PHOTOCATALYSIS USING TiO2 NANOPARTICLES CONTAINING SURFACE METAL SITES

Benjamin D. Stewart

University of New Hampshire, Durham

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PHOTOCATALYSIS USING TiO$_2$ NANOPARTICLES CONTAINING SURFACE METAL SITES

BY

Benjamin D. Stewart
B.S., Gordon College, 2013

THESIS

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

Masters

In

Chemistry

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This thesis has been examined and approved in partial fulfillment of the requirements for the degree of Master of Science in Chemistry by:

Thesis Director, Gonghu Li, Associate Professor, Department of Chemistry

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Christopher F. Bauer, Professor, Department of Chemistry

On August 14th, 2018

Original approval signatures are on file with the University of New Hampshire Graduate School
ACKNOWLEDGEMENTS

Gratitude, for me, is a place from which I strive to live every breath. Therefore, the list of those who I feel deserve my gratitude extends beyond the one or so pages that this section should be limited to. As far as this particular work of scientific inquiry is concerned, I will start by thanking my committee. Chris Bauer, Margaret Greenslade and Gonghu Li, you taught me invaluable secrets of chemical, professional and personal knowledge in every class, presentation and conversation. Those treasures will not go uncherished. Within that group of people, special thanks are due to my advisor and mentor. Gonghu, your patience and supportive demeanor are both exemplary qualities that I hope to emulate throughout my career.

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“by wisdom He laid the Earth’s foundations, by understanding he set the heavens in place…”

- Proverbs 3:19
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<tr>
<td>AOP</td>
<td>Advanced Oxidation Process</td>
</tr>
<tr>
<td>ACS</td>
<td>American Chemical Society</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett, Joyner and Halenda</td>
</tr>
<tr>
<td>bpy</td>
<td>2,2’-bipyridine</td>
</tr>
<tr>
<td>cyclam</td>
<td>1,4,8,11-tetraazacyclotetradecane</td>
</tr>
<tr>
<td>dcbpy</td>
<td>4,4’-dicarboxy-2,2’-bipyridine</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DRIFTS</td>
<td>diffuse reflectance infrared Fourier transform spectroscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>FTO</td>
<td>fluorine doped tin oxide</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>Inductively coupled plasma atomic emission spectrometry</td>
</tr>
<tr>
<td>IET</td>
<td>Interfacial Electron Transfer</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>MLCT</td>
<td>metal to ligand charge transfer</td>
</tr>
<tr>
<td>NHE</td>
<td>normal hydrogen electrode</td>
</tr>
<tr>
<td>PEG-PPG-PEG</td>
<td>poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol)</td>
</tr>
<tr>
<td>RBF</td>
<td>round bottom flask</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Name</td>
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<tr>
<td>SHE</td>
<td>standard hydrogen electrode</td>
</tr>
<tr>
<td>TBAH</td>
<td>tetrabutylammonium hexafluorophosphate</td>
</tr>
<tr>
<td>TDDFT</td>
<td>time dependent density functional theory</td>
</tr>
<tr>
<td>TEA</td>
<td>triethylamine</td>
</tr>
<tr>
<td>TEOA</td>
<td>triethanolamine</td>
</tr>
<tr>
<td>TEOS</td>
<td>tetraethoxysilane</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TN</td>
<td>turnover number</td>
</tr>
<tr>
<td>tpy</td>
<td>2,2':6',2''-terpyridine</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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ABSTRACT

PHOTOCATALYSIS USING TiO$_2$ NANOPARTICLES CONTAINING SURFACE METAL SITES

by

Benjamin D. Stewart

University of New Hampshire

In recent years, exploration of the functionalization of nanoparticle surfaces has gained more interest. This can overcome the high energy band gap problem of a semiconductor such as TiO$_2$. Furthermore, this kind of modification can widen the range of catalytic or other uses for the material. In this work TiO$_2$ in various crystal forms was modified towards both degradation of water contamination as well as the reduction of CO$_2$. Iron was covalently attached to TiO$_2$ using a bottom up synthetic strategy incorporating a photoactive linker designed for photocatalytic applications. The resulting surface Fe(II)-terpyridine complex was characterized with techniques including microscopy and spectroscopy, and was investigated in the degradation of Orange II in the presence of H$_2$O$_2$. Under visible-light irradiation, activity of the photocatalyst was found to be dependent on the crystallinity of the supporting TiO$_2$. Furthermore, the Fe(II)-terpyridine complex grafted on TiO$_2$ showed significantly greater activity than the same complex grafted on zirconia in the degradation of the azo dye, Orange II.

Other modifications are explored as well that make use of tin or copper on the surface of TiO$_2$. Tin and copper are covalently grafted to the surface of TiO$_2$ to explore as a possible CO$_2$ reduction photocatalysts. In each of these explorations, the morphology of the TiO$_2$ nanoparticle was explored as a main factor in determining the efficacy of its function. Sample characterization was conducted via UV/Vis and infrared spectroscopy as well as nitrogen adsorption surface area
analysis, and electron microscopy. Catalyst performance was probed using UV/Vis spectroscopy, in-situ FTIR and gas chromatography.
I. INTRODUCTION

1.1. Motivations

Photocatalysis has been a research topic of intensive interest for a long time. In 1839 Antoine Becquerel was one of the first to report on the photoelectric effect.\textsuperscript{1,2} Since that time, many researchers and innovators have developed new applications of this interesting interaction between light and matter. For example, our modern direction in photocatalysis research is often attributed, deservedly, to Honda and Fujishima from their seminal work in 1972 with TiO\textsubscript{2}.\textsuperscript{3} Their contributions opened up many ideas about how to make photocatalysis practical and cost effective. The potential scope of utility for photocatalytic materials is quite impressive. They can be applied to problems ranging from cleaning polluted natural resources,\textsuperscript{4-11} preserving fruits and vegetables,\textsuperscript{12} catalyzing the synthesis of small molecules,\textsuperscript{13} as well as driving the “uphill” reaction of reverse combustion such as the reduction of CO\textsubscript{2}.\textsuperscript{14-21} The research explored in this thesis will inform the application of photocatalytic materials specifically to the problems of environmental pollution and the production of fuels.

1.2. Photocatalysis

To begin, it is appropriate to introduce green chemistry. This is because the main focus of this work, photocatalysis, goes hand in hand with green chemistry. Green chemistry is an ethic that one can apply to all of the decisions made in designing and executing chemical research.
Like most scientific enterprises, it esteems creativity but also has an emphasis on responsibility at the atomic level. It is the process of forming new chemical ideas and making use of those ideas in ways which minimize the negative impacts for which chemistry is so often infamous\textsuperscript{22,23} by using less hazardous materials and processes in the conception/design phase.\textsuperscript{24-27} I believe that the framework of green chemistry is fundamental for creating a sustainable future for generations to come. It turns out that photocatalysis is a particularly applicable tool when attempting to solve chemical problems within the framework of green chemistry. All of the energy we use to make our current way of life possible comes from the sun. However, we use mostly fossilized solar energy in the form of oil and coal. That solar energy was absorbed and transformed many years ago into the “raw” organic matter we know as oil and coal. Today, we’ve been consuming it at a significant rate for a relatively small number of years from a cosmic perspective (two centuries since the industrial revolution is miniscule relative to the most probable age of the earth).

The reverse reaction of regenerating those fuels from CO\textsubscript{2} and water through the carbon cycle is formidably slow to the point where we can look at this as a reaction that “goes to completion.” The question of when we will reach completion is outside the scope of this thesis, however, some relatively optimistic estimates suggest our fossil fuel supply problems will become extreme near the middle of our current century.\textsuperscript{28,29} This problem is imminent and effects us and our children directly. Without decreased reliance on fossil fuels, the future of man is bleak. Even if we don’t run out of fossil fuels,\textsuperscript{30} burning them at our current rate has and will continue to change the composition of the atmosphere and irreparably alter our planet’s climate and other natural resources in ways that will make our livelihood difficult.\textsuperscript{31-33} Therefore, the application of photocatalysis towards more efficient, \textbf{direct} use of solar energy is highly
consistent with the philosophies of green chemistry and the drive for sustainably maintaining human health and the environment.

Much of the potential for application of photocatalysis, practically, will come from the use of semiconductors. One benefit of using semiconductors is the large variance in electronic structure between different semiconductors as well as the significant dependence upon surface structure of the electronic structure.\textsuperscript{1,14,34} This tunability has the potential to allow for highly controlled systems that direct electron flow as if it were nanoscopic circuitry. Semiconductor photocatalysis as we see it today is a result, in large part, of the work conducted by Fujishima and Honda who used titanium dioxide in the presence of ultraviolet (UV) light for water splitting.\textsuperscript{3} Metal oxides are very commonly used as photocatalysts and unlike metals, have a relatively large band gap. A band gap is the difference in energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In metals this band gap is very small or negligible leading to an energetic surface upon which electrons are mobile called a conduction continuum.\textsuperscript{35} By comparison, insulators such as glass and most plastics are on the other extreme. Their HOMO/LUMO gap is very large causing it to be difficult to excite an electron in these systems.
Figure I.1: Schematic of TiO$_2$ photocatalysis as summarized by He He and coworkers.$^{36}$ Relative positions of redox potentials associated with (a) water splitting, (b) CO$_2$ reduction, and (c) dye-sensitized solar cells. The redox potentials are not shown on scale. Abbreviations: CB (conduction band), VB (valence band), D (electron donor), S (photosensitizer). Reprinted with permission from reference 36. Copyright 2012 American Chemical Society

Semiconductors are useful for photocatalytic applications because their band gap is the right size to interact with some of the most abundant forms of electromagnetic radiation; sunlight. A summary of semiconductor use in a variety of applications is provided in Figure I.1.$^{36}$ This figure, specifically, shows how the energetics of the TiO$_2$ ground and excited states are compatible with a number of different applications such as water splitting, CO$_2$ reduction and dye sensitized solar cells. Through irradiation with UV light, high energy electrons can be injected into the conduction band of TiO$_2$. High energy electrons in the conduction band of TiO$_2$ can be used to reduce CO$_2$ or other target molecules. Excitation of a semiconductor in this way also leaves an unoccupied molecular orbital called a hole in the valence band. These unoccupied holes can accommodate an electron from pollutants or water for environmental or energy applications. The combination of these two separated charge carriers is called an electron/hole pair. These electron/hole pairs (e$^-$/h$^+$) are available at the surface for further reaction. This is often an unfortunately transient event and there are a number of researchers attempting to extend
the lifetime of excited e−/h+ pair.37-39 In our case, the usefulness of semiconductor materials is also in their stability. Most molecular catalysts are quite powerful in rate of reaction but as compared to metal oxide materials are far less stable and often suffer from significant decomposition reactions. Through functionalizing the surface of semiconductor materials with either molecular catalysts or other species such as metal oxides, we may be able to further tune the functionality of these materials for specific applications.

1.3. Pollution Remediation and Advanced Oxidation Processes

Globally, usable drinking water is a relatively rare commodity. A mere 0.77% of the total water on the planet is accessible fresh water (Figure I.2).40 Furthermore, this water is used for more than just drinking, and much of it is polluted to the point where water treatment methods are sorely needed.

![Diagram of accessible water on Earth](image)

Figure I.2: Accessible water on Earth.40

Americans consume 340 L of water per-day through sanitation, cooking and drinking.41,42 Approximately twenty percent of the world’s population does not have access to safe drinking
Many of these people have access to only 5 L of water per day. This is in light of international recommendations that have set the water usage guideline at 20 L per day per person under normal circumstances. However, the water supply will need to meet the demands of the daunting growth of the human population as well as the biodiversity of the Earth.

There are currently many ways in which water contamination can occur. The three general categories of contamination are microbiological contaminants such as bacteria, organic contaminants such as pharmaceuticals, or inorganic contaminants such as heavy metals. Industrial wastewater treatment plants have standardized a set of processes that typically must treat each of these problems with a different chemical or physical technique. Furthermore, these treatment plants are not sustainable for use in processing low concentration pharmaceutical or industrial waste effluent which are still above safety thresholds. These low concentration pollutants are called recalcitrant contaminants. For example, removal of a recalcitrant contaminant through the use of activated charcoal is not sustainable. It is an efficient contaminant removal method, but the charcoal becomes saturated over time. This requires it to be recovered with the pollution still adhered. This material then needs to be processed via incineration or is deposited in a landfill. In either case, the pollution is merely relocated in ways that could be more problematic than simply returning the contaminant to the water stream. Internationally, population growth puts pressure on the need for more viable water treatment methods. Domestically, societal and legal demands are growing as concerns about environmental impact in the Anthropocene grow as well. These factors have contributed greatly to the drive to develop new, effective and economically sustainable methods for pollution prevention and treatment. Scientific exploration in this area has responded in the development of a category of chemical systems called Advanced Oxidation Processes (AOPs).
The term AOP was first published and defined in 1987 by Glaze and coworkers. In Glaze’s work, the authors define an AOP as any processes involving ozone, hydrogen peroxide and/or UV radiation for the purpose of oxidation. In that case, the application focused on was water treatment. Since those days, many other processes have been described as AOPs and the term has come to include reactions in which highly reactive species such as hydroxyl radicals (•OH) are generated. This can be done by hydrogen peroxide and UV light as already established, by semiconductor nanoparticles irradiated with light, or by Fenton process which also employs iron and hydrogen peroxide.

In each of these chemical systems, the goal is to generate reactive radical species which will quickly, and non-selectively eliminate pollutants such as organics. Simpler, conventional methods such as flocculation and filtration tend to be less expensive. However, AOPs are used to treat the chemicals that are not easily removed by these methods. The field of work investigating and applying AOPs refer to these as recalcitrant, or “hard-to-get” chemicals. As a frame of reference, provided below in Table 1.1 is a list of compounds written by an international collaborative from Europe. These compounds are said to be of relatively high priority due to their recalcitrance and should be focused on and potentially monitored in drinking water.
Table I.1 Table of priority compounds for study. These are prioritized targets for AOPs due to their recalcitrance, toxicity, prevalence and/or bioaccumulation. Sample compounds from Ribeiro et al.\textsuperscript{49}

<table>
<thead>
<tr>
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<th>Chemical structure</th>
<th>Compound(s)</th>
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<th>Compound(s)</th>
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<td>Organochlorine pesticides/</td>
<td></td>
<td></td>
<td>Organochlorine pesticides/</td>
<td></td>
<td></td>
<td>Organotin Tributyltin compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclodiene pesticides\textsuperscript{a}</td>
<td>$C_{12}H_8Cl_6$/$364.91$</td>
<td>![Organochlorine pesticides structure]</td>
<td>Cyclodiene pesticides\textsuperscript{a}</td>
<td>$C_{12}H_8Cl_6O$/$380.91$</td>
<td>![Organochlorine pesticides structure]</td>
<td>Tributyltin compounds including tributyltin-cation</td>
<td>$C_{13}H_{27}Sn^+$/$290.05$</td>
<td>![Organotin Tributyltin compounds structure]</td>
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<td>aldrin and isodrin (isomers)</td>
<td></td>
<td></td>
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<td>![Organochlorine pesticide structure]</td>
<td>Organochlorine pesticide/</td>
<td>$C_{14}H_9Cl_3O$/$370.49$</td>
<td>![Organochlorine pesticide structure]</td>
<td>PAH/ Benzo(g,h,i)-perylene</td>
<td>$C_{22}H_{12}$/$276.33$</td>
<td>![PAH/ Benzo(g,h,i)-perylene structure]</td>
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<td>Endosulfan</td>
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<td>Dicofol</td>
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<tr>
<td>Organophosphorus pesticide/</td>
<td>$C_6H_7Cl_O_3P$/$220.98$</td>
<td>![Organophosphorus pesticide structure]</td>
<td>Triazine pesticide/</td>
<td>$C_{11}H_{19}N_5$S/$253.37$</td>
<td>![Triazine pesticide structure]</td>
<td>Industrial compounds/ Perfluorooctane sulfonic acid and its derivatives (PFOS)</td>
<td>$C_{6}HF_{17}O_5$/$500.13$</td>
<td>![Industrial compounds/ Perfluorooctane sulfonic acid and its derivatives (PFOS) structure]</td>
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<td>Cybutryne</td>
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</tbody>
</table>
1.4. Solar Production of Fuels from CO₂

There is a critical need to recycle CO₂ into chemicals, materials and fuels. Research on this topic has developed heavily in recent years. There are multiple pathways for using CO₂. These include hydrogenation, electrochemical reduction, and photochemical reduction. In the future, photo-assisted methods of CO₂ recycling will be better suited to meet the energy needs of the process due to the renewable nature of the Sun as an energy source. The main focus of this aspect of the research described herein is the utility of modified TiO₂ as a photocatalyst for CO₂ reduction.

Given that CO₂ is extremely stable (ΔG° = -400 kJ mol⁻¹) it is a particularly challenging molecule to reduce and therefore requires high potentials to do this directly through electrolysis. Because of the high potential required for single-electron CO₂ reduction (Reaction 1.1), other pathways such as proton-coupled multi-electron steps (Reactions 1.2-1.6) are more favorable.

\[ \text{CO}_2 + e^- \rightarrow \text{CO}_2^+ \quad E^o = -1.9 \text{ V (vs NHE at pH 7)} \quad (1.1) \]
\[ \text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH} \quad E^o = -0.61 \text{ V} \quad (1.2) \]
\[ \text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O} \quad E^o = -0.53 \text{ V} \quad (1.3) \]
\[ \text{CO}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{HCHO} + \text{H}_2\text{O} \quad E^o = -0.48 \text{ V} \quad (1.4) \]
\[ \text{CO}_2 + 6\text{H}^+ + 6e^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad E^o = -0.38 \text{ V} \quad (1.5) \]
\[ \text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad E^o = -0.24 \text{ V} \quad (1.6) \]

An efficient catalytic system for CO₂ reduction should be able to accumulate multiple redox equivalents and will likely proceed through a pathway similar to one of the less
thermodynamically favorable reactions shown in equations 1.2-1.6. One promising means to this end is the attachment of a catalytic site onto the surface of a photoactive material such as a semiconductor nanoparticle. Explored in this thesis is the use of the low-cost, transition metals Sn and Cu grafted onto various forms of TiO$_2$. Sn is less explored than copper and theoretical studies indicate that the interaction between Sn and CO$_2$ may be favorable towards promoting the transient bent CO$_2$ species. This species is commonly cited as important for reduction of CO$_2$ to CO. More on this topic will be explained in Chapter 3, but a discussion of the topic is warranted to orient the reader to the scope of applications that are touched upon in this thesis.
II. VISIBLE-LIGHT DEGRADATION OF ORANGE II USING AN Fe(II)-TERPYRIDINE COMPLEX GRAFTED ONTO TiO$_2$ SURFACE

2.1 Introduction

In 2015, the World Health Organization (WHO) released a report on the progress in both drinking water and sanitation availability since 1990. The report shows a significant improvement, however, there is still much work that is required. The increase of industrialization has many benefits such as increased technological advances and availability of devices and products, which generally increase the standard of living. However, one problem commonly associated with industrialization is an increase in sources of pollution, which degrade both human and environmental health. Furthermore, as human knowledge of mechanistic toxicology grows, pressures to tighten legal concentration thresholds increase as well. However, conventional methods for water treatment are butting up against limitations of meeting new pollution standards. It is possible that photocatalytic degradation of water contaminants could aid in this problem.

Today, much work has been done in the way of homogeneous and heterogeneous photocatalysis of organic pollutants. Traditional photocatalysis using semiconductor nanoparticles commonly uses TiO$_2$ but one limitation to this is its relatively large bandgap of ~3.2 eV. Many of the other semiconductor nanoparticles with smaller band gaps, however, have absolute band positions that render photogenerated electrons and holes inaccessible for environmental pollution remediation applications.
Additionally, TiO$_2$ is very cost effective and relatively non-toxic though investigations into the toxicity of nanoparticles is still ongoing.\textsuperscript{70} In light of this, it may be useful to draw from the large body of knowledge developed in the dye sensitized solar cell field. One major goal of that field has been to overcome these limitations through the use of sensitizing dye molecules. These sensitizers can efficiently inject electrons into the conduction band of TiO$_2$. Until recently, the possibility of using these types of systems was not viable due to the instability of typical dye-TiO$_2$ combinations in oxidative conditions.\textsuperscript{71} However, recent studies have shown that acetylacetonate (acac) is a quite stable surface linker under oxidative conditions.\textsuperscript{71} Therefore, we’ve modified a previously developed system that uses the strength of molecular iron as a photo-Fenton\textsuperscript{9,72-75} type catalyst while bound to TiO$_2$ nanoparticles, which have the benefits of being recyclable.

The Fenton reaction is among the most effective advanced oxidation process for the decomposition of organic pollutants.\textsuperscript{76,77} It involves catalytic activation of hydrogen peroxide (H$_2$O$_2$) with iron species to form reactive oxygen species. In particular, both the ferrous and ferric ions can react to generate radicals such as •OH and •OOH (shown in Reactions 1 and 2). These unstable moieties are suitable to oxidize organic molecules such as pharmaceutical pollutants.\textsuperscript{78,79}

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{•OH} + \text{OH}^- \quad k_1 = 76 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \quad (2.1)
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{•OOH} + \text{H}^+ \quad k_2 = 0.02 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \quad (2.2)
\]

In order to maximize longevity, it is favorable to cycle at equal rates the two main reactions, oxidation and reduction of Fe$^{2+}$ and Fe$^{3+}$, respectively. However, the reduction of Fe$^{3+}$
is typically slow and therefore causes the Fenton reaction to eventually slow to a halt. So any factors which accelerate ferric reduction will also augment the utility of this system. There may be another reaction that is playing a role here. Some experimental evidence in the field indicates that the formation of high-valent oxoiron species such as Fe$^{IV}$=O is possible.$^{80,81}$ This would improve the Fenton system as Fe$^{IV}$=O itself can directly, rapidly oxidize organic pollutants.

Related to the Fenton process is a light assisted reaction called the photo-Fenton reaction. With UV irradiation, the regeneration of Fe$^{2+}$ can be significantly enhanced.$^{82}$ It turns out too that when attempting to use the photo-Fenton reaction to degrade chromophores, visible light irradiation can also improve electron transfer from excited dye molecules to Fe$^{3+}$, thereby assisting to maintain the Fe$^{2+/3+}$ balance.$^{83}$

In addition, it has been found that modification of the ligand environment of the iron species involved in the Fenton reaction can facilitate favorable conditions as well. Coordination complexes of Fe$^{2+}$, such as Fe(bpy)$_3^{2+}$ where bpy is 2,2'-bipyridine, have been employed to activate O$_2$ instead of H$_2$O$_2$ as the oxidant.$^{84}$ Interestingly, Chen and coworkers found that Fe(dcbpy)$_3^{2+}$, where dcbpy is 4,4'-dicarboxy-2,2'-bipyridine, was highly active in visible-light degradation of dye molecules in the presence of either H$_2$O$_2$ or O$_2$.$^{85}$ The dual functional coordination nature (i.e. the –COOH and the bpy moieties) of dcbpy ligand was shown to facilitate cycling between Fe$^{2+}$ and Fe$^{3+}$. This same group showed the photocatalytic activity of a variety of other derivatizations of the bpy Fe coordination environment (Scheme II.1) Furthermore, a hybrid catalyst was prepared by intercalation of Fe(bpy)$_3^{2+}$ into laponite clay, which demonstrated excellent activity in visible-light degradation of dye pollutants in the presence of H$_2$O$_2$.$^{86}$
<table>
<thead>
<tr>
<th>Ligand</th>
<th>Substrate</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Ligand 1" /></td>
<td>Org II</td>
<td>93.7</td>
</tr>
<tr>
<td><img src="image2.png" alt="Ligand 2" /></td>
<td>2,4-DCP</td>
<td>91.2</td>
</tr>
<tr>
<td><img src="image3.png" alt="Ligand 3" /></td>
<td>Org II</td>
<td>6.4</td>
</tr>
<tr>
<td><img src="image4.png" alt="Ligand 4" /></td>
<td>Org II</td>
<td>24.6</td>
</tr>
<tr>
<td><img src="image5.png" alt="Ligand 5" /></td>
<td>Org II</td>
<td>35.1</td>
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<td><img src="image6.png" alt="Ligand 6" /></td>
<td>Org II</td>
<td>13.5</td>
</tr>
<tr>
<td><img src="image7.png" alt="Ligand 7" /></td>
<td>Org II</td>
<td>18.4</td>
</tr>
</tbody>
</table>

Scheme II.1: Photocatalytic activity of Fenton system with ferrous complexes using bpy ligands shown. Dcbpy and bpy are the ligands shown 1st and 2nd, respectively. OrgII is the azo dye orange II (OII in this thesis) and 2,4-DCP is 2,4-dichlorophenol. Conversion % shown are after 8 h of irradiation. Reproduced with permission from ref. 85.

Herein we report the use of a surface Fe(terpy)²⁺ complex, where terpy is 2,2′:6′,2″-terpyridine, as the catalyst for the photo-Fenton reaction. The Fe(terpy)²⁺ complex is covalently grafted onto TiO₂ surfaces via a covalent linkage (Scheme II.2), which as stated above was shown to be stable under strongly oxidative conditions.⁷¹
Unique characteristics of the design shown in Scheme II.2 include (1) a coordination Fe(terpy)$^{2+}$ complex as the catalytic center for the Fenton process, (2) a covalent linkage that can absorb visible light between 400 nm and 600 nm, and (3) a semiconducting TiO$_2$ surface which serves as a robust support. The covalent linkage was previously utilized to graft Mn(terpy)$^{2+}$ complexes on TiO$_2$ for use in photochemical oxidation reactions. It was designed to harvest visible light and subsequently generate redox equivalents for chemical transformations. In comparison, most reported covalent linkages that connect molecular catalysts with surfaces are not light absorbing.

We hypothesize that the semiconducting TiO$_2$ surface could act as an electron acceptor and enhance photo-Fenton reactions using the surface Fe(terpy)$^{2+}$ complex. In order to probe potential effects of TiO$_2$ on the activity of Fe(terpy)$^{2+}$, the Fe(II) complex is also grafted onto zirconia (ZrO$_2$) surface through the same covalent linkage. Orange II (OII) is employed as a
model dye compound in the photo-Fenton reaction. The recyclability of the surface Fe(II) catalyst is also investigated. Electronic properties of this linker and proposed alternatives are also explored computationally.

2.2 Experimental

2.2.1 Catalyst preparation

Nanoscale titanium dioxide was used in three different crystal phases: anatase (Aldrich), rutile (Aldrich) and P-25 (Aeroxide) which is a mixture of 80% anatase and 20% rutile. ZrO$_2$ nanopowder (Aldrich) was used as a larger bandgap material as a comparison. These four nanopowders were all treated in the same way based on a synthetic route reported elsewhere.$^{71}$

400mg of nanopowder was stirred in 30 mL dichloromethane (Pharmco Products) at room temperature for 24 hours with 20.0 mg of the phenylterpyridine-amide-acac ($L$) (synthesized as from literature citation 3) linker shown in Scheme 2.1. The resulting yellow suspension was centrifuged to pellet and supernatant was removed followed by subsequent washing with dichloromethane. After drying under N$_2$ flow, the yellow powder was then stirred in 30 mL ethanol (190 proof Pharmco Products) at room temperature for 2h with 10.0 mg of iron (II) chloride tetrahydrate (Sigma-Aldrich). The resulting purple mixture was centrifuged to pellet and subsequently washed with ethanol followed by N$_2$ drying. The solid powders were ground then heated at $\sim$100 °C for 1 hour prior to use.
2.2.2 Catalyst Characterization

Diffuse reflectance UV/Vis spectroscopy (DRUVS) was conducted using a Cary 50 Bio UV-visible Spectrophotometer. A Barrelino diffuse reflectance probe was used to collect UV-visible spectra of powder samples using BaSO$_4$ as a standard. Infrared spectra were collected on a Thermo Nicolet 6700 Fourier transform infrared (FTIR) spectrometer equipped with a Harrick Praying Mantis diffuse reflectance accessory using spectroscopy grade KBr as background. Scanning electron microscopic (SEM) images were taken on an Amray 3300FE field emission SEM with PGT Imix-PC microanalysis system. Elemental analysis was conducted using inductively coupled plasma atomic emission spectrometer (ICP-AES). Hydrofluoric acid (HF) was used to digest each of the samples for 24 hours. The loadings of Fe were determined to be 50, 95, 59, and 58 µmol/g in Fe-L-P25, Fe-L-Anatase, Fe-L-Rutile, and Fe-L-Zirconia, respectively.

2.2.3 Dye Degradation Studies

Dye degradation was used as a metric for the oxidative ability of this system. The system includes the dye, the catalyst, H$_2$O$_2$, and the solvent. The Fenton reaction is reported to have difficulty degrading the common azo dyes such as Orange II. Therefore this dye was chosen as the target “pollutant.” The catalyst has three components. These are the metal center, the organic visible light absorbing linker, and the support material. Support materials chosen for this study were TiO$_2$ of varying crystallinity or ZrO$_2$. In order to gain an initial understanding of the reactivity of this system, each of these system components were tested for their impact on the dye degradation activity. 30 mg of heterogeneous catalyst was stirred in 44 or 45 mL of 18.2 MΩ
water for 30 s and sonicated for 60 s within a 150 mL beaker. This cycle was repeated once for a total of 3 min. This suspension was placed in line with a visible lamp equipped with a water filter, power off. That lamp was calibrated to be providing the system with 70 mW/cm$^2$ of power when on. While stirring, 5.00 mL of 0.5 mM aqueous OII solution was added. When applicable, oxidant (1.00 mL of .1% aqueous H$_2$O$_2$) was added simultaneously with exposing the system to the light. 1.0 mL samples were taken prior to oxidant addition as well as 30s after then every 15 minutes after that for a total of 120 minutes or until dye absorbance reached below the limits of detection. Each sample was added to a 1.5 mL plastic centrifuge vial and centrifuged at 12,000 rpm for 5 minutes. 500 μL of this sample was taken from the top but below the surface to be measured in a clean, dry, plastic cuvette with a 1.0 cm path length.

2.2.4 Catalyst recyclability testing

Recyclability of the catalyst was probed in a similar manner to the method described above for activity testing. Reactions were conducted in glass 10 mL test tubes on a smaller scale but with the same concentrations as the reaction set up above. 6 mg catalyst was stirred in 8.8 mL of water and 1.00 mL of dye solution followed by the same stirring/sonication cycle described above. This reaction mixture was then stirred for 15 minutes in dark followed by centrifugation at 8,000 rpm for 10 minutes. A UV/Vis spectrum was taken of the supernatant, replaced back into the reaction mixture followed by addition of the oxidant (200 μL of 0.1% H$_2$O$_2$) and exposure to light for 15 minutes. Centrifugation followed by UV/Vis absorption at 485 nm of the supernatant was used to determine percent decomposition. The catalyst was reused immediately by repeating the above steps.
2.2.5 Computational Methods

Geometry optimizations and molecular orbital visualizations were conducted using density functional theory (DFT) computational method. The DFT calculations were performed using Spartan 14 Mechanics Program with the B3LYP density functional and 6-31G** basis set. The geometries of all molecules calculated were relaxed to the optimum structure in vacuum at the B3LYP/6-31G** level of theory. Excited state energies were calculated using time dependent DFT (TDDFT) calculations based on results of DFT B3LYP/6-31G** geometry optimizations. From these calculated excited state energies transition energies (the molecular analog to a band gap) labeled $\Delta E$ could be approximated. Calculations were conducted on molecules shown in Scheme 2.3.
Scheme II.3: Structures of L and alternatives L1 and L2 coordinated and uncoordinated by Fe$^{2+}$.

2.3 Results and Discussion

2.3.1 Catalyst characterization

Figure II.1 shows the DRUVs spectra of the catalyst after each step of the synthesis. The photoactive linker shows a broad absorption in the visible region from about 400-500 nm. Following coordination of the iron (II), the sample turns purple, consistent with the iron terpyridine MLCT band present at 588 nm. Four other support materials were also used in
order to assess the influence of the support’s electronic structure on the activity of the resulting material. Their DRUVs spectra are shown in Figure II.2. Each spectrum shows an absorption peak at 588 nm characteristic of the previously mentioned MLCT band.

Scheme II.4: Synthesis of Fe-L-TiO₂. Powders shown are white, yellow and purple going left to right.

Figure II.1: Diffuse Reflectance Spectra of (a) Bare P25 TiO₂, (b) L-P25, and (c) Fe-L-P25.
Figure II.2: Normalized UV-visible spectra Fe(terpy)$_2^{2+}$ grafted on different surfaces.

Figure II.3 shows the FTIR spectra of P25 with and without surface functionalization. In the spectrum of bare P25 (Figure II.3a), an absorption around 1630 cm$^{-1}$ (O-H bending of surface adsorbed H$_2$O) and several peaks between 3600 cm$^{-1}$ and 3700 cm$^{-1}$ (O-H stretching of surface Ti-OH groups) are clearly seen. The peaks associated with surface Ti-OH groups are absent in the spectrum of L-P25 (Figure II.3b). Instead, multiple absorption bands are seen in the spectral region of 1250-1750 cm$^{-1}$, confirming the presence of L on the TiO$_2$ surface. Likely, this organic linkage (L) is attached to P25 surface through the Ti-OH groups (see Scheme 2.1). The peaks associated with Ti-OH groups and L are all present in the spectrum of Fe-L-P25 (Figure II.3c). Comparison between the spectra of L-P25 and Fe-L-P25 suggests that some of the linkage molecules (L) desorbed from surface during the reaction between Fe$^{2+}$ and L-P25.
Figure II.3: FTIR spectra of (a) bare P25, (b) L-P25, and (c) Fe-L-P25 in the powder form.

SEM images of each of the four functionalized nanoparticles are shown in Figure II.4. Each material has a different particle size with P25 (A) having the apparent smallest size consistent with N2 adsorption surface areas shown Table II.1. The shown particles are also noticeably aggregated. This observation was seen in all four of the samples.
Figure II.4: SEM image of the four functionalized nanopowders: (a) Fe-L-P25 (b) Fe-L-Anatase (c) Fe-L-Rutile (d) Fe-L-Zirconia. Scale bar 200 nm.

Table II.1: Nitrogen adsorption surface area

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m²/g)</th>
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<tbody>
<tr>
<td>P25</td>
<td>57</td>
</tr>
<tr>
<td>Anatase</td>
<td>56</td>
</tr>
<tr>
<td>Rutile</td>
<td>30</td>
</tr>
<tr>
<td>Zirconia</td>
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Analysis of each sample for the amount of iron present is shown in Table II.2. It is shown here that the P25, rutile and zirconia supported catalysts contain similar amounts of iron. This is in contrast to the iron coverage shown in the anatase sample, which is greater than 60% more than the coverage apparent in the rutile sample and almost double the coverage of the P25 sample.
Table II.2: ICP-AES analysis data summarized.

<table>
<thead>
<tr>
<th>Elemental Analysis</th>
<th>Iron content (µmol/mg)</th>
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</thead>
<tbody>
<tr>
<td>P25</td>
<td>5.00</td>
</tr>
<tr>
<td>Anatase</td>
<td>9.52</td>
</tr>
<tr>
<td>Rutile</td>
<td>5.86</td>
</tr>
<tr>
<td>Zirconia</td>
<td>5.79</td>
</tr>
</tbody>
</table>

2.3.2 Dye Degradation Studies

Visible-light degradation of OII by the synthesized catalysts was carried out in the presence of H₂O₂. The concentration of OII in the reaction solution was monitored by UV-visible spectroscopy at different time intervals. Figure II.5 shows a series of UV-visible spectra collected during the degradation of OII by Fe-L-P25 and H₂O₂. Under visible-light irradiation, OII quickly degraded since the intensity of the major absorption band in its UV-visible spectra decreased over time.

In this study, the absorbance at 484 nm in the UV-visible spectrum of Orange II was utilized to quantify its concentration according to Beer’s Law. In particular, the ratio between the absorbance at any given time (Aₜ) and the initial absorbance (A₀) at 484 nm was calculated and plotted against reaction time to provide information regarding reaction kinetics. The trace shown in Figure II.6e quantitatively describes the degradation of Orange II by Fe-L-P25 shown in Figure II.5. Control experiments were also conducted in the absence of any catalyst or H₂O₂. Negligible degradation of OII occurred in photolysis (Figure II.6a), indicating the essential role of catalysts in this degradation process. This is consistent with the hypothesis that all of the components of the Fe-L-P25 system cooperate to form hydroxyl radicals for dye degradation in visible light.
Figure II.5: UV/Vis absorbance plot showing the degradation of Orange II over time. Each trace represents a new 15-minute interval.

Figure II.6: Photodegradation curves (a) simple photolysis (b) the full Fe-L-P25 system without H₂O₂ (c) P25 functionalized with just the organic linker (d) P25 with H₂O₂ and (e) the full Fe-L-P25 system including H₂O₂.
The role of the support material was probed by synthesizing the catalyst using different supports. Initial rate constants were obtained by fitting $A_t/A_0$ values during $t = 0$-45 minutes to the first order kinetics. Figure II.7 summarizes the thus obtained rate constants. It is seen in Figure II.7 that each support material yields a different photocatalytic activity. The initial rates obtained for these materials were obtained from the slopes of the curves in Figure II.9 and show the following trend: Fe-L-P25 (0.051 min$^{-1}$), Fe-L-Anatase (0.039 min$^{-1}$), Fe-L-Rutile (0.027 min$^{-1}$), and Fe-L-Zirconia (0.008 min$^{-1}$), respectively, under visible-light irradiation. The activity of the zirconia supported catalyst is lowest, followed by the activity for rutile, anatase and P25. The functionalized anatase sample has a similar activity compared to the P25 sample. However, in correlating this sample with ICP-AES analysis data, we see that the anatase sample has a far higher iron coverage than the other materials. Therefore, it is less active as a dye degradation material than the P25 sample.

Under visible-light irradiation, L-P25 and P25 demonstrated similar activity in the degradation of OII. Interestingly, the presence of $\text{H}_2\text{O}_2$ had negligible effect on the activity of L-P25 or P25 (Figure II.7). This is consistent with the fact that no Fe$^{2+}$ species exists in these two materials, and therefore the Fenton reaction did not occur on L-P25 or P25 in the presence of $\text{H}_2\text{O}_2$. In comparison, the reaction rate using Fe-L-P25 with $\text{H}_2\text{O}_2$ was more than 5 times greater than that in the absence of $\text{H}_2\text{O}_2$. The extent to which degradation of OII on L-P25 and P25 did occur can be explained via a surface-mediated pathway. That is, oxidation (and decolorization) occurred upon electron transfer from excited dye molecules to P25.

In the presence of $\text{H}_2\text{O}_2$, both Fe-L-Anatase and Fe-L-Rutile showed reasonable activity in the degradation of OII. The initial rate constant obtained for Fe-L-Zirconia was the lowest among the materials tested in the photo-Fenton reaction (Figure II.7).
2.3.3 Recyclability testing

Recyclability tests were conducted to investigate the stability of the prepared P25 catalyst over numerous use cycles. The catalyst was easily centrifuged to pellet and reused multiple times. As shown in Fig II.8, the system was photocatalytically decolorized by about 63% after 15 min of reaction. This level of degradation was maintained for 5 use cycles. This indicates that the catalyst is quite stable and can be reused.
2.3.4 Computational Results

Computational results are presented using visualization of molecular orbitals generated by Spartan Model software. Shown in Figure II.9 is the original ligand bound to iron, FeL, with both HOMO and LUMO on the left and right, respectively. The HOMO is at -2.63 eV and centers around the terpy chelating the iron atom. The LUMO (showing one of a degenerate pair) is at -1.18 eV which yields a “band gap” of 1.45 eV. This would correspond to a $\lambda_{\text{max}}$ of around 855 nm. Proposed alternatives L1 and L2 are shorter as intended in their design. Possibly, a decreased distance between the Fe site and the surface of the TiO$_2$ nanoparticle would improve electronic communication and therefore improve performance of the resulting photocatalyst. L1 being the simpler of the two alternatives retains the phenylacac structure originally designed to integrated well into a TiO$_2$ material.$^{71}$ FeL1 has a calculated HOMO energy of -2.72 eV and is visualized as being fairly dispersed but most of the orbital density weighted towards the terpy. This is similar, qualitatively, to the original FeL results. Similar, also is the resultant energy of the LUMO of FeL1 at -1.22 eV. The HOMO-LUMO $\Delta E$ is calculated to be 1.5 eV which would
correspond to a $\lambda_{\text{max}}$ of around 827 nm. For this application, however, the change in electron density is spatially unfavorable relative to where the binding of TiO$_2$ would be. To promote oxidation of OII, or perhaps just as interestingly, promote the formation of highly reactive oxo-iron species, it would be more favorable for the electron density to be excited towards the acac as is the case in FeL. In order to do this, an electronegative amine group was added to modify the designed alternative. FeL2 computational results are displayed in Figure II.12. With a HOMO of -2.5 eV and a LUMO of -1.09 eV, the HOMO-LUMO $\Delta E$ is calculated to be 1.41 eV which would correspond to a $\lambda_{\text{max}}$ of 879 nm. As shown in Figure II.12, the spatial change in electron density from excitement is calculated to be in favor of excitement-induced charge transfer in the direction of the acetylacetonate linker. Previous studies have shown that this acetylacetonate linker has favorable electronic alignment to favor interfacial electron transfer (IET) and disfavor back electron charge transfer.$^{71}$ The computational results seen here suggest that it may also benefit IET for the MLCT to alter the spatial orientation of the electron density towards the semiconductor surface. It is significant to note that the actual $\Delta E/\lambda_{\text{max}}$ values acquired through calculation are poor approximations. This is due in large part to challenges that the level of theory chosen has with calculations involving d orbitals. Table II.3 highlights some of the quantitative data generated from the computational calculations. From it the metal-coordinated ligand calculations can be compared with the uncoordinated ligands. There is a much greater difference between the HOMO energy comparing coordinated to uncoordinated relative to the LUMO energy. This observation is summarized by the fact that he standard deviation amongst HOMO energies is nearly 10 times as high as the standard deviation amongst the LUMO energies. One contributing difference between the HOMO and LUMO likely determining this is that the HOMO in each of the coordinated ligands is strongly contributed to by Fe d orbitals.
Whereas the LUMO contains far less contribution from the Fe d orbitals due to the transition being categorized as MLCT.

Figure II.9: Spartan visualizations of isosurfaces of the HOMO (left) and LUMO (right) frontier orbitals of FeL computed at the B3LYP/6-31G** level of theory.

Figure II.10: Spartan visualizations of isosurfaces of the HOMO (left) and LUMO (right) frontier orbitals of FeL1 computed at the B3LYP/6-31G** level of theory.
Figure II.11: Spartan visualizations of isosurfaces of the HOMO (left) and LUMO (right) frontier orbitals of $\text{FeL}_2$ computed at the B3LYP/6-31G** level of theory.

Table II.3: Summary of quantitative data generated from computational models.

<table>
<thead>
<tr>
<th></th>
<th>Homo (eV)</th>
<th>Lumo (eV)</th>
<th>$\Delta E$ (eV)</th>
<th>$\lambda_{\text{max}}$</th>
</tr>
</thead>
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<tr>
<td>L</td>
<td>-5.91</td>
<td>-1.61</td>
<td>4.3</td>
<td>288</td>
</tr>
<tr>
<td>L1</td>
<td>-6.28</td>
<td>-1.5</td>
<td>4.78</td>
<td>259</td>
</tr>
<tr>
<td>L2</td>
<td>-5.41</td>
<td>-1.38</td>
<td>4.03</td>
<td>308</td>
</tr>
<tr>
<td>FeL</td>
<td>-2.63</td>
<td>-1.18</td>
<td>1.45</td>
<td>855</td>
</tr>
<tr>
<td>FeL1</td>
<td>-2.72</td>
<td>-1.22</td>
<td>1.5</td>
<td>827</td>
</tr>
<tr>
<td>FeL2</td>
<td>-2.5</td>
<td>-1.09</td>
<td>1.41</td>
<td>879</td>
</tr>
<tr>
<td>Stdev</td>
<td>1.8</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.4 Conclusions

An Fe(II)-terpyridine complex was successfully grafted onto different surfaces through a robust, photo-active covalent linkage. This system is an active catalyst in the photo-Fenton reaction using visible light. The synthesized photo-Fenton catalyst was assessed using an orange azo dye denoted as OII. The nature of the surface on which the complex was grafted was shown to have a significant effect on the reactivity of the system. The Fe(II)-terpyridine complex grafted on TiO$_2$ showed significantly greater activity than the same complex grafted on zirconia in the degradation of OII. Though less pronounced, the effect of different crystal structures of TiO$_2$ on the activity of the system is significant. Presumably, the photophysical properties of the support itself are responsible for this difference. One possible explanation based on previous work conducted by Liu and coworkers\textsuperscript{97,98} on Fe-terpyridine complexes is that the interaction between the complex and the TiO$_2$ support could be favoring the formation of high valent iron-oxo species. The formation of iron-oxo species would be unfavorable on a zirconia material given the more reducing position of the conduction band of zirconia as shown in Figure II.12.
Figure II.12: Energy diagram showing electron injection from \( \textbf{L} \) to TiO\(_2\), but not to ZrO\(_2\). CB: conduction band; VB: valence band. Energies of TiO\(_2\) CB, the lowest unoccupied molecular orbital of \( \textbf{L} \), and ZrO\(_2\) CB are estimated to be -0.3, -0.9, and -1.1, respectively.

Given this possibility, and positive results from the recyclability experiments, a system like this could be interesting to pursue as a re-usable oxidation catalyst for a reaction such as the epoxidation of alkenes. Though, due to the non-selective nature of the reactive species generated in aqueous systems in the presence of H\(_2\)O\(_2\), reaction conditions would need tuning such as the use of a milder oxygen source or modification of the ligand to favor direct, catalytic oxidation of a particular substrate. Future work could also include synthesis of alternative linkers to tune the properties of the resulting catalyst for the application. Computational work such as that shown in this thesis should be used to assist in designing such alternatives.

2.5 Acknowledgements

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences EPSCoR and Solar Photochemistry Programs under
Award Number DE-SC0016417. We are grateful to Prof. Robert Crabtree, Dr. Scott Greenwood, and Kaitlyn D’Orazio for assistance in various aspects of experiments.
III. SYNTHESIS OF Cu and Sn MODIFIED TiO$_2$ MATERIALS FOR CO$_2$ REDUCTION

3.1 Introduction

3.1.1 Motivation

The field of photocatalytic CO$_2$ reduction is motivated by two very important (and related) global problems: overabundance of atmospheric CO$_2$ which is primarily caused by the over-combustion of petroleum fuels, and the search for and application of alternative energy sources. Continued use of fossil fuels at our current rate will eventually lead to greater cost of using them. Furthermore, as humans and other factors greatly shift Earth’s climate stability, greater reliance on alternative/renewable energy sources will be needed.$^{50}$ The ability to feed our excess CO$_2$ back into the fuel cycle would greatly reduce the impact of using carbon fuels for our energy needs. Concurrently, the ability to drive this CO$_2$ recycling with the aid of alternative energy is of great interest to reducing our negative impact on the environment.

The alternative energy source of focus for this work is solar. Solar energy is a particularly promising source in light of its potential for meeting the increasing human energy demand.$^{72}$ Solar energy storage through chemical bond formation is an attractive topic of research, in part, because solar fuels can theoretically be integrated into our current petroleum-based energy infrastructure directly. This would allow for a carbon neutral fuel. However, CO$_2$ is one of the most thermodynamically stable molecules that we encounter day-to-day. Therein lies a formidable research challenge for driving the formation of fuels from a CO$_2$ based feedstock.
Generation of fuels from CO₂ is a reductive process and typically requires high thermodynamic potentials as described by the red/ox potentials listed in Chapter 1. It can be seen there that the direct, one electron reduction of CO₂ (Eq 1.1) is highly unfavorable. The reduction potential required for that process is more than a volt uphill as compared to the next highest energy process listed (Eq 1.2). On the other hand, moving down the list the more favorable, proton assisted, multi-electron reductions (Eq 1.2-1.6) are kinetically challenging in the sense that the simplest of these reactions still require 5 species to come together in order to form products. In our molecular case, though, we need this to happen many moles of times such that usable quantities of fuel can be generated in a reasonable amount at a time. Suffice it to say that a catalyst system is surely needed in order to make this process feasible. This would speed up the multi-electron pathways enabling the field to save energy on this thermodynamically challenging reaction.

3.1.2 Surface modified semiconductor photocatalysis

Significant progress has been made towards using molecular catalysts for this purpose in the past.⁷³ Noteworthy among these catalysts have been the transition metal catalyst Re(bpy)(CO)₃Cl developed by Fujita and coworkers.⁷⁴,⁷⁵ Though molecular catalysts are exemplary in their efficiency of reducing CO₂, they tend to suffer from low stability during photocatalysis. Over the course of using these catalysts, they can degrade leading to poor conversion efficiency. Another problem currently facing the catalysis community is that most of the catalysts used for this application employ expensive metals such as rhenium and ruthenium. This provides an opportunity for discovering new materials to help address these problems. For example, it has been shown that catalyst stability can be increased if these or adapted molecular
catalysts are attached to a support material thus creating what is known as hybrid materials.\textsuperscript{48,51,76,77} These have greatly improved upon the stability-related issues faced in traditional molecular catalysts however there is still much work to be done.

Typically, nanoparticle semiconductors or precious metals are used as the supports for hybrid catalysis. Nanoparticles, generally, show increased reactivity as compared to bulk materials due to their increased surface area to volume ratio. One benefit this provides is the ability to use less material to achieve the same reactivity. Furthermore, they can exhibit unique reactivities due to interesting local surface structures such as low coordination number surface atoms.\textsuperscript{99} For example, the specific nature of the tetrahedral 4+ sites in TiO\textsubscript{2} has been shown to be important for photocatalytic applications.\textsuperscript{14} These factors alone warrant investigation in their use for a variety of different applications. All of this makes semiconductor nanoparticles a logical choice for investigating photocatalysis. Physical modification of the surface of these semiconductor nanoparticles can also change the nature of that charge separation.\textsuperscript{79-82} The surface features can be of different morphologies and crystal phases which changes the energy of the surface thereby directing likely pathways for charged species on the surface.\textsuperscript{83} Furthermore, chemical (as opposed to physical) modifications can be made such as the surface functionalization pursued in hybrid catalysts discussed earlier. The material could also be doped with metals which has been shown to improve efficiency in photocatalytic CO\textsubscript{2} reduction.\textsuperscript{78,84-87} One other way that the surface can be modified is to graft other metals or metal oxides onto the surface of the nanoparticles. Previous work has shown that metals grafted onto the surface of nanoparticles can alter the catalytic and photophysical properties of that material. In particular, tin and copper are relatively unexplored option that may show promise.
This study will explore the influence that support material characteristics such as crystal structure and interfaces can have on photocatalytic reactivity. Specifically, two different materials will be explored. First, materials will be synthesized in order to have the differences depicted in Scheme III.1. In each of the four frames, orange dashes represent surface tin on the represented semiconductor nanoparticle. Frame 1) and 2) depict rutile and anatase TiO$_2$ nanopowders, respectively, with tin adsorbed onto their surfaces. Note, these are certainly not drawn to scale but what is emphasized is that rutile is a much bigger particle than anatase. In the second two frames, tin is adsorbed in a slightly different manner. Frame 3) shows tin adsorbed between two different TiO$_2$ nanoparticles. The last material is a composite constructed using the anatase and rutile nanopowders separately. The result should yield tin modified TiO$_2$ with varying crystal structure as well as differences in interfacial tin sites. The major hypothesis driving this work is that by altering the order in which these reagents are mixed, we may be able to significantly modify the nature of the tin that is available for photocatalysis. The surface structure will be used as an explanatory feature in differences in reactivity.
Scheme III.1: Cartoon portrayal of guiding hypothesis. In each case, orange dashes represent adsorbed/chemisorbed tin species and grey area represents the different crystalline TiO$_2$ nanomaterials.

To go further, in addition to tin, a promising option for modifying the surface of TiO$_2$ is copper.$^{98}$ Recent work has shown that specially fabricated Cu electrodes can transform CO$_2$, under certain conditions to ethanol.$^{99}$ Other promising work conducted by Liu and coworkers showed that photocatalytic CO$_2$ reduction using tetraammonium copper(II) grafted onto a TiO$_2$ support may be possible.$^{19}$

P25 has been used previously to make these materials. Though reactive and a common benchmark for photocatalytic studies, P25 has a poorly controlled surface morphology. Mesoporous silica materials can be synthesized easily and with a higher degree of morphological control. Therefore an approach in which a Ti modified mesoporous silica material is used as the support for the copper catalyst would reduce the variability observed in P25. These materials were analyzed using spectroscopy and BET surface area measurements.

Photocatalysis on many TiO$_2$ materials is relatively inefficient due to electron-hole recombination. This project uses earth-abundant metals to explore how these metals might
improve photocatalysis on TiO$_2$. Spectroscopic techniques will be used to investigate how interfacial sites in metal/TiO$_2$ materials play a role in charge separation and photocatalysis.

3.2 Interfacial Sn sites on TiO$_2$

3.2.1 Experimental

3.2.1.1 Catalyst Preparation

Tin(II) chloride dihydrate (SnCl$_2$·2H$_2$O, ACS Reagent) was obtained from Sigma-Aldrich. Ar (Ultra High Purity) and CO$_2$ (99.999%) were obtained from Airgas. Commercial TiO$_2$ material, Aeroxide P25 (specific surface area 57 m$^2$/g, average particle size ~25 nm, phase composition ~80% anatase and ~20% rutile), was obtained from Evonik. Commercial TiO$_2$ materials, Anatase TiO$_2$ nanopowder (specific surface area 56 m$^2$/g), Rutile TiO$_2$ nanopowder (specific surface area 20 m$^2$/g), and zirconia nanopowder (ZrO$_2$, specific surface area 17 m$^2$/g) were obtained from Sigma-Aldrich. All chemicals were used as received without further purification.

The SnO$_x$/TiO$_2$ nanocomposites were prepared following a method involving acid mediated functionalization of the TiO$_2$ surface with tin cations. Through this method, we aim to synthesize highly dispersed tin oxide (denoted as SnO$_x$) sites on TiO$_2$. In a typical synthesis, 300 mg TiO$_2$ nanopowder dispersed in 20 mL of 18.2 MΩ water was mixed with a 20 mL aqueous solution containing 0.09 M HCl and 300 mg SnCl$_2$·2H$_2$O and sonicated for one hour. The resulting suspension turned yellow instantly upon mixing with the acidic solution of Sn$^{2+}$. 
Following sonication, the suspension was rotovapped to remove the majority of the water and finally dried under gentle nitrogen flow overnight. Five different tin-modified nanomaterials were fabricated in this way with some important modifications described below. To make the final oxide form of these nanopowders, they were calcined for 1 hour at 420°C.

In-house anatase-rutile composite material fabricated using the following method, 300mg Anatase nanopowder and 300mg Rutile nanopowder were combined in 40 mL of 18.2 MΩ water and sonicated for 1 h. The resulting suspension was rotovapped to remove most of the water then dried under gentle nitrogen flow overnight. This material is denoted as AnaRut composite.

**SnOₓ/P25** was fabricated as described above using P25 as the TiO₂ support. This material was used as a benchmark for comparison.

**SnOₓ/Rutile** was fabricated as described above using Rutile TiO₂ nanopowder as the TiO₂ nanomaterial. The intended product is depicted in Scheme III.1, Frame 1.

**SnOₓ/Anatase** was fabricated as described above using Anatase TiO₂ nanopowder as the TiO₂ support. The intended product is depicted in Scheme III.1, Frame 2.

**SnOₓ@ARcomposite** was fabricated as described above using AnaRut composite as the TiO₂ nanomaterial. The intended product is depicted in Scheme III.1, Frame 4.

**SnOₓ/ARmix** was fabricated via the following method: 150 mg Anatase nanopowder dispersed in 10 mL 18.2 MΩ water was mixed with a 10 mL aqueous solution containing 0.09 M HCl and 150 mg SnCl₂·2H₂O and sonicated for one hour. In parallel, 150 mg Rutile nanopowder dispersed in 10 mL 18.2 MΩ water was mixed with a 10 mL aqueous solution containing 0.09 M HCl and 150 mg SnCl₂·2H₂O and sonicated for one hour. The resulting suspensions turned yellow instantly upon mixing with the acidic solution of Sn²⁺. Following sonication, the
suspensions were combined and rotovapped to remove the majority of the water and finally dried under gentle nitrogen flow overnight. The intended product is depicted in Scheme III.1, Frame 3.

### 3.2.1.2 Catalyst Characterization

Infrared spectra of the modified TiO$_2$ were collected using a Nicolet 6700 FTIR spectrometer equipped with a Harrick Praying Mantis diffuse reflectance accessory and a three-window photoreactor. Collection of spectra was conducted at 298 K and KBr was used as background. Diffuse reflectance UV/Vis spectroscopy (DRUVS) was conducted using a Cary 50 Bio UV-visible Spectrophotometer equipped with a Varian Diffuse Reflectance UV-Vis Accessory. Measurements were taken in the 300-800 nm range. Barium sulfate was used as background.

### 3.2.1.3 Photocatalytic testing

In photocatalytic testing, 10 mg tin-modified nanopowder was placed in a Pyrex photoreactor in the configuration shown in Figure III.1. Prior to photocatalytic testing, the photoreactor was purged with CO$_2$ in the dark for 20 min. The photocatalyst was then irradiated with a 200-W Hg lamp equipped with a water filter. Light intensity on the photocatalyst was fixed at 100 mW/cm$^2$. Gaseous products were analyzed using an Agilent 7820 Gas Chromatograph (GC).
3.2.2 Results and Discussion

3.2.2.1 Catalyst Characterization

Figure III.2 shows the DRUVS spectra of P25, SnCl$_2$ adsorbed onto P25 and after calcination, denoted as SnO$_x$/P25. The absorption edge of P25 is close to the UV region and upon adsorbing TiO$_2$ with tin, there is a visual change in color to yellow. This is reflected in the absorption edge red shift away from the UV region. The difference between SnO$_x$P25 and SnCl$_2$ simply adsorbed onto the nanopowder is spectroscopically subtle. Visually, one can see that the SnO$_x$P25 appears to be white, perhaps a little less white than P25. Looking closely at the spectra,
the absorption at ~430nm is higher in the adsorbed Sn$^{2+}$ on P25 as opposed to the calcined SnO$_x$P25. This is consistent with the observation of a more yellow color.

![Absorption Spectra](image)

**Figure III.2**: DRUVS spectra of a) Bare P25 TiO$_2$, b) SnCl$_2$/P25, c) Oxidized SnO$_x$/P25.

Figure III.2 shows the DRIFTS spectra of the P25 TiO$_2$ material after each step of the tin modification. These spectra contain several absorptions around 3000 cm$^{-1}$ and between 1500-1300 cm$^{-1}$ characteristic of surface adsorbed water (1620 cm$^{-1}$). In the case of P25, there are some minor peaks which may be attributed to impurities (1350-1560). Upon treatment we can see these peaks are greatly reduced. Also, upon treatment with SnCl$_2$, the adsorbed water peak at 1620 cm$^{-1}$ broadens and then sharpens subtly after calcination to the SnO$_x$ material. This suggests, as expected, that the coordination environment of the adsorbed water is changing. The broadening could be due to a wider variety of surface sites since perhaps the adsorbed tin is already starting to oxidize under ambient conditions yielding Ti sites, SnCl$_2$ and tin oxide available for adsorbing water. Then as we see the very slight sharpening of that peak, we could suppose that it is due to the removal of the majority of SnCl$_2$ sites from the calcination process.
Focusing on the higher frequency end of the spectrum as in Figure III.4, we note that there are at least two types of surface hydroxyl species present on P25. One that corresponds to a broad band around 3670 cm\(^{-1}\) and one sharp peak at 3630 cm\(^{-1}\). Upon modifying the sample with tin, the sharp peak at 3630 cm\(^{-1}\) very nearly disappears. Interestingly, the band at 3670 changes as well. Its peak shape seems to sharpen. The two bands around 3670 at 3630 cm\(^{-1}\) have been assigned to bridging and tightly bound hydroxyl groups on TiO\(_2\) surfaces, respectively.\(^{100}\) The tin modification causes the tightly bound hydroxyl groups on the TiO\(_2\) to disappear while it looks like the bridging water signal remains. This shows that upon modifying the surface with tin, the surface hydroxyl groups may be getting replaced by the grafted metal center(s). However, given this data, we cannot conclusively determine the specific role of the bridging hydroxyl species. Either the grafted tin has a stronger affinity for the non-bridging hydroxylated sites compared with the bridging or, once replaced, new bridging hydroxyl sites may form either between grafted tin, between low coordination Ti and tin or between liberated Ti sites. No matter the case, this FTIR data is conclusive in showing that the tin is covalently bound and that the bridging OH groups play an important role in the grafting reaction.
Figure III.3: DRIFTS spectra of (a) bare P25, (b) SnCl₂/P25, and (c) SnOₓ/P25 in the powder form.

Figure III.4: DRIFTS spectra of (a) bare P25, (b) SnCl₂/P25, and (c) SnOₓ/P25 in the powder form. Range is 2700-4000 cm⁻¹. Lines shown are for emphasis of particular frequencies.
3.2.2.2 Photocatalytic testing

The concentration of CO was monitored over the course of UV irradiation using GC. Each material tested showed some level of CO production. For each different support material, it was observed that the modification with tin improved performance compared with the unmodified nanopowder. That is, the materials showed a trend in increasing activity in the form of the following; unfunctionalized<tin adsorbed<adsorbed and calcined. One exception to this was the rutile material. In this case, the measured CO ended up being higher than the uncalcined counterpart. Nonetheless, the overall increased CO production resulting from the presence of surfaces tin species suggests that the photo-physical and/or morphological and electronic difference between each step of the synthesis has an observable impact on the reaction. Simply adsorbing tin to the surface seems to improve the transformation of CO$_2$ to CO and further oxidizing that tin on the surface of the nanomaterial further improves the energetics towards this reaction.

Interestingly, each of the modified TiO$_2$ materials outperformed the benchmark material, P25. Each of the calcined materials (highest performing) produced some CO. CO production was observed in the following order of increasing production

P25<Sn/Rut<Sn@AnaRut<Sn/Ana<Sn/AnaRut
Table III.1: Summary of photoreactions using various Sn modified TiO$_2$ materials. Values show the amount of CO (in $\mu$mol) measured in photocatalytic testing after 2 h of irradiation.

<table>
<thead>
<tr>
<th>Support material</th>
<th>TiO$_2$ support</th>
<th>Adsorbed Tin</th>
<th>Calcined</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile</td>
<td>0.15</td>
<td>0.24</td>
<td>0.21</td>
</tr>
<tr>
<td>Anatase</td>
<td>0.16</td>
<td>0.29</td>
<td>0.34</td>
</tr>
<tr>
<td>A/R mix</td>
<td>0.43</td>
<td>0.10</td>
<td>0.58</td>
</tr>
<tr>
<td>A/R composite</td>
<td>0.10</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>P25</td>
<td>0.08</td>
<td>0.04</td>
<td>0.14</td>
</tr>
</tbody>
</table>

A possible explanation could be that the interaction between the anatase and rutile promotes beneficial surface coordination of the grafted tin at the interface between the two crystal phase particles. This possibility is supported by the lower activity of SnOx@AR in which case the tin was grafted after generating interfacial anatase/rutile morphologies. Therefore, in theory, SnOx/AR is likely to have a higher concentration of the proposed interfacial anatase-tin-rutile characteristics than the SnOx@AnaRut.

An interesting observation is the relatively low activity observed with the benchmark material SnOxP25. Given that this is a commercially available composite, the interest is in its low performance as compared with even SnOx@AnaRut which made use of an in-house composite. It is commonly observed that TiO$_2$ materials have relatively low activity towards CO$_2$ reduction. However, given that both P25 and AR composite are anatase/rutile composite materials it may be expected that they would perform similarly. Most likely, the differences observed in activity between the two composites stems from some difference in the morphological features of the nanoparticles.
3.3 Synthesis of Cu-Ti-SBA15 for CO$_2$ reduction

3.3.1 Experimental

3.3.1.1 Catalyst Preparation

Mesoporous SiO$_2$ (silica) material synthesized according to literature.$^{101}$ 2.0 g of amphiphilic block copolymer poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) also known as PEG-PPG-PEG was dissolved in 75 mL of 1.6 M hydrochloric acid at 70°C. 4.61 mL of tetraethylorthosilicate was added to that as the source of silica and allowed to stir overnight. The resulting mixture was heated at 100°C in a sealed, Teflon lined, stainless steel autoclave for 24 hours. The contents were filtered and rinsed with 18.2 MΩ water until the pH>4 monitored with pH paper. Fluffy, off-white powder product was oven-dried at 90°C. then transferred to an aluminum foil carrier to be calcined at 500°C in a tube furnace for 4 hours under oxygen environment to remove organic impurities. Fluffy, white powder was retrieved after calcination. ~257.3 mg product yielded.

Grafting of bimolecular Cu-Ti sites was done using methods derived from literature.$^{101}$ In a 2:1 mass ratio, SBA-15 and titanocene dichloride were stirred in ~35 mL of dry chloroform in a 100 mL round bottom flask (RBF). This was stirred at room temperature for 30 minutes to allow the titanium to diffuse into the pores. 5.0 mL of triethylamine was added dropwise to the flask and this was stirred overnight, filtered and washed with chloroform. The color changed to yellow consistent with synthesis developed by Maschemeyer.$^{102}$ This product was dried and calcined at 500°C yielding a white powder (Ti-SBA-15). Ti-SBA-15 is then stirred in aqueous ammonium hydroxide solution to activate the TiOH moieties to acceptance of the copper cations.
Aqueous copper chloride solution was added dropwise, and the resulting solution was stirred overnight. The product was centrifuged and washed three times with water and allowed to oven dry at 80°C.

3.3.1.2 Catalyst Characterization

100.2 mg of the white powdered SBA-15 sample was added to a BET tube (9mm). The tube was evacuated for 1 hour then flushed with N₂. The tube was inserted into the analyzer and programmed for analysis. Parameters were set to run adsorption and desorption isotherms.

Diffuse reflectance UV/Vis spectroscopy (DRUVS) was conducted using a Cary 50 Bio UV-visible Spectrophotometer equipped with a Varian Diffuse Reflectance UV-Vis Accessory. Measurements were taken in the 200-800 nm range. Barium sulfate was used as background.

To obtain FTIR spectra, ~5mg of the solid catalyst was pressed onto the top of a KBr pellet and placed into a sealed, spherical reaction vessel equipped with multiple windows for spectral reaction monitoring. This vessel was purged with argon and a spectrum was taken.

3.3.1.3 In-Situ FTIR

For tracking progress of the reaction in situ, the vessel was purged with CO₂ and another spectrum was taken as an initial spectrum. Visible light was introduced into the system and spectra were taken at 5, 15, 30 and 60 minutes and the difference spectrum was calculated using the following equation,

\[
\text{Difference Spectrum} = \log\left(\frac{\text{Spectrum}_t}{\text{Spectrum}_0}\right)
\]

Eq. 3.1
where the subscripts \( t \) and \( t_0 \) refer to the “current” reaction time and the initial reaction time, respectively.

3.3.2 Results and Discussion

3.3.2.1 Catalyst Characterization

BET analysis showed that the surface area using the BJH method of calculation was 643 m\(^2\)/g with a pore diameter of 41.9 Å and an overall pore volume of 1.16 cm\(^3\)/g. Significantly higher surface area than commercially available P25, these values are in reasonable agreement with literature.\(^3\)

![Figure III.5: DRUVS spectra of a) SBA15 b) Ti-SBA15 with 1% Ti loading and c) Ti-SBA15 with 5% Ti loading in the feed ratio.](image)
Observed in Figure III.5 are the DRUVS spectra of SBA15 and Ti-SBA15 with two
different Ti loadings. Shown in orange is a batch with a feed ratio of 1% Ti loading but shown in
gray is the sample with a higher feed ratio of 5%. Figure III.6 depicts the DRUVS spectra of 5%
loading Ti- and Cu-Ti-SBA15 in gray and blue, respectively. The SBA15 shows a steep
absorption between 200-300 nm. This is typical for silica materials and represents the large,
electronically insulating band gap. Upon functionalizing with Ti, the band edge becomes
more red shifted. This red shift has been shown to be dependent on the concentration of Ti sites
as can be seen in the figure and has been published elsewhere.\textsuperscript{18} The relatively high feed ratio\textsuperscript{103}
of Ti/Si was set to 12% in the material used for Cu grafting to maximize the availability of Ti
sites. From the spectrum in Figure III.6, it can be seen that upon grafting Cu to the surface of Ti-
SBA-15, the band structure of the material changes significantly. The addition of Cu sites yields
an absorption in the red/near infrared region attributed to the Cu(II) electronic transition d-d*
within CuO. The shoulder that appears to extend the absorption of the Cu-Ti-SBA15 relative to the Ti-SBA15 shows that successful Cu/Ti IET has been achieved.

FTIR characterization of Cu-Ti-SBA15 was also conducted. Figure III.7 shows the DRIFTS spectra of Cu-Ti-SBA15 as well as P25 for reference. The peak “a” at 3745 cm$^{-1}$ can be assigned to the Si-OH groups and the presence of this peak suggests that the grafting of Ti onto SBA-15 may not have completely saturated the surface. The peak “d” at 1628 cm$^{-1}$ may be attributed to surface adsorbed water.$^{100}$ Peaks b and c are related to the SBA-15 material.$^{104}$

![Figure III.7: DRIFTS of uncalcined Cu-Ti-SBA15 (solid black) compared with bare P25 (dotted). Peaks are labeled with dotted lines and left to right with letters a-d.](image-url)
3.3.2.2 In Situ FTIR

CO₂ reduction was also attempted with this catalyst. In-situ analysis of this reaction was done in situ using DRIFTS. The full series of spectra taken at various times is shown in Figure 4.4. It is worthwhile to note that the differences between each of these spectra are very small. The time-dependent difference spectra are shown below in Figure III.8. A small, sharp negative peak is seen at 2077 cm⁻¹ and is attributed to an adsorbed trace gas impurity from the source CO₂.

The growth in absorbance seen around 2120 cm⁻¹ may signify the formation of CO adsorbed on Cu⁺. The broad nature of this peak portends that the formation of highly dispersed, controlled bimetallic sites may have not been achieved. It is possible (based on these
observations) that a broad array of metal sites and possibly clusters and/or nanoparticles have formed. Copper has been known to be catalytically active for CO₂ reduction with other products possible. For example, oxalate, with vibrational modes in the region of 1200-1800 cm⁻¹ could be forming. In this region, it can be observed that a number of small, broad peaks are formed along with the more distinct, surface adsorbed water peak at 1630 cm⁻¹. In this system, however, the main product is CO.

3.4 Conclusions

Successful synthesis of two different metal modified TiO₂ materials was achieved. Though each with limited reactivity, interesting trends were observed relating to support morphology with Sn modified TiO₂. Further, CO was observed to form in a Cu modified Ti-SBA15. It was observed that the material denoted as SnOx/AR produced more CO as compared to the other four Sn modified TiO₂ materials. This observation would be consistent with the hypothesis that the form and structure of the specific interfaces in a nanomaterial play crucial roles in the catalytic performance. Powder XRD analysis could assist in determining the presence and approximate ratios of the crystal structures but more detailed analysis including HRTEM would be needed to investigate the structure more specifically.

To explore the Cu system further, a broader array of Cu/Ti/Si ratios could be explored in order to thermodynamically promote dispersed Cu, and Cu-Ti for catalysis. EPR and XPS could be used to further characterize the oxidation states of species present in the material. Correlating these factors with reactivity could lead to greater insight into mechanistic questions about this system.
IV. Concluding Remarks

Photocatalysis is an area of study in which light is used to drive chemical reactions. Solar energy has amazing potential to meet the energy needs worldwide. In transitioning to solar, this could also reduce our production of greenhouse gases and other pollutants related to combustion. Further, our current pollution remediation techniques could benefit from solar energy through the use of photo-activated AOPs to degrade pollutants but also through solar generation of fuels. Both of these applications can employ semiconductor nanoparticles such as TiO$_2$. This thesis explored several modifications of TiO$_2$ towards these applications.

First reported was an Fe(II)-terpyridine complex grafted onto different surfaces through a robust, photo-active covalent linkage. This system showed activity in the photo-Fenton reaction using visible light. In fact, the activity of this specially designed system showed even greater activity than the degradation of OII with the benchmark P25 under UV irradiation as published elsewhere.\textsuperscript{106} The significance of this is that it may be possible with modifications such as those reported in this thesis, one could design a water purification system using visible light therefore using less energy overall. Also reported were multiple modifications of TiO$_2$ which employed non-precious metal cations as the potential catalytic centers for CO$_2$ reduction, namely tin and copper. These studies were met with less dramatic success as far as application is concerned. However, there was an important theme observed in each of these projects. That is that the nature of the surface on which the modification was done was shown to have a significant effect on the reactivity of the system. For the photo-Fenton process, the interaction between the catalyst and the nanoparticle may influence the red/ox chemistry at the iron center. The possibility of the formation of catalytically active, high valent iron-oxo species was discussed but more experiments would be necessary to confirm. For the metal modification, it was clear that
modification of TiO\textsubscript{2} can produce a more reactive CO\textsubscript{2} reduction surface than the bare TiO\textsubscript{2}. Modification of nanoparticle surface electronics will continue to be a sought-after research topic in search of improving both the performance and longevity of catalytic materials.

**Looking Forward**

The author of this work looks forward to horizons filled with the meaningful pains and joys of teaching at the secondary level. He hopes to shed unique light on students of all ability, demographic and interest levels. The skills acquired in his graduate work will serve him well because he will have a deep insight into what the students might face should they choose college as their own horizon. This new chapter in professional teaching will begin at Pinkerton Academy in Derry, NH at which he will lead freshman students through their “Journey Through Physical Science.”
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