESA spectra, bandgaps from Tauc plots, and the calculated VBM based on the PESA spectra and Tauc plots BiVO₄/Fe-TAML is shown in red, while BiVO₄ is shown in black

3.3. PEC characterisations and applications

3.3.1. PEC characterisations

The PEC performances of BiVO₄ and BiVO₄/Fe-TAML were evaluated through linear sweep voltammetry (LSV). From Figure 3.3.1., the synthesised BiVO₄ was observed to have a current density of about 0.50 mA cm⁻² (at 1.0 V vs relative hydrogen electrode(RHE)) upon illumination by a solar simulator with an AM 1.5 G filter, which is comparable to that reported in literature,²⁵⁻²⁶ indicating that that current methodology were able to produce BiVO₄ that achieves high photocurrent density.

Figure 3.3.1. Linear sweep voltammograms of BiVO_4 in 0.50 M Na_2SO_4 . The black line denotes the data obtained in the absence of light and the red line denotes the data obtained in the presence of illumination from a solar simulator with AM 1.5 G filter.

Upon the dropcasting of Fe-TAML onto the BiVO_4 , the LSV measurements show a significant increase to the photocurrent density. In Figure 3.3.2., the voltammograms indicate an increase of approximately 0.29 mA cm^{-2} at 1.0 V vs RHE upon the addition of Fe-TAML onto the BiVO_4 photoanode. This could be due to the Fe-TAML on the surface of BiVO_4 aiding in the charge separation when the photoanode was illuminated by a solar simulator with an AM 1.5 G filter. A similar enhancement effect was reported for the addition of a FeOOH co-catalyst onto BiVO_4 , and the increase in photocurrent density was attributed to a minimising of electron-hole recombination along the $\text{BiVO}_4/\text{FeOOH}$ interface.²⁷

Figure 3.3.2. Linear sweep voltammograms of BiVO₄/Fe-TAML (red line) and BiVO₄ (black line) in 0.50 M Na₂SO₄ with light from a solar simulator with an AM 1.5 G filter. The blue line denotes the voltammogram of BiVO₄ in the absence of light.

To further evaluate the stability of Fe-TAML on BiVO₄, a series of five LSV experiments was conducted on the same BiVO₄/Fe-TAML photoanode to examine if there was any decrease in the photocurrent density after the initial LSV experiments. This series was conducted at a scan rate of 50.0 mV/s under the illumination from a solar simulator, with Na₂SO₃ being used as a sacrificial hole acceptor to simulate the actual reactions conditions when the desired substrates are used. The use of Na₂SO₃ as a hole acceptor was similarly reported in Kim and team's investigation of the BiVO₄ water oxidation capability.¹⁰ From Figure 3.3.3., the acquired voltammograms were relatively similar and were in general of a higher photocurrent density than the voltammogram of BiVO₄. This suggests that Fe-TAML is relatively stable on BiVO₄, and this stability can also be observed in the IT curve obtained in the subsequent CA experiments.

Figure 3.3.3. Stability test of Fe-TAML in the presence of Na₂SO₃ as a sacrificial reagent.

3.3.2. PEC applications and chronoamperometry (CA) experiments

Following the above characterisation of the PEC properties of both BiVO_4 and $\text{BiVO}_4/\text{Fe-TAML}$, the investigation of the oxidative capabilities of both photoanodes were carried out with substrates such as BPF, BPS, and lignin. In brief, the photoanode was used as the working electrode in a single PEC reaction cell and illuminated by a solar simulator with an AM 1.5 G filter. Ag/AgCl (saturated KCl) was used as the reference electrode and a platinum plate was used as the counter electrode. Appropriate amounts of the substrates were dissolved in the electrolyte before the experiment was carried out over a period of 14 h. Samples were taken at 0 h and 14 h only, with the samples from CA experiments involving BPF and BPS were analysed using HPLC to determine the resulting concentration, while UV-Vis was used to analyse the approximate concentration of lignin from the 0 h and 14 h samples. The results can be seen in Table 3.3.1., where $\text{BiVO}_4/\text{Fe-TAML}$ showed a greater rate of oxidation than BiVO_4 for all three substrates, with illumination from a solar simulator with an AM 1.5 G filter over a period of 14 h. These results agree with our initial hypothesis that the addition of Fe-TAML would help to increase the oxidative potential of $\text{BiVO}_4/\text{Fe-TAML}$.

Table 3.3.1. Reaction parameters and conversion of the substrates by BiVO₄ and BiVO₄/Fe-TAML after 14 h in 50.0 mL of 0.50 M Na₂SO₄.

S/N	Catalyst	Concentration	Substrate	Illumination	Conversion (%)	Potential (V vs Ag/AgCl)
1	BiVO ₄	0.10 mM	BPF	Solar simulator	19.4	0.40
2	BiVO ₄	0.10 mM	BPS	Solar simulator	16.9	0.40
3	BiVO ₄	0.01 g/l	Lignin	Solar simulator	19.4	0.40
4	BiVO ₄ /Fe-TAML	0.10 mM	BPF	Solar simulator	28.2	0.40
5	BiVO ₄ /Fe-TAML	0.10 mM	BPS	Solar simulator	24.9	0.40
6	BiVO ₄ /Fe-TAML	0.01 g/l	Lignin	Solar simulator	22.2	0.40
7	BiVO ₄ /Fe-TAML	0.10 mM	BPF	No	5.00	0.40
8	BiVO ₄ /Fe-TAML	0.10 mM	BPF	Solar simulator	10.0	-

From Figure 3.3.4., BiVO₄/Fe-TAML was observed to generate a greater amount of current over the same period when compared to BiVO₄ in the presence of the substrates. These are prevalent when BPF and BPS were used as the substrate (Figure 3.3.4.), where it was observed that throughout the 14 h, the current drawn by BiVO₄/Fe-TAML was consistently higher than that of BiVO₄. The relatively consistent difference between the current drawn throughout the CA experiment for BiVO₄ and BiVO₄/Fe-TAML would also support the prior investigation of the stability of Fe-TAML on BiVO₄, even over prolonged periods of time. The difference in the current observed over time for BiVO₄/Fe-TAML when used in the different substrates (BPF

and BPS) could be due to a variation of the intermediate from the oxidation of BPF and BPS. These intermediates could potentially interact with the surface of the BiVO_4 or $\text{BiVO}_4/\text{Fe-TAML}$, resulting in the differences in current observed over time.

Figure 3.3.4. Current-time (IT) curve of BiVO_4 and $\text{BiVO}_4/\text{Fe-TAML}$ in 0.50 M Na_2SO_4 with a) 0.10 mM BPF, and b) 0.10 mM BPS.

When lignin was used as a substrate, a similar trend was observed as seen in Figure 3.3.5., where $\text{BiVO}_4/\text{Fe-TAML}$ was shown to have a larger photocurrent over the period of 14 h when compared to BiVO_4 . Similar to the CA experiment using BPF and BPS as substrates, the consistent difference between both IT curves would suggest a similar stability of Fe-TAML on BiVO_4 .

Figure 3.3.5. IT curve of BiVO₄ and BiVO₄/Fe-TAML in 0.50 M Na₂SO₄ with 0.010 g/l lignin.

The PEC properties of BiVO₄/Fe-TAML were further investigated by conducting the PEC experiments in the absence and presence of substrate to see the effects of the substrate on the BiVO₄/Fe-TAML performance. As seen in Figure 3.3.6., it was observed that in the presence of substrate, BiVO₄/Fe-TAML performed slightly better, giving a IT curve that shows a greater current over the same period of time. However, the difference in the current is not as significant as the difference in the presence and absence of Fe-TAML (Figure 3.3.4.a.), suggesting that the increase in current could be due to the activation of Fe-TAML, instead of direct substrate oxidations.

Figure 3.3.6. PEC CA experiments done in the presence and absence of substrate(BPF) with $\text{BiVO}_4/\text{Fe-TAML}$. This setup was done in a H-cell, where the oxidation half-reaction is separated from the reduction half-reaction, thus resulting in a higher current recorded as compared to Figure 3.3.4.

To further improve and optimise the PEC oxidation of the various substrates from the relatively slow rate shown in Table 3.3.1., a higher potential could be used to increase the rate of reactions. Table 3.3.2. entries 1 and 2 show the effect of an increase in applied potential resulting in a 22% increase in BPF conversion. In addition, the use of a H-cell where a Nafion membrane divides the oxidation half-reaction from the reduction half-reaction was shown to increase the conversion of BPF further by about 48.2%, alongside the application of a higher potential (Table 3.3.2., entry 3). It was also observed that when the solvent used for the preparation of the electrolyte was changed to ACN instead of H_2O , 100% conversion of BPF could be achieved, which might indicate the presence of competing water oxidation reactions (Table 3.3.2., entry 5).

Table 3.3.2. PEC experiments conducted in a H-Cell

S/N	Catalyst	Substrate	Potential (V vs Ag/AgCl)	Conversion (%)	Variable conditions
1	BiVO ₄ /Fe-TAML	BPF	0.4	28.2	In water, single cell
2	BiVO ₄ /Fe-TAML	BPF	1.0	50.2	In water, single cell
3	BiVO ₄ /Fe-TAML	BPF	1.0	98.2	In water
4	BiVO ₄	BPF	1.0	85.5	
5	BiVO ₄ /Fe-TAML	BPF	1.0	100	
6	BiVO ₄ /Fe-TAML	BPF	1.0	17.0	No light
7	BiVO ₄ /Fe-TAML	BPF	1.0	26.1	No potential

3.3.3. Reaction kinetics of the PEC reactions

The kinetics of the PEC oxidation of BPF was investigated, with Figure 3.3.7. showing the mean and standard deviation of the conversion of BPF measured at 2 h intervals. In the absence of Fe-TAML, the PEC oxidation of BPF in the presence of BiVO₄ follows a zeroth order rate law and has a rate constant of 6.13 mM⁻¹s⁻¹ (R^2 value = 0.989), with 86% degradation of BPF at the end of 14 h. On the other hand, over the same 14 h time period, BiVO₄/Fe-TAML was able to degrade 100% of the BPF.

Figure 3.3.7. Reaction kinetics of the photoelectrochemical oxidation of 0.10 mM BPF in 30 ml of ACN, with BiVO₄/Fe-TAML (black line) and BiVO₄ (red line). (C/C₀ refers to the value derived when the measured concentration of BPF is divided by the initial concentration of BPF)

However, it is interesting that the deviation in the kinetic curves between BiVO₄ and BiVO₄/Fe-TAML was only observed after 4 h. This is interesting as it could suggest two different rate constants that could be due to the activation of Fe-TAML, or its interactions with intermediates in the solution. Further investigation of the rate constant and the order of the reaction before the 4 h point and after the 6 h point showed the rate order to be a zero-order reaction before 4 h, with a rate constant of 6.96 mM s⁻¹ (R² value = 0.999) and a first order rate reaction after 6 h, with a rate constant 57.48 mM s⁻¹ (R² value = 0.990). In addition, the rate constant of the zero-order reaction up to 4 h has a rate constant which is similar to the rate constant observed for the PEC reactions with BiVO₄.

Furthermore, the reactive species were also investigated through a series of scavenger experiments. Triethylamine (TEA), silver nitrate (AgNO_3), benzoquinone, and isopropanol were added in different experiments to investigate the effects of photogenerated holes, photogenerated electrons, superoxide anions and hydroxyl radicals respectively on the reaction rate. As seen in Table 3.3.3., there are slight decreases to the conversion of BPF at the end of 14 h by about 19.2% and 18.5% in the presence of TEA, acting as a hole scavenger, and in the presence of AgNO_3 , acting as an electron scavenger, respectively. These would suggest that the photogenerated holes and electrons of BiVO_4 have larger roles to play in the PEC reactions, which is expected as seen in the activation of TEMPO by the photogenerated holes of BiVO_4 for the oxidation of hydroxymethylfurfural by Cha *et al.*⁴

Table 3.3.3. Conversion of the BPF in the presence of scavengers, by $\text{BiVO}_4/\text{Fe-TAML}$ after 14 h in 30.0 mL of 0.10 M TBAPF_6 in ACN.

S/N	Catalyst	Scavenger	Conversion (%)	Scavenging target
1	$\text{BiVO}_4/\text{Fe-TAML}$	-	100%	
2	$\text{BiVO}_4/\text{Fe-TAML}$	AgNO_3	81.5%	Photogenerated Electrons
3	$\text{BiVO}_4/\text{Fe-TAML}$	TEA	80.8%	Photogenerated Holes
4	$\text{BiVO}_4/\text{Fe-TAML}$	Benzoquinone	93.0%	Superoxide anions
5	$\text{BiVO}_4/\text{Fe-TAML}$	Isopropanol	96.0%	Hydroxyl radical

In addition, the recyclability of the $\text{BiVO}_4/\text{Fe-TAML}$ plates was examined. The PEC oxidation of 0.10 mM BPF by $\text{BiVO}_4/\text{Fe-TAML}$ in ACN was repeated for four cycles,

with the percentage conversion of BPF decreasing slightly as seen in Figure 3.3.8. After the fourth cycle, the EDX spectrum of the resulting $\text{BiVO}_4/\text{Fe-TAML}$ showed the presence of Fe on the BiVO_4 , but a large portion of the BiVO_4 was observed to have peeled off the FTO plate at the end of the 4th cycle of PEC experiment. This would thus show the stability of Fe-TAML on the BiVO_4 over the PEC experiments.

Figure 3.3.8. a) Conversion of BPF when reusing $\text{BiVO}_4/\text{Fe-TAML}$ plates over multiple 14 h cycles in ACN. b) EDX spectrum of the $\text{BiVO}_4/\text{Fe-TAML}$ plates after the 4th cycle

3.3.4. Product elucidations and substrate scope of PEC experiments

To understand the products obtained from the oxidation of BPF in the PEC system with $\text{BiVO}_4/\text{Fe-TAML}$ as the working electrode, ^1H nuclear magnetic resonance spectroscopy was used to obtain the NMR spectra before and after the 14 h reaction (Figure 3.9.6 and Figure 3.9.7.). The decrease in the peaks at 6.99 ppm and 6.68 ppm indicate the possible degradation of BPF to other products. However, the concentration of the products formed are very low with the signals very close to the noise level and only observable by solvent suppression in the NMR spectroscopy

experiments (Figure 3.9.7.) The wide variety of additional peaks observed between 3 ppm to 10 ppm also suggests that multiple possible products can be seen in Figure 3.3.9..

Figure 3.3.9. Proposed and observed products from the PEC oxidation of BPF.

Other possible substrates were also explored to understand the capabilities of the PEC system. As seen in Table 3.3.4., BPS was found to be oxidised with a conversion of about 89.8%, without showing any additional products formed when examined with ^1H NMR spectroscopy (Figure 3.9.8. and Figure 3.9.9.). This suggests the possibility of BPS being oxidised to give other gaseous or volatile products. On the other hand, when PEG was used as a polymer substrate, singlet peaks were observed in the ^1H NMR spectrum at 9.56 ppm and 8.05 ppm, suggesting the formation of formaldehyde and formic acid as the products respectively (Figure 3.9.12. and Figure 3.9.13.). The additional singlet peaks at 4.65, 4.32, and 4.14 ppm further suggest possible alcohols and aldehyde products such as glycoaldehyde or glycolic acid. Similarly, the oxidation of cellulose acetate was shown to produce small amounts of formic acid and formaldehyde, despite its slow rate of reaction (Figure 3.9.10. and Figure 3.9.11.). Figure 3.9.16. showed that the application of a modified $\text{BiVO}_4/\text{Fe-TAML}$ system to the insoluble PET also yielded

the formation of a singlet peak at 2.31 ppm after 48 h, which could denote the presence of methanol as a potential product.

Table 3.3.4. Expanded substrate scope and their conversion.

S/N	Substrates	Concentration	Time (h)	Conversion (%)	Variable conditions
1	BPS	1.0 mM	14	89.8	-
2	PEG	1.0 mM	16	43.0	-
3	PET	0.105 g	48	*	Fe-TAML in solution
4	Cellulose Acetate	0.50 mM	72	6.0	-
5	Lignin	0.010 g/L	14	66.9	In water, with H-cell

Figure 3.3.10. Proposed and observed products from the PEC oxidation of PEG, Cellulose acetate, PEG and PET.

3.4. Conclusions

In conclusion, dropcasting Fe-TAML onto BiVO₄ was found to be a possible way of adding Fe-TAML as a co-catalyst on BiVO₄ material, and is relatively stable even after 14 h of reaction. The presence of Fe-TAML on the BiVO₄ material was confirmed by XPS, EDX, and by comparison of the DRS spectrum of pure BiVO₄ with that of the BiVO₄/Fe-TAML composite. Furthermore, the addition of Fe-TAML, as seen from the Tauc plots and PESA spectra, had an effect on the band structure of BiVO₄/Fe-TAML. The band gap was found to have narrowed slightly, while the conduction and valence bands have shifted to more negative potentials (vs. vacuum), with the conduction band shifting more than the valence band. The LSV experiments further highlighted the improvement to the photocurrent density when Fe-TAML was added to BiVO₄, and the results of the PEC experiments indicated that BiVO₄/Fe-TAML was able to oxidise substrates such as BPF, BPS, and lignin at a faster rate than BiVO₄. These results thus demonstrate the potential of BiVO₄/Fe-TAML in oxidising lignocellulose and other aromatic bisphenols.

3.5. Materials and equipments

Chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, and Tokyo Chemical Industry (TCI). Unless otherwise stated, the commercial reagents were used as purchased. A Thermolyne™ furnace (Thermo Fischer Scientific) was used for calcination reactions.

The ^1H NMR spectroscopic measurements were conducted using a Bruker AV 500 (500 MHz) NMR spectrometer or a Bruker BBFO 400(400MHz) spectrometer and reported in parts per million (ppm) downfield with reference to the residual protons of the deuterated solvents.

SEM measurements were conducted using a JEOL JSM-7600F Schottky field emission scanning electron microscope operated at 5.00 kV. EDX experiments were performed on the same equipment using Oxford instruments X-max 50mm², equipped with Xstream 2 and micsF+, and the data were processed using the Aztec software.

X-ray absorption fine structure (XAFS) characterisation experiments at the Fe K-edge and the V K-edge were carried out at the XAFCA beamline of the Singapore Synchrotron Light Source (SSLS). All XAS measurements were collected with a ring energy of 0.7 GeV and a ring current of ca. 200 mA. A Si(111) crystal monochromator was used and the data were collected in transmission mode at ambient temperatures. The X-ray energy was calibrated at the inflection point of the absorption edge of a nickel foil. Data analysis was carried out with the programmes

Athena and Artemis included in the Demeter package (version 0.9.25). Each of the powder samples was prepared as a pellet using a pelletizer of diameter 10 mm and mounted on the sample holder for the XAS measurement.

PXRD experiments were done using a Bruker D8 Advance X-ray diffractometer with a copper target ($K_{\alpha 1}$ (1.5406)/ $K_{\alpha 2}$ (1.5444) = 2). The X-ray tube's voltage was set to 40 kV and current set to 40 mA.

XPS experiments were done using a Phoibos 100 spectrometer with a Mg X-ray source (SPECS, Germany) working at 12.5 kV. It is also equipped with dual Al/Mg anodes, with the Mg anode used for the measurements reported. The prominent signal in the XPS spectra for O 1s could be due to the use of carbon tape to attach the samples onto the specimen plates. The spectra were processed using the CASA XPS software, with the C1s peak shifted to 284.6 eV.

UV-visible absorption measurements were carried out on a Shimadzu UV-3600 spectrophotometer. UV-visible diffuse reflectance spectroscopic (UV-Vis DRS) spectra were acquired using a Shimadzu UV-3600 UV-Vis spectrometer with an integrating sphere (Shimadzu ISR-3100). From the reflectance value obtained, the corresponding Kubelka-Munk function values were calculated using the equations below which was then used in figure 3.2.5.

The Tauc plot was then derived from the Kubelka-Munk functions with intersection of the tangent of the first slope with the line where $y=0$ denoting the estimation of the band gap of the material measured.

PESA spectra were acquired using a Model AC-2 from RKI Instruments. The UV light intensity was set to 800 nW. The samples were attached to a glass plate using carbon tape for the measurements. The measurements were then processed using the AC-2 Software with the work function determined by the intersection of the computer generated ground level line, with the tangent line along the slope of the spectra obtained. Both lines are generated as best fit lines through the 5 or more points at the ground level and along the slope respectively.

HPLC was performed using a Shimadzu LC-20AD prominence liquid chromatography instrument, equipped with a SIL-20AC autosampler, CTO-20AC column oven, and a SPD-M20A diode array detector. The column used for HPLC is an Agilent Zorbax Eclipse plus C18 column (4.60 mm x 150 mm, 5 μ m)

Electrochemical experiments were conducted using a Biologic SP300 electrochemical workstation. The electrochemical parameter used in the LSV and CA experiments can be found in Section 3.8. For PEC experiments, the light source used is a 300 W Xenon lamp in a solar simulator with an AM 1.5 G filter, while infrared light were filtered by a constant flow of water. The PEC cell was positioned such that the light intensity on the BiVO₄ and BiVO₄/Fe-TAML substrate is 100 W/cm²

3.6. Synthesis of Fe-TAML

The methods below for the synthesis of Fe-TAML were designed and optimised by Dr. Jia Hui Lim, who had reported them in his thesis. The reaction pathway can be seen in Figure 3.6.1.

Figure 3.6.1. Synthesis pathway of Fe-TAML.

Methyl 4-amino-3-nitrobenzoate (B)

Compound 4-amino-3-nitrobenzoic acid ($C_7H_6N_2O_4$, 3.64 g, 20.0 mmol) was added to an oven-dried two-neck round bottom flask with a dropping funnel under constant N_2 gas flow. Anhydrous MeOH (42.0 mL) was then added to dissolve the compound, before thionyl chloride ($SOCl_2$, 20.0 mL of a 1.00 M solution, 20.0 mmol) was transferred into the dropping funnel. $SOCl_2$ was then added to dropwise to the reaction mixture over 30 min. The resulting reaction mixture was then heated under reflux overnight. Yellow solids were obtained after removing the solvent with a rotary evaporation, which were then suspended in a pH 10.0 sodium carbonate solution (Na_2CO_3 , 80.0 mL) before being filtered. After additional washing with water (40.0 mL) and filtering, the resulting residue was dried *in vacuo*, giving a yellow powder of **B** ($C_8H_8N_2O_4$, 4.00 g, 98%). 1H NMR (DMSO- d_6 , 400 MHz, Figure 3.9.1. in Section 3.9.): δ = 3.79 (s, 3 H, CH_3), 7.03 (d, J = 8.8 Hz, 1 H, ArH), 7.81 (dd, J = 2.0, 8.8 Hz, 1 H, ArH), 7.96 (s, 2 H, NH_2), 8.50 (d, J = 2.0 Hz, 1 H, ArH) ppm. HR-MS (ESI+, m/z) calculated for $C_8H_9N_2O_4$ [$M + H$] $^+$ m/z = 197.0562, found 197.0570. Elemental analyses for $C_8H_8N_2O_4$ calculated: C, 48.98; H, 4.11; N, 14.28%; found: C, 48.99; H, 4.51; N, 14.00%.

Dimethyl 4,4'-((2,2-dimethylmalonyl) bis(azanediyl)) bis(3-nitrobenzoate) (C)

Compound **B** ($C_8H_8N_2O_4$, 2.85 g, 14.5 mmol) was dissolved in anhydrous ACN (25.0 mL) in a two-neck round bottom flask. Both dimethylmalonyl dichloride ($C_5H_6O_2Cl_2$, 1.00 mL, 7.30 mmol) and iodine (I_2 , 184 mg, 0.127 mmol) were then added into the reaction solution, which was subsequently heated up to 70.0 °C and stirred overnight. Flash column chromatography (silica gel, hexane: EA = 2:3) was then used to purify

the residue obtained after removal of solvent from the reaction mixture by rotary evaporation. Further purification of **C** was done by recrystallisation (hexane: EA = 1:9) to give pale yellow crystals of **C** (C₂₁H₂₀N₄O₁₀, 2.60 g, 73%). ¹H NMR (DMSO-*d*₆, 400 MHz, Figure 3.9.2. in Section 3.9.): δ = 1.60 (s, 6 H, CCH₃), 3.89 (s, 6 H, OCH₃), 8.14 (d, *J* = 8.4 Hz, 2 H, ArH), 8.27 (dd, *J* = 2.0, 8.4 Hz, 2 H, ArH), 8.49 (d, *J* = 2.0 Hz, 2 H, ArH), 10.57 (s, 2 H, NH) ppm. HR-MS (ESI-, *m/z*) calculated for C₂₁H₂₀ClN₄O₁₀ [M + Cl]⁻ *m/z* = 523.0868, found 523.0866. Elemental analyses for C₂₁H₂₀N₄O₁₀ calculated: C, 51.64; H, 4.13; N 11.47%; found: C, 51.62; H, 4.55; N, 11.29%.

Dimethyl 4,4'-(2,2-dimethylmalonyl) bis(azanediyl) bis(3-aminobenzoate) (D)

After dissolving compound **C** (0.490 g, 1.00 mmol) in EA (10.0 mL), the solution was transferred into a vial where 10% palladium on carbon (Pd/C, 24.0 mg) was added. The vial containing the reaction mixture was then placed in a hydrogenation pressure vessel, where H₂ gas (10 atm) was introduced and the mixture was stirred for 36 h at room temperature. After filtering the crude product through Celite, the residue obtained was washed with EA (10.0 mL) and MeOH (2.00 mL). DMF (5.00 mL) was then used to dissolve the grey residue to give a dark green solution upon filtration. Further filtration using a 0.200 μ m filter was done for the dark green solution to remove any remaining Pd/C, before the filtrate was dried at 30 °C *in vacuo* to obtain a green paste. Deionised water (25.0 mL) was used to suspend, sonicate and filter the green paste. After further washing with deionised water (30.0 mL) and drying *in vacuo*, a pale green powder of **D** (0.38 g, 90%) was obtained. As the product

undergoes intramolecular condensation while in solution, elemental analysis data of the product is not available since recrystallisation was challenging. ^1H NMR (DMSO- d_6 , 400 MHz, Figure 3.9.3. in Section 3.9.): δ = 1.58 (s, 6 H, CCH_3), 3.80 (s, 6 H, OCH_3), 5.18 (s, 4 H, ArNH_2), 7.15 - 7.20 (m, 4 H, ArH), 7.39 (d, J = 1.2 Hz, 2 H, ArH), 9.19 (s, 2 H, CONH) ppm. HR-MS (ESI-, m/z) calculated for $\text{C}_{21}\text{H}_{24}\text{ClN}_4\text{O}_6$ [$\text{M} + \text{Cl}$] $^-$ m/z = 463.1384, found 463.1383.

Dimethyl 15,15-dimethyl-6,7,14,16-tetraoxo-6,7,8,13,14,15,16,17-octahydro-5H-dibenzo [b, h] [1,4,7,10]tetraazacyclotridecine-3,10-dicarboxylate (E)

To an oven-dried three-neck round bottom flask connected with a dropping funnel, compound **D** (0.28 g, 0.66 mmol) was added and dissolved in anhydrous THF (330 mL). An oxalyl chloride solution (0.81 mL of a 2.00 M solution, 1.6 mmol) was then diluted in anhydrous THF (65.0 mL) in the dropping funnel. Anhydrous Et_3N (0.51 mL, 3.7 mmol) was then added into the solution in the flask before the flask was cooled to 0 °C using an ice-bath. The oxalyl chloride solution was added to the flask at a rate of 1 drop/second, before the resulting cloudy solution was warmed up to room temperature and stirred overnight. A pale yellow solid was obtained after the solvent was removed by rotary evaporation, which was then suspended in deionised water (100 mL), sonicated, followed by filtering off. The resulting residue was washed with large amounts of deionised water before undergoing sonication in Et_2O . A grey solid of **E** (0.20 g, 65%) was obtained after drying the residue *in vacuo*. ^1H NMR (DMSO- d_6 , 400 MHz, Figure 3.9.4. in Section 3.9.): δ = 1.55 (s, 6 H, CCH_3), 3.88 (s, 6 H, OCH_3), 7.58 (d, J = 8.8 Hz, 2 H, ArH), 7.90 (d, J = 8.8 Hz, 2 H, ArH),

8.10 (s, 2 H, ArH), 9.90 (s, 2 H, CONH), 10.0 (s, 2 H, CONH). HR-MS (ESI-, m/z) calculated for $C_{23}H_{21}N_4O_8$ $[M - H]^-$ $m/z = 481.1359$, found 481.1354. Elemental analyses for $C_{23}H_{21}N_4O_8 \cdot 2 H_2O$ calculated: C, 53.28; H, 5.05; N 10.81%; found: C, 53.67; H, 5.32; N, 10.42%.

Sodium salt of Fe-TAML-ester (F)

Compound **E** was added into an oven dried Schlenk flask. It was then suspended in anhydrous THF (130 mL). Sodium hydride (NaH, 60% in mineral oil, 0.130 mg, 3.30 mmol) was subsequently added to the solution and the mixture was stirred vigorously for 15 min to give a pale-yellow suspension. Iron (II) chloride ($FeCl_2$, 0.120 g, 0.950 mmol) was added into the solution and the reaction mixture was stirred overnight to give a brown suspension. Filtering the brown suspension gives a dark brown filtrate and a dark brown residue, which were worked up separately to give two batch of products. The first batch was obtained by the addition of the filtrate into pentane (300 mL) to obtained brown precipitates. These precipitates were then filtered off and dissolved in MeOH, before being dried by rotary evaporator to give a reddish brown crystalline solid. The second crop was obtained by suspending the residue in MeOH (3 x 5.00 mL) and filtered. The filtrate was then collected, and its solvent removed by rotary evaporation to give a similar reddish-brown crystalline solid. The sum of the yield from both batches was 0.320 g (78%). HR-MS (ESI-, m/z) calculated for $C_{23}H_{18}FeN_4O_8^-$ $m/z = 534.0474$, found 534.0477. Elemental analyses for $C_{23}H_{18}FeN_4O_8 \cdot Na^+ \cdot 3 MeOH$ calculated: C, 47.80; H, 4.63; N 8.58%; found: C, 47.58; H, 4.64; N, 8.52%.

Potassium salt of Fe-TAML (G)

Potassium hydroxide (KOH, 0.160 g) was dissolved in anhydrous MeOH (2.40 mL) first, before being added to a reaction tube containing compound **F** (0.400 g, 0.700 mmol). The resulting red solution was heated to 70 °C and stirred for 2.0 h, giving a thick, brown suspension. The suspension was filtered, and the residue was washed with MeOH (3 x 1.0 mL). The filtrate was collected and its solvent was removed *in vacuo*, resulting in a hygroscopic green powder of **Fe-TAML** (0.380 g, ~85%). The crude product **Fe-TAML** was used for anchoring onto photosensitisers without further purification. Complex **Fe-TAML** was demetallated and the remaining solution was examined with ¹H NMR spectroscopy. ¹H NMR (DMSO-*d*₆, 500 MHz, Figure 3.9.5. in Section 3.9.): δ = 1.59 (s, 6 H, CCH₃), 7.48 (d, *J* = 8.5 Hz, 2 H, ArH), 7.82 (dd, *J* = 8.5, 1.5 Hz, 2 H, ArH), 8.18 (d, *J* = 1.5 Hz, 2 H, ArH), 10.12 (s, 2 H, CONH), 10.14 (s, 2 H, CONH).

3.7. Synthesis of the BiVO₄ plates

3.7.1. Electrochemical deposition of bismuth iodate (BiOI) films

Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, 0.970 g, 2.00 mmol) was dissolved in potassium iodide solution (KI, 0.400 M, 50.0 mL). Nitric acid (HNO₃, 69.0 wt%, 100 µl) was added to adjust the pH of the solution to approximately 1.7. Absolute EtOH (20.0ml) containing p-benzoquinone (0.500 g, 4.60 mmol) was then added and the resulting mixture was vigorously stirred for one minute. Electrodeposition of BiOI was done in a three-electrode cell. A fluorine doped tin oxide(FTO) glass plate of lateral dimension 1.00 cm x 1.80 cm was used as the working electrode, an Ag/AgCl (saturated KCl) was used as the reference electrode, and a platinum plate was used as the counter electrode. A SP-300 potentiostat (Biologic) was used for the electrodeposition and subsequent PEC studies. The cathodic deposition was performed at a potential of -0.100 V vs Ag/AgCl (saturated KCl) at room temperature with a deposition time of 5 min. The purpose of using p-benzoquinone is to assist in the precipitation of crystalline BiOI on the working electrode, due to a rise in pH around the working electrode resulting from the reduction of p-benzoquinone to hydroquinone. This results in orange plates of BiOI.

3.7.2. Thermal conversion of BiOI films to BiVO₄ films

A DMSO solution (0.10 mL) containing 0.200 M vanadyl acetylacetonate($\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$) was placed on the BiOI electrode (1.00 cm x 1.80 cm) and heated in a muffle furnace at 450 °C for 2 h (ramping rate: 2.0 °C/min) in air to convert the BiOI to BiVO₄. Excess V₂O₅ was subsequently removed by soaking the plates in 1.0 M NaOH solution for 30 min with gentle stirring. The resulting yellow BiVO₄ plates were rinsed with deionised water and dried at room temperature.

3.7.3. Dropcasting of Fe-TAML onto BiVO₄ plates.

Fe-TAML (10.9 mg, 0.020 mmol) was dissolved in MeOH (4.0 mL) to give a 5.0 mM Fe-TAML solution. The Fe-TAML solution (100 µl) was then dropcasted on the BiVO₄ plates and allowed to dry in air. This was repeated another four times. The resulting plates were eventually washed five times with MeOH before leaving them to dry in air for further use.

3.8. PEC experimental parameters

In all PEC measurements, a three-electrode setup was used with a single PEC cell with a quartz window and a Biologic SP-300 potentiostat. A platinum plate (1.50 cm²) was used as the counter electrode, while an Ag/AgCl (saturated KCl) was used as the reference electrode. The electrolyte used was a 0.500 M Na₂SO₄ solution. The following equation was then used to convert all measured potentials versus Ag/AgCl (saturated KCl) to the corresponding potential versus RHE by the following equation:

$$E \text{ vs RHE} = E \text{ vs Ag/AgCl (saturated KCl)} + E_{\text{Ag/AgCl}}(\text{reference}) + 0.0591 \times \text{pH}$$

Where $E_{\text{Ag/AgCl}}(\text{reference}) = 0.199 \text{ V vs NHE at } 25^\circ\text{C}$

The light source used for the photochemical experiments is a 300 W Xe arc lamp (Ushio, UXL-302-0), with an AM 1.5 G filter. In all the experiments, back-side illumination was done where the light was incident on the FTO side of the prepared plates. The area of the substrates on the FTO plates were 1.50 cm²

3.8.1. LSV experiments in the presence or absence of substrates

LSV experiments were conducted using the setup indicated above. Measurements were made over the range of -0.50 V to 1.30 V. The amount of electrolyte used was 50 mL of 0.50 M Na₂SO₄ solution. All LSV experiments were done without bubbling of N₂ gas and without stirring. The scan velocities of all LSV experiments were set to be at 50.0 mV/s. For LSV experiments involving substrates, the substrates were

dissolved completely in the electrolyte before the experiment was conducted. The concentrations of each substrate are 0.10 mM for BPF and BPS, 0.10 M for Na_2SO_3 , and 10.0 mg/l for lignin

3.8.2. CA experiments in the presence of substrates

For the CA experiments, the same PEC setup was used with the working electrode being either BiVO_4 or $\text{BiVO}_4/\text{Fe-TAML}$. Appropriate amounts of the substrates were then dissolved in the electrolyte to give 0.10 mM BPF, 0.10 mM BPS, or 0.010 g/l lignin solution. Linear sweep voltamograms of the BiVO_4 or $\text{BiVO}_4/\text{Fe-TAML}$ were taken before and after the experiments. Samples were also obtained from the PEC cell at 0 h of the CA experiments and at 14 h. The concentration of BPF or BPS in the sample solutions were then determined by using the HPLC setup described in Section 3.5.. The eluent used was a 1:1 MeOH:water mixture, with a flow rate of 1.00 mL /min, and a column temperature of 30 °C. The volume of sample injected was set to 10.0 μL . The retention time of BPF is at approximately 8 minutes, while the retention time of BPS is at 3 minutes.

Using the UV-Vis setup described in Section 3.5., the concentration and percentage of lignin left in the resulting reaction solution can be determined by the peak at 280 nm. The measurements were done over a range of 200 nm to 800 nm, with a pathlength of 1.0 cm and a slit width of 5.0 nm. Figure 3.8.1. shows the UV-Vis spectra obtained from the reaction samples of lignin

Figure 3.8.1. UV-Vis spectra of solution containing 0.010 g/l of lignin at 0 h with BiVO_4 as the working electrode (black line), at 14 h with BiVO_4 as the working electrode (red line), at 0 h with $\text{BiVO}_4/\text{Fe-TAML}$ as the working electrode (blue line), and at 14 h with $\text{BiVO}_4/\text{Fe-TAML}$ as the working electrode (green line).

Fe-TAML is believed to not significantly interfere with the lignin absorbance at 280 nm despite having similar peaks at the same wavelength as seen in Figure 3.8.2.a. and Figure 3.8.2.c. As discussed in Section 3.3., Fe-TAML had been shown to stay on BiVO_4 even up to the fourth cycle, indicating minimal leaching into the reaction solution. Furthermore, should the Fe-TAML be leeching into the lignin solution during the experiments, one would expect that the absorbance at 280 nm should increase rather than decrease. The molar extinction coefficient of lignin alkali in water was found to be $15.4 \text{ L g}^{-1} \text{ cm}^{-1}$ (R^2 value = 0.996) as seen from Figure 3.8.2.c. This is lower than the reported molar extinction coefficient of $20.9 \text{ L g}^{-1} \text{ cm}^{-1}$, possibly due to the variation of lignin used.²⁸

Figure 3.8.2. a) UV-Vis spectra of lignin dissolved in water at various concentrations. b) Plot of absorbance of lignin in water at 280 nm against the concentration of lignin. c) UV-Vis spectra of Fe-TAML dissolved in water at various concentrations. d) Plot of the absorbance of Fe-TAML in water at 280 nm against concentration of Fe-TAML.

3.8.3. Reaction kinetics experiments in the presence of BPF

Kinetic experiments were conducted using a H-Cell with the anodic chamber separated from the cathodic chamber by a semi-permeable Nafion membrane. A 30.0 ml solution of ACN containing 0.10 M TBAPF₆ and 0.10 mM BPF was added to the anodic chamber for each reaction, while 25.0 ml of water containing 0.50 M Na₂SO₄ was added into the cathodic chamber. The working electrode of BiVO₄/Fe-TAML plates and the Ag/AgCl (Saturated KCl) electrode were then placed in the anodic chamber and a Pt-mesh counter electrode was placed in the cathodic chamber. The experiments were then conducted under a potential bias of 1.00 V vs AgCl/Ag for 14 h, with stirring of the solution in the anodic chamber.

3.8.4. PEC experiments in the presence of scavengers

PEC experiments of other substrates were conducted with the same experimental parameters in Section 3.8.3., with 1.0 mM of the various scavengers (AgNO₃, benzoquinone, isopropanol and TEA) added to the anodic chamber for each reaction.

3.8.5. PEC experiments in the presence of other substrates

PEC experiments of other substrates were conducted with the same experimental parameters in Section 3.8.3., with the different substrates dissolved in the electrolyte instead of BPF. For the PEC experiment with PET as a substrate, 30.0 ml of ACN containing 0.10 M TBAPF₆ containing about 0.104 g of PET pellets were added into the anodic chamber, with 17.0 mg of Fe-TAML dissolved in the same solution

mixture. For the PEC experiment with lignin, lignin was dissolved in 30.0 ml of H₂O containing 0.50 M Na₂SO₄ before being added to the anodic chamber for the PEC experiment

3.9. ^1H NMR Spectra

Figure 3.9.1. ^1H NMR spectrum of **B**.

Figure 3.9.2. ^1H NMR spectrum of **C**.

Figure 3.9.3. ¹H NMR spectrum of **D**.

Figure 3.9.4. ¹H NMR spectrum of **E**.

Figure 3.9.5. ¹H NMR spectrum of **G**, after demetallation.

Figure 3.9.6. The ^1H NMR spectrum of the sample obtained at 0 h from the PEC experiments with BPF as the substrate. The top spectrum shows the full-range from 0 ppm to 10.0 ppm, while the bottom spectrum is the expansion of the above spectrum with a range of 3.0 ppm to 10.0 ppm.

Figure 3.9.7. The ^1H NMR spectrum of the sample obtained at 14 h from the PEC experiments with BPF as the substrate. The top spectrum shows the full-range from 0 ppm to 10.0 ppm, while the bottom spectrum is the expansion of the above spectrum with a range of 3.0 ppm to 10.0 ppm.

Figure 3.9.8. The ^1H NMR spectrum of the sample obtained at 0 h from the PEC experiments with BPS as the substrate. The top spectrum shows the full-range from 0 ppm to 10.0 ppm, while the bottom spectrum is the expansion of the above spectrum with a range of 3.0 ppm to 10.0 ppm.

Figure 3.9.9. The ^1H NMR spectrum of the sample obtained at 14 h from the PEC experiments with BPS as the substrate. The top spectrum shows the full-range from 0 ppm to 10.0 ppm, while the bottom spectrum is the expansion of the above spectrum with a range of 3.0 ppm to 10.0 ppm.

Figure 3.9.10. The expanded ^1H NMR spectrum of the sample obtained at 0 h from the PEC experiments, with cellulose acetate as the substrate. The peak signal at 6.30 ppm is due to the addition of 1,1,2,2-tetrachloroethane as a known standard.

Figure 3.9.11. The expanded ^1H NMR spectrum of the cellulose acetate sample obtained at 14 h from the PEC experiments. The peak at 6.30 ppm is due to the addition of 1,1,2,2-tetrachloroethane as a known standard.

Figure 3.9.12. The ^1H NMR spectrum of the sample at 0 h obtained from PEC experiments with PEG as the substrate.

Figure 3.9.13. The expanded ^1H NMR spectrum of the sample at 14 h obtained from PEC experiments with PEG as the substrate, with a range of 3.0 ppm to 10.0 ppm.

Figure 3.9.14. The ¹H NMR spectrum of the sample obtained at 48 h from the PEC experiments, with PET as the substrate. The top spectrum shows the full-range from 0 ppm to 10.0 ppm, while the bottom spectrum is the expansion of the above spectrum with a range of 2.8 ppm to 3.38 ppm.

3.10. References

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Chapter 4

G-C₃N₄ with PDI for phenolic compound degradation

4.1. Introduction

The material g-C₃N₄ is a metal-free, polymeric semiconductor, with a band gap of 2.70 V, and was found to be capable of splitting water.¹ Its optical absorption edge of 460 nm makes it a potential photocatalyst.² However, the current photocatalytic efficiency of g-C₃N₄ is still comparatively lower than that of other inorganic semiconductors. Small specific surface area, rapid rate of charge recombination, marginal optical absorption of visible light, and generally low electric conductivity are the main factors limiting the photocatalytic efficiency g-C₃N₄.³ On the other hand, studies have shown that making changes to the electronic structure, nanostructure, crystal structure, or heterostructure of the g-C₃N₄ material could improve the photocatalytic abilities of g-C₃N₄.⁴

Regarding the nanostructure modifications of g-C₃N₄, much research has been done in developing extensive methods to exfoliate nanoscale g-C₃N₄. Methods such as chemical⁵ and thermal exfoliation⁶ were explored as ways to exfoliate g-C₃N₄ to nanometer-thick layers, while hard and soft templating methods were developed to make mesoporous g-C₃N₄.⁷⁻⁸ Although such methods are effective for making g-C₃N₄ of high surface area, product yields are sometimes low and thus, such methods are not suitable for preparing large quantities of high-surface area g-C₃N₄. However, if we compare the many different precursors that have to be used for the synthesis of g-C₃N₄, it can be seen that different precursors provide g-C₃N₄ of different morphologies and surface areas. Thus far, the synthesis of bulk g-C₃N₄ has been reported with a variety of precursors, such as melamine,⁹ urea,¹⁰ and dicyandiamide.¹¹ Among these, g-C₃N₄ made from urea has been shown to have a

larger surface area and a thinner morphology than the g-C₃N₄ made from other precursors. This could be because of the O atom of urea that aids in the separation between the layers of g-C₃N₄ during the calcination process.¹⁰ Therefore, we decided to use urea as the precursor in making our g-C₃N₄ material, g-C₃N₄ (urea).

PDMA would then be added to the synthesised g-C₃N₄ (urea) as a form of electronic structure modification in order to improve its ability to absorb more visible light. PDMA is an aromatic diimide, which is known to be an n-type organic semiconductor of high stability and great electron mobility.¹² By incorporating such aromatic diimides into g-C₃N₄, the incorporated pyromellitic diimide (PDI) group would then cause a positive shift of the valence band of g-C₃N₄ due to the group's high electron affinity,¹³ thus increasing the catalytic ability of g-C₃N₄ to favour oxidative reactions.¹⁴ In 2014, Shiraishi *et al.* first reported the incorporation of pyromellitic diimide into melem made from melamine. Melem is a trimer of melamine and is an intermediate in the synthesis of g-C₃N₄ from a melamine precursor. It is usually formed at a lower calcination temperature and has been known to exhibit higher quantum yields compared to bulk g-C₃N₄.¹⁵

It was proposed that g-C₃N₄ was able to photogenerate endoperoxide and hydrogen peroxide in the presence of oxygen as seen in figure 4.1.1. However, ethanol had to be used in the catalytic cycle as the sacrificial electron donor since the valence band of the g-C₃N₄ catalyst was found to be insufficient for water oxidation.¹⁶ On the other hand, when PDI units were mixed with melem(melamine) and calcined, the valence band levels of the resulting materials were altered due to the higher electron affinity of the PDI units, resulting in favourable valence band levels for water oxidation.¹⁷

These would allow the resulting g-C₃N₄/PDI to be able to use water as a sacrificial reagent in the photocatalytic generation of endoperoxide and hydrogen peroxide (Figure 4.1.1.a.) Furthermore, the incorporation of various diimide moieties (Figure 4.1.2.) to g-C₃N₄, expanded the capabilities and applicability of g-C₃N₄ to hydrogen peroxide production,^{14, 17} nitric oxide removal,¹⁸ and hydrogen gas production.¹⁹

Figure 4.1.1. a) Proposed catalytic cycle for the selective H₂O₂ production by g-C₃N₄ in the presence of light. b) Proposed catalytic cycle for the selective H₂O₂ production by melam(melamine)/PDI₅₁ in the presence of light. Adapted with permission from *Angew. Chem. Int. Ed. Engl.* **2014**, 53, 13454-13459. Copyright 2019 John Wiley and Sons.¹⁷

Figure 4.1.2. Various diimide moieties added to melam synthesised from melamine to give the corresponding doped g-C₃N₄

In this chapter, we described the concurrent modifications of both the nanostructure and electronic structure of g-C₃N₄. Bulk g-C₃N₄(urea) were first synthesised by using urea as the precursor, followed by the incorporation of PDI into the resulting g-C₃N₄. These synthesised materials were termed as g-C₃N₄(urea)/PDI as seen in Figure 4.1.2..

Figure 4.1.3. Proposed synthesis route of g-C₃N₄ (urea)/PDI

Bulk g-C₃N₄ made with urea as the precursor, and the literature reported PDI-doped g-C₃N₄ derived from the incorporation of PDI into melem made from melamine, were also synthesised as comparisons and are termed g-C₃N₄(urea) and melem(melamine)/PDI respectively (Figure 4.1.3.). Subsequently, the synthesised materials were applied in the degradation of BPF.

Figure 4.1.4. Chemical structures of a) urea and melamine precursors that could be used in the synthesis of g-C₃N₄ or melem, b) melem(melamine) formed during the calcination process at lower temperature of 425 °C with melamine as the precursor, c) g-C₃N₄ formed commonly by the calcination of the urea precursors at 550 °C, d) melem(melamine)/PDI formed from the further calcination of a mixture of PDMA and melem, and e) g-C₃N₄(urea)/PDI formed from the further calcination of a mixture of PDMA and g-C₃N₄(urea)

4.2. Materials characterisations

The g-C₃N₄(urea)/PDI was synthesised through the concurrent modifications of its nanostructure and the addition of PDI moieties to its g-C₃N₄ framework. Melem(melamine)/PDI₅₁¹⁷ and g-C₃N₄(urea)¹⁰ were synthesised as materials to compare with our g-C₃N₄(urea)/PDI. The characterisation of the g-C₃N₄ materials via Infra-red(IR) spectroscopy was then conducted to identify if PDI moieties were successfully added to the g-C₃N₄(urea).

From Figure 4.2.1., a range of peaks could be identified for all four materials that are characteristic of reported g-C₃N₄ materials.²⁰ Peaks between 1000 and 1600 cm⁻¹ are due to the carbon-nitrogen or carbon-nitrogen double bonds in the aromatic carbon nitride heterocycles, while the broad absorption band at 3100 to 3300 cm⁻¹ can be assigned to the stretching modes of secondary and primary amines and their intermolecular hydrogen-bonding interactions. In addition, a sharp peak at 880 cm⁻¹ corresponds to s-triazine ring mode stretches.

Figure 4.2.1. Full IR spectra of g-C₃N₄ (urea)/PDI (red line), g-C₃N₄ (urea) (black line), melem(melamine)/PDI₅₁ (blue line), and melem(melamine) (pink line)

The presence of the two carbonyl (C=O) peaks at 1729 and 1772 cm⁻¹ are signatures of cyclic imides functional groups and are only observed for g-C₃N₄(urea)/PDI and melem(melamine)/PDI₅₁ (Figure 4.2.2.). The peaks at 1772 cm⁻¹ correspond to the in-phase stretching of the two C=O groups and 1729 cm⁻¹ corresponds to the out-of-phase stretching of two C=O groups with respect to each other. A similar peak at 1749 cm⁻¹ was reported by Zhang *et al.* in their perylene diimide doped g-C₃N₄ as signature peaks of C=O in perylene diimides.²¹ These would therefore indicate the successful condensation of PDMA with both melem(melamine) and g-C₃N₄(urea) through the formation of the diimide functional group.

Figure 4.2.2. Expanded IR spectra of g-C₃N₄ (urea)/PDI (red line), g-C₃N₄ (urea) (black line), melem(melamine)/PDI₅₁ (blue line), and melem(melamine) (pink line) between the range of 1500 to 2000 cm⁻¹.

The successful condensation of PDI moieties to the g-C₃N₄ framework is further investigated through XPS. From the C 1s spectra of g-C₃N₄(urea) and g-C₃N₄ (urea)/PDI (Figure 4.2.3.), the peak at about 285.0 eV would correspond to carbon-nitrogen bonds in the g-C₃N₄ framework. Melem(melamine)/PDI₅₁, was observed to have a peak at 284.6 and 285.0 eV, which would correspond to the carbon-carbon bond in the PDI unit and the carbon-nitrogen bonds in the g-C₃N₄ framework. The peak at about 288.4 eV is often due to the carbon-oxygen double bond (C=O).²² Therefore this could be observed in all three materials, as g-C₃N₄ (urea) would have C=O bonds due to its urea precursors, melem(melamine)/PDI₅₁ would have C=O bonds due to the carbonyl group on the PDI units, and g-C₃N₄ (urea)/PDI would have C=O as a result of both the carbonyl group on the PDI units and the C=O bonds in its g-C₃N₄ framework due to its precursors.

Figure 4.2.3. C 1s XPS data for a) g-C₃N₄ (urea), b) melem(melamine)/PDI₅₁, and c) g-C₃N₄(urea)/PDI.

For the N 1s spectra of g-C₃N₄ (urea) in Figure 4.2.4., the three peaks at 398.5, 399.4, and 401.0 eV were observed. These peaks would correspond to the sp² hybridised N atoms of melem single units, trigonal N atoms of the melem single unit centers in the g-C₃N₄ framework, and the terminal amine N atoms respectively.¹⁷ Furthermore, both g-C₃N₄(urea)/PDI and melem(melamine)/PDI₅₁ were shown to have peaks at about 400.0 eV. This could be assigned to the imide N atoms of the PDI unit, and thus would indicate the presence of PDI moieties on both g-C₃N₄(urea)/PDI and melem(melamine)/PDI₅₁. However, there is an absence of the peaks at 401.0 eV for g-C₃N₄(urea)/PDI, indicating the loss of terminal amine N

atoms as a result of the condensation reaction with PDMA to give imides. In addition, the relative peak intensity of peak at 400.0 eV is much lower than the peak at 398.5 eV which corresponds to the sp^2 hybridised N atoms of melem single units for g- C_3N_4 (urea)/PDI. Using the formula from Shiraishi *et al.*, the mole ratio of the integration of the area from N 1s XPS spectra between the imide N atom and the N atoms of the melem single unit was found to be 0.414 : 1.¹⁷ This would suggest that the amounts of PDI moieties on the g- C_3N_4 framework of g- C_3N_4 (urea)/PDI is small and limited to the amount of terminal NH_2 groups in the g- C_3N_4 (urea) precursor used.

Figure 4.2.4. N 1s XPS data for a) g- C_3N_4 (urea), b) melem(melamine)/PDI₅₁, and c) g- C_3N_4 (urea)/PDI.

From Figure 4.2.5., the XRD pattern analysis reveals that both g-C₃N₄(urea) and g-C₃N₄(urea)/PDI each showed a broad peak at 27.4° and a shoulder at 12.7°. These peaks are characteristic of g-C₃N₄ and have been similarly observed and characterised by both Martin *et al.* and Liu *et al.* as the stacking of π -conjugated layers, with the peak at 27.4° indexed for graphitic material as the (002) peak, and the shoulder at 12.7 indexed as the (100) peaks.^{10, 23} In addition, the broad peak at 27.4° is also characteristic of the amorphous nature of g-C₃N₄.

Figure 4.2.5. XRD patterns of a) melem(melamine), b) g-C₃N₄(urea), c) melem(melamine)/PDI₅₁, and d) g-C₃N₄(urea)/PDI.

On the other hand, we observed that for both melem(melamine)/PDI₅₁ and g-C₃N₄(urea)/PDI, two additional peaks can be observed at 29.0° ($d = 0.302$ nm) and 19.0° ($d = 0.467$ nm), which was similarly reported by Shiraishi *et al.* in their PDI-

doped g-C₃N₄ material.¹⁷ The peak at 29.0° indicates the presence of π - π stacking of PDI units, while the peak at 19.0° would indicate donor-acceptor interactions between melem or g-C₃N₄ and the PDI units.¹⁷ We also observed that for melem(melamine)/PDI₅₁, the peak at 27.4° is not as defined as that of g-C₃N₄(urea)/PDI or g-C₃N₄(urea), while having a relatively higher intensity at 29.0°, suggesting a greater occurrence of π - π stacking of the PDI units than the stacking of π -conjugated g-C₃N₄ layers. This decrease to the peak intensity at 27.4° and increase in peak intensity at 29.0° corresponds to literature reports when increasing amount of PDI units were used in the synthesis of the doped g-C₃N₄ materials.¹⁷

Furthermore, the peak for 29.0° was observed to be less prominent in the synthesised g-C₃N₄(urea)/PDI, which could suggest a decrease in the amounts of π - π stacking of the PDI moieties within the g-C₃N₄(urea)/PDI framework. On the other hand, g-C₃N₄(urea)/PDI displays both a broad peak at 27.4° and a sharp peak at 19.0°. This would suggest that g-C₃N₄(urea)/PDI would have the stacking of π -conjugated layers due to its g-C₃N₄ framework, while the PDI moieties that replace the terminal -NH₂ groups of g-C₃N₄(urea)/PDI would result in further donor-acceptor interactions between the g-C₃N₄(urea)/PDI layers. These would suggest differences in the photophysical and possibly the photocatalytic properties of g-C₃N₄(urea)/PDI, as compared to melem(melamine)/PDI₅₁ and g-C₃N₄(urea), as a result of the differences in interactions between the g-C₃N₄ layers and its retention of its amorphous nature.

In Figure 4.2.2., melem(melamine)/PDI₅₁ can be observed to have a highly layered structure that similar to previous reports.²⁴ In contrasting, the images of g-C₃N₄(urea)

indicate sheet-like morphologies, which had been observed by Yue *et al.*²⁵ These corroborate the supposed amorphous nature as seen by the broad peak at 27.4° in the XRD pattern. In addition, g-C₃N₄ (urea)/PDI was observed to be more aggregated than g-C₃N₄(urea) as a result of having both an amorphous nature as observed by a similar broad peak at 27.4° , and some crystalline behaviour shown by the similar sharp peaks as melem(melamine)/PDI₅₁ at 19.0° and 29.0° .

Figures 4.2.6. SEM images of various synthesised g-C₃N₄: a) g-C₃N₄(urea), b) melem(melamine)/PDI₅₁, and c) g-C₃N₄(urea)/PDI.

The synthesised g-C₃N₄ materials were further investigated by the Brunauer-Emmett-Teller(BET) measurements, as summarised in Table 4.2. 1.. Melem(melamine)/PDI₅₁ was recorded to have the lowest surface area and pore volume, relatively similar to the reported $7.1 \text{ m}^2/\text{g}$.¹⁷ On the other hand, g-C₃N₄ (urea)

was shown to have a surface area of 17.5 m²/g, which is significantly lower than the reported g-C₃N₄(urea). These differences could be due to the reported g-C₃N₄(urea) being synthesised at a higher temperature of 600 °C.² Though g-C₃N₄ (urea)/PDI showed similar morphology as that of g-C₃N₄ (urea), the BET measurements indicate that there are significant increases in their surface areas and pore volumes. The surface area of the synthesised g-C₃N₄ (urea)/PDI was measured to be at 60.7 m²/g. This is higher than the surface area of other reported g-C₃N₄ with the aromatic diimide introduced, with the highest surface area reported being 48.5 m²/g.²⁶ A possible reason could be due to the second heating process of the precursor g-C₃N₄ (urea) with PDMA to synthesise the g-C₃N₄ (urea)/PDI, which resulted in a thermal exfoliation effect during the synthesis.²⁷

Table 4.2.1. Surface area, pore volume, and pore size of g-C₃N₄(urea)/PDI, g-C₃N₄(urea), and melem(melamine)/PDI₅₁.

Catalyst	Surface Area (m ² /g)	Pore volume (cm ³ /g)	Pore size (Å)
G-C ₃ N ₄ (urea)	17.5	0.0818	185
Melem(melamine)/PDI ₅₁	3.51	0.0380	434
G-C ₃ N ₄ (urea)/PDI	60.7	0.631	416

Figure 4.2.7. BET plots of g-C₃N₄(urea)/PDI (red line), g-C₃N₄(urea) (black line), and melem(melamine)/PDI₅₁ (blue line).

4.3. Photophysical properties

In g-C₃N₄(urea)/PDI, the addition of a PDI to bulk g-C₃N₄(urea) saw a slight improvement in its ability to absorb visible light as seen by the increase in the absorption edge from 450 nm to 500 nm (Figure 4.3.2.). This thus allows for a slight improvement in the amount of visible light absorbed by g-C₃N₄(urea)/PDI for an increase in photogenerated electron-hole pairs that could translate to an improvement of its photocatalytic ability. However, the increase in optical light absorption edge by g-C₃N₄(urea)/PDI is comparatively lower when compared to melem(melamine)/PDI₅₁. One reason could be that there is a lower level of PDI moieties that are bound to the terminal -NH₂ group in the synthesis of g-C₃N₄(urea)/PDI, as compared to the larger amount of terminal NH₂ groups for melem single units available before the eventual formation of the complete melem(melamine)/PDI₅₁ framework.

Figure 4.3.1. DRS spectra of g-C₃N₄(urea) (black line), g-C₃N₄(urea)/PDI (red line), and melem(melamine)/PDI₅₁(blue line).

In addition, the introduction of PDI moieties into the g-C₃N₄ framework was reported previously to alter the band gap of the g-C₃N₄ materials, whereby increasing amounts of PDI moieties were observed to decrease the valence band and conduction band values of the resulting g-C₃N₄ materials.¹⁷ In the Tauc plots in Figure 4.3.2., the band gaps of 2.81 eV for g-C₃N₄(urea) and 2.60 eV for melem(melamine)/PDI₅₁ were observed to be similar to the reported values of 2.80 eV for g-C₃N₄(urea)²⁶ and 2.68 eV for melem(melamine)/PDI₅₁.¹⁷ The band gap of g-C₃N₄(urea)/PDI was observed to have increased to 2.92 eV, whereas the inclusion of PDI had previously significantly reduced the band gap. This could be a result of the nanostructure alteration causing the widening of the band gap, while the smaller amounts of PDI moieties in g-C₃N₄(urea)/PDI do not have as significant an effect on narrowing of the band gap.

Figure 4.3.2. Tauc plots of a) g-C₃N₄(urea), b) melem(melamine)/PDI₅₁, and c) g-C₃N₄(urea)/PDI.

The photoluminescence (PL) properties of the synthesised g-C₃N₄ materials were also investigated. From Figure 4.3.5., melem(melamine) was observed to have an emission peak at 400 nm which is relatively similar to the reported literature value.¹⁵ However, upon the addition of PDI moieties into melem(melamine), a red shift of the luminescence center was observed. The emission peak positions of g-C₃N₄(urea), g-C₃N₄(urea)/PDI and melem(melamine)/PDI₅₁ were found to be relatively similar (between 450 nm to 500 nm), with decreasing emission intensities from g-C₃N₄(urea) having the highest emission intensity, to g-C₃N₄(urea)/PDI, and then to melem(melamine)/PDI₅₁. These suggest that the high electron mobility of the PDI

units might result in the effective extraction of photoexcited electrons, thus reducing the immediate recombination of the photogenerated electron-hole pair.

Figure 4.3.3. Photoluminescence spectra of g-C₃N₄(urea)(black line), g-C₃N₄(urea)/PDI(red line), melem (melamine) (pink line) and melem(melamine)/PDI₅₁ (blue line)

To further investigate the effects that both nanostructuring and addition of the PDI moieties have on g-C₃N₄(urea)/PDI, PESA was conducted to measure and compare the work function of the materials. As mentioned in Chapter 3, the work function is the minimum energy required to remove an electron from a semiconductor's Fermi-level to a point in vacuum.²⁸ In an n-type semiconductor such as g-C₃N₄, the Fermi-level would be close to the CBM. Therefore, the work function can be utilised to approximate the CBM of a semiconductor.²⁹ From Figure 4.3.4., we can see that there is a difference of 0.10 eV between the work function of g-C₃N₄(urea)/PDI and its precursor g-C₃N₄(urea). This would suggest that the CBM of g-C₃N₄(urea) would be more positive (vs vacuum), (Figure 4.3.4.).

Figure 4.3.4. PESA spectra of a) g-C₃N₄ (urea), b) melem(melamine)/PDI₅₁, and c) g-C₃N₄(urea)/PDI.

Figure 4.3.5. Illustration of the approximate CBM based on values acquired from PESA experiments, bandgaps from Tauc plots, and the calculated VBM based on the PESA spectra and Tauc plots. $\text{G-C}_3\text{N}_4(\text{urea})/\text{PDI}$ is shown in red, melem(melamine)/ PDI_{51} is shown in blue, while $\text{g-C}_3\text{N}_4(\text{urea})$ is shown in black.

4.4. Photocatalytic activities evaluations

4.4.1. Photocatalytic conversions of BPF by g-C₃N₄(urea)/PDI

To evaluate the photocatalytic ability of g-C₃N₄(urea)/PDI, and to compare it to g-C₃N₄(urea) and melem(melamine)/PDI₅₁, the material was dispersed in an aqueous solution containing BPF as the substrate and the reaction mixture was stirred in the presence of light from a white LED. At the end of 2 h, g-C₃N₄(urea)/PDI was observed to have completely degraded BPF, while g-C₃N₄(urea) and melem(melamine)/PDI₅₁ are slower in their degradation of BPF as seen in Figure 4.4.1. (about 50% for g-C₃N₄(urea) and about 60% for melem(melamine)/PDI₅₁).

Figure 4.4.1. Catalytic photodegradation kinetics of BPF using g-C₃N₄(urea) (black), melem(melamine)/PDI₅₁ (blue), and g-C₃N₄(urea)/PDI (red).

Making a comparison between the rate of BPF degradation g-C₃N₄(urea) (black) and melem(melamine)/PDI₅₁, melem(melamine)/PDI₅₁ was shown to be faster than g-C₃N₄(urea), even though g-C₃N₄(urea) has a surface area that is five times greater

than melem(melamine)/PDI₅₁. This suggests that the presence of PDI moieties in g-C₃N₄ and the resulting alteration to g-C₃N₄ photophysical properties would have an effect on the photocatalytic ability of g-C₃N₄(urea)/PDI on the degradation of BPF.

Furthermore, the high surface area of g-C₃N₄(urea)/PDI would also be another key factor in explaining the higher rate of degradation of BPF. Although both melem(melamine)/PDI₅₁ and g-C₃N₄(urea)/PDI have PDI moieties, g-C₃N₄(urea)/PDI was shown through BET measurements to have a much larger surface area than melem(melamine)/PDI₅₁. The larger surface area would potentially provide a larger area by which the generation of ROS such as hydroxyl radical can take place, which would then go on to degrade BPF. Therefore, both the inclusion of the PDI moieties and the improvement to the surface area are two factors that had resulted in an improvement to g-C₃N₄(urea)/PDI photocatalytic activity, with the changes to the surface area possibly having a greater effect than the PDI moieties.

4.4.2. Investigation of active reactive oxygen species (ROS) in photocatalytic reactions

G-C₃N₄ is known to generate a wide variety of ROS for various types of reactions. Therefore, to further investigate the reaction mechanism of the g-C₃N₄(urea)/PDI photocatalytic system, a series of scavenger experiments was conducted to observe which ROS is the active species in the degradation of BPF. Isopropanol was reported to be able to react with hydroxyl radical to give the corresponding isopropanol radical and water,³⁰ while the oxalate anion in sodium oxalate could react with photogenerated holes from the g-C₃N₄ materials to give carbon dioxide.³¹

Sodium pyruvate was used as a hydrogen peroxide scavenger, where upon reacting with hydrogen peroxide, would give sodium acetate, CO_2 , and water as the products.³² Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) was used as a peroxy radical scavenger, where the mono-anionic form of Trolox would react with peroxy radical to give Trolox radical and peroxy anion, via single electron transfer mechanism.³³

From Figure 4.4.2, when the scavengers for peroxy radicals, hydroxyl radicals, and photogenerated holes were used, it showed that the degradation of BPF had slowed down, such that the resulting yield over the 2 h period was only around 40% degraded BPF.

Figure 4.4.2. Scavenger experiments with no scavengers (black line), isopropanol as hydroxyl radical scavenger (red line), sodium pyruvate as hydrogen peroxide scavenger (blue line), Trolox as a peroxy radical scavenger (grey line), and sodium oxalate as a hole scavenger (green line).

From Figure 4.4.2., the degradation rate for BPF was observed to slow slightly when hydrogen peroxide scavenger was used, which could indicate the formation of small amount of hydrogen peroxide by g-C₃N₄(urea)/PDI. This would agree with the mechanism suggested by Shiraishi *et al.*, where melam(melamine)/PDI₅₁ was shown to produce hydrogen peroxide(Figure 4.1.1.b.).²⁰ On the other hand, there were significant decrease to the degradation rate when the scavengers for peroxy radicals and hydroxyl radicals were used. This would suggest that these two radicals would be most active when g-C₃N₄(urea)/PDI was under the illumination of a white LED. While peroxy radicals could be generated by g-C₃N₄(urea)/PDI, hydroxyl radicals would either be from the partial oxidation of the hydrogen peroxide generated by g-C₃N₄(urea)/PDI or the oxidation of water by g-C₃N₄(urea)/PDI, which could further explain why the scavenging of hydrogen peroxide has a less prominent effect on the reaction rate.³⁴⁻³⁵ Alternatively, it was reported that hydrogen peroxide would be less reactive than other ROS.³⁴ Therefore, it would also seem to indicate that there may be a more complex degradation pathway that requires all three species (photogenerated holes, peroxy radicals, and hydroxyl radicals) for the degradation of BPF.

4.4.3. Investigation of the recyclability of g-C₃N₄(urea)/PDI

The recyclability of g-C₃N₄(urea)/PDI was investigated and it was found that there are morphological changes to the g-C₃N₄(urea)/PDI after just one cycle of reaction. As seen from the IR spectra in Figure 4.4.3.a., the signature peak at 1772 cm⁻¹ that corresponds to the C=O bonds of cyclic imides functional groups, was found to be absent. This would indicate the lost of the imide link between the carbon nitride and PDI moieties. This is further supported by the XRD pattern of the recovered g-

$C_3N_4(\text{urea})/\text{PDI}$ (Figure 4.4.3.b.), with the disappearance of the peaks at 19.0° and 29.0° that correspond to the donor-acceptor interactions between melem or g- $C_3N_4(\text{urea})$ and the PDI units, and the presence of π - π stacking of PDI units respectively. These suggest oxidative degradation of the material along the imide bonds between g- $C_3N_4(\text{urea})$ and the PDI units

Figure 4.4.3. a) IR spectra of fresh $g\text{-}C_3N_4(\text{urea})/\text{PDI}$ (black line) and recovered $g\text{-}C_3N_4(\text{urea})/\text{PDI}$ (red line), b) expanded IR spectra between 1500 cm^{-1} to 2000 cm^{-1} of fresh $g\text{-}C_3N_4(\text{urea})/\text{PDI}$ (black line) and recovered $g\text{-}C_3N_4(\text{urea})/\text{PDI}$ (red line), c)

XRD pattern of fresh g-C₃N₄(urea)/PDI (black line) and recovered g-C₃N₄(urea)/PDI (red line).

4.5. Conclusions

A g-C₃N₄(urea)/PDI material was successfully synthesised with a large surface area and with PDI moieties, and was characterised by various techniques, such as XPS, XRD, SEM, IR and BET. The changes to the photophysical properties of g-C₃N₄(urea)/PDI were then investigated by DRS and PESA, which indicated that g-C₃N₄(urea)/PDI had a wider band gap but exhibited a positive shift to both the valence band edge and the conduction band edge by different magnitudes. This result thus supports the initial idea of performing nanostructuring and electronic structure alteration on g-C₃N₄(urea)/PDI concurrently.

The effects of these alterations made to g-C₃N₄(urea)/PDI affected its photocatalytic abilities when applied in the degradation of BPF. The results indicated that g-C₃N₄(urea)/PDI was able to degrade BPF under white LED light illumination within 2 h. In addition, the effects of each alteration on the resulting photocatalytic abilities of g-C₃N₄(urea)/PDI were shown to vary significantly, with the larger surface area possibly having a greater effect on the photocatalytic ability than the rest. Furthermore, scavenger experiments showed that the photogenerated holes, peroxy radicals, and hydroxyl radicals generated by g-C₃N₄(urea)/PDI had active roles in the degradation of BPF, which might indicate that g-C₃N₄(urea)/PDI favoured their generation or that the substrate degradation pathway involved all three active species.

4.6. Materials and equipments

Chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, and Tokyo Chemical Industry (TCI). Unless otherwise stated, the commercial reagents were used as purchased. In addition to the other equipment used and listed in Section 3.5. of Chapter 3, the following additional equipment used are as detailed.

BET measurements were derived from nitrogen adsorption-desorption isotherms recorded using an Automatic High Resolution Micropore Physisorption Analyzer (ASAP 2020). The sample was first weighed into a glass tube with a bulb at the end, before being left overnight in the oven at 150°C. The glass sample tube was then loaded into the machine while still hot and allowed to cool down under vacuum. The sample tube was then immersed in liquid nitrogen during the measurement.

A Thermo Scientific Sorvall Legend micro 21 centrifuge was used. The operating speed and time of the centrifuge have been added to the experimental section.

Elemental analyses of the synthesised materials were conducted using a PerkinElmer Series II CHNS 10 Analyzer 2400. Before the measurements of the synthesised materials, 2,5-(bis(5-tert-butyl-2-benzo-oxazol-2-yl) thiophene(BBOT) was used as a standard to calibrate the machine. Each measurement was repeated three times and the average value of each element measured recorded.

Solid-state photoluminescence experiments were conducted using PerkinElmer LS-55 fluorescence spectrometer. The excitation wavelength was set to 320 nm. The

measurements and data were processed using FLwinlab as the programme, with the emission slit set at 3 nm and a scan speed of 200 nm/min. A thin layer of material sample was compact on the solid-state PL sample holder, which was then loaded into the instrument for measurement.

4.7. Synthesis parameters

G-C₃N₄(urea)

Urea (3.00 g, 50.0 mmol) was calcined in a crucible to give bulk g-C₃N₄. This was done by first heating it in a furnace at 550 °C at a ramp rate of 5.0 °C/min. Subsequently, the temperature was maintained at 550 °C for a further 2 h. Yellow bulk g-C₃N₄(urea) (0.858 g, 8.66%) was obtained and was ground into a powder using a pestle and mortar. Elemental analysis calculated (%) for g-C₃N₄(urea): C, 44.44; H, 3.73; N, 51.83, found (%): C, 43.28; H, 0.95; N, 27.04.

Figure 4.7.1. Synthetic route of g-C₃N₄(urea)/PDI.

G-C₃N₄(urea)/PDI

G-C₃N₄(urea) (1.00 g) and PDMA (2.00 g, 18.3 mmol) were mixed together in a crucible, before the reaction mixture was heated in a furnace up to 325 °C over a period of 4 h, with the heating rate of 7.0 °C/min. The resulting solid was then ground to obtain brown powders of g-C₃N₄(urea)/PDI (1.42 g, 47.3%) Elemental analysis calculated(%) for g-C₃N₄(urea)/PDI: C, 42.06; H, 1.95; N, 53.65 ,found: C, 34.51; H, 0.2; N, 59.73.

Melem(melamine)

Melamine (8.00 g, 63.4 mmol) was heated in a furnace up to 425 °C for a period of 4 h to obtain white solids, which were then ground into powder. The resulting white powder was then suspended in water and boiled under reflux for 5 h to remove any impurities. The remaining powder was then washed with water before being heated to dryness at 70 °C. This resulted in a white powder of melem (3.96 g, 28.6%) Elemental analysis calculated(%) for melem(melamine): C, 33.03; H, 2.77; N, 64.20 ,found: C, 32.29; H, 0.91; N, 61.40.

Figure 4.7.2. Synthesis of melem(melamine).

Melem(melamine)/PDI₅₁

Melem, (2.00 g, 9.17 mmol) and PDMA, (4.00 g, 18.3 mol) were mixed together in a crucible, before the reaction mixture was heated in a furnace up to 325 °C over a period of 4 h, with the heating rate of 7.0 °C/min. The resulting solid was then ground to obtain brown powders of melem(melamine)/PDI₅₁ (3.55 g, 94.4%) Elemental analysis calculated(%) for melem(melamine)/PDI₅₁: C, 48.67; H, 3.24; N, 39.15. ,found: C, 46.05; H, 1.06; N, 28.82.

4.8. BPF photodegradation experimental parameters

4.8.1. Photocatalytic experiments

To a 25.0 mL Schlenk tube, 0.0100 g of g-C₃N₄(urea)/PDI was added. BPF stock solution (20.0 mL, 0.10 mM) was added to the Schlenk tube, and the reaction mixture was sonicated for 15 min. The reaction mixture is stirred in the dark for 1 h, before O₂ was bubbled into the reaction mixture for 15 min. The resulting reaction mixture was then placed under an oxygen environment and illuminated with a commercially available white LED lamp. 1.5 mL of the reaction mixture was taken at a 20 min interval for over a period of 2 h, and centrifuged twice, at 14800 rpm for 10 min. Subsequently, the centrifuged sample was transferred into a 1.5 mL vial. The concentration of BPF in each sample was then measured by HPLC.

4.8.2. Photocatalytic experiments with the presence of chemical scavengers

For the evaluation of the rate of degradation of BPF in the presence of scavengers, the scavengers were added at the start and sonicated, before stirring in the dark and bubbling of oxygen into the reaction mixture. The scavengers used were isopropanol (10 mM) for the scavenging of hydroxyl radicals, sodium pyruvate (10 mM) for the scavenging of hydrogen peroxide, sodium oxalate (10 mM) for the scavenging of holes from the charge separation in g-C₃N₄(urea)/PDI, and Trolox (10 mM) for the scavenging of peroxy radicals. The work-up and data acquisition process were the same as the experiments without scavengers.

4.8.3. Catalyst recycling experiments

Photocatalytic experiments were conducted as described in Section 4.8.1. At the end of the 2.0 h experiment, the resulting mixture was filtered through a fine frit with g-C₃N₄(urea)/PDI collected as the residue. The g-C₃N₄ (urea)/PDI residue was then washed three times with water followed by three times with ethanol, before being allowed to dry *in vacuo* at room temperature. The resulting dry residues were then examined with XRD and IR-spectroscopy to determine if the recovered g-C₃N₄ (urea)/PDI retained its structural characteristics after reactions.

4.9. References

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Chapter 5

Exploration of alternative photocatalysts and electrocatalysts for eventual tandem cell setup

5.1. Introduction

In the previous two chapters, a potential photoanode in BiVO₄/Fe-TAML for organic reactions, as well as a g-C₃N₄ (urea)/PDI photocatalyst were described to be modified and possibly applied to PEC systems. To achieve the concept of having a tandem PEC cell setup, there is also a need to explore other possible systems or components that could be coupled with the systems mentioned in Chapter 3 and Chapter 4.

Co-TAML as an electrocatalyst

One possible system that photoanode such as BiVO₄/Fe-TAML could be coupled to would be an electrocatalyst as a potential photocathode. In recent times, there had been interests in the variety of electrocatalytic applications to materials,¹⁻³ energy,⁴⁻⁷ and organic chemistry syntheses.⁸⁻¹⁰ Electrocatalysis had also been found to be utilised in artificial photosynthesis systems, as a possible solution to the problem of climate change.¹¹ These were achieved by the utilisation of solar energy and other renewable sources of energy to generate electrical energy, which can then be stored as H₂ and O₂ gas produced through the electrocatalytic splitting of water.¹¹

Currently, there is an increased exploration of other earth-abundant, molecular, first row transition metal systems as alternatives to platinum group metals.¹¹⁻¹⁷ The great promise of molecular electrocatalysts and their customisable ligand systems for proton reduction had similarly increased the attractiveness of employing such first-row transition metal electrocatalysts for proton reduction in aqueous environments.^{14,}

16-17

The usage of Fe-TAML complexes for oxidative reactions and applications had been established and explored since the initial work by Collins *et al.*¹⁸⁻²¹ However, recent work by Nam and Fukuzumi *et al.* of the applications of TAML complexes with other first-row transition metals had helped to extend the range of applications of TAML complexes.²²⁻²⁶ An example of such applications is the oxidative activation of C-H bonds by high valent cobalt (Co) and nickel (Ni) TAML complexes. These give rise to the possibility of using late-transition metal-ate TAML complexes for reductive catalytic activities. As such, a collaborative work in the exploration of Co and Ni-TAML complexes (Figure 5.1.1.) were conducted for the purpose of electrocatalytic proton reduction.

Figure 5.1.1. Ni-TAML and Co-TAML complexes

Hydrophobic lead halide perovskite for photoredox reactions

Similarly, another possible component that could be coupled with the BiVO₄/Fe-TAML photoanode or g-C₃N₄(urea)/PDI photocatalyst for a tandem cell setup could be hybrid metal halide perovskites. The recent decade has seen soaring interest in the performance of the hybrid metal halide perovskites as optoelectronic materials. Even though perovskites such as (MA)MX₃, (FA)MX₃ and CsMX₃ (M = Pb, Sn; X = I, Br, Cl; MA = methylammonium; FA = formadinium; Cs = cesium) have been

commonly applied to light-emitting diodes,²⁷⁻²⁸ lasers,²⁹⁻³⁰ and incorporated into solar cells,³¹⁻³⁵ their light harvesting abilities has been rarely employed for photocatalysis and photoredox reactions.³⁶⁻³⁷

With photoredox catalysis becoming a multifunctional method for the synthesis of organic compounds,^{35, 38 39-40} hybrid metal halide perovskites could be an interesting heterogeneous alternatives to the commonly used ruthenium or iridium based photosensitisers to mediate such reactions. However, some disadvantage of the popular MAPbI₃, FAPbI₃, and CsPbI₃ perovskites are their phase instability and degradation in the presence of moisture in the environment.⁴¹⁻⁴³ Therefore, there is a need for perovskites that could circumvent such degradation, and be stable in a moist environment for applications in photoredox reactions in organic solvents.

Thus, by preparing 2D perovskites with long hydrophobic hexadecylammonium (HDA) cations between the metal halide nanosheets, my collaborators and I seek to increase the stability of the resulting (HDA)₂MI₄ (M = Pb, Sn) perovskites in protic media and other solvents. The synthesised (HDA)₂MI₄ perovskites (Figure 5.1.2.) would subsequently be applied to photoredox decarboxylation and dehydrogenation reactions with indoline carboxylic acids as substrates, to investigate the viability of such perovskites for phototdriven organic syntheses.

Figure 5.1.2. $(\text{HDA})_2\text{Ml}_4$ perovskites ($\text{M} = \text{Pb}$, Sn)

5.2. XPS investigation of the active species of Co-TAML

Figure 5.2.1. shows the two TAML complexes, Ni-TAML and Co-TAML, synthesised for the subsequent proton reduction reactions. Both TAML complexes were characterised by ^1H NMR and UV-Vis spectroscopy, with Co-TAML complex being further characterised with single-crystal X-ray diffraction crystallography analysis, where the structural data was in agreement with the values reported in the literature.⁴⁴ Using the Evan's method, the magnetic susceptibility of the Co-TAML complex was found to have an intermediate spin ground state, with a spin-only magnetic moment of 2.91 mB corresponding to a $S = 1$ ground state.

Figure 5.2.1. Ni-TAML and Co-TAML complexes

Cyclic voltammetry was then conducted, revealing the electron-rich nature of both TAML complexes. From Figure 5.2.2.a., the cyclic voltammogram of Co-TAML in ACN showed a quasi-reversible redox wave with an $E_{1/2}$ at -0.41 V vs Ag/AgCl, which can be assigned to the $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ redox couple. Similarly, Ni-TAML showed a reversible redox wave at +0.24 V, which can be assigned as the $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$ redox couple (Figure 5.2.2.b.).⁴⁵⁻⁴⁶ By conducting the CV experiments at different scan rates (Figure 5.2.2.c. and Figure 5.2.2.d.), the quasi-reversible peak observed in the CV

voltammogram of Co-TAML and the reversible peak found in the CV voltammogram of Ni-TAML can be confirmed.

Figure 5.2.2. Cyclic voltammograms of 1.0 mM a) Co-TAML (black) and b) Ni-TAML (blue) in 0.10 M *n*-Bu₄NPF₆ solutions in ACN. The set of cyclic voltammograms at scan rates of 100 (black), 200 (red), 400 (blue), and 1000 (teal) mVs⁻¹ for complexes (c) Co-TAML and (d) Ni-TAML. The black arrows correspond to the direction in which the initial potential was applied.

However, upon their application in electrocatalytic proton reduction reactions, only Co-TAML displayed a significant increase in the catalytic current at an onset potential beyond the redox couple of Co^{III}/Co^{II} (Figure 5.2.3.). Further investigations indicate chemical changes of the Co-TAML complexes, with the Tafel plot suggesting the

heterogeneous catalytic generation of H₂ gas by Co oxides or Co nanoparticles (Figure 5.2.4.a.).⁴⁷⁻⁴⁹

Figure 5.2.3. Cyclic voltammograms of a) 1.0 mM of Co-TAML in the absence (blue) and presence (black) of 1.0 M of water in ACN. b) CVs of 1.0 mM of Co-TAML with different concentrations of water in ACN at scan rates of 100 mVs⁻¹. c) Expansion of the data in a) to show the detailed behaviour. d) Expansion of the data in b) to show the detailed behavior.

These were confirmed by controlled potential electrolysis (CPE) with the Co-TAML complex, where a constant potential of -2.0 V vs Ag/AgCl was applied for 50 min. From Figure 5.2.3.c., the current-time curve indicated at least two different processes occurring during the electrolysis of Co-TAML, the first being a transformation of Co-TAML to another species during the initial 1300 s, and the subsequent stabilization of the current in the following 1200 s due to H₂ production

by the resulting heterogeneous catalyst. The low Faradaic efficiency of 18.2% observed from the H_2 evolution by Co-TAML after 50 min could therefore be due to the consumption of current necessary to convert Co-TAML to the active HER catalyst. A rinse test was then conducted, where the same glassy carbon electrode was rinsed with DI water and acetone to remove any remaining Co-TAML before being re-used as the working electrode in a second round of the CPE experiment. The resulting H_2 gas was detected as the electrolysis product, confirming that the active HER catalytic species was a heterogeneous catalyst that was deposited during the first cycle of the electrolysis.

Figure 5.2.4. a) Tafel Plot obtained from Co-TAML HER reactions. b) The amount of H_2 produced (μmol) in the presence (black) and absence (red) of Co-TAML. c) Plots of current against time using 1.0 mM of Co-TAML in ACN (1.0 M of water).

The oxidation states and chemical nature of the electrodeposited film were further investigated by XPS experiments. Figure 5.2.2.a. shows the XPS spectrum in the Co 2p window for a sample of the nanoparticulate layer that was scraped off the glassy carbon electrode onto carbon tape. The peak and shoulder of the Co 2p_{3/2} band can be fit to three distinct peaks with binding energies of 779.9, 782.1, and 785.9 eV. These three peaks' binding energies are like those of the anhydrous CoCl₂ that we used as a reference for materials containing Co^{II} (Figure 5.2.2.b.). For the CoCl₂ sample, the two peaks of the Co 2p_{3/2} band are fitted with two components at higher binding that could be satellite or shake-up peaks, while the two more components at lower binding energies are consistent with Co^{II} interacting with Cl.⁵⁰ By comparing the data from the nanoparticulate film with those from CoCl₂, it appeared that there may be some Co^{II} present in the electrodeposited material, likely due to partial oxidation of the surface Co⁰ by air.

Figure 5.2.5. XPS spectra of (a) Co-TAML complex after CPE and (b) anhydrous CoCl₂.

As electrodeposited Co-based heterogeneous catalysts were previously reported to be capable of proton reduction in aqueous buffer solutions,⁵¹ the Co⁰ nanoparticulate film on the electrode was investigated for properties similar to those of the reported

catalysts. Linear sweep voltammetry experiments were then conducted with Co-TAML to determine the overpotential needed for H₂ evolution for the Co⁰ nanoparticulate layer in a phosphate buffer solution (KH₂PO₄/K₂HPO₄, 0.50 M, pH=7.2). As seen in figure 5.2.6., the Co⁰ nanoparticulate film has an onset of the catalytic current occurring at a potential of -1.1 V Vs Ag/AgCl, regardless of the presence or absence of Co-TAML, which is different from what was reported.⁴⁷ These results suggest that the nature of the electrodeposited Co⁰ heterogeneous catalyst could be dependent on the precursors that were used to generate them. The electrodeposited Co⁰ nanoparticulate film derived from Co-TAML mainly showed electrocatalytic H₂ evolution activity at intermediate concentrations of water.

Figure 5.2.6. Linear sweep voltammogram in the presence (red) and absence (black) of the electrodeposited Co⁰ in phosphate buffer (KH₂PO₄/K₂HPO₄, 0.50 M, pH = 7.2).

Different electrochemical activities of Co-TAML in varying amounts of water were

then attributed to the changes in the electronic structure of Co-TAML. From Figure 5.2.7., Co-TAML complex was observed to have three different molecular geometries: octahedral geometry in the presence of two solvent molecules, square planar geometry in the absence of any solvent molecules, and square pyramidal in the presence of one solvent molecule. These varying geometries would affect the electronic structures of complexes and they would thus exhibit different electrochemical activities.

Figure 5.2.7. Walsh diagram illustrating a change in the electronic configuration and kinetic stability in Co-TAML after it binds different number of water molecules and is reduced.

5.3. VBM measurements and AFMs of (HDA)₂PbI₄

Both (HDA)₂PbI₄ and (HDA)₂SnI₄ were synthesised and characterised by X-ray crystallography and PXRD measurements, as seen in Figure 5.3.1. XPS was also conducted which verified the oxidation state of +2 for the metal centers of both perovskites, while the IR spectra obtained revealed the presence of peaks corresponding to HDA in the perovskites.

Figure 5.3.1. a) PXRD patterns of (HDA)₂PbI₄ and its precursors. b) Crystal structures of (HDA)₂PbI₄ and (HDA)₂SnI₄.

The stabilities of the perovskites in moist atmospheres were also investigated through contact angle measurements and pXRD measurements of the synthesised perovskites before and after exposure to water. Only (HDA)₂PbI₄ was found to be stable, with the pXRD of the (HDA)₂PbI₄ being similar before and after being suspended and stirred in water for 30 min (Figure 5.3.2.a). It also exhibited hydrophobic characteristics with a contact angle of 98.4° (Figure 5.3.2.b). In addition, variable temperature photoluminescence (VTPL) and time-resolved

photoluminescence (TRPL) studies were also conducted on $(\text{HDA})_2\text{PbI}_4$ to better understand the photophysical properties of $(\text{HDA})_2\text{PbI}_4$. The VTPL data (Figure 5.3.3.a.) showed a blue shift upon cooling, which could be due to a stronger interaction of overlapping orbitals in Pb-I bonds as their bond contract at the lower temperature. In Figure 5.3.3.b., the TRPL experiments conducted at variable temperature yielded PL decay transients that can be fitted bi-exponentially and indicates a two decay processes. The faster process occurs due to exciton recombination in the defect-rich region, and the slower process results from intrinsic exciton recombination. The slower process was identified to be longer-lived than diffusion control.^{11, 52-53} These information therefore further support the viability of $(\text{HDA})_2\text{PbI}_4$ to undergo charge transfers upon photoexcitation.

Figure 5.3.2. a) pXRD of $(\text{HDA})_2\text{PbI}_4$ before and after being suspended and stirred in water for 30 min, b) Photo of a contact angle measurement on $(\text{HDA})_2\text{PbI}_4$

Figure 5.3.3. a) VTPL and b) VT-TRPL spectra of (HDA)₂PbI₄ after exciting at 390 nm.

To further characterise the photophysical character of the hydrophobic perovskites, DRS experiments were conducted and the Tauc plots calculated from the DRS data (Figure 5.3.4.a.) showed (HDA)₂PbI₄ and (HDA)₂SnI₄ to have band gaps of 2.3 eV and 1.9 eV respectively (Figure 5.3.4.b.). PESA was also conducted for (HDA)₂PbI₄ to measure the work function (Figure 5.3.4.c.).⁵⁴ The resulting PESA spectrum indicates that (HDA)₂PbI₄ has a work function of 5.70 eV, corresponding to a potential of 1.20 V vs normal hydrogen electrode (NHE), and can be assigned to the VBM of (HDA)₂PbI₄. In addition, the VBM value obtained for (HDA)₂PbI₄ is relatively similar and within the range of the VBM of other Pb based perovskites, which generally reports VBM of about 5.49 eV to 5.70 eV dependent on the organic component and the halide used.⁵⁵ This suggests that using HDA cations instead of other common cations had not significantly altered the general photophysical properties of the synthesised (HDA)₂PbI₄ perovskites, while increasing its hydrophobicity for its stability, thus increasing its promise for being applied to the subsequent photoredox reactions.

Figure 5.3.4. a) DRS spectra, b) Tauc plot, and c) PESA data of $(\text{HDA})_2\text{PbI}_4$ with the intercept at the abscissa for the VBM.

In the application of the perovskites to photoredox reactions, $(\text{HDA})_2\text{PbI}_4$ was shown to be able to oxidatively decarboxylate indoline-2-carboxylic acids to give indolines in the presence of light from a white LED under an inert atmosphere (Figure 5.3.5.a.). The $(\text{HDA})_2\text{PbI}_4$ was found to catalyse the decarboxylation of indoline-2-carboxylic acid to give indoline at 98% under a N_2 atmosphere, while catalysing the dehydrogenation of indoline-2-carboxylic acid to give indoles under an O_2 atmosphere.

Figure 5.3.5. a) The photoredox catalytic reaction scheme. b) Scope of substrates used in the photoredox reactions. **1** Indoline-2-carboxylic acid **2** 5-bromoindoline-2-carboxylic acid, **3** 5-trifluoromethylindoline-2-carboxylic acid, **4**. 5-methylindoline-2-carboxylic acid, **5**. 5-chloroindoline-2-carboxylic acid, **6**. 2-methylindoline.

Similarly, 5-methylindoline-2-carboxylic acid, 5-chloroindoline-2-carboxylic acid, and 5-bromoindoline-2-carboxylic acid were also investigated as potential substrates, and their respective decarboxylations into indolines were found to be about 82%. The 5-trifluoromethylindoline and 2-methyl-indoline were evaluated as substrates for dehydrogenation, yielding 48% and 17% of the respective indoles. With the use of diethyl ether (DE) as the solvent, the yield of 2-methylindole could be increased to 71%. On the other hand, decarboxylation of 5-methylindoline acid by the lead-free $(\text{HDA})_2\text{SnI}_4$ yielded only 30% of the indoline, while the dehydrogenation of 2-methylindoline led to a 47% yield of the indole in DE. This is most likely due to the oxidative instability and the abundance of traps for Sn(II) perovskites. Figure 5.3.6. illustrates the proposed mechanisms for the photocatalytic decarboxylation and the photocatalytic dehydrogenation reactions.

Figure 5.3.6. Proposed mechanisms for the decarboxylation (left) and dehydrogenation (right) reactions. [P] represents the perovskites.

To further investigate the mechanisms proposed in Figure 5.3.6., ferrocene and AgBF₄ were added as the hole and the electron scavengers, respectively. It was found that the presence of ferrocene would impede the decarboxylation reaction, whereas AgBF₄ behaved as a sacrificial electron acceptor with little effect on the decarboxylation reaction. This observation indicates that the rate determining step is the photooxidation of the perovskite. The product yield of the photocatalytic dehydrogenation reaction was found to decrease to 32% when an excess of Tiron (disodium 4,5-dihydroxy-1,3-benzenedisulfonate-4,5-dihydroxy-1,3-benzenedisulfonate) as a superoxide scavenger is added⁵⁶ which verified the role of superoxide radicals for the proposed dehydrogenation mechanism.

Moreover, the perovskites were recoverable and could be reused, with PXRD and XPS indicating minute changes to the chemical structure, elemental composition, and elemental oxidation states of the recycled perovskites. However, the initial polycrystalline perovskites had fragmented to smaller nanocrystals after the first

cycle of reaction, as observed by the decrease in the size distribution of the perovskites before and after reaction shown in Figure 5.3.7.. The fragmentation is similarly observed when the perovskites were examined with SEM, as seen in Figure 5.3.8.

Figure 5.3.7. The AFM image and height profile of $(\text{HDA})_2\text{PbI}_4$ a) before and b) after a catalytic reaction. The micron-sized polycrystalline material has clearly disintegrated into nanocrystals.

Figure 5.3.8. SEM of $(\text{HDA})_2\text{PbI}_4$ a) before and b) after a catalytic reaction.

5.4. Conclusions

Two alternate systems were explored in this chapter, as collaborative projects with my colleagues, for possible use alongside with the PEC and photocatalytic systems proposed in Chapter 3 and Chapter 4. Firstly, the Co-TAML complex **8** was able to electrocatalytically reduce protons to H_2 . However, the main reactive species of the electrocatalysis was shown to be an electrodeposited Co^0 nanoparticulate film. This was verified with XPS and was further confirmed by electron microscopy and EDS. Secondly, the use of HDA cations between the metal halide nanosheets was shown to retain their photophysical properties, while seeing improvements to the hydrophobic properties of $(HDA)_2PbI_4$ only. Furthermore, both perovskites were applied to photoredox reactions and $(HDA)_2PbI_4$ was recoverable after the reactions. However, the initial $(HDA)_2PbI_4$ micron-sized polycrystalline structures were observed to have fragmented to nanocrystals as observed by AFM and SEM. It would therefore be interesting to couple the systems described within with either the $BiVO_4/Fe-TAML$ or the $g-C_3N_4(urea)/PDI$ systems, to possibly add value to the overall PEC or photocatalytic systems.

5.5. Materials and equipments

Chemicals were obtained from Sigma-Aldrich, Merck, Alfa-Aesar, and Tokyo Chemical Industry Co., Ltd. (TCI). Unless otherwise mentioned, the commercial reagents were used as purchased. All reactions involving air- or moisture-sensitive compounds were performed by standard Schlenk techniques in oven-dried reaction vessels under an argon atmosphere. Compounds 5-chloroindoline-2-carboxylic acid hydrochloride monohydrate (Sigma-Aldrich, 99%) and 5-methylindoline-2-carboxylic acid hydrochloride (Sigma-Aldrich, 99%) were treated with NaHCO_3 under N_2 to remove HCl to provide the respective substrates 5-chloroindoline-2-carboxylic acid and 5-methylindoline-2-carboxylic acid before usage. Dichloromethane was desiccated using CaH_2 , degassed, and stored in a glove box before use. Tetrahydrofuran (THF) was distilled and stored in a glove box to minimize the moisture and O_2 contents. In addition to the other equipment used and listed in Section 3.5. of Chapter 3, the following additional equipment used are as detailed.

PL spectra were acquired using a Varian Cary Eclipse fluorescence spectrophotometer. Variable temperature PL (VTPL) studies were carried out and ultrafast femtosecond optical spectroscopic methods were employed to measure the VTPL data and the full width at half maximum (FWHM) of the crystal flakes. Samples were contained in an encapsulation equipped with liquid N_2 circulation. A Coherent Libra regenerative amplifier (50 fs, 1 kHz, 800 nm) seeded by a Coherent Vitesse Oscillator (100 fs, 80 MHz) were used as the pump laser sources. For pump wavelength tuning, the Coherent OPerA Solo optical parametric amplifier was used. Upon optically pumping the samples, the respective PL emissions were collected at

a backscattering angle of 150° by a collimating lens pair, guided into an optical fiber that was coupled to a spectrometer (Acton, SpectraPro 2500i and SP2300), and detected by a charge coupled device (CCD; Princeton Instruments, Pixis 400B). Time-resolved PL (TRPL) was collected using an Optronis Optoscope streak camera system.

PXRD experiments were conducted using a Bruker D8 Advance X-ray diffractometer with a copper ($K_{\alpha 1}$ (1.5406)/ $K_{\alpha 2}$ (1.5444) = 2) target X-ray tube set to 40 kV and 40 mA. Air-sensitive samples were prepared and loaded into an air-tight specimen holder purchased from Bruker (A100B33) in a glovebox before analysis.

The AFM experiments were conducted on a Bruker MultiMode 8 with a NanoScope V controller. The images were acquired using a silicon tip with a nitride lever from Bruker.

5.6. Experimental parameters for Co-TAML and Ni-TAML experiments

5.6.1. Electrochemical experimental parameters

The electrochemical experiments were performed using a Biologic SP-300 potentiostat. A three-electrode electrochemical cell was used with a glassy carbon referenced to the Ag/AgCl scale using $E(\text{NHE}) = E(\text{Ag/AgCl}) + 0.197 \text{ V}$. Before each experiment, the working electrode (glassy carbon, 3 mm in diameter) was polished using a 0.05 μm alumina suspension on a polishing pad, followed by sonication in deionized (DI) water for 10 min, and dried in air. The saturated Ar solutions were prepared by bubbling Ar through the solvents for 30 min.

Cyclic voltammetry of Co-TAML and Ni-TAML were conducted in acetonitrile containing 1.0 mM of Co-TAML or Ni-TAML, and 0.10 M *n*-Bu₄NPF₆ as the electrolyte salt. The scan rate used was 100 mVs⁻¹. To determine the quasi-reversible and reversible nature of the peaks observed for Co-TAML and Ni-TAML respectively, CV of the respective complex was conducted with increasing scan rate of 100 mVs⁻¹, 200 mVs⁻¹, 400 mVs⁻¹ and 1000 mVs⁻¹.

Controlled potential electrolysis (CPE) experiments were conducted with a glassy carbon electrode to confirm the identity of and quantify the product via gas chromatography (GC). The CPE measurements were performed with the same three-electrode setup as the CV experiments in 1.0 M of DI water in ACN with a glassy carbon rod as the working electrode. A constant potential of -2.0 V was

applied for 50 min. Samples of the headspace were removed by a gas-tight syringe and H₂ was identified as the product by GC

5.6.2. Magnetic susceptibility by the Evans method

The Evans method is used to determine the spin-only magnetic moment for a sample and provide an estimate of the number of unpaired electrons present. In a typical experiment, the difference in the NMR chemical shift caused by the presence of paramagnetic species in solution is measured.⁵⁷ It is summarized in the following equation:

$$\chi_M = 3\Delta f/4\pi f m + \chi_0 + \chi_0(d_0 - d_s)/m$$

- χ_M : mass susceptibility in cm³g⁻¹
- Δf : observed frequency difference in Hz
- f : 400 MHz on Bruker AV 400 NMR spectrometer
- m : mass of paramagnetic substance in g mL⁻¹
- χ_0 : mass susceptibility of solvent in cm³g⁻¹
- d_0 : density of solvent in g cm⁻³
- d_s : density of solute in g cm⁻³

Since d_s is not applicable,

$$\chi_M = 3\Delta f/4\pi f m + \chi_0$$

$$\mu_{eff} = \sqrt{(8 \chi_M T)}$$

In our experiment, 5.0 mg of Co-TAML was dissolved in 0.50 mL solvent and used for a ¹H NMR spectroscopic measurement. A 400 MHz NMR spectrometer was used. A peak separation of 0.281 ppm was observed, which was then introduced into the

equations above to give a χ_M of 3.55×10^{-3} and hence a μ_{eff} of $2.91 \mu_B$. This μ_{eff} value is close to the expected spin-only magnetic moment of an $S = 1$ complex, which has 2 unpaired electrons.

Table 5.6.1. Summary of the data used for the calculations of the magnetic susceptibility *via* the Evans method.

	Co-TAML	ACN
Mass (g)	5.0 mg	0.39
MW (g/mol)	474.2	N.A.
n (mol)	1.05×10^{-5}	N.A.
Density (g/mol)	N.A.	0.79
Volume (mL)	N.A.	0.50
Concentration (mol/ mL)	2.10×10^{-5}	
NMR shift		
δ (ppm)	2.245	1.964
Δ (ppm)	0.281	

5.7. Hydrophobic (HDA)₂MI₄ photocatalytic experimental parameters

5.7.1. Synthesis of (HDA)₂MI₄ perovskites

A two-step method was developed to synthesize HDA based perovskites. The HDAI salt was first prepared and isolated as a solid precursor. Metal halides were then mixed with HDAI in THF to give the precursor solutions. The perovskite products crystallized from the precursor solutions by vapor diffusion of diethyl ether into the THF at room temperature.

Compound 1-hexadecylammonium hydroiodide (HDAI): HDA (1.8 g, 7.5 mmol) was mixed with 1.1 mL of HI (57% wt. aq.) in 20 mL methanol with vigorous stirring for 3 h at 0 °C. The solvent was then removed under vacuum using a rotary evaporator. The residue was dissolved in a minimal amount of ethanol to give a concentrated solution, after which diethyl ether was added to yield a white solid. The product was washed with diethyl ether for three times and stored in a glovebox for further usage (2.55 g, 92% yield). ¹H NMR (DMSO-*d*₆, 500 MHz): δ = 0.85 (t, *J* = 6.8 Hz, 3 H), 1.24 (bs, 26 H), 1.50 (q, *J* = 7.5 Hz, 2 H), 2.71 – 2.81 (m, 2 H), 7.58 (s, 3 H) ppm. MS (ESI+, *m/z*) calculated for C₁₆H₃₆N⁺ [*M*⁺] *m/z* 242.46, found 242.23. Elemental analysis calculated (%) for C₁₆H₃₆IN: C, 52.03; H, 9.82; N, 3.79, found: C, 52.23; H, 9.64; N, 3.96.

(HDA)₂PbI₄ perovskite: The HDAI salt (184 mg, 0.500 mmol) and PbI₂ (115 mg, 0.250 mmol) were mixed in 5.0 mL of THF with stirring for 2 h at room temperature to yield a clear, light yellow solution. The perovskite product crystallized after vapor diffusion of diethyl ether into the as-prepared solution as pale yellow, thin flakes (136

mg, 52% yield). Elemental analysis calculated (%) for $C_{32}H_{72}I_4N_2Pb$: C, 32.03; H, 6.06; N, 2.34, found: C, 32.22; H, 5.83; N, 2.43.

(HDA) $_2$ SnI $_4$ perovskite. In a glove box filled with N_2 , the HDAI salt (184 mg, 0.500 mmol) and SnI $_2$ (93 mg, 0.25 mmol) were mixed in 5.0 mL of THF with stirring for 2 h at room temperature to yield a clear yellow solution. The perovskite product crystallized after vapor diffusion of diethyl ether into the as-prepared solution as dark red, thin flakes (166 mg, 60% yield). Elemental analysis calculated (%) for $C_{32}H_{72}I_4N_2Sn$: C, 34.59; H, 6.53; N, 2.52, found: C, 34.89; H, 6.41; N, 2.58.

5.7.2. Photocatalytic experimental parameters

All the photocatalytic experiments were carried out in 25 mL reaction tubes that were sealed under a N_2 atmosphere. For the reactions with O_2 , the reaction mixtures were cooled with liquid N_2 until the solvents froze, degassed under vacuum and refilled with O_2 . The reaction mixtures were then exposed to visible light radiation under a white LED lamp (equipped with a 48 W LED chip and a cooling fan) with vigorous stirring. The products were collected by removing the solvents under vacuum. Dibromomethane (2 H at $\delta = 5.41$ in DMSO- d_6) was used as an internal standard to calculate the yield by NMR spectroscopy. All the NMR spectra are from crude samples without further purification and only the product peaks are processed.

5.8. References

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Chapter 6

Conclusions and future works

6.1. Summaries and future works

6.1.1. BiVO₄/Fe-TAML PEC system

Through the current work presented in Chapter 3, Fe-TAML was shown to have been successfully incorporated on BiVO₄ and the resulting BiVO₄/Fe-TAML utilised in a PEC system. In the PEC system, the novel photoanode was able to oxidise variety of substrates in the presence of light and with an applied potential.

However, further improvements of the PEC oxidation reactions can be done by optimisation of the reaction rates and characterisation of the reaction products. Previous studies indicated that bisphenols were generally oxidised to a variety of aromatic intermediates before finally producing CO₂,¹ while lignin was converted to its monomers via cleavage of β -O-4 bonds in native lignin.² Thus, it would be beneficial to determine the extent of the reaction and propose a plausible reaction mechanism, as a measure to evaluate the viability of eventual industrial application.

6.1.2. A g-C₃N₄(urea)/PDI photocatalytic system

As reported in Chapter 4, a g-C₃N₄(urea)/PDI material was successfully synthesised with a high surface area and with PDI dopants. It was shown that g-C₃N₄(urea)/PDIs have a slightly wider band gap than that of its precursor g-C₃N₄(urea), and that there is a positive shift to both the valence band edge and conduction band edge by different magnitudes. The g-C₃N₄ (urea)/PDI material was then applied to the photocatalytic degradation of BPF and was able to completely degrade BPF in 2 h under illumination from a white LED. The high surface area had a greater effect on the rate generation of the photogenerated holes, peroxy radicals, and hydroxyl radicals than the addition of the PDI moieties.

In the future, the investigation would be the utilisation of the photogenerated holes in g-C₃N₄(urea)/PDI for the activation of co-catalyst, such as Fe-TAML. The photogenerated holes could activate the co-catalyst by increasing the metal center's oxidation state so that it could oxidise other substrates in the solution. In addition, the characterisation of the products from the BPF degradation reaction would provide additional insights for the reaction mechanism. Other phenolic substrates, including BPS and lignin, could also be examined for reactivity in order to assess the oxidative capabilities of g-C₃N₄(urea)/PDI more thoroughly.

6.1.3. Alternative photocatalysts and electrocatalyst

Through the collaborative works, Co-TAML was first observed to be electrocatalytically active for proton reduction in water-ACN mixtures. However, it is not ideal as its active catalytic form is a result of demetallation of the Co-TAML to a Co^0 nanoparticle film. Therefore, other alternative electrocatalytic reduction reactions could be attempted for Co-TAML, as a way to investigate and subsequently utilise the catalyst as a plausible co-catalyst on a photocathode in a tandem PEC cell.

Secondly, the use of HDA cations between the metal halide nanosheets was shown to increase the stability of the $(\text{HDA})_2\text{PbI}_4$ in moist environments, and as such was able to catalyse photoredox decarboxylation and dehydrogenation reactions in organic solvents. One possible way forward is to investigate the direct application of the perovskites in similar reactions, but with bisphenols and lignocellulose as the potential substrates. Studies had shown that the photocatalytic carbon-carbon bond cleavage of β -O-4 bonds in lignin model compounds is a viable way to obtain aromatic monomers from lignin.² Thus it would be potentially viable for perovskites to effect the same reaction for lignin.

6.2. Future directions

Having demonstrated that the $\text{BiVO}_4/\text{Fe-TAML}$ PEC systems are capable of oxidising phenolic compounds, and $\text{g-C}_3\text{N}_4(\text{urea})/\text{PDI}$ was able to degrade BPF via the generation of ROS through the reduction of oxygen, the usage of either system in a tandem PEC cell should be investigated. Nanoporous BiVO_4 photoanode has previously been applied in tandem with a-Si photocathode(a-SiC:H film) for H_2 and O_2 evolution.³ Therefore, it would be plausible to couple the $\text{BiVO}_4/\text{Fe-TAML}$ PEC system with a photocathode for the concurrent oxidation of phenolic compounds, while generating other value-added products or H_2 at the photocathode. Similarly, recent studies regarding the usage of $\text{g-C}_3\text{N}_4$ in a PEC setup have led to an expansion of its application and capabilities, such as in organic photovoltaic cells and supercapacitors.⁴ Therefore, it would be interesting to use the novel $\text{g-C}_3\text{N}_4(\text{urea})/\text{PDI}$ in similar applications to develop a sustainable method for reducing chemical pollutants and meet the increasing demands for chemical products.

Furthermore, the investigations into Co-TAML and hydrophobic metal halide perovskites had shown interesting results in proton reduction reactions and decarboxylation reactions respectively. Their ability to work in conjunction with a corresponding photoanode or photocathode would be an interesting concept to explore further, such that a greater value of each photocatalytic system can be obtained from such tandem setups.

6.3. References

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