Characterization and evaluation of novel nano-structured bismuth vanadate and hybrid nanomaterials as more sustainable and enhanced photocatalysts in organic transformations

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**NANYANG
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SINGAPORE

**CHARACTERIZATION AND EVALUATION OF
NOVEL NANO-STRUCTURED BISMUTH
VANADATE AND HYBRID NANOMATERIALS AS
MORE SUSTAINABLE AND ENHANCED
PHOTOCATALYSTS IN ORGANIC
TRANSFORMATIONS**

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**INTERDISCIPLINARY GRADUATE SCHOOL
ENERGY RESEARCH INSTITUTE @ NTU (ERI@N)**

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TRANSFORMATIONS**

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

2019

Statement of Originality

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

10 February 2019

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Date

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NG KIA SHEUN LEONARD

Supervisor Declaration Statement

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

10 February 2019

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Date

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Assistant Professor Dr. Soo Han Sen

Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journals where I was the first and co-author.

Chapter 4 is published as L. K.-S. Ng, E. J.-C. Tan, T. W. Goh, X. Zhao, Z. Chen, T. C. Sum, H. S. Soo. Mesoporous SiO₂/BiVO₄/CuO_x nanospheres for Z-Scheme, visible light driven aerobic photoredox coupling of amines. *Applied Materials Today* **15**, 192-202 (2019). DOI: 10.1016/j.apmt.2019.01.010.

The contributions of the co-authors are as follows:

- A/Prof. H. S. Soo provided the initial project direction and edited the manuscript drafts.
- I wrote and revised the manuscript drafts.
- I performed all the materials synthesis, characterization, and application studies.
- I collected X-ray diffraction patterns, electron microscopy data, most spectroscopic data, and conducted data evaluation. All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation, and in School of Physical and Mathematical Sciences, Chemistry of Biological Chemistry division.
- Mr. E. J.-C. Tan assisted with the synthesis of mesoporous silica nanoparticles, and some of the substrates screening.
- Mr. T. W. Goh assisted in the collection of UV photoelectron spectroscopy, photoluminescence, and TR-PL spectroscopy data. Mr. T. W. Goh and Prof. T. C. Sum provided guidance in the interpretation of the spectroscopic data.

- Dr. X. Zhao assisted in the collection photocurrent measurements data and provide guidance in the interpretation of the data.
- Prof. Z. Chen provided insightful suggestions in the material synthesis.

Chapter 5 is published as D. Ghosh, B. Febriansyah, D. Gupta, L. K.-S. Ng, S. Xi, Y. Du, T. Baikie, Z. Dong, H. S. Soo. Hybrid nanomaterials with single-site catalysts by spatially controllable immobilization of nickel complexes *via* photoclick chemistry for alkene epoxidation. *ACS Nano* **12**, 5903-5912 (2018). DOI: 10.1021/acsnano.8b02118.

The contributions of the co-authors are as follows:

- A/Prof. H. S. Soo provided the initial project direction and edited the manuscript drafts.
- Mr. D. Ghosh wrote and revised the drafts of the manuscript. The part of the manuscript with electron microscopy data and some X-ray spectroscopic data were revised by me.
- Mr. D. Ghosh performed all the metal complexes and materials synthesis, some of the characterization, all application studies, and conducted data evaluation.
- Mr. B. Febriansyah assisted with the synthesis and characterization of the metal complexes. I assisted with the synthesis of the mesoporous silica nanoparticles.
- Ms. D. Gupta assisted in the collection of X-ray absorption spectroscopy data. Ms. D. Gupta, Dr. Dr. S. Xi, and Dr. Y. Du provided guidance in the interpretation of the spectroscopic data.
- I collected all electron microscopy data, and conducted data evaluation. All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation, and in School of Physical and Mathematical Sciences, Chemistry of Biological Chemistry division. I may have about 25% contribution to the work.

- Dr. T. Baikie, and Prof. Z. Dong provided insightful suggestions during the manuscript preparations.

10 February 2019

Date

A handwritten signature in black ink, appearing to read 'Leonard', written diagonally across the line.

NG KIA SHEUN LEONARD

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- ¹. Adapted with permission from *ACS Nano* 2018, 12, 5903-5912. Copyright 2018 American Chemical Society.¹ 129
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Abstract

In light of the growing demand for alternative energy sources, artificial photosynthesis (AP) has shown great potential as one of the solutions in the production of chemicals by harnessing renewable solar energy from the sun. In recent years, extensive research has been done for photocatalytic (PC) processes with semiconducting metal oxides as potentially efficient, low cost, and environmentally friendly catalysts for AP to produce solar chemicals.

We have synthesized and fully characterized a mesoporous bismuth vanadate-copper oxide-silica semiconductor nanocomposite ($\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$) to act as a chromophore in a Z-scheme system for effective light harvesting and charge separation in the synthesis of solar chemicals. Notably, the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres perform seven times faster than bulk BiVO_4 and provide higher yields for oxidative coupling of amines to imine products. The superior photocatalysis of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ is attributed to the surface CuO_x nanoparticles that increase the average PL lifetime from 2.3 to 4.5 ns, which improved the charge separation and decreased the unproductive recombinations of electron-hole pairs. To the best of our knowledge, this is the first report of uniform nanoparticulate $\text{BiVO}_4/\text{CuO}_x$ catalysts that absorb light *via* a Z-scheme for photoredox organic synthesis. We envision that this work will pave the way for the use of more ideas from AP in the synthesis of fine chemicals, agrochemicals, and active pharmaceutical ingredients.

Apart from being a photocatalyst, $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres and various metal oxides including titanium dioxide (TiO_2), cerium oxide (CeO_2), and tungsten oxide (WO_3) can be employed as light harvesting supports for the immobilization of molecular complexes to enhance the performance of their homogeneous molecular counterparts. An oxidatively stable anchoring group, maleimide, is shown to form covalent linkages with surface hydroxyl

functionalities of metal oxide nanoparticles by photoclick chemistry. Definitive evidence of the active site molecular structure was achieved from a broad range of characterization techniques. The hybrid nanomaterials function with essentially quantitative oxidative conversions of internal and terminal alkenes with molecular selectivity, but can operate in a broader range of solvents, including more eco-friendly ones.

In conclusion, a novel photocatalyst $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ was successfully fabricated and tested in this project. Apart from being a photocatalyst, $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ has the potential to function as a light harvesting support for the immobilization of molecular complexes that can synergize the benefits of both homogeneous and heterogeneous catalysts and enhance the PC performance.

Abbreviations

Symbol	Definition
°C	Centigrade degree
Å	Angstrom
¹ H NMR	Proton nuclear magnetic resonance spectroscopy
¹³ C NMR	Carbon nuclear magnetic resonance spectroscopy
ACN	Acetonitrile
aq.	Aqueous
a.u.	Arbitrary unit
BET	Brunauer Emmett Teller method
Bi	Bismuth
BiVO ₄	Bismuth vanadate
BJH	Barret-Joyner-Halenda method
cald.	Calculated
CB	Conduction band
CBM	Conduction maxima
CD ₃ CN	Deuterated acetonitrile
CeO ₂	Cerium oxide
CTAC	Cetyltrimethylammonium chloride
Cu	Copper
Cu ₂ O	Copper(I) oxide
CuO	Copper(II) oxide
DRS	Diffuse reflectance spectroscopy
e ⁻	electrons
eq.	Equivalent (s)
EDS	Energy dispersive X-ray spectroscopy
EDX	Energy dispersive X-ray
<i>E_g</i>	Band gap(s)
EPR	Electronic paramagnetic resonance

eV	Electron volt
FE-SEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
FTO	Fluorine-doped tin oxide
GC	Gas chromatography
h	Hour(s)
h ⁺	holes
HR-TEM	High resolution transmission electron microscopy
ICP-OES	Inductively coupled plasma optical emission spectroscopy
M	Molar
Me	Methyl group
min	Minute(s)
mol	Moles
mol%	Mole percent
mg	milligrams
mmol	Millimoles
ml	Millilitres
m/z	Mass to charge ratio
NHE	Normal hydrogen electrode
Ni	Nickel
nm	Nanometres
NMR	Nuclear magnetic resonance spectroscopy
PC	Photocatalytic
PL	Photoluminescence
PXRD	Powder X-ray diffraction
PV	Photovoltaic
rpm	rotations per minute
r.t	room temperature
SC	Semiconductor
SiO ₂	Silica/Silicon dioxide

TEM	Transmission electron microscopy
TEOA	Triethanolamine
TEOS	Tetraethyl orthosilicate
TiO ₂	Titanium dioxide
TOF	Turnover frequency
TR-PL	Time-resolved photoluminescence
UV	Ultraviolet
VB	Valence band
VBM	Valence band maxima
Vis	Visible
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
WO ₃	Tungsten oxide
wt%	weight percent
V ^v	Vanadium (5+)
%	percent
δ	chemical shift scale (delta)
λ	wavelength
τ	excited lifetime
μ l	microliters
μ mol	micromoles

Chapter 1

Introduction

This chapter describes the problems that the thesis address. At present, it is well-established that a growing demand for energy, the need for improved chemicals production, and increasingly severe environmental challenges constitute paramount issues for the 21st century. Consequently, fast depleting, unsustainable fossil fuel resources and strict environmental regulations motivate the search for sustainable and environmentally friendly renewable chemical sources. The key research challenges, objectives, and scope of work are clearly stated. Hypotheses are laid out clearly. Moreover, the dissertation overview is depicted in which the gist of each chapter is described.

1.1 Motivation: Solar energy generation, and storage; climate change, and sustainability

The rapidly growing human population has placed tremendous stress on the planet for energy and raw materials. At present, the world relies greatly on non-renewable fossil fuels, which account for approximately 80% of the global energy needs to maintain economic growth.¹ Moreover, these limited fossil fuels are being burnt on an unprecedented scale, releasing carbon dioxide (CO₂) into the environment at amounts exceeding 30 billion tonnes annually.² CO₂, one of the principal “greenhouse gases”, is believed to be a major contributor to global warming and the extraordinary climate change phenomena. Regardless of climate change, the argument for greater sustainability in energy production is irrefutable and perhaps a more unifying argument for change. Future generations will eventually be left with a world void of easily accessible fossil fuels, and this will require strategies to find alternatives.

In addition, as the global population and affluence increase, the use of various materials will also increase in volume and diversity. For the past century or more years since the start of industrialization, society has been increasingly reliant on the products of the petrochemical industry to supply man-made fibers for clothing, plastic artefacts, cosmetics, and paints. Hence, the increasing global demand for energy, depletion of fossil fuel reserves, and environmental concerns over rising CO₂ emissions warrant urgent actions on the development of renewable sources of chemicals and fuels as well as mitigation of environmental problems.

Addressing power generation using renewable and/or green energy sources would lead to a dramatic change in the global consumption of fossil fuels. Renewable or green energy are sources that are inexhaustible and have low or net zero CO₂ production.³⁻⁴ Among various renewable energy sources, solar energy is believed to be the most promising alternative as it is one of the most abundant

and sustainable natural energy resources. Every hour, the sun emits about 4.3×10^{20} joules of energy to the Earth's surface, which is more than what the entire world consumes annually (4.1×10^{20} joules) from fossil fuels.⁵ Visible light, ranging from 380 nm to 700 nm, is one of the strongest output range of the Sun's total irradiance spectrum that reaches the Earth's surface.⁶ The solar spectrum comprises 50% and 45% of visible light and infrared respectively, while ultraviolet (UV) light only occupies about 5% of the solar spectrum.⁷

Photosynthetic organisms participate in complex biological processes in order to accumulate and utilize solar energy while involving only natural elements that can be found in different ecosystems to store this energy in the form of chemical bonds in carbon compounds.⁸⁻⁹ A vital feature of the light absorbing mechanism in green plants is the incorporation of two visible light harvesters in Photosystems I and II (chlorophylls P700 and P680, respectively), where photo-induced electrons are transferred between the interfaces in a “Z-scheme” fashion. In principle, a “molecular photodiode” is constructed for effective charge separation and light absorption, allowing P680 to accumulate the four photo-generated holes to oxidize water, while P700 gains the four photoelectrons to reduce two NADP^+ to NADPH.¹⁰ As a result, it is possible that a unique self-sustaining system can be re-created by mimicking natural photosynthesis to address our current demands.

Scientists have devoted research efforts to the development of AP for the synthesis of solar fuels *via* water splitting or CO_2 reduction.¹¹⁻²⁰ However, AP is not restricted to produce only H_2 and O_2 *via* water splitting but also includes alternative approaches to synthetically fabricate other chemicals using light as the energy source, as the term, AP suggests. From this perspective, a number of research groups have broadened the scope of light utilization applications in the production of solar chemicals and fuels, while using only earth abundant elements.¹⁰

Currently, silicon-based photovoltaic (PV) cells are widely used to harness solar energy and convert it directly to electrical energy. However, silicon-based PV cells are limited by the high cost of producing highly crystalline silicon needed for high efficiency solar cells. Invented by Michael Grätzel, dye-sensitized solar cells (DSSCs) represent new and cheaper strategy to efficiently convert solar energy into electricity via ultrafast charge separation events.²¹ This kind of chemistry can form the basis of a photosynthetic unit provided that the separated charges are able to drive multi-electron catalytic reactions. Extensive studies have utilized the concept of the DSSC and one them is a hybrid artificial photosynthetic system that stores light energy in the chemical bonds of a solar fuel (Figure 1.1).²² A DSSC's main function is to convert light energy to electrical energy. Conversely, a hybrid artificial photosynthetic system mimics the natural photosynthesis system, which converts light energy to chemical energy. When visible photons are absorbed by the light harvesting agent, charge separation occurs, generating holes and electrons at the valence band (VB) and conduction band (CB) respectively. Subsequently, electrons at the CB are transported to the reduction cocatalyst to drive reduction reactions, while the oxidation cocatalyst performs oxidation by drawing electrons back into the holes of the VB. This process repeats, driving the redox reactions.²²⁻²³

Figure 1.1. Proposed artificial photosynthetic unit that couples molecular cocatalysts to a semiconductor light absorber. Adapted with permission from *Acc. Chem. Res.* 2013, 46, 2355-2364. Copyright 2018 American Chemical Society.²²

To date, molecular photosensitizers and semiconductors (SCs) have been used as light harvesting agents to absorb light efficiently. While the utilization of a

molecular photosensitizer for AP is promising,²⁴⁻²⁵ SCs seem to receive more attention due to their broad spectral absorption and relatively higher stability, allowing a wider range of potential applications.^{22, 26} SCs have been widely applied in various areas ranging from renewable energy to environmental clean-up where they can play two roles: that of catalysts and/or light absorbing supports.

1.2 SCs as photocatalysts

Since the pioneering studies on water splitting with TiO_2 ,²⁷ there has been impressive progress on using SCs as chromophores in AP systems, with work on nanostructuring and doping among the many popular routes. TiO_2 is recognized as one of the most practical and prevalent SC owing to its chemical stability, non-toxicity, abundance, and cost-effectiveness. So far, TiO_2 has been used for various applications such as PC self-cleaning,²⁸ PC antibacterial systems,²⁸ photo-induced super hydrophilicity,²⁸⁻²⁹ photodegradation of pollutants and environmental remediation,^{28, 30-34} as well as sensors,³⁵ photovoltaics,^{34, 36-44} and water splitting for solar hydrogen production.^{27, 45-47} However, TiO_2 only absorbs light in the UV region due to the large band gap (E_g) of 3.0 eV for rutile and 3.2 eV for anatase. Since UV light accounts for only approximately 5% of the solar spectrum, the practical application of TiO_2 SC is limited. Therefore, in order to fully utilize the full solar spectrum, visible light harvesters such as BiVO_4 , Cu_2O , WO_3 , and Fe_2O_3 are being explored.

1.3 SCs as light harvesting support

Catalyst deactivation is a persisting problem for homogeneous inorganic complexes. Heterogenization of molecular complexes supported on high surface area nanoparticles to form isolated single-site catalysts can potentially overcome issues on catalyst oligomerization, ligand oxidation, and demetallation pathways.⁴⁸ Moreover, intermediates that are extremely reactive such as first row

transition metal hydrides,⁴⁹ molecular-imprinted cavities with ruthenium catalysts,⁵⁰ and iron-based water oxidation catalysts,⁵¹ which would then be unstable in solution, have been characterized and employed through anchoring of the catalyst on bulk metal oxide surfaces. The immobilization of molecular complexes to fabricate isolated single-site heterogeneous hybrid nanomaterials⁵² is thus still an emerging field that can address many catalyst deactivation problems and also present alternative reactivity and durability in environmentally benign solvents with supposedly high selectivity using homogeneous catalysts.

1.4 Key research challenges

- 1) Heterogeneous photocatalysts, in particular metal oxides, have proven to be effective in various applications such as water splitting and removal of some toxic organic contaminants. So far, TiO_2 has been shown to be one of the most affordable and effective photocatalysts. However, it is only capable of absorbing UV light due to its wide energy band gap of 3.2 eV. Unfortunately, UV light only accounts for 5% of the entire solar spectrum. Therefore, it is necessary to explore other visible light absorbing semiconductors to effectively utilize more of the solar spectrum. Moreover, much work has been dedicated to extend the light absorption of a variety of metal oxide semiconductors into the visible light region, but only limited success has been reported.
- 2) Metal oxide semiconductors face the problem of electron and hole pair recombinations. This reaction hinders the charge extractions that are necessary for useful photoreactions and thus, contributes to inefficiency in the photocatalytic process. Moreover, the size of the particle plays an important role in influencing the charge transport, recombination rate, and hence the system efficiency. Therefore, the introduction of mesoporosity as well as nanoscaling of the material could increase the surface active sites and

further improve the charge extraction efficiency that could improve the overall PC activity.

- 3) The adsorption of chemical molecules on heterogeneous photocatalysts is rarely emphasized in photocatalytic reactions. The ability of a material to adsorb organic molecules on its surface greatly enhances the overall performance since it provides a shorter path for charge interaction. It is challenging to modify surfaces of photocatalytic materials to adapt to this criterion.
- 4) Heterogenization of molecular metal complexes by anchoring them on metal oxide supports could potentially address a number of catalyst deactivation problems. However, it is important to ensure that the complexes are covalently anchored on the support and not simply adsorbed. This is to ensure recyclability of the hybrid nanomaterials. Furthermore, the accurate characterization of these heterogeneous hybrid nanomaterials is challenging, though it is important to provide definitive evidence for the successful anchoring.

The motivation of this thesis thus lies in the development of a variety of novel photocatalysts that have enhanced properties for more efficient and green organic transformations that can lead to more sustainable and environmentally friendly renewable chemical sources.

1.5 Objectives and scope

The objectives (number bullets) and scope (black dot bullets for $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ and white dot bullets for hybrid nanomaterials) encompass the following milestones:

- 1) Development of a novel and efficient visible light absorbing metal oxide materials to be used as photocatalysts and/or light absorbing supports for PC applications
 - Fabrication of a visible light active mesoporous $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ composite to act as a photocatalyst in a heterojunction system.
 - Fabrication of heterogeneous hybrid nanomaterials by stabilization of molecular scaffolds on the mesoporous $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ composite support and a select number of well-defined metal oxides through cooperative anchoring groups.
- 2) Full characterization of the novel materials
 - The mesoporous $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ composite and heterogeneous hybrid nanomaterials will be characterized in an attempt to link the structural, electronic, and optical properties of the materials to their PC activity. Some common characterization of the materials can be done with diffuse reflectance UV-vis spectroscopy (UV-DRS), electron microscopy, powder X-ray diffraction spectroscopy (PXRD), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS).
 - Characterization of the heterogeneous hybrid nanomaterials to affirm that the molecular complexes were anchored on the metal oxide and not leached out.
- 3) Photocatalytic activity evaluation
 - Evaluation of the mesoporous $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ composite PC performance by comparing to bulk BiVO_4 particles in the conversion and yield efficiency from primary amines to imines (“solar chemicals”). This is achieved by performing the reaction in the presence of the photocatalyst, in which the conversion efficiency is assessed by proton nuclear magnetic resonance (^1H NMR) spectroscopy.
 - Propose possible mechanisms for the observed enhanced activity of the

composite photocatalyst, and experimentally demonstrate their validity.

- Evaluation of the heterogeneous hybrid nanomaterials PC performance by comparing to its homogeneous counterpart in the conversion and yield efficiency with various organic reactions. This is achieved by performing the reaction in the presence of the photocatalyst, in which the conversion efficiency is assessed by gas chromatography-mass spectrometry (GC-MS) or ^1H NMR spectroscopy.
- Demonstrate various metal oxides as suitable light absorbing support for the anchoring of molecular complexes, such as metal complexes and dye molecules. I plan to improve the performance of both homogeneous and heterogeneous catalysts. The metal oxides that can be used as the light absorbing supports are for example TiO_2 , WO_3 , and BiVO_4 .

4) Recyclability studies

- Evaluation of the recyclability of the mesoporous $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ composite with multiple PC runs. Characterization methods such as SEM-EDS, XPS, and fourier transform infrared (FT-IR) spectroscopy.
- The recyclability the hybrid nanomaterials will be evaluated with multiple PC runs. Characterization methods include SEM-EDS, XPS, and FT-IR.

1.6 Hypotheses

- 1) Loading BiVO_4 precursors into silica can prevent aggregation of BiVO_4 nanoparticles and induce greater PC abilities compared to bulk BiVO_4 microparticles due to improvement of the charge extraction efficiency
- 2) Mesoporous BiVO_4 nanoparticles induce greater PC ability than bulk BiVO_4 crystals due to the increase in surface active sites
- 3) The presence of copper oxide nanoparticles on BiVO_4 nanostructures might extend the light absorption and also form a heterojunction system, which can

improve charge separation that will enhance the overall PC activity.

- 4) The anchoring of molecular complexes on the metal oxides as supports creating an isolated single-site to overcome the issue on catalyst oligomerization, ligand oxidation, and demetallation.

1.7 Dissertation overview

The thesis include 7 separate chapters.

Chapter 1 describes the problem statement and provides the motivation for the research. The objectives and scope as well as the hypotheses are also outlined.

Chapter 2 addresses the research gaps that mainly focus on BiVO₄-based SCs and review the literature concerning the physical and optical properties of BiVO₄ as well as its limitations as a photocatalyst. Relevant and interesting emerging research efforts to overcome these limitations with an emphasis on the development of BiVO₄ related heterojunctions are described. Finally, alternative strategies to enhance the PC performance of BiVO₄ are reviewed.

Chapter 3 discusses the principles of the synthesis and characterization techniques. Also, the rationale for the choice of the experimental methods used is described followed by the detailed protocols of how the techniques are carried out.

Chapter 4 details the design, synthesis, characterization, and the PC performance of the SiO₂/BiVO₄/CuO_x nanospheres in the photo-oxidation of primary amines to imines. The proposed mechanism and the recyclability of the photocatalyst will be discussed as well.

Chapter 5 details the development of hybrid nanomaterials with single-site catalysts by immobilization of Ni molecular complexes on TiO_2 , WO_3 , and CeO_2 acting as the supports, with photoclick chemistry. Mesoporous SiO_2 and bulk BiVO_4 from Chapter 4 were also selected as the solid supports for the anchoring of Ni complexes to mimic the surface composition in $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres as a proof of concept.

Chapter 6 presents an outlook for a potential platform technology on the photo-oxidative C-C bond cleavage of lignin to obtain renewable sources of aromatic compounds, following the initial success of the work reported in Chapter 5. A preliminary study on the anchoring of V^{V} complex on $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres and TiO_2 was attempted.

Chapter 7 summarizes the findings and provides insights about the implication and novelty of the research. It reiterates the extent to which the hypotheses are proven and evaluates if the design requirements have been met. Finally, opportunities and strategies for future work are presented.

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Chapter 2

Literature Review

This chapter addresses the research gaps, which mainly focus on BiVO₄ based SCs and reviews the literature concerning the physical and optical properties of BiVO₄ as well as its limitations as a photocatalyst. Relevant and interesting emerging research efforts to overcome these limitations, with emphasis given to the development of BiVO₄ related heterojunctions are described. Finally, alternative strategies to enhance the PC performance of BiVO₄ are reviewed.

2.1 Visible light active photocatalysts

In recent years, pristine visible light-active SCs are being actively sought after for better utilization of the full solar spectrum.¹ It is important to note that different types of visible light-active SCs that are characterized by certain activities under sunlight irradiation represent two specific groups: metal oxides and metal chalcogenides such as WS₂, PbSe, FeS₂, CdS, CdSe, and MoS₂. The latter possess relatively narrow E_g , which can efficiently absorb a broad range of solar irradiation, but they often demonstrate limited stability because of photo-corrosive phenomena that affect the photoactivity.

Researchers have historically studied metal oxides because of their chemical- and photo-stability, ease of fabrication, and comparably low cost. Still, in most cases, binary metal oxides have wide E_g energies related to positive VB, usually including O 2p orbitals that are situated at +3.0 V in comparison to the normal hydrogen electrode (NHE), which restricts their ability to absorb light; for examples, with E_g energies of 3.2–3.3 eV for ZnO, 3.0–3.2 eV for TiO₂, and 2.7 eV for WO₃.² In order to use solar energy efficiently, the design of metal oxides with smaller E_g is required. For efficient photo-responses, metal cations in metal oxide SCs typically consist of empty d orbitals (d^0 electronic configuration), or fully filled d orbitals, (d^{10} electronic configuration) that are not considerably negative.³ Hence, lowering these energy bands becomes thermodynamically undesirable. To reduce the E_g of metal oxides, it is necessary to use a new VB formed by orbitals of the elements that are not related to O 2p.⁴ Thus, the focus is on ternary metal oxides that have VBs related to atomic orbitals of more than one element. Orbitals of Ag 4d in Ag⁺, Bi 6s in Bi³⁺, Sn 5s in Sn²⁺, and Pb 6s in Pb²⁺ influence the VB formation by O 2p orbitals in metal oxides.⁵ Therefore, it has been observed that Bi, Ag, Pb, and Sn (BiVO₄,⁵ Bi₂WO₆,⁶ AgNbO₃,⁷ PbCrO₄,⁸ and SnNb₂O₆ ⁹) in ternary metal oxides have somewhat narrower E_g with promising abilities to absorb visible light.

2.2 Introduction to BiVO₄ photocatalyst

In recent years, BiVO₄-based materials have emerged as alternatives to binary oxides due to their optimal electronic and optical properties that make them suitable candidates for efficient visible light driven photocatalysis. In 1963, BiVO₄ was first synthesized by Roth and co-workers by just heating a mixture of vanadium(V) oxide and bismuth oxide at high temperatures,¹⁰ Due to its non-toxic nature,¹¹ BiVO₄-based compounds became actively studied because of their potential to be used as substitutes for cadmium-, lead-, and chromate-based pigments. These components are generally utilized in the coating and plastics industry (for example, BASF). During the past four decades, researchers demonstrated their interest in BiVO₄ by examining its technological properties, including acousto-optical features,¹² ferroelasticity,¹²⁻¹⁷ and ionic conductivity,¹⁸ as they significantly depend on the crystal structures of BiVO₄.

2.2.1 Crystal structures and phase transitions

There are three main crystal structures commonly obtained with BiVO₄. One of them is a scheelite structure with a tetragonal phase, another is a scheelite structure with a monoclinic phase, and a third is a zircon structure with a tetragonal phase.^{13, 19} Vanadium (V) ions in these structures are coordinated with four oxygen (O) atoms in a specific tetrahedral site. The bismuth (Bi) ions, are coordinated to eight O atoms. There is a difference between the scheelite and zircon structures. In a scheelite structure, each Bi ion is connected to eight vanadate (VO₄) tetrahedral units. In a zircon structure, there are only six VO₄ related to one Bi ion.²⁰ For BiVO₄ with a specific scheelite structure, a monoclinic scheelite (m-s) BiVO₄ is distorted with two different V–O bond lengths (1.77 Å and 1.69 Å), while the V–O bonds in the tetragonal scheelite (t-s) BiVO₄ are all of an equal length (1.72 Å).²¹ The (m-s) BiVO₄ structure is stable at a high temperatures, and they can be obtained from the irreversible phase transformation from a tetragonal zircon (t-z) structure at 400 to 500°C.²²

Irreversible phase transition from (t-z) to (m-s) BiVO_4 structures was also achieved through mechanical crushing.¹⁷ The (m-s) BiVO_4 can be obtained via an aging and crystallization process of (t-s) BiVO_4 at room temperature.²²⁻²³ Thus, the formation of (t-s) BiVO_4 under these conditions is kinetically favorable, but (m-s) BiVO_4 can be viewed as a more thermodynamically stable form. In addition, it is important to note that heat treatment can catalyze phase transitions because the transformation of scheelite BiVO_4 with monoclinic into tetragonal phases is observed at 255°C.

2.2.2 Optical properties and electronic structures

Among the three polymorphs of BiVO_4 , (m-s) BiVO_4 , in particular, became actively researched after the publication of a paper by Kudo and co-workers on the visible light-triggered water oxidation over the three polymorphs of BiVO_4 in the presence of Ag^+ ions as electron scavengers.²⁴ They observed higher O_2 evolution activity (water oxidation) from aqueous AgNO_3 solutions for (m-s) BiVO_4 mainly due to the wider E_g of (t-z) BiVO_4 .⁵ In the scheelite BiVO_4 , it is possible to find out a hybridized band structure with Bi 6s and O 2p orbitals. Therefore, with reference to a hybridized Bi 6s–O 2p linked to VB and the O 2p VB, the electronic transition to the V 3d CB can result in the formation of a lower E_g energy of scheelite BiVO_4 (2.4 eV) in comparison to the energy associated with zircon BiVO_4 (2.9 eV) with V–O transitions.⁵ Computational methods using density functional theory (DFT) calculations to study the BiVO_4 crystal structure were reported in 2009, suggesting that the hybridized VB may exist.²⁵ However, it was only in 2011 that Payne and co-workers conducted experiments with the help of XPS, XAS, and X-ray emission spectroscopy (XES)²⁶ to find evidence to support the hybridization of Bi 6s and O 2p orbitals at the VB maximum (VBM) of monoclinic BiVO_4 .

Contrary to the report by Walsh and co-workers,²⁵ BiVO_4 is viewed as an indirect E_g SC, which was supported by the recent study by Cooper and co-workers, where they provided a rigorous analysis of the band structure of the BiVO_4 . The

researchers combined DFT calculations and experimental evidence from X-ray spectroscopies including XAS, XES, resonant inelastic X-ray scattering (RIXS), and XPS.²⁷ Furthermore, the E_g energy was identified to be 2.5 eV (absorption edge: *ca.* 500 nm) and the Fermi level at the surface was 2.0 eV above the VBM. These measures showed that BiVO₄ is an n-type SC. The CB edge was 0.10 V_{RHE} and the VB edge was 2.6 V_{RHE}, as a result of conducted UPS measurements and Mott-Schottky analysis.²⁸ Consistently, the DFT calculations by Walsh and co-workers²⁵ and Zhao and co-workers²⁹ suggest that the effective masses of both holes and electrons in (m-s) BiVO₄ are smaller than other metal oxide in most cases. The drift velocity of holes and electrons is inversely proportional to the effective mass.³⁰ Thus, smaller effective masses are associated with easier charge separation and migration of electrons to reach the surface reaction sites. Therefore, monoclinic scheelite BiVO₄ is viewed as an effective photocatalyst.

2.2.3 Limitations of BiVO₄

Based on the near to optimal E_g of 2.5 eV and VB edge located at *ca.* 2.6 eV, as well as the relatively small effective carrier masses mentioned in the previous section, the actual solar-to-hydrogen (STH) conversion efficiency obtained by BiVO₄ has been far below its theoretical value of 9.3%, with a maximum photocurrent of 7.6 mA cm⁻² under standard AM 1.5 solar spectrum.³¹ The limitations are as follows:

- 1) Poor electron transport.³² The poor electron transport properties of BiVO₄ can be attributed to the disconnected VO₄ tetrahedral units observed in the material's crystal structure. This suggests that the photoexcited electrons in the V 3d CB may be bounded between the VO₄ tetrahedra.³¹
- 2) Slow water oxidation kinetics, although this only applies to water splitting.
- 3) Low carrier mobility that can significantly add to the poor charge separation of BiVO₄ also leads to approximately 60%–80% of the electron–hole pairs' recombinations before they reach the interfaces.^{2, 27, 33-34}

- 4) Weak surface absorption properties drastically limit the efficiency of the reactions at the interfaces.³⁵

The main reason for the poor charge separation of BiVO₄ is its intrinsic low carrier mobility, which is only about 0.044 cm² V⁻¹s⁻¹ (measured under 1 sun illumination condition).³⁶ On the other hand, the comparably long carrier lifetime (40 ns) and the charge diffusion length (70 nm) seem to balance this poor carrier mobility. However, charge carriers move by diffusion if an external field is absent. Diffusion, in this case, depends on the carrier lifetime and specific mobility. The charge carriers move by diffusion, and the average physical distance a charge carrier moves after generation and before recombination is defined as diffusion (L), which is dependent on the carrier excited lifetime (τ) and mobility (μ), as shown in Eqn. 2.1³⁶ below:

$$L = \sqrt{D\tau}, \quad D = \mu \frac{kT}{q} \quad (\text{Eqn. 2.1})$$

where D is the carrier diffusion coefficient that is related to μ by the Einstein relation.³⁷

Again, apart from its low carrier mobility, BiVO₄ seems to be superior in terms of its carrier lifetime and diffusion length compared to the dynamic properties of other typical visible light absorbing SCs, which include WO₃, Fe₂O₃, and Cu₂O (Table 2.1). Clearly, the carrier lifetime of BiVO₄ is one to three orders of magnitude longer than the other metal oxides, and its diffusion length is just second to WO₃.³⁶

Table 2.1. Comparison of the carrier mobility, lifetime, and diffusion length of BiVO₄ with those of several typical metal oxides. Adapted with permission from *J. Phys. Chem. Lett.* 2018, 4, 2752-2757. Copyright 2013 American Chemical Society³⁶

	SCs	Carrier mobility, μ (cm ² V ⁻¹ s ⁻¹)	Carrier lifetime, τ	Diffusion length, (nm)
1	BiVO ₄	0.044	40 ns	70
2	WO ₃	10	1-9 ps	150-500
3	Cu ₂ O	6	40 ps	25
4	Fe ₂ O ₃	0.5	3 ps	2-4

In recent years, numerous attempts with different strategies have been developed to improve the PC performances of BiVO₄. These strategies include doping, loading co-catalysts, surface modification, and other alternative strategies including crystal facet engineering, annealing, and nanoscaling.

However, before moving on to the strategies to enhance the performance of BiVO₄, we have to first understand the basic principles of photocatalysis, as well as the requirements for photocatalysis to occur.

2.2.4 Basic principles of photocatalysis

The mechanism of photocatalysis is illustrated in Figure 2.1. When a SC photocatalyst is irradiated with photon energy equal to or greater than the SC's E_g , charge separation occurs promoting an electron (e^-) to the CB and leaving a hole (h^+) in the VB (Figure 2.1a). The excited state CB e^- and VB h^+ are kinetically as well as thermodynamically favored to recombine and dissipate heat or emit light (Figure 2.1b). However, without recombination, the photo-excited e^- and h^+ can migrate to the surface, and can be involved in electrochemical processes with species adsorbed at the SC surface. The photoexcited e^- act as reducing agents to react with electron acceptors (A, Figure 2.1c), while the h^+ act

as oxidizing agents to react with electron donors (D, Figure 2.1d). It is important to note that, the photo-excited e^- and h^+ pair can get trapped in metastable surface states (Figure 2.1e and f) that are caused by crystalline defects or scavengers that facilitate in the recombination.

Figure 2.1. A schematic illustration of the principle of SC photocatalysis.

Furthermore, the band edge positions (or flat band potential) of the SC indicate the thermodynamic limitations that must be considered as the choice photocatalyst for a particular photoreaction that can be carried out with the charge carriers. From a thermodynamic viewpoint, the adsorbed species can be reduced by the CB e^- if they have redox potentials more positive than the flat band potential of the CB and can be oxidized by the VB h^+ if they have redox potentials more negative than the flat band potential of the VB.³⁸

2.2.5 Strategies to enhance BiVO₄ PC performance

2.2.5.1 *Surface Modification*

Surface modification to improve water oxidation kinetics with the use of various rare-earth transition metal catalysts such as IrO₂, RuO₂, and RhO₂ is costly³⁹⁻⁴¹. Co-catalysts containing earth abundant elements are favourable to reduce the cost of the SC. Recently, the potential of CoPi,^{32, 42} Co₃O₄,⁴³ FeOOH,⁴⁴ and NiOOH⁴⁴ as earth-abundant water oxidation co-catalysts for BiVO₄ have been demonstrated. Among these co-catalysts, CoPi is the most commonly studied to improve the water oxidation kinetics of BiVO₄ in PEC and PS systems. The performance enhancement (i.e. negative shift of onset potential) resulted primarily from a hole transfer process from BiVO₄ to CoPi to suppress surface recombination.

2.2.5.2 *Doping*

One approach that has been widely proven to effectively improve the electron transport in BiVO₄ involves doping of the material of interest. Substitutional doping involves replacing one of the host original atoms, i.e., effective doping by atom incorporation. In contrast, interstitial doping is based on attracting a foreign atom to an interstitial space, as well as within the lattice of a specific host matrix, when the existing atoms remain non-replaced. Still, in comparison to interstitial doping, substitutional doping has more strength in terms of its electrical and optical properties. Features similar to qualities of substituted atoms or atoms with different valence states can also be possessed by impurities, leading to increases in the numbers of electrons or holes to stimulate the charge carrier mobility and affect the minority carrier diffusion length. In order to contribute to the increased photoactivity, transition metal doping stimulates an enhanced trapping of electrons that results in the inhibition of electron-hole recombination observed during irradiation, when the conductivity rises because of doping BiVO₄ with Mo

and/or W since $\text{Mo}^{6+}/\text{W}^{6+}$ replaces the V^{5+} in VO_4 tetrahedron positions.^{35, 39} The mid-gap deep-level states only partially contribute to the visible-light PC activity due to the low charge carrier mobility associated with these states that perform as charge recombination centers despite the fact that they can broaden the spectral range of light absorption related to E_g of the SCs.⁴⁵

2.2.5.3 *Heterojunction Photocatalysts*

The basic principles of SC photocatalysis explain the recombination between holes and electrons as undesirable for a SC photocatalyst. In order to increase PC efficiency, electron–hole pairs are expected to be separated. Moreover, to constrain the recombination, charges should be quickly transferred to the surface/interface. The PC performance can potentially be improved by forming a SC heterojunction with a secondary material. Four typical categories of heterojunction photocatalysts are known, but only a SC-SC heterojunction will be discussed in the following section of this Chapter:

- 1) a SC–metal (SC–M) heterojunction
- 2) a SC–SC heterojunction**
- 3) a SC–carbon group (SC–C) heterojunction
- 4) a multicomponent heterojunction

Typically, a SC-SC heterojunction can be further classified into three different types: Type I (straddling gap), Type II (staggered gap), and Type III (broken gap) as shown in Figure 2.2.⁴⁶ The SC-1 CB is more negative than the band of SC-2 in Types I to III. However, the VB for SC-1 is more positive compared to the VB band of SC-2 in Type I, whereas the VB of SC-1 is less positive in Type II. The CB and VB of SC-2 is more positive compared to both the CB and VB in SC-1 for Type III. In Type I heterojunctions, electrons and holes then amass in the SC with the smaller E_g and often recombine, resulting in no improvement in the PC performance. In Type II heterojunctions, electrons and holes are separated to the two SCs, with an overall separation of charge carriers. In Type III heterojunctions,

electrons and holes are localized in only one SC and do not transfer to the other, essentially resulting in no heterojunction between the SCs.

Figure 2.2. Possible band alignments for two SCs at a heterojunction. Reprinted from the journal *Appl. Surf. Sci.* 2018, 430, 2-17, Copyright 2018, with permission from Elsevier.⁴⁶

2.2.6 Type II heterojunction

The Type II heterojunction system can be represented in two subtypes as shown in Figure 2.3. In the first subtype, SC 1 has higher CB and VB positions and a smaller work function (Figure 2.3a). Another subtype is when a typical p-n junction is observed (Figure 2.3b). In the first subtype (Figure 2.3a), when SC-1 and SC-2 are in contact, free electrons move from SC-1 to SC-2 after photoexcitation in order to stabilize and balance their Fermi levels. Band bending occurs with the SC-1 side being positively charged while SC-2 is negatively charged at the interface. This results in the formation of built-in electric fields in both SCs, where the photo-generated electron-hole pairs can be transferred *via* a Z-scheme mechanism after visible light excitation.⁴⁷ The electrons from the CB of SC-1 and holes from VB of SC-2 that are separated can participate in reductive and oxidative photocatalytic reactions, respectively.

Figure 2.3. (a) An illustration of a Z-scheme heterojunction with staggered band configurations. (b) An illustration of a typical p-n heterojunction with staggered band configurations. Reprinted from the journal *Appl. Surf. Sci.* 2018, 430, 2-17, Copyright 2018, with permission from Elsevier.⁴⁶

On the other hand, the charge transfer mechanism in the second subtype is significantly different from the first subtype. When a p-type SC-1 comes into contact with a n-type SC-2, free electrons from the n-type SC-2 are transferred to the p-type SC-1, forming a built-in electric field (Figure 2.3b). In addition, an extra potential barrier will be induced as a result of band bending and Coulombic repulsion will cause the charge carriers to be transferred *via* a double charge transfer mechanism instead of the direct Z-scheme mechanism.⁴⁸⁻⁴⁹ Therefore, the photogenerated charge carrier transfer mode that is typically observed in a p-n heterojunction cannot be viewed as appropriate in a Z-scheme heterojunction.

2.2.7 Artificial Z-scheme photocatalyst

An artificial Z-scheme photocatalyst usually consists of two connected oxidation and reduction SC photocatalysts, and often demonstrates greater PC performance.⁵⁰⁻⁵¹ Typically, the oxidation photocatalysts have low VB positions with strong oxidation abilities, whereas reduction photocatalysts possess high CB positions with strong reduction abilities. There are many advantages that are associated with the performance of a Z-scheme photocatalyst with excellent PC

activity, including: 1) the preservation of strong reduction and oxidation abilities due to the extended lifetimes of the photogenerated charge carriers, 2) the separation of specific oxidative and reductive active sites, 3) the high separation efficiency of photogenerated charge carriers that result in the inhibition of charge recombinations, 4) a broad range of photocatalysts for different reactions, and 5) an extended light absorbing spectrum.

The Z-scheme photocatalysts can be classified into three types with reference to the type of the introduction of a charge carrier mediator and its type. These types are known as traditional Z-scheme photocatalysts, all-solid state Z-scheme photocatalysts, and direct Z-scheme photocatalysts. In traditional Z-scheme photocatalysts, a reversible redox ion pair ($\text{Fe}^{3+}/\text{Fe}^{2+}$ and IO_3^-/I^-) is used in order to transport charge carriers. In all-solid state Z-scheme photocatalysts, electron conductors (e.g. Au and Ag nanoparticles) are utilized in order to enhance transporting charge carriers. Lastly, in direct Z-scheme photocatalysts, two SCs contact directly without any charge carrier transfer mediators involved in the process.⁵⁰⁻⁵³

Direct Z-scheme photocatalysts are most remarkable because they are able to function without any transfer mediator contrary to the traditional variant of the Z-scheme system as seen above.⁵⁴⁻⁵⁵ As a result, the absence of any redox mediators causes the backward reactions to be significantly suppressed, as well as significantly reducing the shielding effect that was caused by the charge carrier mediators. Moreover, direct Z-scheme photocatalysts are less susceptible to corrosion. For example, when an Ag-based photocatalyst serves as an oxidation component *via* a Z-scheme, photogenerated electrons in an Ag-based photocatalyst are consumed through recombination with photogenerated holes on the other component, which reduces any possibilities for Ag-based compounds to be photocorroded into metallic Ag.⁵⁶ It is also important to examine the charge transfer mode in a specific PC reaction. It is noteworthy, that a work function

difference between two SC photocatalysts is a prerequisite for stimulating specific charge redistribution and the formation of an internal electric field in order to affect the photogenerated charge carrier separation and transfer process.⁵⁷⁻⁵⁸

In conclusion, the advantages of a Z-scheme heterojunction PC systems are as follows:

- 1) the inhibition of charge recombinations;
- 2) an improvement of the charge separation;
- 3) an extension of the life time for energy excited electrons;
- 4) the utilization of the full solar spectrum.

Therefore, we are keen to improve the efficiency of BiVO₄ PC oxidation in organic reactions using the concept of a heterojunction by combining it with another metal oxide that possess appreciable visible light absorption, high efficiency and reasonable stability. Indeed there has been some progress in the use of complex oxides, for instance, several metal oxides were associated with BiVO₄ as shown in Table 2.2.

Table 2.2. Selected nanocomposites with BiVO₄ for PC application

Composites	Hetero-junction (proposed)	Degradation efficiency	Source of light irradiation	Application ^a	Ref.
TiO ₂ /BiVO ₄	Type I	~84% (2h)	50W halogen lamp with 185 mW cm ⁻²	MO degradation	59
CuO/BiVO ₄	Type II	2 times compared to BiVO ₄	300 W Xe lamps, $\lambda_{\max} > 420$ nm	RhB degradation	60
Cu ₂ O/BiVO ₄	Type II	1.2 times compared to BiVO ₄	300 W Xe lamps, $\lambda_{\max} > 420$ nm	MB degradation	61
WO ₃ /BiVO ₄	Type II	7.3 times compared to BiVO ₄	Solar simulator lamp (AM1.5G)	Water oxidation	2
Fe ₂ O ₃ /BiVO ₄	Type I	27 and 31 times to BiVO ₄	500 W Xe light $\lambda_{\max} > 420$ nm	RhB degradation	62
Bi ₂ O ₃ / BiVO ₄	Type I	Complete degrade after 40-80 min.	350 W Xe Solar simulator lamp	MB degradation	63

^a MO: methyl orange, MB: methylene blue, RhB: Rhodamine B

Among the nanocomposites, three of the nanocomposites were reported with a type II heterojunction, namely CuO/BiVO₄, Cu₂O/BiVO₄, and WO₃/BiVO₄. Furthermore, the band edge position of the SC is one of the most important and useful parameters that must be considered for use as a photocatalyst as mentioned in Section 2.2.4.

Figure 2.4. Band edge positions of SCs in contact with the aqueous electrolyte at pH = 0 relative to NHE and the vacuum level.

Therefore, the heterojunction material of choice (in red box of Figure 2.4) have to fulfil these criteria:

- 1) A BiVO₄ based SC
- 2) A type II heterojunction
- 3) The redox potential (i.e. reduction of O₂ and oxidation of amines) lies within the E_g domain of the nanocomposite.

2.2.8 Alternative strategies to enhance BiVO₄ PC performance

Another approach to better utilize the photocatalyst is to fabricate nano-sized materials and/or introduce mesoporosity to the catalyst. The use of nano-sized materials decreases the charge transport length and recombination rate, which increases the system efficiency. Introducing mesoporosity to the photocatalyst allows access to more active sites and facilitates the diffusion of the reactants and products. Incorporating mesoporosity into a nano-sized photocatalyst yields a catalyst with much shorter charge diffusion length, which in turn greatly reduces the recombination rate of the electron-hole pairs generated below the metal oxide surface.^{38, 64} Therefore, the photo-generated electron-hole pairs can be fully utilized not just on the surface but also in the bulk of the mesoporous catalyst particles. More recently, mesoporous SC metal oxides have attracted great interest due to their unique physical and chemical properties, and potential applications for catalysis and gas sensing.⁶⁵⁻⁸¹ Introducing a highly ordered, mesoporous, crystalline framework to the SC allows access to more active sites, facilitates diffusion of the reactants and products, and enables efficient charge transport pathways.⁷⁵ Aside from providing superior mechanical and thermal stability, a crystalline framework offers high charge mobility as well. In particular, a single crystalline framework is able to provide longer range mobility of the CB electrons as opposed to a polycrystalline framework which is compromised by intergrain boundaries.^{78, 82}

In conclusion, I aim to develop a nanoparticulate BiVO₄ based SC material with high surface area to demonstrate that it can be applied to the AP of solar chemicals. To further improve the overall PC activity, copper oxide nanoparticles will be loaded to achieve a Type II BiVO₄/CuO_x heterojunction through enhancement of the charge extraction efficiency.

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Chapter 3

Experimental Methodology

This chapter describes the experimental methodologies and characterization techniques used to address the objectives and hypotheses of this thesis. It begins with the rationale for the selection of materials, followed by the preparation and fabrication of test samples. Lastly, the characterization of materials to assess the functionality of the novel material, the principles underlying the syntheses, and the characterization methods are discussed and the analytical parameters of the methodologies are described in detail.

3.1 Materials

Tetraethyl orthosilicate (TEOS, $\geq 99\%$, GC grade), *n*-propyltriethoxysilane ($\geq 98\%$), *n*-cetyltrimethylammonium chloride (CTAC, 25 wt % in water), and cyclohexane ($\geq 99.9\%$) were purchased from Sigma-Aldrich. Triethanolamine (TEOA, 98%) was purchased from Sinopharm Chemical Reagent Co. Ltd. Sodium hydroxide (NaOH, 99.9%), hydrochloric acid (HCl, 36%), and toluene (99.5%) were purchased from Avantor Inc., while absolute ethanol (99.99%) was obtained from Fischer Scientific. The BiVO_4 precursors used were bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 98%) and ammonium metavanadate (NH_4VO_3 , $\geq 99\%$), which were purchased from Sigma-Aldrich. Nitric acid (69%) was purchased from Honeywell. Copper(II) acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\geq 98\%$) was purchased from Alfa Aesar. The internal standard, 3,5-dimethylanisole (99.9%), was purchased from Sigma-Aldrich. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Distilled water was obtained using a Milli-Q Advantage A10 water purifier with a total organic carbon content < 5 parts per billion. The radical traps, 2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO, 98%) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO, $> 97\%$) were purchased from Sigma-Aldrich and Tokyo Chemical Industry Co. Ltd. All the chemicals used in this work were of analytical grade and were used as received.

3.2 Experimental procedures for $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$

3.2.1 Preparation of 3-dimensional (3D) dendritic mesoporous nanoparticles (DMSN)

The dendritic mesoporous silica nanoparticles (DMSN) were prepared using a method previously reported by Zhao and coworkers.¹ CTAC solution (24 mL) and TEOA (0.16 mL, 1.2 mmol) were added in a 100 mL round bottom flask

filled with distilled water (36 mL) and the mixture was stirred gently at 60 °C for 1 h. Subsequently, TEOS (2.0 mL, 9.0 mmol) in cyclohexane (18 mL) was carefully added to the surfactant solution in an oil bath at 60 °C, with stirring at a rate of about 150 rpm. The reaction flask was then stirred at 60 °C for 16 h to obtain the product as a white suspension. The crude product was collected by centrifugation and washed three times with absolute ethanol. Subsequently, the crude product was extracted once with hydrochloric acid (1.2% v/v in absolute ethanol), washed with distilled water twice, and once with absolute ethanol before being left to dry overnight at 70 °C. The white powder was then transferred into a crucible and calcined at 550 °C for 5 h at a ramp rate of 2 °C per min. After calcination, a white, powdery mesoporous dendritic silica was obtained (0.14 g, 25%).

3.2.2 Hydrophobic functionalization of DMSN²

DMSN (1.2 g, 20 mmol) was pre-dried under vacuum on a Schlenk line at 130 °C for 3 h before anhydrous toluene (150 mL) and subsequently *n*-propyltriethoxysilane (1.6 mL, 7.0 mmol) were added to the silica. The suspension was stirred for 10 min and heated to reflux for 3.5 h. Subsequently, the propyl-functionalized DMSN (propyl-DMSN) was collected by centrifugation and washed three times with dry toluene and twice with absolute ethanol. The product was then dried overnight at 70 °C to obtain a slightly off-white powder.

3.2.3 General procedure for the preparation of SiO₂/BiVO₄ nanospheres

BiVO₄ nanospheres with different BiVO₄ loadings were prepared via an incipient wetness impregnation-calcination procedure.³ As a representative example, for SiO₂/BiVO₄ (59 wt%) nanospheres, Bi(NO₃)₃•5H₂O (110 mg, 230 μmol) was added to a solution of NH₄VO₃ (33 mg, 280 μmol) that was dissolved in nitric

acid (3.0 M, 2.0 mL) and ethylene glycol (0.20 mL) to obtain a yellow, homogeneous BiVO_4 precursor solution. Excess NH_4VO_3 was added so that the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ reacts with a sufficient amount of the vanadium source during the annealing process. The resulting solution was added to the propyl-DMSN (100 mg) and ground using a hot pestle and mortar (70 °C) to obtain a dry powder. The addition of ethylene glycol to the BiVO_4 precursors was necessary to wet the pores of the propyl-DMSN given its hydrophobicity, thus easing the penetration of the precursor into the silica pores. The light-brown powder was then transferred to a crucible and calcined at 500 °C for 2 h at a ramp rate of 1 °C/min to convert the BiVO_4 precursor to $\text{SiO}_2/\text{BiVO}_4$ nanospheres. Subsequently, the product was stirred in an aqueous NaOH solution (1.0 M, 20 mL) for 30 min to remove excess vanadium oxide. The photocatalyst powder was obtained after washing and centrifugation with water once, with nitric acid (0.20 M, 10 mL) once, finally with ethanol twice, and dried overnight at 70 °C. The procedure was repeated for the fabrication of $\text{SiO}_2/\text{BiVO}_4$ (45 wt%) nanospheres, $\text{SiO}_2/\text{BiVO}_4$ (56 wt%), and $\text{SiO}_2/\text{BiVO}_4$ (63 wt%) with the following quantities: $\text{SiO}_2/\text{BiVO}_4$ (45 wt%) nanospheres: $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (65 mg, 130 μmol) and NH_4VO_3 (19 mg, 160 μmol); $\text{SiO}_2/\text{BiVO}_4$ (56 wt%) nanospheres: $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (97 mg, 200 μmol) and NH_4VO_3 (28 mg, 240 μmol); $\text{SiO}_2/\text{BiVO}_4$ (63 wt%) nanospheres: $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (130 mg, 270 μmol) and NH_4VO_3 (37 mg, 320 μmol).

3.2.4 General procedure for the preparation of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres⁴

$\text{SiO}_2/\text{BiVO}_4$ (59 wt%) nanospheres (50 mg, 47 μmol) were added to a 100 mL round-bottom flask with a stir bar. $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.43 mL, 25 μM in absolute ethanol) and absolute ethanol (40 mL) were added, and the solution was stirred for 6 h. The ethanol was then removed by rotary evaporation. Subsequently, diethylene glycol (40 mL) was added, and the solution was sonicated for 10 min before it was heated to 180 °C for 2 h. The product was

collected by centrifugation and washed with distilled water three times and then washed twice with ethanol. The product was then dried overnight at 70 °C to provide a green powder (46 mg, 88%).

3.3 Instrumental details

3.3.1 Transmission electron microscopy (TEM) imaging

Transmission electron microscopy (TEM) is employed to acquire high atomic resolution images of materials. TEM transmits a focused, high-energy electron beam through a sample. The electrons scatter off the nuclei of atoms in the sample and are projected onto a fluorescent screen. Through this process, atomic scale images can be collected. Furthermore, a selected area electron diffraction (SAED) pattern can be obtained from single nanostructures to present information about the crystallographic planes orientation. By combining the information gained from diffraction patterns and atomic scale imaging, the surface crystallographic planes of a material can be characterized. Scanning transmission electron microscopy (STEM) can be combined with the high-angle annular dark field (HAADF) imaging technique to provide Z contrast images, which can differentiate particles of different atomic number. The elemental composition of a sample can be resolved by energy-dispersive X-ray spectroscopy (EDS). EDS involves ionization of the sample from the X-rays of the microscope that results in the X-ray emissions from the sample, which are then analyzed with a solid-state energy dispersive detector. Each element gives out a unique pattern of X-ray lines from the K, L, and M shells for a simple analysis. This technique is also useful for constructing elemental maps to characterize the elemental distribution of multicomponent catalysts and microstructural composition on a nanometric scale.

In this study, the morphology and structure of the samples were characterized by TEM with a JEOL JEM-1400 operated at 100 kV and a high-resolution TEM (HRTEM) with a JEOL JEM-2100F operated at 200 kV. The HRTEM is equipped with a scanning transmission electron microscope (STEM) and an energy-dispersive X-ray spectrometer for STEM images and elemental analysis, respectively. The sample preparation involved sonicating an aliquot of the nanocrystalline powder in analytical-grade ethanol for 10 min. A single drop of the homogeneous colloidal solution was deposited on a thin, lacey, carbon-coated copper TEM grid and dried in air.

3.3.2 Field emission scanning electron microscopy (FESEM) imaging

FESEM analyzes the surface characteristics, such as morphology, and chemical composition of the sample. The electrons interact with the atoms in the sample, resulting in informative signals on the sample's topographical information, elemental composition, and homogeneity. In contrast to a SEM, the FESEM uses a field-emission cathode as the electron gun delivering narrow probing beams at low currents as well as high electron energy beam under high vacuums (10^{-1} Torr). With these instrumental parameters, analyses are achieved by the improved spatial resolution with minimal sample charging, and less sample damage.

In this study, an FESEM equipped with an energy-dispersive X-ray spectrometer was used to examine the samples using a JEOL JSM-7600F operated at 5 kV. Each sample was prepared by coating a uniform layer of the materials on SPI double-sided adhesive carbon tape and mounted on an aluminum SEM specimen stub. Accelerating voltage and variable slit sizes were adjusted for proper focus on samples, with manually corrected astigmatism and beam shape. Chemical composition analyses were measured by an OxfordEDS detector supported by Aztec software for a JEOL SEM.

3.3.3 Powder X-ray diffraction (PXRD)

PXRD is a non-destructive technique used to characterize solid-state materials. The structure of a crystal is analyzed by the X-ray diffraction patterns. When X-rays with a wavelength λ are incident on a crystal, diffraction peaks occurs if the Bragg condition (Eqn. 3.1) is satisfied:

$$n\lambda = 2d\sin\theta \quad (\text{Eqn. 3.1})$$

From the X-ray diffraction pattern, we can obtain the following information:

- 1) types of crystalline phases present in the solid-state samples,
- 2) unit cell structure, lattice parameters and Miller indices,
- 3) estimation of the crystalline/amorphous contents in the sample,
- 4) evaluation of the mean crystalline domain size from the widths of the peaks with higher intensity in a particular phase pattern by using of the Scherrer equation (Eqn. 3.2).⁵ A large crystal size gives rise to sharp peaks, while the peak width increases with decreasing crystal size.

$$\tau = \frac{K\lambda}{\beta\cos\theta} \quad (\text{Eqn. 3.2})$$

where τ is the mean crystalline domain size, $K = 0.94$ is a dimensionless shape factor, $\lambda = 1.54178 \text{ \AA}$ is the Cu K_α X-ray wavelength, β is the full width at half maximum (FWHM) in radians, and θ is the Bragg angle.

In our study, the XRD profiles were obtained using a Bruker D8 Advance powder X-ray diffractometer with Cu K_α radiation at 40 kV and 40 mA and step-size scans of 0.02° from 10° to 80° . The mean crystallite size was estimated by the Scherrer equation using the full-width at half-maximum (FWHM) height of the peaks at $2\theta = 28.9^\circ$ and 30.6° .

3.3.4 Specific surface area and pore size measurements

Surface area and pores size distribution of given materials are mainly determined by using gas sorption techniques. In these techniques, the samples are exposed to a gas (adsorptive) atmosphere under a controlled pressure to let the gas cover the external and accessible internal pore surfaces of a solid sample. The amounts of gas adsorbed on the surface and pores, which dependant on the relative pressure are monitored. The data is then used to obtain gas adsorption isotherms. For pure gases, there are basically six types of isotherms as shown in Figure 3.1.

Figure 3.1. Different types of adsorption isotherms.

A Type I isotherm is typical of microporous solids and chemisorption isotherms. A Type II is shown by finely divided non-porous solids. Type III and V are typical of vapor adsorption (i.e. water vapor on hydrophobic materials). Type IV and V feature hysteresis loops generated by the capillary condensation of the adsorbate in the mesoporous solid. Finally, a Type VI step-like isotherm is shown by nitrogen adsorbed on a unique carbon.

The surface area is determined by monitoring the amount of gas involved in creating the multilayer using a Brunauer, Emmett, and Teller (BET) model⁶ (Eqn. 3.3)

$$\frac{p}{(P_o - P)V} = \frac{1}{aV_{max}} + \frac{a-1}{aV_{max}} \frac{P}{P_o} \quad (\text{Eqn. 3.3})$$

where p is the gas pressure, P_o is the saturation pressure of gas at a given temperature, V is the volume of the multilayer adsorbed, V_{max} is the volume of the monolayer, and a is a constant depending upon the nature of the gas. Since a and V_{max} are constant for a given gas-solid system, a plot of $\frac{p}{(P_o - P)V}$ against P/P_o should be a straight line, which will allow determination of V_{max} using intercept and slope.

In this study, the nitrogen sorption isotherms of each sample were measured at 77 K using a Micrometrics Tristar II 3020 version 2.00 automated gas analyzer. Each sample was degassed in a Micrometric Smart Vacprep 061 unit at 140 °C for 10 h before analysis. The adsorption data obtained at P/P_o between 0.05 and 0.2 atm were modeled according to the Brunauer, Emmett, and Teller (BET) adsorption isotherm equation to calculate the surface area of the material.

3.3.5 UV-DRS measurements

Diffuse reflectance is similar to UV-Vis spectroscopy applied to crystalline or amorphous materials. Diffuse reflectance depends on the focused projection of the spectrometer beam onto the sample where it is reflected, scattered, transmitted through, and absorbed partially by the sample material. The reflected, diffusely scattered light is then collected and directed to the detector optics. Generally, the sample is ground up appropriately and also mixed with a non-light-absorbing matrix such as barium sulfate (BaSO_4).

A Kubelka-Munk conversion can be applied to a diffuse reflectance spectrum to compensate for these differences. The Kubelka-Munk equation (Eqn. 3.4) is shown below:

$$F(R) = \frac{(1-R)^2}{2R} \quad (\text{Eqn. 3.4})$$

where $F(R)$ is equivalent to the absorption coefficient. The E_g energies of the samples were calculated from the UV-vis spectra by using a Tauc plot following the Eqn. 3.5,⁷

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (\text{Eqn. 3.5})$$

where α , h , A , and ν are the absorption coefficient, Planck's constant, proportionality constant, and photon frequency, respectively. Among them, n is determined by the type of optical transition of a SC ($n = 1$ for a direct transition and $n = 4$ for an indirect transition). Thus, the E_g of the samples could be estimated from plots of $(\alpha h\nu)^{2/n}$ versus the photon energy ($h\nu$).

In this study, the UV-visible DRS spectra were collected with a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer mounted with an ISR-3100 integrating sphere attachment. The sample was applied onto the surface of the barium sulfate powder that was packed on a sample holder of the ISR-3100 integrating sphere attachment. BaSO₄ was used as a background reference. The Tauc plot obtained from the DRS measurement can be used to determine the E_g of the samples.

3.3.6 XPS experiments

XPS is used for the qualitative and quantitative analyses of the chemical composition and electronic state of a surface region. Under an ultra high vacuum environment, the sample surface is bombarded by X-rays with a certain amount of energy to eject the electrons, beginning with the outermost electrons bound least tightly to the nucleus of the atom. Depending on the amount of irradiation,

electrons from the bound states are excited. These ejected electrons are collected by the electron analyzer and the kinetic energy (KE) is measured. Since energy is conserved, the binding energy (BE), also known as the ionization energy required to eject the electron can be calculated by the equation: $BE = \text{total irradiation energy } (h\nu) - KE$ ($1/2 mv^2$), where h is planck constant and ν is frequency. The energy spectrum recorded produces a plot of intensity corresponds to the number of photo-ejected electrons against the BE. Given that each energy peak corresponds to a specific element, XPS is equipped to identify the elemental compositions and their electronic state. By resolving the area intensities of each elements, the quantities of each can be known.

In this study, XPS analysis was performed using a Kratos AXIS Supra spectrometer with a monochromatic Al K_{α} source (15 mA, 10 kV). A 3.1-volt bias was applied to the sample to neutralize positive charge build up on the sample surface. Individual core levels were measured with a pass energy of 20 eV. XPS measurement was performed on solid powder samples pressed onto SPI double-sided adhesive carbon tape. The XPS data obtained were processed using the CasaXPS software. The spectra were calibrated internally by setting the C 1s signal at 284.6 eV. Photoemission from the samples will cause them to be positively charged, which results in a shift of the peak position to higher binding energies. To eliminate any positive charging effect, a low energy electron flood gun was used for charge compensation during spectrum acquisition. The XPS spectra reported here are referenced to C 1s at 285.0 eV. The estimated uncertainty in the BE for a spectrum peak was at most ± 0.2 eV based on repeated measurements.

3.3.7 UV photoelectron spectroscopy (UPS) experiments

UPS using a He-I ($h\nu = 21.2$ eV) excitation source was performed to obtain the work function and VB maximum of the samples. The experiment was conducted

in an UHV chamber at 1×10^{-9} torr pressure. The samples were biased at -10 V, and photoelectrons were collected at a surface normal using the CAE mode at 2.00 eV pass energy with a hemispherical electron energy analyzer (Omicron EA-125).

3.3.8 Photoluminescence spectroscopy (PL) experiments

PL is a process by which a chemical compound absorbs photons thus promoting to a higher electronic energy state, and then radiates photons, returning to a lower energy state. Photo-excitation causes electrons within the material to move into excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light, or luminescence. This process is relevant to the study of photocatalyst systems since photoluminescence occurs when electrons in the CB recombine with holes in the VB.⁸ The PL intensity can then be used to compare recombination rates for different photocatalyst systems.

Time resolved-PL (TR-PL) is similar to steady-state PL spectroscopy and gives information detailing the lifetimes of photo-excited species. In PL, there is a continuous excitation from a light source, while TR-PL spectroscopy relies on pulsed excitation and measures the photoluminescence at certain time intervals after the pulse excitation. The PL emission intensity over time is then fitted to an exponential decay model to determine the lifetimes of the photo-generated e^-/h^+ pairs.

The laser source was a regenerative amplifier (Coherent Libra, 50 fs, 1 KHz, 800 nm) seeded by an oscillator (Coherent Vitesse, 50 fs, 80 MHz). The 400 nm wavelength laser pulses were obtained using a BBO doubling crystal. The laser pulse (circular spot, diameter 3 mm) were directed to the films. The emission from the samples was collected at a backscattering angle of 150° by a pair of

lenses into an optical fiber that was coupled to a spectrometer (Acton, Spectra Pro 2500i) and subsequently detected by a charge coupled device (Princeton Instruments, Pixis 400B). An Optronis Optoscope streak camera system was used to measure the time resolved-PL (TR-PL), which has a temporal resolution of around 10 ps. PL and TR-PL experiments were performed on $\text{SiO}_2/\text{BiVO}_4$ and $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$, with photoexcitation at 400 nm with $\sim 30 \mu\text{J}/\text{cm}^2$ fluence.

3.3.9 FT-IR spectroscopy measurements

Infrared radiation interacts with chemical bonds to cause stretches, bends, and various other atomic vibrations. For a vibration to give rise to absorption of infrared radiation, it must cause a change in the dipole moment of the molecule. The larger this change, the more intense the absorption band will be.

In this study, FT-IR spectroscopic measurements were carried out with a Bruker Vertex 80v FT-IR spectrometer. In a typical experiment, about 1.5 mg of the sample was mixed with about 30.0 mg of potassium bromide (KBr) to make a pellet. The pellets were made with a Specac Atlas manual hydraulic press 15T at 10 ton pressure. The FT-IR experiments were conducted in transmission mode with data collected from 400 to 4000 cm^{-1} .

3.3.10 Photoelectrochemical measurements

Photoelectrochemical measurements were performed using a three-electrode configuration (PCI4/300™ potentiostat with PHE200™ software, Gamry Electronic Instruments, Inc.). In each experiment, the BiVO_4 composite samples were used as the working electrode, Pt foil as the counter electrode, and Ag/AgCl as the reference electrode in 0.5 M Na_2SO_4 electrolyte. A solar simulator (HAL-320, Asahi Spectra Co., Ltd.) with power intensity of $100 \text{ mW}\cdot\text{cm}^{-2}$ was used as the light source for the photoelectrochemical measurements. The photocurrents

were measured in aqueous solutions, each with a scan rate of $30 \text{ mV} \cdot \text{s}^{-1}$. Under similar conditions, the electrochemical impedance spectroscopy (EIS) measurements were carried out at the applied potential of $0.50 \text{ V vs AgCl/Ag}$ using a PCI4/300TM potentiostat.

3.3.11 Radical trapping experiments

A spin-trapping agent, DMPO, was added to the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ suspension (1 mg/mL) during photocatalytic reactions to trap superoxide radicals. The suspension was first irradiated under visible light for 30 s and around $250 \text{ }\mu\text{L}$ of the reaction mixture was withdrawn, transferred into a quartz EPR tube, and probed in a X-band electronic paramagnetic resonance (EPR) spectrometer (JEOL FA200, 10 mW) to verify the formation of superoxide radicals during photocatalysis.

To an oven-dried 10 mL quartz Schlenk tube, $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ (30 mg , 0.050 mmol , $10 \text{ mol\%}$ of BiVO_4 , 1 eq.), 4-methoxybenzylamine ($6.5 \text{ }\mu\text{L}$, 0.050 mmol), and the radical trapping agent TEMPO (39 mg , 0.25 mmol , 5 eq.) or diisopropyl azodicarboxylate ($49 \text{ }\mu\text{L}$, 0.25 mmol , 5 eq.) were added to the Schlenk tube containing the acetonitrile (4.0 mL). The suspension was irradiated under visible light for 4 h and a portion of the reaction mixture was withdrawn, centrifuged, and the supernatant was transferred to a NMR tube for ^1H NMR analysis on a Bruker Avance 400 NMR spectrometer. In addition, liquid chromatography-mass spectrometry (LC-MS) measurements were performed on a quadrupole ion trap mass spectrometer equipped with a Thermo Accela LC (ThermoFinnigan LCQ Fleet MS) to verify the formation of the trapped amine radical cation intermediate during photocatalysis.

3.4 References

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Chapter 4

Development of SiO₂/BiVO₄/CuO_x for PC Applications

*This chapter discusses the development of a novel mesoporous SiO₂/BiVO₄/CuO_x to act as a chromophore in a Z-scheme system for effective light harvesting and charge separation to facilitate the synthesis of “solar chemicals”. The SiO₂/BiVO₄/CuO_x nanospheres are more efficient catalysts than the constituents, with catalytic reactivity over seven times faster than bulk BiVO₄ and its nanoparticles. Notably, our new nanocatalysts outperform previously reported papers in this field, and provide higher yields for the oxidative coupling of amines to imine products. Moreover, the SiO₂/BiVO₄/CuO_x nanospheres are effective for the PC oxidative coupling of a broad range of benzylamines, which are valuable precursors for fine chemicals, agrochemicals, and active pharmaceutical ingredients. This study has been published in *Applied Materials Today* and forms the bulk of Chapter 4.¹ I am the first author and completed all of the synthesis, characterization, and optimization of the material, as well as the screening of all substrates. Eugene Jun-Ching Tan assisted me with some of the substrate screening. Teck Wee Goh and Prof. Tze Chien Sum assisted me with the UPS, PL, and TR-PL analysis studies. Dr. Xin Zhao assisted me with the photocurrent measurements and analysis studies. Prof. Zhong Chen provided some ideas for the material synthesis.*

Mesoporous SiO₂/BiVO₄/CuO_x Nanospheres for Z-Scheme, Visible Light Driven Aerobic Photoredox Coupling of Amines

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4.1 Abstract

In light of the growing demand to use renewable energy, we have synthesized a mesoporous bismuth vanadate-copper oxide-silica photocatalyst (SiO₂/BiVO₄/CuO_x) to act as a chromophore in a Z-scheme system. These photocatalysts are intended for effective light harvesting and charge separation in the synthesis of solar chemicals, using air as an environmentally benign oxidant. Full characterization of the SiO₂/BiVO₄/CuO_x was conducted, including XPS, UPS, and scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDS), which confirm the presence of CuO_x at the heterojunction of the nanostructures. The other characterization methods that were employed included PXRD, TEM, HRTEM, elemental mapping, UV-vis DRS, N₂ sorption experiments, PL, electrochemical impedance spectroscopy (EIS), and photocurrent measurements. Notably, the SiO₂/BiVO₄/CuO_x nanospheres perform seven times faster than bulk BiVO₄ and provide higher yields for the oxidative coupling of amines to imines, which are valuable precursors for agrochemicals and active pharmaceutical ingredients. The superior photocatalysis of SiO₂/BiVO₄/CuO_x is attributed to the surface CuO_x nanoparticles that increase the average PL lifetime from 2.3 to 4.5 ns, which improved the charge separation and decreased the unproductive recombinations of electron-hole pairs. In addition, the photocurrent density of the SiO₂/BiVO₄/CuO_x electrode was about 3.5 times higher than that of SiO₂/BiVO₄, while lower charge transfer resistance was observed by EIS. Meanwhile, chemical scavenging experiments revealed that holes and superoxide radicals were the main reactive oxygen species in the photocatalytic reaction. The

nanospheres also show broad functional group tolerance, good recyclability with high conversions, and high to moderate yields for the oxidatively coupled imine products after eight runs. Thus, we demonstrate that an effective and green approach in artificial photosynthesis is applicable for organic synthesis as well.

4.2 Introduction

The exploitation of solar energy in the production of fuels and chemicals has taken on greater urgency lately due to the increasingly palpable environmental and economic effects of global climate change. To address this challenge, several groups, including ours,²⁻¹⁰ have been inspired by the effectiveness of natural photosynthesis in capturing sunlight and coupling the separated charges for multielectron redox catalysis. A fundamental feature of the light harvesting mechanism among green plants is the integration of two visible light absorbers in Photosystems I and II to create a “Z-scheme”. The two chromophores, chlorophylls P680 and P700, are organized so that electrons flow from P680 to P700 with high fidelity by interfacing with both thermodynamically and kinetically favorable intermediates. This essentially creates a “molecular photodiode” for effective light absorption and charge separation, allowing P680 to build up four holes to oxidize water, while P700 acquires two electrons to reduce NADP⁺.¹⁰

To mimic this vital capability of photosynthesis, the groups of Domen, Li, Nocera, Yang, and others have assembled visible light absorbing, Z-scheme SC systems to harvest solar energy for the production of solar fuels *via* water splitting or CO₂ reduction, as well as to mitigate the environmental impact of water pollution.¹¹⁻²⁹ Complementary to these pioneering studies, a number of research teams have started to focus on the production of solar chemicals to broaden the scope of light utilization applications. For instance, T. J. Meyer, G. J. Meyer, and co-workers have used dye-sensitized photoelectrochemical cells to simultaneously oxidize

halides to halogens and hypohalites as solar chemicals while producing H_2 as well.³⁰⁻³³ Likewise, Reisner and his team have employed alcohols and lignocellulosic biomass in photodriven oxidative processes,³⁴⁻³⁵ while Sun and co-workers utilized biomass-derived furfuryl alcohol and 5-hydroxymethylfurfural (HMF) as the substrates in cadmium sulfide/nickel (CdS/Ni) photocatalyzed water splitting.³⁶⁻³⁷ Z. Li and his co-workers have also used metal organic frameworks (MOFs)³⁸⁻³⁹ and ZnIn_2S_4 ⁴⁰ in the oxidation of amines to imines, which are important building blocks for the synthesis of fine chemicals. In the same vein, our team has been developing alternative approaches to harness sunlight in the production of solar chemicals and fuels, while using exclusively earth abundant elements.¹⁰ We have developed molecular complexes and metal oxide SCs as chromophores,⁴¹⁻⁴² molecular Ni electrocatalysts capable of H_2 evolution from seawater,⁴³ and molecular V photocatalysts that mediate C-C bond cleavage in biomass lignin model compounds, with the intention of integrating them into one unit for solar chemicals production.^{10, 44-45}

Some candidates that have emerged for solar to chemical energy conversion are Bi-based materials, due to their efficient PC performance, high stability, low cost, and modest toxicity.⁴⁶ Bi-based nanomaterials have been introduced for photoinduced water splitting and environmental remediation, among other applications.⁴⁷ One example is BiVO_4 , which commonly exists in three phases: tetragonal zircon, monoclinic scheelite, and tetragonal scheelite.⁴⁸ Among these, monoclinic BiVO_4 has the best reported PC performance, with a narrow E_g of about 2.4 eV for visible light absorption,^{47, 49} and a moderate charge diffusion length of 100 nm.⁵⁰ Furthermore, the VB potential is around +2.5 V vs. normal hydrogen electrode (NHE), ample to oxidize many organic compounds.⁵¹⁻⁵⁵ Consequently, BiVO_4 has been employed in the partial oxidation of secondary amines to imines⁵³ and methane to methanol in the presence of O_2 ,⁵⁶ underscoring its value in harvesting light for solar chemicals production.

Here, we have developed mesoporous $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres as chromophores in a Z-scheme system for effective light harvesting and charge separation in the synthesis of solar chemicals. Mesoporous nanomaterials are attractive due to their large surface areas, open pore systems, controllable pore sizes and morphologies, and high chemical and thermal stability.⁵⁷⁻⁵⁸ Previous reports on the poor PC activity of BiVO_4 when in nanoparticulate form were attributed to the poor crystallinity, for the generation of O_2 from aqueous AgNO_3 solutions for instance.⁵⁹ Heat treatment did not improve the activity due to severe sintering, which reduced the nanoparticles' surface areas.⁶⁰ In contrast, we have overcome these problems by preparing dispersible $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres and established that they are efficient visible light photocatalysts for the aerobic oxidative coupling of amines and dehydrogenation of indolines in the presence of molecular O_2 in air as a green oxidant under ambient conditions. Moreover, loading $\text{BiVO}_4/\text{CuO}_x$ in the mesoporous SiO_2 nanoparticles could potentially inhibit the aggregation that often occurs for photocatalytic reactions using dispersed materials; such agglomeration is known to be a major factor in the loss of catalytic activity among nanomaterials over time.⁶¹⁻⁶³ The staggered type II heterojunction between BiVO_4 and CuO_x facilitated concurrent absorption of two photons over a broader visible spectrum and also more effective charge separation. Notably, the mesoporous $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres perform seven times faster than BiVO_4 nanospheres alone and provide higher yields for imine products, which are valuable precursors for fine chemicals, agrochemicals, and active pharmaceutical ingredients.⁶⁴⁻⁶⁶

4.3 Experimental Procedure

See Chapter 3 for preparation of SiO₂/BiVO₄/CuO_x

4.3.1 Typical procedure for aerobic oxidative imine preparation from primary amines, catalyzed by SiO₂/BiVO₄/CuO_x nanospheres

As a representative example, SiO₂/BiVO₄/CuO_x nanosphere samples (6.0 mg, 0.010 mmol, 10 mol%) were added to 4-methoxybenzylamine (13 μ L, 0.10 mmol) and CD₃CN (0.80 mL) in an 8 mL vial with a stir bar, and the vial was irradiated with a white LED (48 W) for 3.5 h with the temperature maintained at 30 °C. The internal standard 3,5-dimethylanisole (14 μ L) was then added, before the solution was centrifuged. The supernatant was analyzed by ¹H NMR spectroscopy.

4.4 Results and Discussions

4.4.1 Synthesis and structural characterization

Figure 4.1. An illustration of the fabrication of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres.

Figure 4.1 illustrates the synthesis of mesoporous $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres. Mesoporous dendritic silica was synthesized via a soft templating approach from tetraethyl orthosilicate (TEOS),⁶⁷ and then used as a template to load the metal oxides (Figure 4.2).⁵⁷ Surface modification of the DMSN with *n*-propyltriethoxysilane (propyl-DMSN) was found to be necessary to ensure effective BiVO_4 precursor loading in the next step.

Figure 4.2. TEM images of (a) DMSN and (b) propyl-DMSN. SEM images of (c) DMSN and (d) propyl-DMSN.

Four samples of DMSN, with increasing amounts of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NH_4VO_3 loaded (45, 56, 59, and 63 wt% of BiVO_4 relative to SiO_2), were prepared *via* an incipient wetness impregnation procedure (IWI).⁵⁷ The samples were annealed in air at 500 °C for 2 h, and the amount of BiVO_4 was found to be 12, 14, 18, and 22 mol% with SEM-EDS analyses, corresponding to the increasing loadings of the BiVO_4 (Figure 4.3).

Figure 4.3. Determination of BiVO_4 content in silica (a-d) from samples loaded with the following quantities of Bi and V precursors: (a) 45 wt%, (b) 56 wt%, (c) 59 wt%, (d) 63 wt%. Carbon (C) comes from the SPI double-sided adhesive carbon tape and Al comes from the SEM specimen stubs.

The transmission electron microscopic (TEM) images of $\text{SiO}_2/\text{BiVO}_4$ samples showed well-defined, non-aggregated, mesoporous dendritic nanospheres (Figure 4.4). The average particle size for all the $\text{SiO}_2/\text{BiVO}_4$ samples are about

100 nm, with the exception of the 63 wt% loading, which had aggregated particles outside the nanospheres due to overloading. Finally, CuO_x was incorporated on the mesoporous SiO₂/BiVO₄ nanospheres by a polyol process. After evaluating the samples, we identified 59 wt% SiO₂/BiVO₄ with 20 mol% CuO_x (relative to BiVO₄) as the optimal catalyst (*vide infra*) and characterized this one rigorously.

Figure 4.4. TEM images of propyl-DMSN loaded with different quantities of Bi and V precursors (a-d), with the following specific weight percentages: (a) 45 wt%, (b) 56 wt%, (c) 59 wt%, (d) 63 wt%. TEM images of SiO₂/BiVO₄ nanospheres after calcination at 500 °C for 2 h (e-h) with the following specific weight percentages loaded: (e) 45 wt%, (f) 56 wt%, (g) 59 wt%, (h) 63 wt%. TEM images of SiO₂/BiVO₄ nanospheres after calcination and washing with 1 M NaOH (i-l). (i) 45 wt%, (j) 56 wt%, (k) 59 wt%, (l) 63 wt%

Powder XRD (PXRD) measurements were conducted to verify the crystalline properties of the nanospheres. Figure 4.5 reveal discernible peak splitting at 2θ of 35°, diagnostic of a single monoclinic scheelite phase for all samples (JCPDS 00-044-0081).⁶⁸ The crystalline domain sizes of the as-prepared BiVO₄ samples based on the PXRD were calculated using the Scherrer equation (Eqn. 3.2 in Chapter 3). Peak broadening was observed for the sample with 45 wt% loading, which does not show obvious splitting pattern at 35° (red boxes), likely attributed to the low crystallinity due to the decreasing crystallite size.⁶⁹ Although no diffraction peaks corresponding to CuO_x could be observed due to the low CuO_x loading levels, their presence was confirmed by electron microscopy.

Figure 4.5. PXRD pattern of BiVO₄ loadings of a) 45 wt%, b) 56 wt%, c) 59 wt%, d) 63 wt%, e) SiO₂/BiVO₄/CuO_x, and f) bulk BiVO₄ crystals.

The high resolution TEM (HRTEM) images of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres (Figure 4.6a) further demonstrates that the dendritic particles are composed of BiVO_4 nanocrystals, with the lattice fringe d-spacing of 0.309 nm corresponding to the (112) plane of monoclinic BiVO_4 (Figure 4.6b).

Figure 4.6. (a) HRTEM images of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres, (b) lattice fringe with a d-spacing of 0.309 nm corresponds to the (112) plane of BiVO_4 in $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres.

Moreover, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) together with elemental mapping evidently verify the uniform distribution of Bi, V, and Cu within the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres (Figures 4.7). In addition, the energy-dispersive X-ray spectroscopic (EDS) experiments (Figure 4.8) with scanning electron microscopy (SEM) confirm that 19 mol% (relative to BiVO_4) of Cu has been incorporated on the surface of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres (Figure 4.8g). The morphology of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres was also examined by SEM (Figure 4.9) reveals that the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres have porous and rough surfaces with average sizes of 100 nm, in accordance with the TEM results.

Figure 4.7. HAADF-STEM image (a), and elemental mapping images of Bi (b, magenta), V (c, cyan), Cu (d, yellow), Si (e, green), and O (f, red).

Figure 4.8. (a) Selected scan area for EDS, elemental mapping analysis of Bi (b, magenta), V (c, cyan), Cu (d, yellow), Si (e, light green), and O (f, red). (g) EDS of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres.

Figure 4.9. SEM images of SiO₂/BiVO₄/CuO_x at (a) 3000x magnification, (b) 7000x magnification, (c) 14,000x magnification, (d) 100,000x magnification.

The surface area and pore structure of the as-prepared SiO₂/BiVO₄ samples were studied by the Brunauer-Emmett-Teller (BET) method. The nitrogen sorption isotherms of the samples display the type IV isotherm (Figure 4.10a-g) with the most abundant pore size ranging from 9 to 13 nm (Table 4.1), implying the presence of mesoporous structures.⁷⁰ Furthermore, a trend was observed where the propyl-DMSN with a maximum pore size of 13 nm decreases to 10 nm with loadings of the BiVO₄ and CuO_x (Figure 4.10h).

Table 4.1. Physical properties of the as-prepared BiVO₄ samples

Samples	BET surface		
	area (m ² g ⁻¹)	Pore size (nm)	Crystallite size (nm)
1 SiO ₂ /BiVO ₄ (45 wt%)	172	13	14
2 SiO ₂ /BiVO ₄ (56 wt%)	122	12	17
3 SiO ₂ /BiVO ₄ (59 wt%)	119	11	21
4 SiO ₂ /BiVO ₄ (63 wt%)	87.7	9.0	31
5 ^a SiO ₂ /BiVO ₄ /CuO _x	122	10	21
6 Bulk BiVO ₄ crystals	2.60	-	37

^a Copper loading (20 mol%) based on SiO₂/BiVO₄ (59 wt%).

Figure 4.10. Nitrogen sorption isotherms of (a) DMSN, (b) propyl-DMSN, (c) $\text{SiO}_2/\text{BiVO}_4$ (45 wt%) nanospheres, (d) $\text{SiO}_2/\text{BiVO}_4$ (56 wt%) nanospheres (e) $\text{SiO}_2/\text{BiVO}_4$ (59 wt%) nanospheres, (f) $\text{SiO}_2/\text{BiVO}_4$ (63 wt%) nanospheres (g) $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres. (h) Pore size distribution of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres (blue), $\text{SiO}_2/\text{BiVO}_4$ (59 wt%) nanospheres (red), and propyl-DMSN (black)

4.4.2 Redox and optical properties

XPS measurements were then performed to investigate the chemical states of the SiO₂/BiVO₄/CuO_x nanospheres. As shown in Figure 4.11a, Bi, O, V, and C are observed in SiO₂/BiVO₄, while Cu was detected only in the SiO₂/BiVO₄/CuO_x sample. The Cu 2p core level spectrum can be fitted to four peaks (Figure 4.11b). The two major peaks at 932.5 and 952.4 eV are characteristic Cu⁺ 2p_{3/2} and 2p_{1/2}, respectively. The shake-up peaks at 933.8 and 954.1 eV and the two strong satellites at about 942.2 and 961.9 eV correspond to Cu²⁺ 2p_{3/2} and 2p_{1/2}, which are characteristic of a 3d⁹ ground state configuration for CuO.⁷¹ It is noteworthy that the intensity of Cu⁺ is stronger than Cu²⁺ on the surface, implying that CuO_x is predominantly composed of Cu₂O. By comparing the spectral area intensities of the peaks in Figure 4.11b, it was found that the ratio between Cu₂O:CuO in SiO₂/BiVO₄/CuO_x was 7:2. For both SiO₂/BiVO₄ and SiO₂/BiVO₄/CuO_x nanospheres, the binding energies of the Bi 4f band, in which two peaks are located at about 158.8 and 164.1-164.2 eV, can be indexed to the Bi 4f_{7/2} and Bi 4f_{5/2} bands, respectively (Figure 4.11c and g). Similarly, the binding energies at 516.5-516.6 and 524.0-524.1 eV, correspond to the V 2p_{3/2} and V 2p_{1/2} bands, respectively (Figure 4.11d and h). Two O 1s bands (for both SiO₂/BiVO₄ and SiO₂/BiVO₄/CuO_x nanospheres, 4.11e and f) were fitted and the binding energies at 529.3-529.4 and 530.2-530.4 eV are ascribed to lattice oxygen in SiO₂/BiVO₄/CuO_x and adsorbed H₂O or surface hydroxyl groups, respectively. The O 1s bands at 532.7-532.9 eV correspond to the lattice oxygen in SiO₂. Based on the HRTEM and XPS results, we believe that there is mixed valent CuO_x on the surface of the heterojunction of the SiO₂/BiVO₄/CuO_x heterogeneous nanostructures.

Figure 4.11. (a) XPS survey spectra of $\text{SiO}_2/\text{BiVO}_4$ (red), and $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ (green) samples. High resolution XPS spectra of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres for the elements, (b) Cu 2p, (c) Si 1s and Bi 4f, (d) V 2p, and (e) O 1s. High resolution XPS spectra of $\text{SiO}_2/\text{BiVO}_4$ nanospheres for the elements, (f) O 1s, (g) Si 1s and Bi 4f, and (h) V 2p.

We then evaluated the optical properties of the nanospheres and bulk BiVO₄ (Figure 4.12) with UV-vis DRS. The E_g energies of the samples were calculated from the UV-vis spectra by using a Tauc plot following the equation (Eqn. 3.5, Chapter 3).⁷² The coefficient n was found to be 4, consistent with the direct band properties of BiVO₄.⁷³ From the Tauc plots, the E_g was estimated to be 2.42, 2.60, and 2.60 eV for bulk BiVO₄, SiO₂/BiVO₄, and SiO₂/BiVO₄/CuO_x respectively (Figure 4.12b, d).

Figure 4.12. (a, and c) UV-vis DRS and (b, and d) Tauc plots of the as-prepared BiVO₄ samples.

The absorption edge of SiO₂/BiVO₄ and SiO₂/BiVO₄/CuO_x were slightly blue-shifted compared to bulk BiVO₄. Such a blue shift in the absorption edge of SiO₂/BiVO₄ concurs with the report by Iwase and Kudo, which explained that it was likely due to quantum confinement effects in the BiVO₄ nanocrystals.⁵⁹ Despite the weak absorption around the NIR region, the SiO₂/BiVO₄/CuO_x

nanospheres have similar E_g as their corresponding SiO₂/BiVO₄ samples, likely due to the low CuO_x loading.

The VB energies (E_{VB}) of SiO₂/BiVO₄/CuO_x, SiO₂/BiVO₄, and bulk BiVO₄ were determined by the addition of the work function (Φ relative to vacuum) and VBM measured using UPS, and they were determined to be and -6.86, -7.20, and -6.54 eV, respectively (Figure 4.13). The CB maxima (CBM) of SiO₂/BiVO₄/CuO_x can be estimated by subtracting E_g (2.60 eV) from the VBM, giving an CBM of -4.26 eV. The corresponding relative VB and CB levels are thus 2.42 V and -0.18 V *vs.* the normal hydrogen electrode (NHE), respectively, by assuming that the reference of 0 V *vs.* NHE corresponds to 4.44 eV *vs.* the vacuum level.⁷⁴ From these results, the highly positive VB implies a high oxidation ability of BiVO₄,⁷⁵ which favors the oxidation of benzylamine.⁷⁶

In addition, the UPS results support the staggered type II heterojunction upon incorporating CuO_x onto SiO₂/BiVO₄, with the VBM position at 3.13 ± 0.05 shifted to 2.89 ± 0.05 eV (or -7.20 shifted to -6.86 eV when normalized to vacuum) after band alignment (Figure 4.14). This shift favors the transfer of photogenerated electrons in the CB of BiVO₄ to the holes in the VB of Cu₂O upon visible light irradiation. This promotes the charge separation efficiency of the SiO₂/BiVO₄/CuO_x, which resulted in the superior PC oxidation from amine to imines.

Figure 4.13. Work function and UPS of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres (a and b, respectively), $\text{SiO}_2/\text{BiVO}_4$ nanospheres (c and d, respectively), and bulk BiVO_4 particles (e and f respectively).

Figure 4.14. A schematic diagram of a staggered type II heterojunction between SiO₂/BiVO₄ and CuO_x (based on a reported E_g of Cu₂O).⁷⁷

4.4.3 Optimization of photocatalytic conditions

With the SiO₂/BiVO₄/CuO_x nanospheres in hand, we applied them for the visible light-driven PC oxidative coupling of 4-methoxybenzylamine using molecular O₂ in air as the terminal oxidant, with bulk BiVO₄ as a reference for comparison (Table 4.2).⁵³ In each experiment, a 10 mol% loading level of BiVO₄ relative to the substrate was used. Although the bulk BiVO₄ sample apparently exhibited the highest turnover frequency per unit surface area (TOF/SA), all the SiO₂/BiVO₄ samples showed faster overall photocatalytic activity due to the substantially higher surface areas. Among the different loadings of BiVO₄, SiO₂/BiVO₄ (59 wt%), exhibited the optimal catalytic performance with 100% conversion only after 12 h giving a turnover frequency (TOF) over twice as high as bulk BiVO₄, with 99% yield (Table 4.2 entry 5). We propose that the higher exposed surface area (Table 4.1) and shorter charge transport distances ensure efficient charge extraction and improved PC activity in the nanospheres over bulk BiVO₄, without aggregation since the particles are well dispersed in SiO₂. The variation in PC performance among the different loading levels is also correlated with the size of the nanocrystallites (Table 4.2 entries 3-6) according to the following trend: 59 wt% $\approx$ 56 wt% > 45 wt%. A thicker depletion layer is

typically found to induce greater band bending in larger crystals and promote charge separation,⁶⁹ while small BiVO₄ nanocrystals contain higher surface defects with low crystallinity, resulting in lower activity (Table 4.2 entry 3). On the other hand, the highest loading level we examined (63 wt%) resulted in aggregation of the nanospheres as depicted in the TEM images (Figure 4.41). Negligible conversion and yield was observed in control experiments in the absence of any catalysts (Table 4.2, entry 1). Thus, we believe that the higher exposed surface area (Table 4.1) and shorter charge transport distances, attributable to the nano-sized mesostructure of the composite, ensure efficient charge extraction and improved photocatalytic activity in the nanospheres over bulk BiVO₄ (Table 4.2, entry 2).

After the optimizing the BiVO₄ loading at 59 wt% (Table 4.2 entries 3-6), CuO_x was introduced as a co-catalyst to further improve the catalytic performance (entries 9-11). Furthermore, in order to investigate the effects of using more eco-friendly solvents, the reaction was performed in acetone and ethyl acetate (Table 4.2, entries 7 and 8). Alcohols and water are unsuitable solvents because they can interfere in the oxidative coupling as competing nucleophiles. Among the solvents we tested, acetonitrile was the greenest solvent for this organic transformation, although we expect the heterogeneous photocatalysts to be stable in alcohols and water for other catalytic processes. The staggered type II heterojunction formed between BiVO₄ and CuO_x could facilitate simultaneous absorption of two photons in a Z-scheme over a slightly broader visible spectrum as well as more effective charge separation. The optimal Cu loading level is 20 mol% with respect to BiVO₄. Using this catalyst (Table 4.2 entry 10), the catalytic reaction showed 100% conversion and 99% yield after only 3.5 h, giving a TOF around 7 times higher than bulk BiVO₄. Low conversions and yields were recorded with just Cu₂O or CuO, or a mixture of Cu₂O and CuO with ratio of 7:2 (to mimic the surface composition determined by XPS studies above) in control experiments (Table 4.2, entries 12, 13, and 14, respectively).

Table 4.2. Evaluation of the optimized photocatalyst for the oxidative coupling of 4-methoxybenzylamine.^a

Entry	Photocatalyst	t (h)	Conv (%) ^b	Yield (%) ^b	TOF/SA (h ⁻¹ m ⁻² g) ^c	TOF (h ⁻¹)
1	-	12	4	3	-	0.025
2	Bulk BiVO ₄ crystals	24	100	98	0.16	0.41
3	SiO ₂ /BiVO ₄ (45 wt%)	12	66	65	0.0031	0.54
4	SiO ₂ /BiVO ₄ (56 wt%)	12	98	97	0.0066	0.81
5	SiO₂/BiVO₄ (59 wt%)	12	100	99	0.0070	0.83
6	SiO ₂ /BiVO ₄ (63 wt%)	12	87	87	0.0083	0.73
7 ^d	SiO ₂ /BiVO ₄ (59 wt%)	12	100	99	0.0036	0.83
8 ^e	SiO ₂ /BiVO ₄ (59 wt%)	12	100	99	0.0028	0.83
9 ^f	SiO ₂ /BiVO ₄ /CuO _x (10 mol%)	3.5	60	58	0.014	1.66
10^f	SiO₂/BiVO₄/CuO_x (20 mol%)	3.5	100	99	0.023	2.83
11 ^f	SiO ₂ /BiVO ₄ /CuO _x (50 mol%)	3.5	100	99	0.023	2.83
12	Cu ₂ O	3.5	3	3	-	0.086
13	CuO	3.5	3	3	-	0.086
14	Mixture of Cu ₂ O & CuO (7:2)	3.5	4	4	-	0.11

^a Reaction conditions: 0.10 mmol of 4-methoxybenzylamine, 10 mol% “BiVO₄” photocatalyst, 0.80 mL of CD₃CN in air, 48 W white LED lamp, 30 °C; ^b Determined by ¹H NMR yield with 3,5-dimethylanisole as an internal standard; ^c TOF normalized by the BET surface area (SA, Table 4.1); ^d Conducted in acetone; ^e Conducted in ethyl acetate; ^f Copper loading (mol% relative to BiVO₄) based on SiO₂/BiVO₄ (59 wt%).

We then proceeded to expand the substrate scope of the SiO₂/BiVO₄/CuO_x photocatalyst for the general oxidative coupling of benzylamines. Electron-rich benzylamines (methoxy, methyl, and *tert*-butyl derivatives) and electron-deficient ones (fluoro, chloro, bromo, and trifluoromethyl derivatives) were all compatible substrates (Table 4.3). Also, the reaction rate of the regio-isomer

increased in the order of ortho < meta < para, indicating the effect of steric hindrance on the rate (Table 4.3, entries 9-13), although the yields remained high regardless.

Table 4.3. PC oxidative coupling of various substrates by SiO₂/BiVO₄/CuO_x nanospheres.^a

$\text{R-CH}_2\text{NH}_2 \xrightarrow[\text{CD}_3\text{CN, 30 } ^\circ\text{C, air, white LED (48 W)}]{\text{photocatalyst (10 mol\%)}} \text{R-CH=N-CH}_2\text{R'}$					
Entry	Substrates	Products	t (h)	Yield (%) ^b	TOF (h ⁻¹)
1			4	99	2.48
2			6	99	1.65
3			5	99	1.98
4			7.5	99	1.32
5			9	98	1.09
6			6	99	1.65
7			7	99	1.41
8			11	99	0.90
9			3.5	99	2.83
10			5	99	1.98
11			6.5	99	1.52

12			4	99	2.48
13			6.8	99	1.46
14			6	96	1.60
15			11	96	0.96
16			10	99	0.99
17			7	99	1.41
18 ^c			13	83	0.64
19 ^c			9	86	0.96
20 ^c	$\text{H}_3\text{C}(\text{H}_2\text{C})_6\text{NH}_2$	$\text{H}_3\text{C}(\text{H}_2\text{C})_6\text{NH}_2$	22	77	0.35
21 ^c			30	61	0.20

^a Reaction conditions: 0.10 mmol of substrate, 6.0 mg SiO₂/BiVO₄/CuO_x nanospheres, 0.80 mL of CD₃CN, in air, 48 W white LED lamp, 30 °C. ^b Determined by ¹H NMR spectroscopy with 3,5-dimethylanisole as an internal standard; All reactions proceeded with quantitative conversion. ^c Reaction under O₂ (1 atm).

The SiO₂/BiVO₄/CuO_x nanospheres are also tolerant to heterocycles such as 2-thiophenemethylamine, which is known to poison metal catalysts *via* the sulfur atom (Table 4.3, entry 17). In addition to the homocoupling reactions, an oxidative cross-coupling between benzylamine and heptylamine was also conducted, showing moderate yield (Table 4.3, entry 20). Benzaldehyde was

formed as a minor by-product in all reactions (~1-4%), which is likely due to hydrolysis of the imines in the presence of water from the reduction of O₂. We further performed the oxidative dehydrogenation of 2-methylindoline and gratifyingly, the reaction proceeded with quantitative conversion of 100% and reasonable yield of 61% under visible light irradiation (Table 4.3, Entry 21).

4.4.4 Mechanistic insights by radical scavenging

To derive insights into the PC mechanism of SiO₂/BiVO₄/CuO_x, the reaction rates have been compared for different *para*-substituted benzylamines and in the presence of disparate chemical scavengers. The Hammett plot for a series of benzylamine derivatives of increasing electron-deficiency (methoxy, methyl, hydrogen, chloro, and trifluoromethyl) evidently exhibit a negative slope ($\rho = -0.27$, $R^2 = 0.93$), implying the intermediacy of a carbocationic PhCH₂NH₂^{•+} formed by the holes during oxidation by the SiO₂/BiVO₄/CuO_x nanospheres (Table 4.4 and Figure 4.15).⁷⁸

Table 4.4. Comparison of the conversion ratio of selected *para*-substituted benzylamines after photooxidation over a reaction time of 60 min with SiO₂/BiVO₄/CuO_x nanospheres as the photocatalyst.^a

Entry	Substituent	Conversion (%) ^b
1	<i>p</i> -OCH ₃	40
2	<i>p</i> -CH ₃	35
3	<i>p</i> -H	30
4	<i>p</i> -Cl	25
5	<i>p</i> -CF ₃	17

^a Reaction conditions: 0.10 mmol of *para*-substituted benzylamine, 0.80 mL of CD₃CN, in air, 48 W white LED lamp, 30 °C. ^b Determined by ¹H NMR yield with 3,5-dimethylanisole as internal standard.

Figure 4.15. Hammett plot for the photo-oxidative coupling of *para*-substituted benzylamines over SiO₂/BiVO₄/CuO_x.

Scavenging experiments were then conducted to compare the rates for the oxidative coupling of compound 4-methoxybenzylamine (Figure 4.16a). The scavengers include triethylamine (TEA) for holes, silver nitrate (AgNO₃) for electrons, benzoquinone (BQ) for superoxide, and isopropanol (IPA) for hydroxyl (•OH) radicals. IPA had little effect, whereas TEA, and both AgNO₃ and BQ especially dramatically diminished the conversion after 7 h, indicating

that holes and superoxide radicals were the main reactive species. EPR spectroscopy was used to detect the superoxide radicals with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as the radical trap. We observed EPR signals that are characteristic of a superoxide adduct of DMPO^{29, 79}, confirming that superoxide radicals are generated during the photocatalytic reaction with $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ (Figure 4.16b). To detect an amine radical cation intermediate formed due to oxidation by the holes during the reaction, a stable radical (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) was employed as a radical trap. We observed inhibition of the reaction by TEMPO, confirming that the reaction proceeded *via* a radical process (Appendix I, Figure 4.50). Subsequently, the amine radical cation intermediate was successfully trapped by diisopropyl azodicarboxylate, and the product from this trapping was confirmed by ^1H NMR spectroscopy and liquid chromatography-mass spectrometry (Appendix I, Figure 4.51 and 4.52).

Figure 4.16. (a) Comparison of conversion rate with addition of different chemical scavengers. (b) EPR spectra of the photocatalytic reaction mixture after addition of DMPO as a superoxide trap under visible light illumination (red line on top) and in the dark (black line at the bottom). The signal under illumination is characteristic of superoxide radicals trapped by DMPO.

In addition, the “on-off” experiment suggested that this photocatalysis was not a radical chain reaction (Figure 4.17).

Figure 4.17. Conversion rate against time for the oxidative coupling of 4-methoxybenzylamine with consecutive light and dark exposure.

There are at least two possible, commonly recognized mechanisms for the migration and separation of electron and hole pairs: a double charge transfer and a Z-scheme mechanism (Figure 4.18). A mechanism via a double charge transfer mode⁷⁴ (Figure 4.18a) is probably not operating since the more positive CB electrons of BiVO_4 (+0.2 V vs. NHE)⁸⁰ would not be able to reduce O_2 to superoxide radicals (-0.16 V vs. NHE).⁸¹ On the other hand, the more negative CB of CuO_x is able to reduce O_2 to superoxide radicals and hence, the Z-scheme mechanism (Figure 4.18b) is likely to be energetically more feasible.⁸²

Figure 4.18. Proposal for the photoexcited electron–hole separation processes: (a) a double charge transfer mechanism and (b) a Z-scheme mechanism.

On the basis of the type II heterojunction band alignment of BiVO₄ and CuO_x, we propose light absorption and charge separation *via* a Z-scheme (Figure 4.19). The excited electrons are transferred to O₂ to produce superoxide radicals, while the holes migrate to the VB of CuO_x and oxidize the amine to amine radical cations. A reaction between the superoxide radical and the amine radical cation forms the intermediate imine, which leads to the desired product after addition of a second amine and loss of NH₃.

Figure 4.19. Proposed mechanism for the oxidative coupling of benzylamine photocatalyzed by SiO₂/BiVO₄/CuO_x nanospheres.

4.4.5 Photoluminescence and photoelectrochemical studies

PL and TR-PL experiments were then performed on SiO₂/BiVO₄ and SiO₂/BiVO₄/CuO_x to determine the recombination efficiency of charge carriers, both of which were found to exhibit emission around 505 nm (Figure 4.20a).⁷³ TR-PL measurements were performed (Figure 4.20b) to understand the origin of the charge recombination components. By fitting the TR-PL decay curves to an exponential model, the PL lifetime of SiO₂/BiVO₄ was found to increase from 2.3 ns to 4.5 ns with the addition of CuO_x on the surface and this corresponds to the recombination rate of photogenerated carriers under light excitation. Therefore, the longer PL lifetime indicates slower charge recombination rate for

$\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ after the introduction of CuO_x on the surface, which improves the charge separation lifetime and extraction of photogenerated electron-hole pairs, leading to the improved photocatalytic performance.

The photocatalytic activities of the prepared composites are closely related to the separation and transport ability of the photogenerated electron-hole pairs. EIS and photocurrent measurements were thus used to investigate the separation efficiency of the charge pairs. Typically, a Nyquist plot obtained from an EIS measurement gives an arc, where a smaller arc radius indicates a lower charge transfer resistance across the electrolyte/semiconductor, which correlates to more effective separation of the electron-hole pairs.^{29, 82} Instead, we observed almost linear plots for both $\text{SiO}_2/\text{BVO}_4$ and $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$, which could be due to the high charge transfer resistance caused by the insulation of the SiO_2 . Similar observations had been made in reports by Zeng and co-workers.^{29, 82} Nonetheless, the EIS “radius of the arc” of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ is smaller than that of $\text{SiO}_2/\text{BiVO}_4$, implying that the photoexcited charge carriers in $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ have lower recombination efficiency than in $\text{SiO}_2/\text{BiVO}_4$ (Figure 4.20c).^{29, 82} Therefore, the EIS results indicated that the $\text{BiVO}_4/\text{CuO}_x$ heterojunction could facilitate the separation of photoinduced charge pairs, leading to the improved photocatalytic performance.

Figure 4.20. (a) Time-integrated PL spectra, (b) time-resolved PL spectra, (c) EIS spectra, and (d) transient photocurrent response against time for $\text{SiO}_2/\text{BiVO}_4$ (black) and $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ (red). In (b), the fits are the solid lines. PL and TR-PL experiments were performed on $\text{SiO}_2/\text{BiVO}_4$ and $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$, with photoexcitation at 400 nm and $\sim 30 \mu\text{J}/\text{cm}^2$ fluence.

Transient photocurrent experiments were also performed to support the EIS studies and investigate the charge separation abilities⁸³ of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ and $\text{SiO}_2/\text{BiVO}_4$ electrodes (Figure 4.20d). The photocurrent density of the electrodes were recorded for six “on-off” cycles with pulses of 10 seconds under visible light irradiation. The photocurrent density of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ electrode was about 3.5 times higher than that of $\text{SiO}_2/\text{BiVO}_4$ when taken at 0.50 V vs AgCl/Ag. This further highlighted that the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ photocatalyst was superior to $\text{SiO}_2/\text{BiVO}_4$ for more effective charge-pair separation and transfer *via* a Z-scheme system.

4.4.6 Recyclability of the photocatalysts

To determine the stability and recyclability of the SiO₂/BiVO₄/CuO_x nanospheres, photo-oxidative coupling of 4-methoxybenzylamine was repeated for at least ten cycles with the catalyst recycled after each run (Figure 4.21). After each catalytic run, the heterogeneous catalysts could be recovered by centrifugation, and the residue was rinsed with solvent, dried, and recycled. It appeared that the BiVO₄ nanocrystals after multiple catalytic cycles did not aggregate when stabilized in the SiO₂ scaffold, as we anticipated (Figure 4.22).

Figure 4.21. Recycling performance of SiO₂/BiVO₄/CuO_x towards photo-oxidative coupling of 4-methoxybenzylamine.

High conversions of the substrate were maintained for the first three catalytic runs, after which a gradual decrease in the conversion was observed, although high yield for the imine product was maintained (Figure 4.21).⁶¹⁻⁶³

Figure 4.22. TEM images of SiO₂/BiVO₄/CuO_x nanospheres after (a) 2nd, (b) 4th, (c) 8th, and (d) 10th cycles of photocatalysis.

To investigate the chemical composition of the SiO₂/BiVO₄/CuO_x nanospheres after photocatalysis, we conducted XPS measurements on the recovered nanomaterials after the 2nd and 4th cycles (Figure 4.23). The XPS data of the SiO₂/BiVO₄/CuO_x nanospheres after the 2nd and 4th cycles show the presence of Cu 2p, Si 1s and Bi 4f, and V 2p bands in the samples. The binding energies of Bi 4f and V 2p bands were found to be similar to those in Figure 4.11, thus confirming that no significant change in the oxidation states of Bi and V had occurred after the photocatalytic reaction. The Cu 2p core level spectra of SiO₂/BiVO₄/CuO_x after the 2nd and 4th cycles can be fitted with two components each (Figure 4.23a and d). The two peaks at 931.7-932.9 and 951.7-952.8 eV are characteristic of Cu⁺ 2p_{3/2} and 2p_{1/2}, respectively. The two weak shake-up satellites correspond to the Cu²⁺ species.^{71, 84}

Figure 4.23. High resolution XPS of SiO₂/BiVO₄/CuO_x nanospheres after 2nd cycle of photocatalysis for elements (a) Cu 2p, (b) Si 1s and Bi 4f, and (c) V 2p. High resolution XPS of SiO₂/BiVO₄/CuO_x nanospheres after 4th cycle of photocatalysis for elements (d) Cu 2p, (e) Si 1s and Bi 4f, and (f) V 2p.

It is noteworthy that the intensities of the Cu²⁺ signals became negligible after the reaction compared to before the reaction (Figure 4.11b), implying that the Cu²⁺ species in CuO_x was further reduced to Cu₂O. In addition, this observation provided more definitive evidence that the electrons from BiVO₄ were transferred to CuO_x, which reduced Cu²⁺ to Cu⁺ *via* a Z-scheme mechanism instead of oxidation of CuO_x to generate more Cu²⁺ species *via* a double charge transfer mechanism (Figure 4.18).⁸²

To understand this decay in catalytic activity, we investigated the elemental composition of the catalysts after the 2nd, 4th, 8th, and 10th cycles (Figure 4.24) by SEM-EDS, and found that the slow decay in catalytic performance was due to dissolution of V first, followed by Bi and Cu later. After each run, the heterogeneous catalysts could be recovered by centrifugation, and the residue was rinsed with solvent, dried, and recycled. Apart from incomplete recovery of the photocatalyst, it was found that the levels of V decreased as the catalysts were recycled, with the V:Bi ratio deviating from a 1:1 ratio. This indicated that small

amounts of V leached during the catalytic process. Furthermore, although the Bi and Cu contents remained stable up to the 8th cycle, by the 10th cycle, both Bi and Cu were also starting to deplete from the nanospheres.

Figure 4.24. Elemental composition of SiO₂/BiVO₄/CuO_x nanospheres after a) 2nd cycle, b) 4th cycle, (c) 8th cycle, and 10th cycle of photocatalysis.

4.5 Conclusions

In summary, we have fabricated mesoporous SiO₂/BiVO₄/CuO_x nanospheres as a chromophore in a Z-scheme system for effective light harvesting and charge separation. The SiO₂/BiVO₄/CuO_x nanospheres are effective for the PC oxidative coupling of a broad range of benzylamines and are also viable for the dehydrogenation of indolines under ambient atmospheric conditions. The superior PC performance of SiO₂/BiVO₄/CuO_x is attributed to the presence of CuO_x nanoparticles on the surface, which extend the light absorption and dramatically improve charge separation. To the best of our knowledge, this is the first instance of uniform nanoparticulate BiVO₄/CuO_x catalysts that absorb light *via* a Z-scheme for photoredox organic synthesis. We envision that this work will

pave the way for the use of more solutions from AP in the synthesis of fine chemicals.

4.6 Characterization of products

***N*-(4-methoxybenzylidene)-4-methoxybenzylamine** (See Appendix I, Figure 4.25). ¹H NMR (400 MHz, CD₃CN): δ = 3.76 (s, 3 H), 3.82 (s, 3 H), 4.65 (s, 2 H), 6.89 (d, J = 8.7 Hz, 2 H), 6.97 (d, J = 8.8 Hz, 2 H), 7.24 (d, J = 8.8 Hz, 2 H), 7.69 (d, J = 8.8 Hz, 2 H), 8.34 (s, 1 H) ppm. HRMS (ESI+, m/z) calculated for C₁₆H₁₈NO₂ [M + H]⁺ m/z = 256.1338, found 256.1335. The spectroscopic data matches those from a previous report.⁸⁵

***N*-benzylidenebenzylamine** (See Appendix I, Figure 4.26). The reaction mixture was irradiated for 4 h. ¹H NMR (400 MHz, CD₃CN): δ = 4.77 (s, 2 H), 7.25 – 7.30 (m, 1 H), 7.35 (d, J = 4.4 Hz, 4 H), 7.44-7.46 (m, 3 H) 7.77 – 7.79 (m, 2 H), 8.46 (s, 1 H) ppm. HRMS (ESI+, m/z) calculated for C₁₄H₁₄N [M + H]⁺ m/z = 196.1126, found 196.1128. The spectroscopic data matches those from a previous report.⁸⁵

***N*-(4-fluorobenzylidene)-4-fluorobenzylamine** (See Appendix I, Figures 4.27 & 4.28). The reaction mixture was irradiated for 6 h. ¹H NMR (400 MHz, CD₃CN): δ = 4.73 (s, 2 H), 7.08 (t, J = 8.9 Hz, 2 H), 7.18 (t, J = 8.9 Hz, 2 H), 7.36 (dd, J = 8.7, 5.6 Hz, 2 H), 7.80 (dd, J = 8.8, 5.7 Hz, 2 H), 8.42 (s, 1 H) ppm. ¹⁹F[¹H] NMR (CD₃CN, 282.40 MHz): δ = -117.69, -111.35 ppm. HRMS (ESI+,

m/z) calculated for C₁₄H₁₂F₂N [M + H]⁺ m/z = 232.0938, found 232.0943. The spectroscopic data matches those from a previous report.⁸⁵

***N*-(4-chlorobenzylidene)-4-chlorobenzylamine** (See Appendix I, Figure 4.29).

The reaction mixture was irradiated for 5 h. ¹H NMR (400 MHz, CD₃CN): δ = 4.74 (s, 2 H), 7.32 – 7.37 (m, 4 H), 7.45 (d, J = 8.5 Hz, 2 H), 7.75 (d, J = 8.5 Hz, 2 H), 8.42 (s, 1 H) ppm. HRMS (ESI⁺, m/z) calculated for C₁₄H₁₂Cl₂N [M + H]⁺ m/z = 264.0347, found 264.0345. The spectroscopic data matches those from a previous report.⁸⁵

***N*-(2-chlorobenzylidene)-2-chlorobenzylamine** (See Appendix I, Figure 4.30).

The reaction mixture was irradiated for 7.5 h. ¹H NMR (400 MHz, CD₃CN): δ = 4.92 (s, 2 H), 7.28 – 7.38 (m, 3 H), 7.42 – 7.45 (m, 4 H), 8.04 (d, J = 7.3 Hz, 1 H), 8.88 (s, 1 H) ppm. HRMS (ESI⁺, m/z) calculated for C₁₄H₁₂Cl₂N [M + H]⁺ m/z = 264.0347, found 264.0357. The spectroscopic data matches those from a previous report.⁸⁶

***N*-(2,4-dichlorobenzylidene)-2,4-dichlorobenzylamine** (See Appendix I,

Figure 4.31). The reaction mixture was irradiated for 9 h. ¹H NMR (400 MHz, CD₃CN): δ = 4.88 (s, 2 H), 7.34 (dd, J = 8.3, 2.0 Hz, 1 H), 7.39 (dd, J = 8.5, 2.0 Hz, 1 H), 7.45 (d, J = 8.3 Hz, 1 H), 7.53 (dd, J = 14.7, 2.0 Hz, 2 H), 8.01 (d, J = 8.5 Hz, 1 H), 8.82 (s, 1 H) ppm. HRMS (ESI⁺, m/z) calculated for C₁₄H₁₀Cl₄N [M + H]⁺ m/z = 331.9567, found 331.9581. The spectroscopic data matches those from a previous report.⁸⁵

***N*-(4-bromobenzylidene)-4-bromobenzylamine** (See Appendix I, Figure 4.32).

The reaction mixture was irradiated for 6 h. ¹H NMR (400 MHz, CD₃CN): δ = 4.72 (s, 2 H), 7.28 (d, J = 8.5 Hz, 2 H), 7.50 (d, J = 8.4 Hz, 2 H), 7.61 (d, J = 8.5 Hz, 2 H), 7.69 (d, J = 8.5 Hz, 2 H), 8.41 (s, 1 H) ppm. HRMS (ESI+, m/z) calculated for C₁₄H₁₂Br₂N [M + H]⁺ m/z = 351.9336, found 351.9329. The spectroscopic data matches those from a previous report.⁸⁷

***N*-(3-trifluoromethylbenzylidene)-3-trifluoromethylbenzylamine** (See

Appendix I, Figures 4.33 & 4.34). The reaction mixture was irradiated for 11 h.

¹H NMR (400 MHz, CD₃CN): δ = 4.88 (s, 2 H), 7.53 – 7.70 (m, 5 H), 7.77 (d, J = 7.8 Hz, 1 H), 8.04 (d, J = 7.8 Hz, 1 H), 8.09 (s, 1 H), 8.55 (t, J = 1.3 Hz, 1 H) ppm. ¹⁹F[¹H] NMR (CD₃CN, 282.40 MHz): δ = -63.42, -63.15 ppm. HRMS (ESI+, m/z) calculated for C₁₆H₁₂F₆N [M + H]⁺ m/z = 332.0874, found 332.0870.

The spectroscopic data matches those from a previous report.⁸⁶

***N*-(4-trifluoromethylbenzylidene)-4-trifluoromethylbenzylamine** (See

Appendix I, Figure 4.35 & 4.36). The reaction mixture was irradiated for 7 h. ¹H

NMR (400 MHz, CD₃CN): δ = 4.89 (s, 2 H), 7.56 (d, J = 8.1 Hz, 2 H), 7.67 (d, J = 8.2 Hz, 2 H), 7.76 (d, J = 8.2 Hz, 2 H), 7.96 (d, J = 8.1 Hz, 2 H), 8.56 (s, 1 H) ppm. ¹⁹F[¹H] NMR (CD₃CN, 282.40 MHz): δ = -63.41, -62.99 ppm. HRMS (ESI+, m/z) calculated for C₁₆H₁₂F₆N [M + H]⁺ m/z = 332.0874, found 332.0878.

The spectroscopic data matches those from a previous report.⁸⁶

***N*-(2-methoxybenzylidene)-2-methoxybenzylamine** (See Appendix I, Figure 4.37). The reaction mixture was irradiated for 6.5 h. ¹H NMR (400 MHz, CD₃CN): δ = 3.82 (s, 3 H), 3.86 (s, 3 H), 4.74 (s, 2 H), 6.91 – 6.97 (m, 3 H), 7.04 (d, J = 8.4 Hz, 1 H), 7.24 – 7.29 (m, 2 H), 7.42 (ddd, J = 8.5, 7.4, 1.8 Hz, 1 H), 7.89 (dd, J = 7.7, 1.8 Hz, 1 H), 8.80 (s, 1 H) ppm. HRMS (ESI+, m/z) calculated for C₁₆H₁₈NO₂ [M + H]⁺ m/z = 256.1338, found 256.1340. The spectroscopic data matches those from a previous report.⁸⁶

***N*-(3-methoxybenzylidene)-3-methoxybenzylamine** (See Appendix I, Figure 4.38). The reaction mixture was irradiated for 5 h. ¹H NMR (400 MHz, CD₃CN): δ = 3.77 (s, 3 H), 3.81 (s, 3 H), 4.73 (s, 2 H), 6.79 – 6.86 (m, 1 H), 6.93 – 6.90 (m, 2 H), 7.02 (ddd, J = 7.8, 2.5, 1.7 Hz, 1 H), 7.26 (t, J = 8.1 Hz, 1 H), 7.31 – 7.38 (m, 3 H), 8.41 (t, J = 1.3 Hz, 1 H) ppm. HRMS (ESI+, m/z) calculated for C₁₆H₁₈NO₂ [M + H]⁺ m/z = 256.1338, found 256.1336. The spectroscopic data matches those from a previous report.⁸⁶

***N*-(2-methylbenzylidene)-2-methylbenzylamine** (See Appendix I, Figure 4.39). The reaction mixture was irradiated for 6.8 h. ¹H NMR (400 MHz, CD₃CN): δ = 2.39 (s, 3 H), 2.51 (s, 3 H), 4.80 (s, 2 H), 7.16 – 7.25 (m, 5 H), 7.28 – 7.34 (m, 2 H), 7.86 (d, J = 8.8 Hz, 1 H), 8.76 (s, 1 H) ppm. HRMS (ESI+, m/z) calculated for C₁₆H₁₈N [M + H]⁺ m/z = 224.1439, found 224.1443. The spectroscopic data matches those from a previous report.⁸⁵

***N*-(4-methylbenzylidene)-4-methylbenzylamine** (See Appendix I, Figure 4.40).

The reaction mixture was irradiated for 4 h. ¹H NMR (400 MHz, CD₃CN): δ = 2.31 (s, 3 H), 2.36 (s, 3 H), 4.69 (s, 2 H), 7.16 (d, J = 7.9 Hz, 2 H), 7.20 – 7.26 (m, 4 H), 7.65 (d, J = 8.1 Hz, 2 H), 8.39 (s, 1 H) ppm. HRMS (ESI+, m/z) calculated for C₁₆H₁₈N [M + H]⁺ m/z = 224.1439, found 224.1437. The spectroscopic data matches those from a previous report.⁸⁵

***N*-(4-(*tert*-butyl)benzylidene)-4-(*tert*-butyl)benzylamine** (See Appendix I,

Figure 4.41). The reaction mixture was irradiated for 6 h. ¹H NMR (400 MHz, CD₃CN): δ = 1.30 (s, 9 H), 1.32 (s, 9 H), 4.71 (s, 2 H), 7.26 (d, J = 8.5 Hz, 2 H), 7.39 (d, J = 8.4 Hz, 2 H), 7.48 (d, J = 8.4 Hz, 2 H), 7.69 (d, J = 8.4 Hz, 3 H), 8.41 (s, 1 H) ppm. HRMS (ESI+, m/z) calculated for C₂₂H₃₀N [M + H]⁺ m/z = 308.2378, found 308.2382. The spectroscopic data matches those from a previous report.⁸⁵

***N*-(2,4,6-trimethylbenzylidene)-2,4,6-trimethylbenzylamine** (See Appendix I,

Figures 4.42 & 4.43). The reaction mixture was irradiated for 11 h. ¹H NMR (400 MHz, CD₃CN): δ = 2.23 (s, 6 H), 2.28 (s, 6 H), 2.34 (s, 6 H), 4.84 (s, 2 H), 6.85 (s, 2 H), 6.87 (s, 2 H), 8.61 (s, 1 H) ppm. ¹³C[¹H] NMR (CD₃CN, 100 MHz): δ = 20.3, 21.1, 21.4, 21.5, 60.3, 129.5, 130.1, 130.5, 131.7, 131.8, 134.0, 137.9, 138.6, 138.7, 140.0, 142.6, 162.2 ppm. HRMS (ESI+, m/z) calculated for C₂₀H₂₆N [M + H]⁺ m/z = 280.205, found 280.2066.

N-(1-naphthylmethylimine)-1-naphthylmethylamine (See Appendix I, Figure 4.44). The reaction mixture was irradiated for 10 h. ¹H NMR (400 MHz, CD₃CN): δ = 5.35 (s, 2 H), 7.48 – 7.60 (m, 7 H), 7.85 (d, J = 8.2 Hz, 1 H), 7.91 – 7.95 (m, 4 H), 8.32 (d, J = 8.5 Hz, 1 H), 9.06 (d, J = 9.2 Hz, 1 H), 9.16 (s, 1 H) ppm. HRMS (ESI⁺, m/z) calculated for C₂₂H₁₈N [M + H]⁺ m/z = 296.1439, found 296.1440. The spectroscopic data matches those from a previous report.⁸⁸

N-(α -methylbenzylidene)- α -methylbenzylamine (See Appendix I, Figure 4.45). The reaction mixture was irradiated for 9 h. ¹H NMR (400 MHz, CD₃CN): δ = 1.45 (d, J = 6.5 Hz, 3 H), 2.28 (s, 3H), 4.91 (q, J = 6.5 Hz, 1 H), 7.21 – 7.25 (m, 1 H), 7.34 (t, J = 7.8 Hz, 2 H), 7.39 – 7.41 (m, 3 H), 7.48 (d, J = 7.8 Hz, 2 H), 7.85 – 7.87 (m, 2 H) ppm. HRMS (ESI⁺, m/z) calculated for C₁₆H₁₈N [M + H]⁺ m/z = 224.1439, found 224.1443. The spectroscopic data matches those from a previous report.⁸⁵

N-(2-thiophenemethylimine)-2-thiophenemethylamine (See Appendix I, Figure 4.46). The reaction mixture was irradiated for 7 h. ¹H NMR (400 MHz, CD₃CN): δ = 4.88 (s, 2 H), 6.99 – 7.00 (m, 2 H), 7.12 (dd, J = 5.0, 3.6 Hz, 1 H), 7.30 (dd, J = 3.9, 2.5 Hz, 1 H), 7.42 (dd, J = 3.6, 1.0 Hz, 1 H), 7.51 (d, J = 5.0 Hz, 1 H), 8.51 (s, 1 H) ppm. HRMS (ESI⁺, m/z) calculated for C₁₀H₁₀NS₂ [M + H]⁺ m/z = 208.0255, found 208.0254. The spectroscopic data matches those from a previous report.⁸⁵

***N*-(3,4-(methylenedioxy)benzylidene)-3,4-(methylenedioxy)benzylamine**

(See Appendix I, Figure 4.47). The reaction mixture was irradiated for 13 h and reaction was conducted with 1 atm O₂. ¹H NMR (400 MHz, CD₃CN): δ = 4.61 (s, 2 H), 5.92 (s, 2 H), 5.99 (s, 2 H), 6.79 (s, 2 H), 6.83 (s, 1 H), 6.88 (d, J = 8.0 Hz, 1 H), 7.17 (d, J = 8.0 Hz, 1 H) 7.32 (s, 1 H), 8.27 (s, 1 H) ppm. HRMS (ESI+, m/z) calculated for C₁₆H₁₄NO₄ [$M + H$]⁺ m/z = 284.0923, found 284.0930. The spectroscopic data matches those from a previous report.⁸⁵

***N*-benzylideneheptylamine** (See Appendix I, Figure 4.48). The reaction mixture

was irradiated for 22 h and the reaction was conducted with 1 atm O₂. ¹H NMR (400 MHz, CDCl₃): δ = 0.89 (t, J = 6 Hz, 3 H), 1.27–1.35 (m, 8 H), 1.65–1.74 (m, 2 H), 3.61 (t, J = 7 Hz, 2 H), 7.37–7.41 (m, 3 H), 7.70–7.74 (m, 2 H), 8.27 (s, 1 H) ppm. HRMS (ESI+, m/z) calculated for C₁₄H₂₂N [$M + H$]⁺ m/z = 204.1752, found 204.1756. The spectroscopic data matches those from a previous report.⁸⁸

Compound 2-methylindole (See Appendix I, Figure 4.49). The reaction mixture

was irradiated for 30 h and the reaction was conducted with 1 atm O₂. ¹H NMR (400 MHz, CD₃CN): δ = 2.40 (s, 3 H), 6.14 (s, 1 H), 6.97 (t, J = 7.4 Hz, 1 H), 7.03 (t, J = 7.7, 1 H), 7.29 (d, J = 8.0 Hz, 1 H), 7.42 (d, J = 7.8 Hz, 1 H), 9.06 (s, 1 H) ppm. HRMS (ESI+, m/z) calculated for C₉H₁₀N [$M + H$]⁺ m/z = 132.0813, found 132.0815. The spectroscopic data matches those from a previous report.⁸⁹

4.7 References

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4.8 Appendix I

Figure 4.25. The ¹H NMR spectrum of *N*-(4-methoxybenzylidene)-4-methoxybenzylamine.

Figure 4.26. The ¹H NMR spectrum of *N*-benzylidenebenzylamine.

Figure 4.27. The ^1H NMR spectrum of *N*-(4-fluorobenzylidene)-4-fluorobenzylamine.

Figure 4.28. The ^{19}F NMR spectrum of *N*-(4-fluorobenzylidene)-4-fluorobenzylamine.

Figure 4.29. The ¹H NMR spectrum of *N*-(4-chlorobenzylidene)-4-chlorobenzylamine.

Figure 4.30. The ¹H NMR spectrum of *N*-(2-chlorobenzylidene)-2-chlorobenzylamine.

Figure 4.31. The ¹H NMR spectrum of *N*-(2,4-dichlorobenzylidene)-2,4-dichlorobenzylamine.

Figure 4.32. The ¹H NMR spectrum of *N*-(4-bromobenzylidene)-4-bromobenzylamine.

Figure 4.33. The ^1H NMR spectrum of *N*-(3-trifluoromethylbenzylidene)-3-trifluoromethylbenzylamine.

Figure 4.34. The ^{19}F NMR spectrum of *N*-(3-trifluoromethylbenzylidene)-3-trifluoromethylbenzylamine.

Figure 4.35. The ^1H NMR spectrum of *N*-(4-trifluoromethylbenzylidene)-4-trifluoromethylbenzylamine.

Figure 4.36. The ^{19}F NMR spectrum of *N*-(4-trifluoromethylbenzylidene)-4-trifluoromethylbenzylamine.

Figure 4.37. The ¹H NMR spectrum of *N*-(2-methoxybenzylidene)-2-methoxybenzylamine.

Figure 4.38. The ¹H NMR spectrum of *N*-(3-methoxybenzylidene)-3-methoxybenzylamine.

Figure 4.39. The ^1H NMR spectrum of *N*-(2-methylbenzylidene)-2-methylbenzylamine.

Figure 4.40. The ^1H NMR spectrum of *N*-(4-methylbenzylidene)-4-methylbenzylamine.

Figure 4.41. The ¹H NMR spectrum of *N*-(4-(tert-butyl)benzylidene)-4-(tert-butyl)benzylamine.

Figure 4.42. The ¹H NMR spectrum of compound *N*-(2,4,6-trimethylbenzylidene)-2,4,6-trimethylbenzylamine.

Figure 4.43. The ¹³C NMR spectrum of compound *N*-(2,4,6-trimethylbenzylidene)-2,4,6-trimethylbenzylamine.

Figure 4.44. The ¹H NMR spectrum of *N*-(1-naphthylmethylimine)-1-naphthylmethylamine.

Figure 4.45. The ¹H NMR spectrum of *N*-(α -methylbenzylidene)- α -methylbenzylamine.

Figure 4.46. The ¹H NMR spectrum of *N*-(2-thiophenemethylimine)-2-thiophenemethylamine.

Figure 4.47. The ¹H NMR spectrum of *N*-(3,4-(methylenedioxy)benzylidene)-3,4-(methylenedioxy)benzylamine.

Figure 4.48. The ¹H NMR spectrum of *N*-benzylideneheptylamine.

Figure 4.49. The ^1H NMR spectrum of 2-methylindole.

Figure 4.50. The ^1H NMR spectrum from the radical trap experiment with $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$, 4-methoxybenzylamine, and TEMPO. The signals belonging to the 4-methoxybenzylamine reagent are indicated by the orange circles, while the signals

from the *N*-(4-methoxybenzylidene)-4-methoxybenzylamine product are indicated by the blue triangles. The reaction was inhibited, confirming that the reaction likely proceeded *via* a radical process.

Figure 4.51. The ¹H NMR spectrum from the radical trap experiment with SiO₂/BiVO₄/CuO_x, 4-methoxybenzylamine, and diisopropyl azodicarboxylate. The signals belonging to 4-methoxybenzylamine are indicated by the orange circles, *N*-(4-methoxybenzylidene)-4-methoxybenzylamine is indicated by the blue triangles, diisopropyl azodicarboxylate is indicated by the black squares, and the trapped radical is indicated by the red stars.

Figure 4.52. Liquid chromatography-mass spectrum at a retention time of 6.77 sec from the radical trap experiment with SiO₂/BiVO₄/CuO_x, 4-methoxybenzylamine, and diisopropyl azodicarboxylate, confirming the detection of the trapped amine radical cation.

Chapter 5

Stabilization of Nickel Catalysts on Metal Oxide Supports via Photoclick Chemistry for Alkene Epoxidation

*This chapter details the development of hybrid nanomaterials with single-site catalysts by immobilization of Ni molecular complexes on TiO_2 , WO_3 , and CeO_2 , with photoclick chemistry. The mesoporous SiO_2 and BiVO_4 from Chapter 4 were also employed as solid supports for the photochemical anchoring reaction to mimic the surface composition in $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres as a proof of concept. We have utilized maleimide as a photoactivated anchoring group, and have definitive evidence of the active site molecular structure from a range of characterization techniques. The hybrid nanomaterials function with quantitative oxidative conversions of internal and terminal alkenes and can operate in a broader range of solvents. We have also verified the stability and recyclability of the nanocatalysts. The results of this study were published in ACS Nano (ACS Nano, **2018**, 12, 5903–5912) and form the bulk of Chapter 5.¹ My colleague, Dwaipayan Ghosh is the first author and is responsible for all the syntheses of the nickel complexes, the hybrid nanomaterials, and the application studies. I synthesized the mesoporous SiO_2 and performed the electron microscopy-EDS sample preparations for all the hybrid nanomaterials, which included the sample preparations, characterization, and the analyses. I was also involved in the XPS sample preparations and analyses for Ni-1@ TiO_2 and Ni-1@ SiO_2 .*

Hybrid Nanomaterials with Single-Site Catalysts by Spatially Controllable Immobilization of Nickel Complexes *via* Photoclick Chemistry for Alkene Epoxidation

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5.1 Abstract

Catalyst deactivation is a persistent problem not only for the scientific community but also in industry. Isolated single-site heterogeneous catalysts have shown great promise to overcome these problems. Here, a versatile anchoring strategy for molecular complex immobilization on a broad range of semiconducting or insulating metal oxide (e.g. TiO₂, mesoporous SiO₂, CeO₂, and WO₃) nanoparticles to synthesize isolated single-site catalysts has been studied systematically. An oxidatively stable anchoring group, maleimide, is shown to form covalent linkages with surface hydroxyl functionalities of metal oxide nanoparticles by photoclick chemistry. The nanocomposites have been thoroughly characterized by techniques including UV-DRS, HRTEM, XPS, IR, and XAS. The IR spectroscopic studies confirm the covalent linkages between the maleimide group and surface hydroxyl functionalities of the oxide nanoparticles. The hybrid nanomaterials function as highly efficient catalysts for essentially quantitative oxidations of terminal and internal alkenes, and show molecular catalyst product selectivities even in more eco-friendly solvents. XAS studies verify the robustness of the catalysts after several catalytic cycles. We have applied the photoclick anchoring methodology to precisely control the deposition of a luminescent variant of our catalyst on the metal oxide nanoparticles. Overall, we demonstrate a general approach to use irradiation to anchor molecular complexes on oxide nanoparticles to create recyclable, hybrid, single-site catalysts that function with high selectivity in a broad range of solvents. We have achieved a facile, spatially and temporally controllable

photoclick method that can potentially be extended to other ligands, catalysts, functional molecules, and surfaces.

5.2 Introduction

Catalyst deactivation is a perennial problem for homogeneous inorganic catalysts supported by organic ligands. Catalyst oligomerization, ligand oxidation, and demetallation are some of the commonly reported pathways for the degradation of catalytic activity.²⁻³ Heterogenization of molecular compounds on high surface area nanoparticulate solid supports to form isolated single-site catalysts can potentially overcome many of these inactivation pathways.⁴ Moreover, highly reactive intermediates such as early transition metal hydrides,⁵ iron-based water oxidation catalysts,⁶ and molecular-imprinted cavities with ruthenium catalysts,⁷ which would otherwise be unstable in solution, have been characterized and utilized through catalyst immobilization on bulk metal oxide surfaces. The anchoring of molecular compounds to produce isolated single-site hybrid heterogeneous nanocatalysts⁸ is thus still a nascent field that can address a number of catalyst deactivation problems and also offer alternative reactivity and longevity in eco-friendly solvents for highly selective, nominally homogeneous catalysts.

Several approaches have been presented for the immobilization of molecules on surfaces, especially metal oxides. Some of the most popular strategies include physisorption by electrostatic attraction or non-covalent π - π stacking in applications such as proton reduction by hydrogels⁹ or CO₂ reduction with graphitic carbon electrodes,¹⁰ respectively. However, physisorption is typically reversible, especially under aqueous and/or aerobic conditions. Chemisorption can be more robust and often involves hydrolysis of silyl esters or alkynes,¹¹⁻¹³ dealkylation of metal alkyls and hydrides⁵ as well as deposition of carboxylates, phosphonates,¹⁴ hydroxamates, and amines on metal oxides.^{12, 15-16} Nonetheless, the functional groups required are often incompatible with metallation of the

ligand and there is little spatial and temporal control, since the same functional groups such as phosphonates and carboxylates are also excellent donors to Lewis acidic catalytic centers. Consequently, protection-deprotection protocols will be necessary to prevent the anchoring groups from binding and interfering with the metal catalytic activity.

Photochemical grafting of molecules by UV radiation has emerged as a strategy for the orthogonal deposition of small molecules on surfaces such as silicon, diamond, and numerous metal oxides.¹⁷⁻²⁰ Especially notable is the work by Hamers and co-workers, where *terminal* alkenes have been grafted on hydrogen-terminated metal oxides and diamond, and employed in applications such as nanomaterial self-assembly, molecular electronics, and chemical sensing.²⁰⁻²² This strategy is attractive in having a good surface substrate scope, and is often orthogonal to the catalytic and metallation reactivity since alkenes are relatively innocuous functional groups, although terminal alkenes can be vulnerable under oxidative conditions. Also, spatial and temporal control is possible with established masking approaches. To the best of our knowledge, however, even though there has been some precedence for reductive chemistry,²³ there has not been any report of photochemical covalent immobilization of molecular oxidation catalysts on metal oxide nanoparticle surfaces and their applications in catalysis.

Recently, the electron-deficient maleimide group with an internal instead of a terminal alkene has been shown to be a dipolarophile that reacts rapidly with tetrazoles in a “photoclick” modification of DNA strands.²⁴ The maleimide group is more oxidatively robust than terminal alkenes, and can be installed at the periphery of ligands with a reasonably small number of synthetic steps. Furthermore, metal oxide SC nanocrystals readily absorb UV or visible radiation, leading to effective charge extraction from the SC surfaces.

Herein, we describe an exceptionally mild protocol to use UV radiation to immobilize molecular complexes on the surface of metal oxide nanoparticles through a maleimide group. The maleimide is saturated by addition of surface hydroxyl groups to the alkene to form the hydrolytically more robust succinimide group. We have further demonstrated that the functional molecular nickel (Ni) catalysts anchored on the nanoparticles can be used as heterogeneous oxidation catalysts for the epoxidation of styrene and other alkenes, with comparable reactivity *vis a vis* their homogeneous congeners. Moreover, we show that the operational stability of the catalysts increases since we are able to recycle the heterogeneous nanomaterials more effectively, and more eco-friendly non-halogenated solvents can be used. Apart from the deposition of Ni epoxidation catalysts, the photoclick methodology has been successfully applied to attach a luminescent variant of the Ni catalyst on the metal oxide nanoparticles. Our work thus illustrates a proof of concept that this orthogonal, facile, photoclick protocol can create functional nanomaterials with improved single-site catalytic activity and lifetime, using modular, independently optimized components. In addition, we can realize spatial and temporal attachment of catalysts, luminophores, and potentially other functional molecules in specifically desired amounts on nanomaterials.

5.3 Experimental Section

5.3.1 Synthesis of dendritic SiO₂ nanoparticles

See Chapter 3 section 3.2.1

5.3.2 Processing of TiO₂ P25 nanoparticles

Prior to use in the anchoring reaction, the commercially purchased TiO₂ P25 nanoparticles (Sigma-Aldrich) were treated with piranha solution to remove any surface organic impurities and hydroxylate the surface to facilitate anchoring. In a typical procedure, TiO₂ P25 nanoparticles (40 mg, 0.50 mmol) were soaked in freshly prepared piranha solution (conc. H₂SO₄: H₂O₂ = 3:1) for 2 h. Subsequently, it was washed thoroughly with de-ionized water and dried in a furnace at 300 °C for 3 h to remove traces of H₂SO₄. It was then dried at 120 °C for 5 h under vacuum to remove any remaining surface moisture.

5.3.3 Preparation of Ni-1 anchored on (@) metal oxide

Ni-1@TiO₂

A degassed, anhydrous DCM (5 mL) solution of Ni-1 (10 mg, 0.013 mmol) was added to an oven dried quartz glass Schlenk tube. Pre-processed TiO₂ P25 nanoparticles (21 mg, 0.26 mmol) was then added. The Schlenk tube was sonicated for 5 min before the solvent was removed under vacuum. The solid mixture was stirred under UV irradiation (254 nm, 125 watt) for 8 h. After the reaction, the nanoparticles were collected and washed several times by DCM to remove any excess and unbound **Ni-1** present.

Ni-1@SiO₂ was prepared using the same method as for **Ni-1@TiO₂**. Instead of TiO₂, dendritic SiO₂ nanoparticles (30 mg, 0.50 mmol) from Chapter 4 were used.

Ni-1@BiVO₄ was prepared using the same method as for **Ni-1@TiO₂**. Instead of TiO₂, bulk BiVO₄ particles (33 mg, 0.10 mmol) were used.

5.3.4 Alkene epoxidation using heterogeneous **Ni-1@TiO₂** catalyst

To a solution of alkene (0.10 mmol) in 2 mL DCM, was added **Ni-1@TiO₂** (23.5 mg), *n*-decane (19.5 μ L, 0.100 mmol), tetra-*n*-butylammonium bromide (2.0 mg, 6.0 μ mol), and aqueous sodium hypochlorite (0.36 mL, 0.70 M). The mixture was stirred vigorously at room temperature. After the reaction was complete, the reaction mixture was carefully transferred to a centrifuge tube and the catalyst was recovered by centrifugation and washed with water, ethanol, and DCM. Finally, it was dried under vacuum before being re-used for subsequent cycles. To prepare the GC-MS sample, 500 μ L of the organic layer was withdrawn using a syringe and diluted with DCM in a 10 mL volumetric flask.

5.3.5 Alkene epoxidation using heterogeneous **Ni-1@SiO₂** catalyst

The alkene epoxidation was conducted following the same procedure as for **Ni-1@TiO₂**, but **Ni-1@SiO₂** (25.5 mg) was used instead of **Ni-1@TiO₂**.

5.4 Results and Discussion

Salicylaldimine ligands are known for their relative ease of synthesis and ability to stabilize multiple transition metal oxidation states.²⁵ In particular, Ni salicylaldimine complexes have been reported to homogeneously catalyze reactions such as the asymmetric aldol reaction of β -keto esters,²⁶ tetralin oxidation,²⁷ Michael addition reactions,²⁸ and epoxidation of alkenes.²⁹⁻³¹ Some Ni alkene oxidation catalysts had been encapsulated in zeolites previously, but there was no structural characterization, the epoxide selectivity was low, and there was little evidence that the catalyst could be recycled.³² Here, we have prepared a Ni^{II} salicylaldimine complex, **Ni-1** (Figure 5.1a) *via* a templated condensation of 5-chloro-2,3-diamino pyridine, a maleimide-substituted salicylaldehyde, and Ni^{II} acetate.¹ A variant **Ni-3** was also prepared as a luminescent reporter. Another Ni^{II} congener, **Ni-2** (Figure 5.1b), without the maleimide anchoring group was synthesized in a similar fashion for comparison in control experiments. The synthesis of Ni^{II} salicylaldimine complex, **Ni-1**, **Ni-2**, and **Ni-3** were carried out by authors Dwaipayan Ghosh, and Benny Febriansyah and therefore the synthetic procedure will not be discussed (See published Manuscript and Supporting Information for details.¹)

Figure 5.1. a) Chemical structures of **Ni-1** bearing the maleimide anchoring group and b) **Ni-2**, without the maleimide group. c) Reaction scheme of the anchoring experiment. Covalent anchoring *via* the maleimide group is shown. Adapted with permission from *ACS Nano* 2018, 12, 5903-5912. Copyright 2018 American Chemical Society.¹

Titanium(IV) oxide (TiO₂), silica (SiO₂), cerium oxide (CeO₂), tungsten oxide (WO₃) nanoparticles, and bulk bismuth vanadate (BiVO₄) were chosen as the hydroxy-terminated solid supports due to their high surface area, ease of synthesis, oxidative stability, and relative abundance. Furthermore, nanomaterials offer the versatility of photocatalysis in the future since charge extraction is expected to be more expedient. Each of the photochemical anchoring reactions was carried out using a 254 nm (125 W) UV lamp in a sealed quartz Schlenk tube under an argon atmosphere. Briefly, **Ni-1** was added into a

dispersion of TiO₂ nanoparticles in anhydrous dichloromethane (DCM) under argon and the mixture was stirred vigorously for 15 minutes before the solvent was removed under reduced pressure. The flask was then filled with argon and subjected to UV irradiation for 12 hours under stirring (Figure 5.1c). Likewise, **Ni-2** was also irradiated with TiO₂ nanoparticles under the same conditions. Upon UV irradiation, the hydroxyl groups on the nanoparticle surfaces form covalent linkages by reacting with the C=C double bonds of the maleimide groups to convert into alkoxy succinimides. Both product mixtures were then washed several times with DCM and characterized by UV-DRS.

The DRS spectrum of the reaction product between **Ni-1** and TiO₂ (**Ni-1@TiO₂**) exhibits an absorption maximum at 515 nm and a shoulder at 370 nm (black, Figure 5.2a), which corresponds to the d-d transitions and ligand-to-metal charge transfer, respectively, in **Ni-1** (red, Figure 5.2a).³³⁻³⁴ On the other hand, the sample from the reaction between **Ni-2** and TiO₂ (**Ni-2+TiO₂**) shows almost no visible light absorption (navy blue, Figure 5.2a), indicating that **Ni-1** is not merely physisorbed on the TiO₂ surface and also the critical role of the maleimide group for the covalent anchoring. Similar spectral signatures were observed in the DRS spectra when TiO₂ nanoparticles were replaced by SiO₂ nanoparticles (Figure 5.2c), commercially available CeO₂ nanoparticles (Figure 5.2e), and WO₃ nanoparticles (Figure 5.2g) under similar reaction conditions. This highlights the generality and effectiveness of our approach on insulating, semiconducting, and visible light absorbing oxide materials. The DRS spectrum of the hybrid composite between **Ni-1** and CeO₂ nanoparticles (**Ni-1@CeO₂**) exhibits a broad absorption shoulder at 515 nm, corresponding to the same Ni centered d-d transition (sky blue, Figure 5.2e), and likewise for the molecular-nanoparticle hybrid between **Ni-1** and WO₃ (**Ni-1@WO₃**, light green, Figure 5.2g). The broad absorption shoulder at 515 nm could not be observed with the UV-vis DRS for **Ni-1@BiVO₄** due to the masking of strong absorption edge at about 520 nm by the bulk BiVO₄. However, a preliminary elemental analysis

with the SEM-EDS, did not detect any Ni on the surface of the bulk BiVO_4 , which indicates no or extremely low amount of Ni complex was anchored on BiVO_4 . Therefore, from this result, further test on bulk BiVO_4 particles was not pursued.

Figure 5.2. a) DRS spectra of **Ni-1** (red), **Ni-1@TiO₂** (black), TiO₂ P25 nanoparticles (green), **Ni-2** (grey), and **Ni-2+TiO₂** (navy blue). b) The FT-IR spectra of **Ni-1** (red), **Ni-1@TiO₂** (black), TiO₂ P25 nanoparticles (green), and **Ni-1+TiO₂** (royal blue) in absorbance mode. c) DRS spectra of **Ni-1** (red), **Ni-1@SiO₂** (orange), SiO₂ nanoparticles (magenta), **Ni-2** (grey), and **Ni-2+SiO₂** (dark cyan). d) The FT-IR spectra of **Ni-1** (red), **Ni-1@SiO₂** (orange), SiO₂ nanoparticles (magenta), and **Ni-1+SiO₂** (light cyan) in absorbance mode. e) DRS spectra of **Ni-1** (red), **Ni-1@CeO₂** (sky blue), **Ni-2+CeO₂** (brick red), and CeO₂ nanoparticles (violet). f) The FT-IR spectra of **Ni-1** (red), **Ni-1@CeO₂** (sky blue), CeO₂ nanoparticles (violet), and **Ni-1+CeO₂** (olive green) in absorbance mode. g) DRS spectra of **Ni-1** (red), **Ni-1@WO₃** (light green), **Ni-2+WO₃** (dark yellow), and WO₃ nanoparticles (beige). h) The FT-IR spectra of **Ni-1** (red), **Ni-1@WO₃** (light green), WO₃ nanoparticles (beige), and **Ni-1+WO₃** (light grey) in absorbance mode. For **Ni-1** and all the **Ni-1@MO_x** samples (MO_x = TiO₂, SiO₂, CeO₂, and WO₃), the absorbance band at 515 nm corresponds to the Ni centered d-d transition. Adapted with permission from *ACS Nano* 2018, 12, 5903-5912. Copyright 2018 American Chemical Society.¹

To confirm the UV stability of **Ni-1** and verify that the maleimide group was involved in covalent bond formation with the surface hydroxyl groups during the photoclick reaction, we conducted FT-IR spectroscopic measurements. The FT-IR spectra of **Ni-1** in the solid state before and after 254 nm UV irradiation remained essentially identical (Figure 5.3), suggesting that the Ni^{II} complex was stable under our photochemical deposition conditions.

Figure 5.3.(a) Comparison of FT-IR spectra of **Ni-1** before (red) and after (purple) 254 nm UV irradiation from 400 cm⁻¹ to 4000 cm⁻¹. b) Expanded spectra of **Ni-1** before (red) and after (purple) 254 nm UV irradiation from 500 cm⁻¹ to 2000 cm⁻¹. Adapted with permission from *ACS Nano* 2018, 12, 5903-5912. Copyright 2018 American Chemical Society.¹

The FT-IR spectra in the range 1400–1800 cm⁻¹ reveal that a vibrational stretching band at 1608 cm⁻¹ for **Ni-1@TiO₂** (black, Figure 5.4b) has diminished, whereas for a control reaction in which **Ni-1** and TiO₂ have been physically mixed without any UV irradiation (**Ni-1**+TiO₂), this stretching band remains intact (royal blue, Figure 5.4b). We propose that this vibrational band at 1608 cm⁻¹ corresponds to the C=C stretch of the maleimide group, which is lost upon covalent anchoring on the nanoparticle surface.³⁵ We observed similar spectral changes for **Ni-1@SiO₂** (orange, Figure 5.4d), **Ni-1@CeO₂** (sky blue, Figure 5.4f), and **Ni-1@WO₃** (light green, Figure 5.4h) in comparison to the controls (Figure 5.4) fully consistent with our model that the **Ni-1** had become covalently

attached by conversion of the maleimide group to a succinimide after reacting with the surface hydroxyls.

Figure 5.4. Comparison of the FT-IR spectra from 1000 cm^{-1} to 2000 cm^{-1} of (a) **Ni-2**+ TiO_2 before (light pink) and after washing (blue); (b) **Ni-2**+ SiO_2 before (pink) and after washing (dark cyan); (c) **Ni-2**+ CeO_2 before (light sky blue) and after washing (brick red); and (d) **Ni-2**+ WO_3 before (light yellow) and after washing (dark yellow). After washing with DCM, the peaks corresponding to **Ni-2** are no longer present, confirming that little to no anchoring or physisorption occurred. Moreover, the peaks at 1608 cm^{-1} and 1709 cm^{-1} , corresponding to the maleimide $\text{C}=\text{C}$ and $\text{C}=\text{O}$ stretches respectively, are not detectable in the spectra of the rinsed samples. Adapted with permission from *ACS Nano* 2018, 12, 5903-5912. Copyright 2018 American Chemical Society.¹

To further ascertain the coordination environment and oxidation state of the Ni center upon anchoring to the nanoparticle surface, XAS and XPS measurements were conducted on **Ni-1@TiO₂**, **Ni-1@SiO₂**, and **Ni-1**. XAS measurements and

analyses of the materials were done by authors Disha Gupta, and Dr. Yonghua Du and therefore detailed analyses of all XAS will not be discussed here (See published Manuscript and Supporting Information for details.¹)

The XPS spectra of **Ni-1@TiO₂** (Figures 5.5a, and 5.5b) show the presence of Ni 2p, Cl 2p, and Ti 2p signals in the sample. Similarly, the XPS spectra of **Ni-1@SiO₂** (Figures 5.5d, and 5.5e) show the presence of Ni 2p, Cl 2p, and Si 2p signals in the sample. The Ni 2p binding energies of **Ni-1@TiO₂** (Figure 5.5b), **Ni-1@SiO₂** (Figure 5.5e), and **Ni-1** (Figure 5.7) were found to be similar (Figure 5.6), confirming the presence of Ni^{II} on the nanoparticle surfaces. The Ni 2p_{3/2} signals for **Ni-1**, **Ni-1@TiO₂**, and **Ni-1@SiO₂** appear at 853.8 eV, 853.7 eV, and 853.8 eV, respectively. The slight differences in the binding energies are likely within experimental error, although there have been reports of interfacial interactions between nanoparticles and surface-attached Ni complexes.³⁶⁻³⁸ In aggregate, we are confident that the molecular Ni^{II} catalysts remain structurally intact and are covalently anchored on the different metal oxide supports.

Figure 5.5. a) XPS survey spectrum of **Ni-1@TiO₂** showing the binding energies corresponding to Ni 2p, Ti 2p, and Cl 2p. b) Ni 2p XPS data for **Ni-1@TiO₂** with the Ni 2p_{3/2} signal at 853.7 eV and Ni 2p_{1/2} signal at 870.9 eV. c) HRTEM image of **Ni-1@TiO₂**.

d) XPS survey spectrum of **Ni-1@SiO₂** showing the binding energies corresponding to Ni 2p, Si 2p, and Cl 2p. e) Ni 2p XPS data for **Ni-1@SiO₂** with Ni 2p_{3/2} signal at 853.8 eV and the Ni 2p_{1/2} signal at 871.1 eV. f) HRTEM image of **Ni-1@SiO₂**. Adapted with permission from *ACS Nano* 2018, 12, 5903-5912. Copyright 2018 American Chemical Society.¹

Figure 5.6. Comparison of the Ni 2p XPS spectra for Ni-1 (red), **Ni-1@TiO₂** (black), and **Ni-1@SiO₂** (orange), also demonstrating that the oxidation states of Ni in these samples are almost identical. Adapted with permission from *ACS Nano* 2018, 12, 5903-5912. Copyright 2018 American Chemical Society.¹

The catalysts were then employed in catalytic alkene epoxidation reactions to evaluate the activities. The conditions were first optimized with **Ni-1** as a homogeneous catalyst. Different oxidants including hydrogen peroxide (H₂O₂), TEMPO, sodium periodate, sodium hypochlorite (NaOCl), and oxygen were screened (Table 5.1). Moreover, since **Ni-1** is poorly soluble in ethyl acetate, methanol, and acetonitrile, they are unsuitable solvents for homogeneous catalysis. The combination of **Ni-1** (5 mol%), NaOCl (8 equivalents) as the oxidant, and DCM as the solvent gave the highest (>99%) conversion of styrene (Table 5.2). This performance is comparable with or better than previously reported alkene epoxidation catalysis.^{29, 32} We also found that less than 8 equivalents of NaOCl relative to the substrate resulted in incomplete conversions of the alkenes. Using these same optimized conditions, a number of internal and terminal alkene substrates were successfully oxidized at room temperature using

Ni-1 (Table 5.2). The homogeneous reactions showed very high conversions and the selectivity for the epoxides were found to vary from moderate for cyclooctene oxide (54%) to good (78%) for 4-chlorostyrene oxide.

For the homogeneous catalysis, the TOF was calculated using the formula:

$$\text{TOF} = \frac{(\text{number of mmol of product formed})}{(\text{number of mmol of Ni - 1 used}) \times (\text{time of the reaction in hour})}$$

For example, in Table 5.1, entry 1, the reaction was performed with 0.50 mmol of styrene and 0.025 mmol of **Ni-1**. The reaction took 3.5 hours to complete and the styrene oxide yield by GC was found to be 63%. Hence, the TOF for this reaction was calculated using the aforementioned formula and found to be 3.60 h⁻¹. For the heterogeneous catalysis experiments, 5.0 μmol of **Ni-1** content was used in each run. The weight of catalyst added was calculated based on their respective Ni contents. The reactions were performed with 0.10 mmol of alkenes and the TOFs were calculated using the same formula above.

Table 5.1 Homogeneous alkene epoxidation by **Ni-1** with different oxidants.

Entry	Oxidant	% Conversion of substrate ^{a,b}	Time (h)	% GC yields of epoxide product ^b
1	Hydrogen peroxide	<5	6	<1
2	TEMPO	<1	6	-
3	Aerial oxygen	-	12	-
4	Sodium periodate	28	6	<10
5	NaOCl	98	3.5	63

^a The compound styrene was used as the substrate. ^b The compound *n*-decane was used as the internal standard.

Table 5.2 Conversion, selectivity, and substrate scope of alkene epoxidation by **Ni-1**^a.

Entry	Substrate	% Conversion	Time (h)	Epoxide product	% GC yields of	TOF (h ⁻¹)
-------	-----------	--------------	----------	-----------------	----------------	------------------------

		of substrate ^b			epoxide products ^b	
1		>99	3.5		63	3.60
2		>99	2		75	7.50
3		>99	5		78	3.12
4		>99	2.5		74	5.92
5		95	5		54	2.16

^a The reactions were performed in DCM and the compound *n*-decane was used as the internal standard. ^b NaOCl was used as the oxidant.

Ni-1@TiO₂, **Ni-1@SiO₂**, **Ni-1@CeO₂**, and **Ni-1@WO₃** were all then applied as heterogeneous catalysts for alkene oxidation under similar reaction conditions, although notably, we were no longer limited by the solubility constraints of **Ni-1** in the solvents mentioned above. The conversions of the substrates in the heterogeneous reactions and selectivities were found to be similar to the homogeneous version, with the highest epoxide selectivity of 68% for 4-chlorostyrene oxide (Table 5.3, Entry 3). **Ni-1@TiO₂** performed better than **Ni-1@SiO₂**, **Ni-1@CeO₂**, and **Ni-1@WO₃** (Table 5.3, Entries 8, 9, and 10, respectively) both in terms of substrate conversion and selectivity for the epoxide products. Notably, all of the heterogeneous catalysts displayed higher substrate conversion as well as epoxide selectivity compared to the best previously reported metal organic framework (MOF) heterogeneous catalysts embedded with Ni salicylaldehyde complexes.³⁹ This could be due to better accessibility of the Ni catalytic centers, which are on the surface of the nanoparticles (Figures

5.5c, 5.5f, 5.7, 5.8, and Table 5.4) unlike the MOF-based catalysts that have Ni centers embedded deep inside the porous framework.

Table 5.3 Conversion, selectivity, and substrate scope of alkene epoxidation by heterogeneous catalysts

Entry	Substrate	% conversion of substrate ^c	Time (h)	Epoxide product	% GC yields of epoxide product ^{a,b}	TOF (h ⁻¹)
1 ^b		92	4		53	2.64
2 ^b		96	2.5		63	5.04
3 ^b		95	5.5		68	2.47
4 ^b		93	8		54	1.35
5 ^b		96	3.5		62	3.54
6 ^b		84	5		42	8.40
7 ^c		85	4		45	2.25
8 ^c		88	5.5		64	2.32
9 ^d		90	5.5		61	2.21
10 ^e		94	5.5		66	2.64
11 ^f		<1	6		-	-
12 ^{h,g}		<1	6		-	-

^a Compound *n*-decane was used as the GC internal standard. ^b **Ni-1@TiO₂** was used as the catalyst. ^c **Ni-1@SiO₂** was used as the catalyst. ^d **Ni-1@CeO₂** was used as the catalyst. ^e **Ni-1@WO₃** was used as the catalyst. ^f Control reaction with TiO₂ P25 nanoparticles as

catalyst. ^g Control reaction without NaOCl. ^h Other products obtained were aldehydes and 1,2-diols.

Figure 5.7. HRTEM images of a) **Ni-1@WO₃** and b) **Ni-1@CeO₂** nanoparticles. Adapted with permission from *ACS Nano* 2018, 12, 5903-5912. Copyright 2018 American Chemical Society.¹

Figure 5.8. a) STEM image of **Ni-1@TiO₂**. b) EDX overlay of Ti (cyan) and Ni (red) for **Ni-1@TiO₂**. c) EDS overlay of Ti (cyan) and Cl (magenta) for **Ni-1@TiO₂**. d) EDX spectrum of **Ni-1@TiO₂**. Adapted with permission from *ACS Nano* 2018, 12, 5903-5912. Copyright 2018 American Chemical Society.¹

Table 5.4. STEM-EDS elemental composition table for **Ni-1@TiO₂**

Element	Weight %	Atom %
O(K)	44.8	70.9
Cl(K)	1.10	0.79
Ti(K)	51.5	27.2
Ni(K)	2.64	1.14

In order to determine the stability and recyclability of the **Ni-1@TiO₂** catalysts, catalytic alkene epoxidation was repeated for at least ten cycles. After the

reaction, the heterogeneous catalysts could be recovered by centrifugation, and the residue was rinsed with solvent, dried, and recycled. Remarkably, the reused catalyst showed essentially quantitative conversions of the substrate for the first few recycling experiments, although the conversion and the epoxide selectivity decreased over extended reuse (Figure 5.9). Despite the fact that the heterogeneous catalyst sample could not be completely recovered after every experiment (some remained in the reaction flasks and the centrifuge tubes) and some sample was also lost for FT-IR spectroscopic analysis, **Ni-1@TiO₂** could still be used for at least 10 consecutive cycles with 4-chlorostyrene as the substrate. In contrast, the physical mixtures of **Ni-1** and TiO₂ or SiO₂ do not survive after the first catalytic cycle and neither the supernatant (containing the dissolved Ni by-products) nor the recovered nanoparticles showed any catalytic activity in the second run (Figure 5.10 and Table 5.5). The decrease in the catalytic activity of **Ni-1@TiO₂** could be due to inactivation of some of the Ni catalysts as insoluble Ni oxides on the nanoparticle surface. We observed that the Ni concentrations in the reaction aliquots were below the detection limit of our inductively coupled plasma optical emission spectroscopy (ICP-OES) experiments, indicating that little Ni leached out during the catalytic process. To demonstrate the robustness and scalability of **Ni-1@TiO₂**, we performed four cycles of 4-chlorostyrene oxidations (0.28 g, 2.0 mmol in each cycle) since the percentage conversion remained fairly high, and isolated 0.66 g of 4-chlorostyrene oxide (53%) by reusing the same catalyst.

Figure 5.9. (a) Percentage conversion of 4-chlorostyrene (black) and selectivity for epoxide (red) obtained over 10 cycles by reusing the **Ni-1@TiO₂** catalyst. b) FT-IR spectra of **Ni-1@TiO₂** before (black), and after four (light brown), eight (lilac), and 10 cycles of catalysis (light green). Adapted with permission from *ACS Nano* 2018, 12, 5903-5912. Copyright 2018 American Chemical Society.¹

Figure 5.10. DRS spectra of (a) **Ni-1+TiO₂** (blue) and after one cycle of epoxidation catalysis (brick red), and (b) **Ni-1+SiO₂** (light cyan) and after one cycle of epoxidation catalysis (dark magenta). Comparison of the FT-IR spectra of (c) **Ni-1+TiO₂** (blue) and after one cycle of epoxidation catalysis (brick red), and (d) **Ni-1+SiO₂** (light cyan) and after one cycle of epoxidation catalysis (dark magenta) from 1000 to 2000 cm⁻¹. Adapted with permission from *ACS Nano* 2018, 12, 5903-5912. Copyright 2018 American Chemical Society.¹

Table 5.5 Heterogeneous alkene epoxidation by the physically mixed Ni-1+TiO₂ and Ni-1+SiO₂.

Entry	Catalyst	% Conversion of substrate ^a	Time (h)	% GC yields of epoxide products ^b	TOF (h ⁻¹)
1	Ni-1+TiO ₂ in 1 st cycle	>99	4.5	73	3.24
2	Ni-1+TiO ₂ residue after centrifugation in 2 nd cycle	<2	6	-	-
3	Ni-1+TiO ₂ supernatant from 1 st cycle	<2	6	-	-
4	Ni-1+SiO ₂ 1 st cycle	>99	4.5	70	3.11
5	Ni-1+SiO ₂ residue after centrifugation in 2 nd cycle	<2	6	-	-
6	Ni-1+SiO ₂ supernatant from 1 st cycle	<2	6	-	-

^a The substrate 4-chlorostyrene was used for this study. ^b The epoxide product is 4-chlorostyrene oxide. ^c After the nanoparticles were separated by centrifugation, another 0.10 mmol of 4-chlorostyrene was added.

This selective photoclick reaction of the maleimide anchoring group could be utilized to spatially and temporally attach luminescent reporters on the metal oxide nanoparticles, which is an advantage over indiscriminate grafting functionalities like carboxylates and phosphonates. We have been able to successfully graft a different luminescent nickel salicylaldimine complex (**Ni-3**, Figure 5.11a), bearing the maleimide anchoring group, on SiO₂ and TiO₂ coated flourine-doped tin oxide (FTO) films (**Ni-3@SiO₂-FTO** and **Ni-3@TiO₂-FTO**, respectively) using 254 nm UV radiation. The designs (Figures 5.11b and 5.11c) were achieved by using a simple paper mask, which allows the photoclick reaction to occur only at specifically exposed areas of the coated FTO films. The DRS spectra of **Ni-3@SiO₂-FTO** and **Ni-3@TiO₂-FTO** (Figure 5.11d) shows the absorbance maxima corresponding to **Ni-3**, indicating the presence of the complex after the photoclick reaction. The successful grafting was again confirmed by the SEM-EDX spectrum of **Ni-3@SiO₂-FTO** (Figure 5.12) as well

as FT-IR spectra of **Ni-3@SiO₂-FTO** and **Ni-3@TiO₂-FTO** (Figure 5.13e), which show the loss of the 1605 cm⁻¹ peak, corresponding to the maleimide C=C stretch present in the **Ni-3** (wine red) spectrum.

Figure 5.11. a) Chemical structure of **Ni-3** bearing the maleimide anchoring group. Photograph of the spatially controlled photoclick deposition of **Ni-3** on b) SiO₂ and c) TiO₂ coated FTO plate. In each figure, the mask is shown on the top right. The dashed lines highlight the boundaries of the deposited patterns. A ruler has been provided to facilitate size comparison. d) DRS spectra, e) FT-IR spectra from 1400 cm⁻¹ to 1800 cm⁻¹ in absorbance mode, and f) photoluminescence spectra with 395 nm excitation of **Ni-3** (wine red), **Ni-1@SiO₂-FTO** (light magenta), and **Ni-1@TiO₂-FTO** (light violet). Adapted with permission from *ACS Nano* 2018, 12, 5903-5912. Copyright 2018 American Chemical Society.¹

Figure 5.12. a) SEM image of **Ni-3@SiO₂-FTO**. b) EDS overlay of Si (green) and Ni (red) for **Ni-3@SiO₂-FTO**. EDX mapping of c) Si (green) and d) Ni (red) for **Ni-3@SiO₂-FTO**. e) EDX spectrum of **Ni-3@SiO₂-FTO**. Adapted with permission from *ACS Nano* 2018, 12, 5903-5912. Copyright 2018 American Chemical Society.¹

The solid state PL spectra of the films exhibit the luminescent behavior of the parent **Ni-3** complex (Figure 5.11f). The PL spectrum of **Ni-3** shows an emission maximum at 530 nm when excited at 395 nm. A small blue-shift of 3 nm in the emission maximum was observed in each of the **Ni-3@SiO₂-FTO** and **Ni-3@TiO₂-FTO** samples. The **Ni-3** coated regions in the **Ni-3@SiO₂-FTO** sample were found to show PL when irradiated with a TLC lamp emitting 365 nm UV light (Figure 5.13). However, the PL intensity for **Ni-3@TiO₂-FTO** was found to be attenuated compared to **Ni-3** and **Ni-3@SiO₂-FTO** (Figures 5.11f and 5.13). This could be due to PL quenching after charge injection into the semiconducting TiO₂ layer, in contrast to the insulating SiO₂, a feature that will be further investigated for catalytic applications.

Figure 5.13. a) Photograph of spatially controlled deposition of **Ni-3** on SiO₂ and TiO₂ coated FTO under visible light. The dashed lines highlight the edges. b) The coated plates under 365 nm UV from a TLC lamp. The **Ni-3@SiO₂-FTO** (left) plate shows better brighter photoluminescence compared to **Ni-3@TiO₂-FTO** (right). Adapted with permission from *ACS Nano* 2018, 12, 5903-5912. Copyright 2018 American Chemical Society.¹

In conclusion, we have utilized maleimide as an oxidatively stable, photoactivated anchoring group to synthesize several hybrid single-site catalysts comprising covalently grafted Ni complexes on SiO₂, TiO₂, CeO₂, and WO₃ nanoparticles. Characterization by DRS, FT-IR spectroscopy, XAS, and XPS verified that the Ni salicylaldimine complexes remained intact and were anchored covalently. Remarkably, the heterogeneous catalysts displayed conversions and selectivities for alkene epoxidation similar to their corresponding homogeneous molecular congener, but were found to be more robust, recyclable, and stable up to 10 catalytic cycles under the harsh oxidative reaction conditions in a wider range of more eco-friendly solvents. We have also been able to utilize the photoclick protocol of the maleimide anchoring group to precisely deposit the Ni complexes on specific regions. Our study thus forms the basis for future discoveries on using light to deposit functional molecular catalysts on inert or semiconducting scaffolds to create hybrid (photo)catalysts that can synergize the benefits of both homogeneous and heterogeneous catalysts. Moreover, we

believe that this spatially and temporally controlled photoclick reaction to deposit functional molecules can be applied in other fields, including biosensing, renewable energy, and optoelectronic devices, for example.

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5.6 Appendix II

Figure 5.14. (a) Selected scan area for EDS, elemental mapping analysis of Bi (b, cyan), V (c, light green), O (d, red). (e) EDS of Ni-1@BiVO₄.

Chapter 6

Project Outlook: Stabilization of Vanadium Catalysts on Metal Oxide Supports via Cooperative Anchoring Groups for Photoredox Carbon-Carbon Bond Cleavage

This chapter discusses the continuation of similar work following the initial success on the immobilization of Ni complexes on mesoporous SiO₂ and various metal oxides with photoclick chemistry reported in Chapter 5. Briefly, a preliminary study on the anchoring of V^v complexes on SiO₂/BiVO₄/CuO_x nanospheres and TiO₂ was attempted. We have utilized alkynes as anchoring groups in the V^v complexes to undergo a copper(I)-catalyzed 1,3 dipolar azide–alkyne cycloaddition, referred to as a “click” reaction. To this point, we have yet to uncover promising PC activity from the hybrid nanomaterials although evidence of the active site molecular structure from FT-IR spectroscopy and SEM-EDS was observed. On the other hand, it shows potential as a platform technology for the photooxidative C-C bond cleavage of lignin and to obtain renewable sources of aromatic compounds.

6.1 Introduction

Biomass has attracted tremendous interest lately as it is sustainable and it is one of the biggest sources to provide abundant, renewable organic carbon resources that can reduce our reliance on fossil fuels for chemical feedstocks.¹⁻⁹ Furthermore, biomass is carbon neutral, which implies that the net CO₂ emissions would be zero and it would thus be able to diminish the effect of global warming.

Among the various types of biomass, lignocellulose is regarded as a major raw material for the future biorefinery.¹⁰ Lignocellulose consists of three basic components, cellulose, hemicellulose, and lignin. They are non-food biomass and thus there will be no competition with food resources. Each year, vast amounts of waste are generated from lignocellulosic biomass exceeding 200 billion tonnes worldwide.¹¹ Lignin is nominally considered as “waste” with little or no application compared to cellulose and hemicellulose, which are converted to valuable platform chemicals such as hydroxymethylfurfural and levulinic acid.¹² In addition, lignin is the only lignocellulosic biomass that is rich in aromatic moieties and can be potentially transformed into valuable chemical feedstocks, which can subsequently be utilized as precursors for specialty chemicals such as polymer, dyes and drugs (Figure 6.1).¹³ Considering the emerging biomass industry, enormous amounts of lignin will be generated in future. As a consequence, there is an urgent need to develop new technologies that can create new applications for lignin.

Despite the increasing need for potential feedstocks of valuable aromatic compounds, selective depolymerisation of lignin into valuable chemicals remains a major unsolved problem.¹⁴ This is primarily due to an extensive C-O and C-C crosslinking network, and the low molecular weight by-products tend to form intractable species.¹⁰

Figure 6.1. Valuable products potentially obtained from lignin with development and integration of new and current technology. Adapted with permission from *Chem. Rev.* 2010, 110, 3552-3599. Copyright 2018 American Chemical Society¹³

Catalysis plays an important role in the development of selective lignin conversion processes. Several attempts have been made in lignin valorization, which include hydrogenolysis, oxidation, biodegradation, and fast pyrolysis.¹⁰ However, although much effort has been devoted to the valorization of lignin into fuels through thermal and microbial reactions, majority of the valuable aromatic units and functional groups are destroyed. Not only do these methods require harsh conditions, costly rare-earth transition metals, and/or enzymes, they often exhibit poor chemoselectivity.

In order to improve the selectivity of lignin degradation, an understanding of the lignin structure at the molecular level is required. The most abundant structural motif in lignin is the β -O-4 linkage, which is weak and easily cleaved.¹³ Lignin model compounds mimic the β -O-4 linkage and they are often used to study the mechanism of the catalytic system so as to convert lignin more effectively.¹³

Some examples of published work by various authors demonstrated the two-steps degradation of lignin model compounds where the first step involves the chemoselective oxidation of the benzylic alcohol, which activates the β -O-4 for

subsequent C-O cleavage.^{12, 15-17} The drawback of this degradation is the lack of a direct C-O or C-C bond cleavage. Furthermore, excess additives as well as high temperatures are required to drive lignin degradation reactions. Meanwhile, Toste *et. al.* and Hanson *et. al.* have successfully reported direct C-O bond or C-C cleavage of the lignin with high conversion and good selectivity.¹⁸⁻²³ However, the reactions require high temperature conditions for the conversion.

In recent work on lignin model compounds, Gazi and co-workers from our team have revealed a unique V^V (oxovanadium with +5 oxidation state) photocatalyst that is able to induce a highly selective and unprecedented C-C bond scission in aliphatic alcohols under visible light irradiation and ambient, atmospheric conditions.²⁴ Following Gazi *et. al.*'s initial success on the photooxidative C-C bond activation in aliphatic alcohols, they have improved their original design and developed a library of modified V^V photocatalysts.²⁵ As anticipated, one of the more strongly oxidizing photocatalysts reacted up to 7 times faster than the earlier complex by introducing strong electron withdrawing groups such as nitro (-NO₂) and fluorine (F) group(s) that resulted in the stabilization of the HOMO energy level, and thus increased the oxidative potential of the V^V photocatalyst (Figure 6.2).²⁵

Figure 6.2: Selective C-C bond cleavage lignin model compound A.

Therefore, to further expand the work by Gazi *et. al.*, an attempt has been made to synthesize heterogeneous catalysts by anchoring the V^v photocatalyst to solid supports like metal oxide nanoparticles. By doing this, we envision that the hybrid PC system could further improve the recyclability and stability of the complex. We also hope to be able to use a wider range of more eco-friendly solvents, similar to what was reported in Chapter 5.

In addition to the objectives and scopes on page 8 of Chapter 1, this ongoing project consists of the following. 1) The development of a modified V^v photocatalyst based on the design similar to what was reported by our teammates,²⁵ so that the complex can be anchored on the metal oxide surface with minimal leaching after recycling. 2) Subsequently, the modified V^v complex will be fully characterized by NMR, UV-vis, and FT-IR spectroscopies, HRMS, as well as single crystal XRD of the V^v complex crystals after recrystallization. 3) In order to provide definitive evidence of the active site molecular structure anchored on the metal oxide, a broad range of characterization techniques will be employed, such as FT-IR spectroscopy, XAS, XPS, and SEM-EDS. 4) Lastly, lignin model compounds will be synthesized and characterized, which will be used as the substrates to evaluate the performance of the hybrid nanomaterials in the photooxidative C–C bond cleavage of lignin model compounds.

6.2 Results & Discussion *(The following are preliminary results an ongoing project)*

6.2.1 Synthesis of modified V^v photocatalyst bearing anchoring group *(Refer to Appendix III for detailed experimental methods for compound I – 3 and V-I)*

Based on the V^v photocatalyst that has been established by our teammates, our target is to synthesize a V^v based complex bearing a anchoring group. To anchor

the V^V photocatalyst effectively on a metal oxide support, terminal alkyne and alkene substituents are introduced on two different V^V photocatalysts, **V-1** and **V-2**, as shown in Figure 6.3, respectively.

Figure 6.3. (a) V^V complex with an alkyne anchoring group, **V-1**, (b) V^V complex with an alkene anchoring group, **V-2**.

Out of the two complexes, only **V-1** was synthesized at the time that this thesis was completed. Therefore, only **V-1** will be used for the following preliminary studies.

The synthetic route to the V^V complex, **V-1** (Figure 6.4), started from the commercially available compound 2,3-dihydroxybenzaldehyde and propargyl bromide. De-protonation of 2,3-dihydroxybenzaldehyde, followed by nucleophilic substitution of propargyl bromide gives the alkyne tethered aldehyde **1**, which can act as an anchoring group. Amide coupling reaction between 2,3,4,5,6-pentafluorobenzoyl chloride and *tert*-butyl carbazate, followed by de-protection of the *tert*-butoxycarbonyl (BOC) protecting group gives hydrazide compound **2**. Subsequently, condensation of **1** and **2** gives ligand **3**. The desired V^V complex, **V-1** is expected to be obtained by treatment of the ligand **3** with trialkyl orthovanadate.

Figure 6.4. Proposed synthesis for complex **V-1**

6.2.2 Anchoring of **V-1** complex via sequential functionalization approach on metal oxide (*Refer to Appendix III for detailed experimental methods*)

Subsequently, with **V-1** complex at hand, we proceeded with the copper(I)-catalyzed 1,3 dipolar azide–alkyne cycloaddition, referred to as a “click” reaction, for the purpose of covalently linking **V-1** to the metal oxide.²⁶ The as-prepared $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ (see Chapters 3 and 4), and commercial available TiO_2 were chosen as the hydroxy-terminated solid supports. Before undergoing the “click” reaction to bind **V-1** onto the metal oxide, the pre-treated metal oxide has to first undergo anchoring with the allyl bromide to form **allyl bromide@metal oxide**. The anchoring reaction was carried out in a sealed quartz

Schlenk tube under an argon atmosphere, irradiated using a 254 nm (125 W) UV lamp, which was followed by a substitution reaction to obtain an azide ($-N_3$) functionalized metal oxide, **allyl azide@metal oxide**. Lastly, the azide group on the metal oxide underwent a “click” reaction with the alkyne group on **V-1** in the presence of copper(I) iodide (CuI) and *N,N*-diisopropylethylamine (DIPEA) as a base to give **V-1/R@metal oxide** (Figure 6.5). Finally, the product mixture was washed several times by water and methanol to remove dimethylformamide (DMF), CuI, DIPEA, and any excess unbound **V-1** present. The **V-1/R@metal oxide** hybrid nanomaterial was characterized by FT-IR spectroscopy and SEM-EDS to verify the successful anchoring of **V-1** on the metal oxide.

Figure 6.5. A schematic representation of **V-1** anchoring via sequential functionalization approach on a select number of metal oxides.

According to the preliminary FT-IR spectrum, the strong azide stretch peak at wavelength 2105 cm^{-1} was diminished after the “click” reaction (Figure 6.6a), suggesting that complete reaction was achieved with the alkyne group on **V-1** or the allyl azide had dissociated. The presence of the elements fluorine and vanadium (5:1 ratio) with Ti observed in the SEM-EDS provided additional definitive evidence of **V-1/R@TiO₂** (Figure 6.7). Other analytical techniques to further affirm the anchoring of **V-1** on TiO₂ with UV-DRS and XPS are ongoing at present.

Figure 6.6. FT-IR comparison expanded portion around 2000 to 2200 cm^{-1} (a) between TiO₂, allyl bromine@TiO₂, allyl azide@TiO₂, **V1/R@TiO₂**, indicating the azide peak for allyl azide@TiO₂, (b) between **V-1/APS@SiO₂/BiVO₄/CuO_x** nanospheres and **APS@SiO₂/BiVO₄/CuO_x** nanospheres, indicating the azide peak for **APS@SiO₂/BiVO₄/CuO_x**.

Next, the anchoring of **V-1** complex on SiO₂/BiVO₄/CuO_x was investigated with the same method as shown above. However, the results of both FT-IR and SEM-EDS show no evidence of **V-1** anchored on SiO₂/BiVO₄/CuO_x even after two trials.

Figure 6.7. (a) Selected scan area for EDS, elemental mapping analysis of O (b, cyan), Ti (c, red), V (d, green), and F (e, magenta). EDS of **V-1/R@TiO₂** hybrid nanomaterial.

An alternative method to anchor **V-1** on both **SiO₂/BiVO₄/CuO_x** is *via* chemisorption that involves substitution of the ethoxide group on silyl esters in the presence of the –OH groups on the **SiO₂** and **BiVO₄** of the nanospheres (Figure 6.8). Similarly, the FT-IR spectrum (Figure 6.6b) reveals a strong azide stretch peak around 2103 cm⁻¹ for **APS@SiO₂/BiVO₄/CuO_x**, suggesting that the hydrolytic anchoring was successful. After the “click” reaction, the peak diminished, suggesting that the azide functional groups reacted with the alkyne anchoring groups on complex **V-1** to give **V-1/APS@SiO₂/BiVO₄/CuO_x**. SEM-EDS indicated a significant amount of hydrolytic-anchoring had occurred (Figure 6.9).

Figure 6.8. A schematic representation of hydrolytic-anchoring is given below: 3-azidopropyl-triethoxysilane is abbreviated as APS.

Figure 6.9. (a) Selected scan area for EDS, elemental mapping analysis of Bi (b, red), V (c, dark green), Si (d, green), Cu (e, magenta), F (f, brown). (g) EDS of V-1/APS@SiO₂/BiVO₄/CuO_x.

With these hybrid nanomaterials at hand, the PC performance of the photocatalysts was evaluated. Table 6.1 presents the preliminary results of the PC performance over V-1@TiO₂ and V-1/APS@SiO₂/BiVO₄/CuO_x and the results did not seem to be promising. Compound 1-phenyl-2-propyl alcohol that is structurally similar to lignin was employed as the substrate for the PC reaction.

Table 6.1.

Catalyst	Type of anchoring before “click” reaction	Catalyst loading (mg, 5 mol% relative to V-1)	Time (h)	Yield of benzaldehyde, 4 (%)
V-1@TiO₂	photo	20	40	5%
V-1@SiO₂/BiVO₄/CuO_x	chemisorption	15	40	0%

Up to the submission of this thesis, the PC results were still inconclusive, although some activity over **V-1/R@TiO₂** was observed. Therefore, further characterizations and catalytic experiments are needed to analyze the full potential of these catalysts.

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6.4 Appendix III

6.4.1 Synthesis and characterization of compounds

General procedure: All experiments were carried out in oven-dried Schlenk glassware and an inert nitrogen (N₂) atmosphere unless otherwise stated. The reaction mixtures were degassed under vacuum to remove molecular oxygen (O₂) and trace amounts of moisture.

Synthesis of 3-propargyloxy-2-hydroxybenzaldehyde, **1**:

Sodium hydride (60% dispersion in oil, 0.75 g, 19 mmol) and 2,3-dihydroxybenzaldehyde (1.4 g, 10 mmol) were placed in 25 mL Schlenk flask. DMSO (10 mL) was then added to the mixture dropwise at 0 °C with continuous stirring. The resulting reaction mixture was stirred for 1 h at room temperature before adding propargyl bromide (1.1 mL, 10 mmol, 80% dispersion in toluene) to the mixture. After addition was completed, the reaction mixture was stirred overnight at room temperature under a continuous N₂ flow. After completion, the reaction mixture was poured into deionized water (100 mL) and extracted with DCM (3 × 50 mL). The organic layer was dried over anhydrous Na₂SO₄. The resulting solution was evaporated to dryness under reduced pressure to provide a brown colored oily compound, **4** (1.4 g, 79%). ¹H NMR (300MHz, CDCl₃): δ = 2.52 (t, *J* = 2.3 Hz, 1 H), 4.80 (s, 2 H), 6.98 (t, *J* = 7.9 Hz, 1 H), 7.24-7.35 (m, 2 H), 9.92 (s, 1 H), 11.12 (s, 1 H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 57.3, 76.4, 78.2, 119.5, 121.3, 122.0, 126.4, 145.9, 152.4, 196.6 ppm.

Synthesis of pentafluorobenzhydrazide, 2:

Pentafluorobenzoylchloride (3.1 mL, 22 mmol) and *tert*-butylcarbazate (3.6 g, 27 mmol) were added in a Schlenk flask. Subsequently, the anhydrous dichloromethane (DCM, 220 mL) was added to the flask under continuous cooling at 0 °C with an inert N₂ atmosphere. Triethylamine (4.5 mL, 33 mmol) was added dropwise with stirring and the reaction mixture was maintained under a N₂ atmosphere at 0 °C for 2 h to obtain **2'**. Compound **2'** was used without further purification in the next step. Next, to the cooled solution of **2'**, trifluoroacetic acid (TFA, 27 mL, 0.35 μmol) was added dropwise and the reaction mixture was then warmed to room temperature and stirred for 16 h in order to allow deprotection of the *tert*-butyloxycarbonyl group to take place. DCM was then evaporated under reduced pressure and the white solid obtained was re-dissolved in ethyl acetate (150 mL) before it was neutralized using saturated Na₂CO₃ solution (19 mL) during the work-up. The pH was monitored using pH paper strips. The organic phase was washed with deionized water (3 x 25 mL) and the collected organic layer was dried over Na₂SO₄. Finally, the solvent was removed under rotary evaporation to give the product as a white solid, **2** (4.70 g, 95%). ¹⁹F{¹H} NMR (282.40 MHz, MeOD): δ = -142.1 (s, 1 F), -154.0 (s, 2 F), -163.3 (s, 2 F) ppm.

Condensation reaction to form ligand, 3

Compound **2** (0.50 g, 2.2 mmol) and ethanol (8.0 mL) were added to the flask under N₂. The mixture was stirred and heated to 65 °C to dissolve the solid completely. Next, **1** (0.39 g, 2.2 mmol) was added to the reaction mixture under a positive N₂ flow. The reaction mixture was then heated and stirred for 3 h under reflux conditions. The precipitate that formed was washed with hexane and filtered off using a Buchner funnel to remove any excess aldehyde present. The crude product was purified with a column chromatography (ethyl acetate:hexane = 1:4) to obtain a white solid, **3** (0.78 g, 92%). ¹H NMR (300 MHz, CD₃CN-*d*₃): δ = 2.81 (s, 1 H), 4.75 (s, 1 H), 4.79 (s, 2 H), 6.89–6.93 (m, 2 H), 7.01–7.12 (m, 3 H), 8.23 (s, 1 H), 8.36 (s, 1 H), 8.81 (s, 1 H), 10.48 (s, 1 H) 10.93 (s, 1 H) ppm. ¹⁹F {¹H} NMR (282.40 MHz, CDCl₃): δ = -159.9 (s, 1.5 F), -159.1 (s, 2 F), -149.4 (s, 0.6 F), -148.9 (s, 1 F), -139.6 (s, 1.5 F), -139.4 (s, 2 F) ppm.

Complexation reaction to form the complex, V-1

Ligand **3** (0.25 g, 0.64 mmol) was added in a 5 ml methanol solution of Vanadium(V) oxytriisopropoxide was added at 40°C and the mixture was further heated to reflux for an hour. Solvent is subsequently removed in vacuum yielding the desired vanadium complex, **V-1** (0.21 g, 67 %). ¹H NMR (300 MHz, MeOD-*d*₄): δ = 2.89 (s, 1 H), 4.78 (s, 2 H), 6.91 (t, 1 H, *J* = 9.0 Hz), 7.27 (d, 2 H, *J* = 24 Hz), 8.71 (s, 1 H) ppm. ¹⁹F {¹H} NMR (282.40 MHz, MeOD-*d*₄): δ = -164.5 (m,

2 F), -154.8 (m, 1 F), -140.7 (m, 2 F) ppm. ^{51}V NMR (105.25 MHz, $\text{MeOD-}d_4$) $\delta = -547.8$ ppm.

Pretreatment of TiO_2 P25 Nanoparticles

See Chapter 5 section 5.3.2

Allyl bromide@ TiO_2 :

A degassed, allyl bromide (5.0 mL) was added to an oven dried quartz glass Schlenk tube. Pre-processed TiO_2 P25 nanoparticles (80 mg, 1.0 mmol) was then added. The Schlenk tube was sonicated for 5 min before the solvent was removed under vacuum. The suspension was stirred under UV irradiation (254 nm, 125 watt) for 10 h. After the reaction, the nanoparticles were collected and washed several times by methanol to remove any excess and unbound allyl bromide present.

Allyl Azide@ TiO_2 :

The allyl bromide@ TiO_2 nanoparticles (60 mg, 0.75 mmol) was dried under vacuum at 120 °C for 3 h to remove any surface moisture in a Schlenk flask. In

another Schlenk flask, sodium azide (130 mg, 2.0 mmol) was dissolved in DMSO while being heated at 80 °C. The mixture containing sodium azide was then added into the other Schlenk flask containing the nanoparticles and the resulting suspension mixture was heated at 75 °C with stirring for 48 h. After the reaction, the nanoparticles were collected and washed several times with H₂O to remove DMSO and any excess and unbound NaN₃ present.

V-1@TiO₂

CuI (6.0 mg, 0.032 mmol) and DIPEA (60 μ L, 0.34 mmol) were charged with anhydrous DMF (3.0 ml). The reaction mixture was stirred until the color of the solution turned green. Next, the mixture was transferred to a suspension mixture containing tetrahydrofuran (THF, 4.0 mL) and **allyl azide@TiO₂** (40 mg). Subsequently, complex **V-1** (24 mg, 0.050 mmol) was added to the mixture and the mixture was heated at 60 °C with stirring for 72 h. After the reaction, the nanoparticles were collected and washed several times with water and methanol to remove DMF, CuI, DIPEA, and any excess and unbound Complex **V-1** present.

3-Azidopropyl-triethoxysilane@SiO₂/BiVO₄/CuO_x (APS@SiO₂/BiVO₄/CuO_x):

SiO₂/BiVO₄/CuO_x nanoparticles (40 mg, 0.067 mmol relative to BiVO₄) was added in a Schlenk tube, followed by addition of 3-azidopropyl-triethoxysilane (50 μ L, 0.20 mmol, 3 eq.) and toluene (5.0 mL). Subsequently, the resulting mixture was stirred for 18 h at 80 °C. After completion, the nanoparticles were collected and washed by toluene followed by ethanol to remove any excess and unbound 3-azidopropyl-triethoxysilane present.

V-1/APS@ SiO₂/BiVO₄/CuO_x

CuI (6.0 mg, 0.032 mmol) and DIPEA (60 μ L, 0.34 mmol) were charged with anhydrous DMF (3.0 ml). The reaction mixture was stirred until the color of the solution turned green. Next, the mixture was transferred to a suspension mixture containing tetrahydrofuran (THF, 4.0 mL) and APS@SiO₂/BiVO₄/CuO_x (40 mg). Subsequently, complex V-1 (24 mg, 0.050 mmol) was added to the mixture and the mixture was heated at 60 °C with stirring for 72 h. After the reaction, the

nanoparticles were collected and washed several times with water and methanol to remove DMF, CuI, DIPEA and any excess and unbound complex **V-1** present.

Figure 6.10. The ¹H NMR of 3-propargyloxy-2-hydroxybenzaldehyde, **1**.

Figure 6.11 The ¹³C NMR of 3-propargyloxy-2-hydroxybenzaldehyde, **1**.

Figure 6.12. The ^1H NMR of the ligand, **3**.

Figure 6.13. The ^{19}F NMR of the ligand, **3**.

Figure 6.14. The ^1H NMR of the vanadium complex, V-1.

Figure 6.15. The ^{19}F NMR of the vanadium complex, V-1.

Figure 6.16. The ^{51}V NMR of complex, **V-1**.

Chapter 7

Overall Conclusions and Future Work

This chapter discusses the overall results of the research and highlights the importance in the value of the work. Lastly, it discusses some of the future work and directions of the project.

7.1 Overview of research findings

At present, it is well-established that the growing demand for energy, chemicals production, and environmental challenges constitute paramount issues for the 21st century. Consequently, unsustainable fossil fuel resources, and strict environmental regulations motivate the search for more sustainable, and environmentally friendly renewable chemical sources. Apart from obtaining solar fuels *via* water splitting, AP has great potential in the production of solar chemicals by harnessing renewable solar energy from the sun.

To date, most of the AP systems studied either require energy intense UV light or have low activity due to the recombination of photogenerated species. To overcome the drawbacks of fast charge recombination and limited visible light absorption, many strategies have been developed in the past few decades. Among these strategies, constructing a heterojunction with two or more SCs is most widely used. This dissertation explored multiple aspects in the construction of the heterojunction photocatalysts and its use toward AP to generate solar chemicals. The major objectives of this research were to prepare visible light active heterojunction SCs and study their performance 1) as photocatalysts, 2) as a light harvesting supports toward solar chemical generation. The objectives illustrated in Section 1.5 shall be recapped here again.

7.1.1 Key findings and outcomes

In Chapter 4, we have successfully synthesized 1) a mesoporous bismuth $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ to act as a chromophore in a Z-scheme system for effective light harvesting and charge separation in the synthesis of solar chemicals. 2) Full characterization of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ was conducted, including XPS and STEM-EDS, which confirm the presence of CuO_x at the heterojunction of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanostructures. 3) Notably, the $\text{SiO}_2/\text{BiVO}_4$ nanospheres perform two times faster than bulk BiVO_4 and provide higher yields for oxidative

coupling of amines to imine products. 4) We have obtained insights into the PC mechanism of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ by comparing the reaction rates of different *para*-substituted benzylamines in the presence of disparate chemical scavengers. Moreover, the mechanism of the enhanced activity was proposed on the basis of a type II heterojunction band alignment between BiVO_4 and CuO_x . 5) Furthermore, the stability and recyclability of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres were evaluated, with a reaction repeated for at least ten cycles. High conversions of the substrate were maintained for the first three runs, after which a gradual decrease in the conversion was observed, although high selectivity for the imine product was maintained.

In Chapter 5, we have successfully 6) utilized maleimide as a photoactivated anchoring group to synthesize several hybrid single-site catalysts comprising covalently grafted Ni complexes on SiO_2 , TiO_2 , CeO_2 , and WO_3 nanoparticles. 7) Characterization by DRS, FT-IR, XAS, and XPS verified that the Ni salicylaldimine complexes remained intact and were anchored covalently. 8) Remarkably, the heterogeneous catalysts displayed conversions and selectivities for alkene epoxidation similar to their corresponding homogeneous molecular congener, but were found to be more robust, recyclable, and 9) the heterogeneous catalysts were stable up to 10 catalytic cycles under harsh oxidative reaction conditions in a wider range of more eco-friendly solvents.

Finally, in Chapter 6, we have also been able to 10) utilize a similar protocol to deposit the V^v complexes on TiO_2 and $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$. 11) Characterization by FT-IR spectroscopy and SEM-EDS verified that the V^v complex remained intact. Up to the submission of this thesis, the PC results showed that none of hybrid nanomaterial were active for C-C bond cleavage, although some different reactivity over **V1-R1@TiO₂** was observed. Further characterizations and catalytic experiments are needed to analyze the full potential of these catalysts.

Therefore, the finding in Chapters 4 and 5 successfully showed that the objectives have been met, although there is further work to be completed in Chapter 6.

Overall, the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ SC heterojunction was synthesized as more efficient catalysts than the constituents only. Remarkably, the new nanocomposites performed seven times faster than reported articles in this field, and afford better yields for the oxidative coupling of amines to imines, as reported in Chapter 4. Although we have yet to obtain promising PC activity from the **V-1@SiO₂/BiVO₄/CuO_x** hybrid nanomaterials, the anchoring of V^v complex on $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ as a light harvesting support was successful, as shown in Chapter 6. Moreover, we are able to illustrate this idea with the mesoporous SiO_2 (from Chapter 4) and other pristine metal oxide as a proof of concept in Chapter 5. Therefore, the hypothesis of the thesis has been addressed successfully.

7.2 Future studies and potential research directions

The present thesis work is devoted toward the synthesis and characterization of BiVO_4 with a CuO_x heterojunction and investigations of its related physical features with the aim of PC applications. There are some possible future work aspects and potential directions toward the enhancement of PC efficiencies.

- 1) One of the main objectives of this thesis work is the fabrication of mesoporous BiVO_4 nanomaterials and the procedure used was focused on the incipient wetness impregnation-calcination method. We could potentially explore other methods to synthesize pristine mesoporous BiVO_4 nanoparticles, such as hard templating and soft templating approaches before loading it with CuO_x . This may further improve the PC performance by increasing the surface area and number of active sites, which are currently blocked by the SiO_2 support in $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$.
- 2) Synthesis of other combinations of visible light active heterojunctions with similar synthesis reported in Chapter 4 instead of limiting to BiVO_4 , such as WO_3/CuO_x ¹⁻² and $\text{Fe}_2\text{O}_3/\text{CuO}_x$,³ since the addition of CuO_x has proven to be effective in extending the charge separation lifetime and thus improve the

overall PC performance. It is important that the band positions of the individual components of the heterojunction should be aligned in such a way that the photogenerated species can be transferred from one material to the other and to the surface without recombination.

- 3) Although the CO_2 reduction (to form methane, methanol, or formic acid) potential is more negative than the water reduction potential in NHE, the CuO_x on BiVO_4 might have sufficient CB overpotential to be used for these reduction reactions. Hence, an extension of the research scope toward other applications is recommended.⁴
- 4) Furthermore, the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres can potentially be used as the photocatalyst for water splitting applications. The investigation on the water splitting ability can be compared among $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ to the doped version of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ (W and/or Mo). In other words, the activity of $\text{SiO}_2/\text{W-BiVO}_4/\text{CuO}_x$, $\text{SiO}_2/\text{Mo-BiVO}_4/\text{CuO}_x$, and $\text{SiO}_2/(\text{W+Mo})\text{-BiVO}_4/\text{CuO}_x$ can be compared.⁵⁻⁷ Also, instead of loading CuO_x , it would be interesting to study nanoparticulate $\text{SiO}_2/\text{BiVO}_4$ modified with a water oxidation co-catalyst such as FeOOH and Co-Pi to improve water oxidation kinetics.⁸⁻⁹
- 5) It was proposed that metal-doped BiVO_4 nanoparticles are efficient for the degradation of organic pollutants, but it is also possible to use the metal-doped $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres simultaneously for water splitting (hydrogen production) using the same setup.¹⁰
- 6) The loading of metals such as Au, Ag, Pt, and Cu on the BiVO_4 nanocomposites is very attractive, especially if the synthesis of such materials can be achieved in a short time (e.g. photodeposition) as compared to other chemical routes such as sol-gel or hydrothermal processes. It would be

interesting to check and compare all the physico-chemical properties as well as conduct PC studies with these metal/BiVO₄ nanocomposites under the same PC conditions.¹⁰

- 7) Lastly, in order to proceed with anchoring a V^v complex on the nanocomposites, a new V-2 complex (containing an alkene moiety), could be a potential candidate to be anchored on both SiO₂/BiVO₄/CuO_x and TiO₂ separately. Alternatively, SiO₂/BiVO₄/CuO_x modified as described above could serve as better supports.

Finally, we have also been able to utilize the photoclick protocol of the maleimide anchoring group to deposit molecular complexes on various metal oxides as proof of concept. Our study thus forms the basis for future discoveries on using light to deposit functional molecules on SCs to create hybrid (photo)catalysts that can synergize the benefits of both homogeneous and heterogeneous catalysts. Moreover, we believe that this type of anchoring protocol to deposit functional molecules can be applied in other fields, including biosensing, renewable energy, and optoelectronic devices, for example.

7.3 References

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