BLACK PHOSPHORUS/CARBON NITRIDE HETEROJUNCTIONS FOR SOLAR FUEL GENERATION

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BLACK PHOSPHORUS/CARBON NITRIDE HETEROJUNCTIONS FOR SOLAR FUEL GENERATION

By

Nicholas Pollak

B.S., Lebanon Valley College, 2018

DISSERTATION

Submitted to the University of New Hampshire

In Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

in

Chemistry

September 2023
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Dedication

I dedicate this dissertation to my wife and best friend, Hannah Rae Pollak. Her constant encouragement and belief in me even when I didn’t believe in myself helped me through this long process, and I feel as if I can do anything with her by my side. My work is dedicated to her so that I can help make the world a better place for our family.
Acknowledgement

I would first like to acknowledge my advisor, Christine Caputo. Her dedication to science and work ethic has driven me to be the best scientist I could be. She truly taught me what it means to be a researcher, how to ask important questions, and how to think critically about what, why, and how I am doing something. If I become half the scientist she is today, I will have achieved more than I ever thought possible. Thank you so much for everything; there aren’t enough words to describe how much you have helped me.

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ABSTRACT

BLACK PHOSPHORUS/CARBON NITRIDE HETEROJUNCTIONS FOR SOLAR FUEL GENERATION

By

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University of New Hampshire, May 2023

Solar fuel generation has garnered attention in recent years as a renewable source for syngas (hydrogen and carbon monoxide) evolution. Difficulty in designing one-pot systems that can generate tunable ratios of hydrogen and carbon monoxide gases has persisted. In this thesis, a photocatalytic system for the generation of syngas under simulated solar irradiance is described that satisfies these challenges using black phosphorus (BP) and carbon nitride loaded with Co²⁺ active sites (Co@C₃N₄) to form a heterojunction. This thesis will present the ability to tune the syngas ratio by controlling the %wt of BP in the heterojunction.

The oxidative power of this heterojunction was also explored by employing non-sacrificial reagents, specifically 4-methylbenzyl alcohol and glucose, as oxidation substrates in an effort to generate value-added oxidized organic by-products. We present our preliminary findings that show
overall low conversion of oxidation substrates as well as syngas ratios significantly higher than what was observed in previous experiments with a sacrificial reagent.

Fundamental electron dynamics for both reductive and oxidative pathways, as determined using transient absorption spectroscopy, are also described herein. The implications of these electron transfer rates for tuning the activity of the heterojunction and to promote targeted and selective product generation are discussed. Finally, the development of C₃N₄ electrodes for use in electrocatalytic schemes is also described.
CHAPTER I

Global Crisis and Introduction of 2D Photocatalytic Systems

1.1 The State of the Climate

The global rise in temperature since the Industrial Revolution can be directly linked to anthropomorphic sources. Global average temperatures have been rising steadily since the mid 1970’s (Figure 1.1), and as of the writing of this thesis in early 2023, the last 9 years have been the warmest on record.¹ The idea of the temperature going up by only a small amount is an abstract danger that makes it hard to conceptualize the fear in this increase, but the severe results of these few degrees can be seen in many much more concrete ways. The United Nations has pointed to a myriad of issues caused by climate change, including: mass displacements by sea level rise, threats to food security, widening global economic inequality, and increased extreme weather events.² The US Geological Survey notes that “since 2000, the western United States is experiencing some of the driest conditions on record”³ and this drought catastrophe is seen throughout the world, primarily in less developed regions. Locations including central Asia, northern and central Africa, and central and southern South America have been dealing with ongoing droughts, some dating all the way back to 2008.⁴
These climate events threaten the livelihoods and the lives of the people who contribute the least to the emission of greenhouse gases. The US and China combined to release 45% of all CO\textsubscript{2} emissions in 2014, with CO\textsubscript{2} making up 76% of total greenhouse gas emissions in the same year (Figure 1.2).\textsuperscript{5} Other greenhouse gasses, like methane and nitrous oxides, are more effective at trapping heat than CO\textsubscript{2}, but the combination of the sheer amount of CO\textsubscript{2} released each year that continues to increase (Figure 1.3) and the long atmospheric lifetime of the molecule make it a prime target for concerted efforts to reduce the amount currently present in the atmosphere and the present emissions. The combustion of fossil fuels is a major source of CO\textsubscript{2} emissions, and the wide range of uses for fossil fuels makes it critical to develop new methods for generating alternative fuel sources.

Figure 1.1. Average global temperature increase compared to a baseline value derived from the average temperature between 1951 and 1980.\textsuperscript{1}

Figure 1.2. Total greenhouse gas emissions in 2014 by (a) gas and (b) country.\textsuperscript{5}
Figure 1.3. Measurements of atmospheric CO₂ levels since 1956 at Mauna Loa Observatory.

1.2 Impacts of Nonrenewable Energy

The two main sources of nonrenewable energy are fossil fuels and nuclear energy, with fossil fuels, primarily natural gas and coal, accounting for 61% of the electricity generated in the US in 2021. Nuclear energy lags behind at 18.9% in the US, but these numbers are higher in countries across Europe, including France and Sweden. Nuclear energy is considered a green energy due to very low amount of greenhouse gasses released by this low carbon fuel source, but since fissile materials are finite in nature it cannot be classified as renewable energy.

Natural gas, coal, and oil are the three main types of fossil fuels that supply nearly 80% of the world’s energy. In the United States in 2020, the majority of CO₂ emissions from all sectors was oil due to the large reliance on this by the transportation sector. This is reflected in the processing of crude oil in refineries to generate gasoline, as well as heating oil and petroleum. In addition to the environmental impacts of the combustion of oil and oil-derived products, the process of accessing oil can also have devastating impacts on the environment. On April 10, 2010, the offshore oil rig Deepwater Horizon in the Gulf of Mexico exploded and released approximately 134 million gallons of oil into the ocean over the course of 87 days. This incident was the largest marine oil spill in history, and claimed 11 lives in the process. Years earlier, in 1989, the Exxon
Valdez tanker spilled 11 million gallons of oil in the Prince William Sound located in Alaska after running aground. These spills take many years to clean and restore the environment to its previous condition, and the cleanup of the Deepwater disaster is ongoing as of this writing. In addition to the environmental impacts of spills, wildlife is also greatly affected by these incidents. The EPA indicates that contamination with oil can result in the loss of insulative properties of fur or feathers, stomach and intestinal disorders upon ingestion of contaminated sources, and negative impacts on reproductive systems and juveniles. Oil consumption decreased in 2020 as a result of decreased travel due to the COVID-19 pandemic, but experts expect this number to rise back to pre-pandemic levels.

Coal is primarily responsible for CO$_2$ emissions from electrical power generation, while natural gas was the main culprit in the residential, commercial, and industrial sectors. Coal production peaked in 2008, and has subsequently fallen in recent years as the prices of competing fossil fuel sources have decreased. In fact, CO$_2$ emissions from coal have been reduced by nearly 50% from 2006 to 2019, with the Energy Information Administration predicting this decline to continue until 2050. Even with coal on the decline, the mining practices that have been used to date have had a devastating impact on the environment. Water pollution is specifically of major concern, whether an underground or above ground mining method is being used. Dust and particulates from the mining process, as well as undetonated explosive materials, make their way into water in the mines, and the runoff from these sites can infiltrate the surrounding water table. This runoff can also be acidic if it comes into contact with rock containing FeS$_2$ or other sulfuric minerals. Any dust that is not suppressed by water will enter the atmosphere, and inhalation can lead to “coal workers’ pneumoconiosis” which can lead to other fatal diseases. Technologies
exist now to mitigate these concerns, but the high coal extraction in the past has caused significant damage to the environment.

Natural gas is most commonly used to produce heat and electricity for commercial or industrial structures, with the US consuming roughly 22% of the world’s natural gas in 2020.\textsuperscript{11} Compared to other fossil fuels, natural gas releases less CO\textsubscript{2} during combustion, but the rapidly increasing use of natural gas has led to a 36% share of the total energy related CO\textsubscript{2} emissions in the US in 2020. In addition to CO\textsubscript{2}, natural gas is a significant emitter of methane, a molecule that is significantly more effective at trapping heat in the atmosphere. The main concern with natural gas, however, is found in the typical way it is extracted. Hydraulic fracturing, or “fracking” is the most common method to access the natural gas found in sedimentary rocks and shale. The process of fracking involves cracking the rocks containing natural gas with water, chemicals, and sand forced at high pressures into wells dug for extracting natural gas. An average well can use up to 9.7 million gallons of water according to the United States Geological Survey, and fracking that occurs in regions susceptible to drought puts an increased strain on water availability for residents.\textsuperscript{15} Handling wastewater is also a significant concern, as studies have shown that between 5 and 40% of injected water returns to the surface, carrying contaminants used in and produced by the fracking process.\textsuperscript{16} One of the most common methods for disposing of this wastewater involves injecting it into deep wells that exist below the water table in the region. Studies have shown little water table contamination using this method,\textsuperscript{15} but this disposal method has the potential to induce seismic activity if these deep wells exist in regions near fault lines. The largest earthquake confirmed to be caused by this method of wastewater removal occurred in Pawnee, Oklahoma in 2016, and registered a magnitude of 5.8 on the Richter scale.
1.3 Alternative Energy Sources

The implementation and optimization of renewable energy techniques has become a major focus in the fight to lower CO₂ emissions as a response to global climate change. In 2021, nearly 20% of all electricity in the US was generated by renewable sources, with wind leading the way at 9.2% followed by hydro and solar power.⁶ The US lags behind the global trends of renewable energy usage for electricity generation, where 29% of global electricity came from primarily hydropower in 2020.¹⁷ A recent report from the International Energy Agency (IEA) found that from 2022-2027, the “global renewable power capacity is now expected to grow by 2,400 gigawatts”¹⁸. Projections by the IEA indicate the increase of solar and wind energy, with the former actually surpassing coal and natural gas in the year 2027 to have the highest share of cumulative power capacity (Figure 1.4). The increased projected total amount of global renewable power generation is still below the 3,800 gigawatts of renewable capacity growth needed by 2027 to reach the Net Zero by 2050 target set forth in the Paris Agreement. Increased investment and development of these technologies is a critical aspect to reaching the zero-emission goal, and reduced cost of materials and installation in recent years makes that more possible. The combination of rising climate threat and lowered cost of installation is leading governments to be able to see past the higher initial cost of implementing renewable energy to prevent the catastrophic economic damage that climate change will impose on the world.
Traditional sources of renewable energy have more downfalls than simply the high cost of installation when compared to traditional coal-fired power plants. One of the most critical is the lack of infrastructure to facilitate power delivery from renewable sources to consumers. In the US, the current electrical grid is nearing the expected lifetime of the structures. These structures were not built to be able to withstand the severe weather that has become more common as a result of climate change, with outages between 2015 and 2020 more than double what was observed over the previous six-year period. The instability of the current system makes extending the power grid more difficult, which is an issue because many large scale renewable energy projects are located in remote or hard to reach areas. Offshore wind farms and large solar farms have become more prevalent as methods for generating renewable energy, but the ability to harvest the electricity generated by these systems is limited by the ability to integrate the farms into the grid. A massive amount of money needed to update the grid, estimated at $2.4 trillion by the year 2050 if the US is to reach zero emissions by that date. The high cost of these projects will almost inevitably be turned on to consumers, angering the electorate and endangering the chances of reelection for the public officials that implement the changes that necessitate this high level of spending. This in turn disincentives the politicians to move to enact legislation that will expand
and improve the grid to make large scale renewable farms a viable way to transfer clean energy from remote areas to population centers.

The issue of energy storage is also a critical challenge that must be faced to make renewable energy, and more specifically wind and solar energy, viable. Critics of these types of renewable energies tend to point to the fact that the sun isn’t always shining, or the wind isn’t always blowing, thus rendering these non-reliable sources of energy. While this is a very juvenile argument, akin to bringing snow into the Senate to dispute global warming,\textsuperscript{21} it does bring up the issue that the peak production time for solar energy does not correspond to peak consumer electricity consumption times.\textsuperscript{22} Coal-fired powerplants are able to be activated whenever they are needed to meet the demand of the consumers, because the energy is effectively stored in the coal. The research and development of batteries for storage is a massive field of research\textsuperscript{23–26} outside of the scope of this thesis, but the development of battery technology must happen in lockstep with the development of alternative energy sources to make these systems overall viable.

1.4 Solar Fuels

1.4.1 Hydrogen

Direct use of hydrogen as a source of energy storage is advantageous due to a high specific energy of 33.3 kWh/kg compared to 13.9 kWh/kg of natural gas and the only byproduct of combustion being water.\textsuperscript{27} Hydrogen fuel cells are capable of continuous electricity production in the continued presence of H\textsubscript{2} and air sources. Interestingly, hydrogen fuel cell engines can operate at an efficiency nearly 2.5 times higher than that of gasoline-powered engines due to fuel cells not being impacted by the limitations of the Carnot cycle. These promising results, however, are
tempered by the very low energy density of gaseous H₂. Gaseous H₂ has an energy density of 0.53 kWh/dm³ at 200 bar, and liquid H₂ only increases to 2.37 kWh/dm³ compared to 9.5 kWh/dm³ for gasoline. Due to these restrictions, efforts have been undertaken to develop methods for storing the energetic potential of H₂ in other molecules. The ideal solution would be a molecule with high energy density while remaining a low or ideally carbon-free source, thus overcoming the low energy density of gaseous or liquid H₂ while maintaining the benefits of carbon-free emissions.

1.4.2 Photocatalytic Generation of Hydrogen

A photocatalytic system is one that can absorb incident radiation, typically sunlight or simulated sunlight, to excite electrons that are then capable of initiating a redox reaction. There are three types of photocatalytic systems: homogenous, where all species are soluble in the reaction media; heterogeneous, where all species are insoluble in the reaction media; and hybrid, where the light absorbing semiconductor is not soluble in the reaction media but electrons are transferred to a soluble catalyst. The work reported in this thesis focuses on heterogeneous and hybrid photocatalytic systems which will be discussed in further detail. There are many examples of these systems in the literature, but the two main types involve the use of material surfaces such as semiconductor coated electrodes or semiconductor nanoparticle suspensions. When the semiconducting material absorbs light, electrons in the valence band are promoted to the conduction band. If this conduction band exists at or above the proton reduction potential, then the chosen system may be capable of proton reduction to generate H₂. These reductive events occur at the surface of the semiconductor. If the semiconductor is capable of visible light absorption but shows low catalytic activity, a co-catalyst may be added to the system. If the thermodynamics of the catalyst and the semiconductor are properly aligned, the semiconductor is then able to transfer excited electrons into the co-catalyst, where the reductive events then take place. The generation
of an excited electron leaves behind a hole, or the absence of the electron that was excited and subsequently transferred out of the species that was excited, either through electron transfer or through the reductive process. These holes are filled by a substrate in the solvent the catalysis is taking place in, thus allowing the cycle to continue.

The earliest example of heterogeneous photocatalytic H₂ production was published in 1975 by Fujishima, Kohayakawa, and Honda.²⁸ This team of researchers from Japan created titanium dioxide (TiO₂) films on titanium metal plates to be used as anodes in alkaline solution in a photocell. Platinum cathodes were used in acidic solution and the cell was completed using a salt bridge. The maximum amount of H₂ collected was 6.6 liters of H₂ per m² of the anodic surface upon exposure to sunlight during a sunny August day. Research into the use of TiO₂ in photocatalytic systems has taken on many more applications than just H₂ production, including organic dye degradation²⁹,³⁰ and neutralization of harmful atmospheric gases.³¹,³² However, the use of TiO₂ and other oxide-based semiconductors suffers from the difficulty of possessing a conduction band properly aligned for proton reduction as well as having a band gap small enough to efficiently absorb visible light. As the band gap of the semiconductor increases in size, an incident photon with increased energy is needed to excite electrons in that semiconductor. D. E. Scaife reported in 1980 that this difficulty is due to the O 2p orbitals involved in forming the oxide pushing the valence band to more positive potentials and increasing the size of the band gap.³³ Tantalates (TaₓXₜ₋ₓ where X is a halogen or oxo group) have shown high H₂ evolution, but suffer from the issue of large band gaps to the point that they can only be excited by UV radiation, a comparatively small part of the solar spectrum that reaches earth.³⁴ A 2014 review of water splitting semiconductors ranked over 40 different semiconductor systems, many using various doping methods or introduction of co-catalysts, and subsequently grouped the systems into their
base semiconductor components. The authors found that in terms of both $\mu$mol h$^{-1}$ g$^{-1}$ and $\mu$mol h$^{-1}$ m$^{-2}$, Zn/In/S based systems performed the best due to the proper alignment and size of the bandgaps typically found in this class of material.

The two main ways to help mitigate the detrimentally large band gaps of many semiconducting materials used in photocatalysis are doping the materials and by introduction of co-catalysts. Doping requires the replacement of an atom in the semiconductor structure with a foreign atom to introduce a new energy level in the system that exists within the bandgap of the material to allow for absorption of lower energy light. These dopant sites do have the potential to promote recombination, where the excited electron falls back into the photogenerated hole and is no longer available for catalysis, but the introduction of co-dopants, a second doping element on the same material, can serve to mitigate these issues. The use of a second doping element allows for changes to the properties of the materials in more than one way, for example one dopant changing the conduction band and the other changing the valence band. Co-catalysts are used in situations where the band gap of a semiconducting material may be conducive to visible light absorption, but the band edge is not aligned thermodynamically for proton reduction. Metals such as Pt, Pd, Ag, and Au have been used as active sites leading to increased charge separation by providing a thermodynamic sink for electron migration and simultaneously acting as a catalytic site for proton reduction.

Melo and co-workers improved the visible light H$_2$ evolution of TiO$_2$ through the addition of Pt and CdS. These researchers saw a maximum H$_2$ production of 65 $\mu$mol g$^{-1}$ h$^{-1}$ with a 0.3 wt% Pt/CdS/TiO$_2$ system under visible light. Previous work using 0.5 wt% Pt/TiO$_2$ had H$_2$ production ranging from 350 to 435 $\mu$mol g$^{-1}$ h$^{-1}$. Different semiconducting materials (other than TiO$_2$) also benefit from additions of co-catalysts. Gao and co-workers used CdS and PdAg as
co-catalysts on carbon nitride, and found that with a 40 wt% CdS and 4 wt% PdAg on C$_3$N$_4$ led to a maximum 3779 µmol g$^{-1}$ h$^{-1}$ with additions of K$_2$HPO$_4$ as a sacrificial agent in the electrolyte solution.\textsuperscript{41} Cao and co-workers experimented with different shapes of Pt nanoparticles deposited on C$_3$N$_4$, and found a maximum H$_2$ evolution rate of 29.4 µmol h$^{-1}$ using spherical nanoparticles.\textsuperscript{42} in both of these cases, the addition of co-catalysts increased the H$_2$ evolution of the bare material by a significant amount.

1.4.3 Syngas

According to the US Department of Energy, natural gas reforming accounts for 95% of all hydrogen production in the United States.\textsuperscript{43} This process, also known as methane-steam reforming, first came to America in the early 1930s.\textsuperscript{44} Methane-steam reforming is a highly energy intensive process with an enthalpy of 206 kJ/mol.\textsuperscript{45} This energy demand requires the use of high temperature and pressure even in the presence of a catalyst to convert methane and steam into H$_2$ and CO, more commonly referred to as syngas (Equation 1.1). A large number of different catalysts have been explored to vary the ratio of H$_2$/CO ratio produced by this reaction, achieving ratios as high as 3:1 H$_2$:CO.\textsuperscript{46} The ability to alter the ratio of syngas produced is critical, as different applications for syngas require different amounts of H$_2$ and CO (Figure 1.5). The catalyst chosen for the reaction is what determines the ratio of gas produced, but as these catalysts are not photocatalysts they fall outside of the scope of this thesis and will not be discussed further.

\[
\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow 2\text{H}_2(g) + \text{CO}(g)
\]

Equation 1.1. Methane-steam reforming equation.
1.4.4 Photocatalytic Generation of Syngas

Forays into using heterogeneous photocatalytic systems for syngas production began with the report of CO₂ reduction using TiO₂, ZnO, and other semiconductors by Inoue and co-workers in 1979. These researchers found relatively low yields of methanol and formic acid upon irradiation of the suspended semiconductors in aqueous media, but this opened the door to the potential of systems like these being used for simultaneous proton and CO₂ reduction. However, syngas generation requires selective reduction of CO₂ to CO which can prove challenging, as other products such as methane or ethanol can be produced by CO₂ reduction. This difficulty is increased if the syngas generation is happening in one pot, as proton reduction is more thermodynamically favorable and thus will dominate in the system. Examples exist for electrocatalytic syngas production, but few systems have shown similar product evolution using photocatalytic methods.

Li and co-workers demonstrated tunable syngas production using a MnOₓ and CuPt loaded TiO₂ shell. The spatially separated nanospheres help to drive charge separation through electron
migration to the CuPt sites with subsequent hole migration to the MnOx sites. The researchers found that the addition of Cu in the system greatly expanded the visible light absorption capabilities of the system are greatly increased. It also had an impact on the ratio of H2 to CO produced, where both a low and high Cu content led to low yields of CO, but a moderate Cu content increased by roughly a factor of 7. This led to the discovery that the H2:CO ratio ranges from 2:1 to 14:1 based on the amount of Cu loaded into the system. A maximum CO evolution rate of 84.2 µmol g⁻¹ h⁻¹ with a H2:CO ratio of 2:1 was achieved at the moderate Cu loading with an overall solar energy conversion yield of 0.108%. This value outperforms traditional oxide-based systems by over a factor of 2.

Similar H2:CO syngas ratios of 1.3:1 to 15:1 were achieved by Qiu and co-workers using a CoAl-layered double hydroxide/MoS2 nanocomposite photocatalyst. A major advantage of this work was the ability to alter the ratio of products based only on the concentration of catalyst in solution (Figure 1.6). The maximum CO evolution rate was found to be 14.15 µmol g⁻¹ h⁻¹ at a catalyst loading of 0.2 mg mL⁻¹. At lower concentrations of catalyst, a larger proportion of CO was produced compared to the products observed at higher catalyst concentrations. This is an exciting result as the synthesis of the two materials that form the heterojunction is difficult, but in this case a bulk amount of material can be made to make any desired ratio of H2:CO within the experimentally determined range. The researchers determined that this property was due to the electronic levels of the materials changing as they interacted and formed heterojunctions in solution. H2 evolution was attributed to both the CoAl and MoS2 materials, while CO2 reduction mainly occurred on the CoAl material. It was reasoned that CO2 reduction occurred on the MoS2 because the presence of surface hydroxyl groups drives the absorption of CO2 on the surface of MoS2.
Wang and co-workers added Pd to the same CoAl material Qui and co-workers used and saw an increase in CO evolution rates to 1.68 mmol g\(^{-1}\) h\(^{-1}\).\(^{53}\) PdCl\(_2\) was added to the CoAl material through a simple stirring method to generate a material with a disperse coating of Pd nanoparticles. Increased loadings of Pd lead to a decrease in CO evolution and an initial increase in H\(_2\) evolution with a slight decrease at the maximum Pd loading. The most significant finding in this study was the ability for the Pd/CoAl material to produce syngas at a ratio of roughly 1:1 with 600 nm irradiation. This greatly extends the typical working range for photocatalytic systems, and the enhanced range allows for a larger proportion of solar photons to be used for excitation. Evolution rates and syngas ratios stayed relatively constant over 4 cycles using the same catalyst, and the researchers were able to use XPS to determine metallic Pd\(^0\) sites were mainly responsible for CO\(_2\) reduction due to the increase in CO evolution observed in subsequent trials after the first (Figure 1.7). These active sites were also crucial in promoting charge carrier separation as determined using photoluminescence spectroscopy.
Figure 1.7. H$_2$ and CO evolution rates of Pd/CoAl-7.57 after repeated photocatalytic experiments (left) and XPS spectra showing the reduction of Pd$^{(2-n)+}$ to Pd$^0$ after the first photocatalytic experiment (right).$^{53}$
CHAPTER II

BP and C$_3$N$_4$ for Solar Fuel Generation

2.1 Background

Bulk black phosphorus was first discovered in 1914 by the physicist Percy W. Bridgman, whose work focused on synthesizing materials under extremely high pressure and analyzing their properties. Black phosphorus (BP) is one of the three main allotropes of elemental phosphorus, the other two being red and white, and has attracted interest in the last 10 years due to BP possessing unique qualities as a material as well as showing the greatest propensity towards catalytic activity of the three allotropes. Bulk BP is comprised of individual stacked, puckered sheets called phosphorenes in analogy to the more well studied carbon analogue graphene (Figure 2.1). Each phosphorene has a thickness of ~0.85 nm with an interspatial distance between the phosphorene layers in the bulk material of 0.53 nm. BP has a thickness-dependent band gap, ranging from 0.3 eV for the bulk material up to 2.0 eV for a single layer. Additionally, BP exhibits high charge-carrier mobility of approximately 1000 cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature, making it an ideal candidate for use in heterojunction systems. However, black phosphorus does present two main difficulties, namely stability and exfoliation techniques. Black phosphorus is moisture, light, and oxygen sensitive, and degrades rapidly in the combined presence of all three. Density functional theory and molecular dynamics simulations point to this oxidation occurring initially through the oxidation of surface P atoms. Ambient humidity is then able to cleave these oxidized P atoms off the surface as phosphoric acid units, thus exposing new P atoms.
at the edge for this process to continue. The removal of one or more of these BP degradation factors significantly reduces the rate at which the material degrades.

Exfoliation is an issue due to sample uniformity and scalability issues. Sample uniformity is critical due to the thickness dependent band gap, as exfoliated flakes with different thicknesses may interfere with the catalytic capabilities of the system due to potential incompatibility of the band edge energy levels between the semiconductors. Any method employed for exfoliation must also be scalable so that any future system involving BP can be used on a larger scale. Exfoliation of BP unlocks the thickness-dependent band gap, with the band edges of few layer BP positioned well for proton reduction. Mathews and co-workers were able to exfoliate bulk BP to an average thickness of 8 layers through first turning the bulk material into a powder, then probe and bath sonicating the powder in N-methyl pyrrolidone. The highest reported turnover number was 64 µmol H₂ h⁻¹ g⁻¹ from the exfoliated BP nanosheets.

Yang and co-workers utilized ball-milling to exfoliate bulk BP to achieve exfoliated flakes ranging from 8 to 1 layers. The addition of anhydrous LiOH to the bulk BP prior to ball milling capped the reactive ends of the material with OH groups, which they hypothesize inhibits the transition of BP to red phosphorus catalyzed by the ball milling process. The authors report a hydrogen evolution rate up to 512 µmol h⁻¹ g⁻¹ after 10 hours of visible light irradiation in aqueous solutions containing 0.75 M Na₂S and 1.05 M Na₂SO₃. These two publications are some of the first studies into the use of BP as a H₂ evolution catalyst, and the large difference between the reported turnover numbers is somewhat indicative of the inconsistency in the field. Most efforts moving forward from these initial studies include the use of molecular catalysts or other 2D materials in combination with BP leading to enhanced photocatalytic activity.
Carbon nitride (C₃N₄) was originally discovered by Jöns Jacob Berzelius and reported by Justus von Liebig in 1834. It was named “melon”, and consisted of tri-s-triazines linked through secondary nitrogens to form a linear polymer.⁷² There are different forms of C₃N₄, but the most studied is graphitic carbon nitride (g-C₃N₄) due to being the most stable form of C₃N₄ in ambient atmosphere.⁷³ g-C₃N₄ is stable up to 600 °C in air, and possess conduction and valence bands positioned at -1.1 eV and 1.6 eV vs normal hydrogen electrode, respectively, allowing this material to absorb visible light.⁷⁴ Proton⁷⁵ and CO₂ reduction⁷⁶ have been observed using g-C₃N₄, showcasing the ability for this material to perform metal-free catalysis generating a range of products under visible light irradiation. However, attempts to reduce gaseous CO₂ even at high pressure proved fruitless for Antonietti et. al., indicating that metal free g-C₃N₄ is not a good candidate for reducing atmospheric CO₂. The addition of single atom Co²⁺ active sites onto C₃N₄ (Co@C₃N₄) by Dr. Peipei Huang in the Dr. Gonghu Li lab at UNH greatly enhanced the catalytic ability of this material (Figure 2.2). A simple microwave method for depositing single atoms of Co²⁺ was used to create Co@C₃N₄, which demonstrated a high selectivity towards CO₂ reduction to CO resulting in a turnover number greater than 200 after 24 hours of visible light irradiation.⁷⁷
The combination of carbon nitride and black phosphorus is particularly attractive due to the naturally complementary nature of the two materials. Two of the main detriments of BP are the lack of visible light absorbance and the rate of degradation in systems typically used for photocatalysis. Significant conduction band overlap between C$_3$N$_4$ and BP allows for efficient electron transfer from C$_3$N$_4$ to BP, and, combined with the ability of C$_3$N$_4$ to absorb visible light, creates a system in which excited electrons can populate the conduction band of BP under visible light. C$_3$N$_4$ also lends an element of stability to BP through the formation of P–N bonds as the two materials interact in solution. This prevents the formation of P–O bonds at those sites, thus inhibiting the rate of degradation. These physical interactions may also enhance the electron transfer capabilities, as the bonds formed keep the materials in close contact to greatly reduce the reliance on random collisions in solution. The addition of Co$^{2+}$ active sites on C$_3$N$_4$ does not affect the spectral properties of bare C$_3$N$_4$. These additions enhance the overall catalytic capabilities of a heterojunction formed between BP and Co@C$_3$N$_4$ without limiting the largely beneficial impact that C$_3$N$_4$ has on BP.
Majima and co-workers were the first to report on the capabilities of the BP/C₃N₄ heterojunction as a metal-free photocatalyst for H₂ production under visible light utilizing a >420 nm cutoff filter.⁸⁰ The group found a maximum H₂ evolution rate of 427 µmol g⁻¹ h⁻¹ from a BP:C₃N₄ weight ratio of 1:4. The presence of P–N bonds was confirmed through the use of FT-IR, and the increased stability of the combined materials showed consistent H₂ over three consecutive 3 hour cycles and after being stored for 2 weeks. Liu and co-workers utilized an exfoliation method to develop BP quantum dots (BPQD) and found that a 7 wt% loading of BPQD on C₃N₄ gave an H₂ evolution rate of 1900 µmol g⁻¹ h⁻¹ under full spectrum irradiation (using a Xe lamp).⁸¹ The increased amount of UV irradiation used by Liu and co-workers is most likely the cause of the higher H₂ evolution rate compared to what was observed by Majima.

Moon and co-workers grew a Ni₂P catalyst on the surface of BP utilizing a solvothermal method starting from sonication-exfoliated BP and NiCl₂•6H₂O.⁸² The resulting Ni₂P@BP was combined with C₃N₄ using a hydrothermal treatment and subjected to visible light irradiation with a >420 nm cutoff filter. At a 2 wt% loading of Ni₂P@BP on C₃N₄, an impressive H₂ evolution rate of 858.2 µmol g⁻¹ h⁻¹ was observed. The enhanced catalytic activity in the presence of Ni₂P is a result of the lower H₂ production overpotential compared to BP. These authors also observed that increased loadings of Ni₂P@BP on C₃N₄ resulted in decreased photoactivity, most likely due to limited photoexcitation of the C₃N₄ which hampers the overall efficiency of the heterojunction. BP/C₃N₄ heterojunctions have also been used for many other reductive processes, including nitrogen fixation,⁸³ CO₂ reduction,⁸⁴–⁸⁶ and pollutant removal.⁸⁷–⁸⁹

Nearly all reports involving BP/C₃N₄ heterojunctions describe the interaction of the two materials as a Type I heterojunction, where the conduction and valence band of BP is contained within the bandgap of C₃N₄ (Figure 2.3) Photons with sufficient energy are absorbed by the C₃N₄,
resulting in a charge separated state. The excited electron is able to undergo recombination, or alternatively, to relax into the conduction band of BP, where proton reduction is more likely due to the electronic and physical properties of BP. This electron transfer has two distinct advantages, namely: a lower overpotential is crucial to efficient proton reduction, and physical charge separation inhibits recombination thus increasing the likelihood of proton reduction. There is potential for hole transfer from the valence band of C₃N₄ to the valence band of BP as well, which reintroduces the potential for fast recombination when the excited electron and photoinduced hole reside in the same material. The use of an appropriate sacrificial electron donor (SED) can rapidly fill this hole and prevent recombination. The addition of catalytically active sites can also work to inhibit recombination, as the excited electrons are able to move onto these active sites where they are subsequently used in reductive processes and are effectively separated from the photogenerated holes.

Figure 2.3. Bandgap alignment of the Type I heterojunction formed between BP and Co@C₃N₄, with proposed electron and hole transfer. ED is a sacrificial electron donor.
2.2 Hypothesis

We hypothesize that the use of Co@C₃N₄ and BP will form a heterojunction in solution capable of simultaneous proton and CO₂ reduction to form H₂ and CO, respectively. The heterojunction is likely comprised of stacked, alternating sheets of BP and C₃N₄. However, we expect the lateral dimensions of C₃N₄ to be significantly larger than BP due to the physical properties and structure of each material, thus it may more closely resemble BP nanoflakes on large C₃N₄ sheets. The reported physical interaction between these materials, as well as the energy level overlaps between them indicate the potential for efficient electron transfer from Co@C₃N₄ to BP. The broad visible light absorption exhibited by C₃N₄ materials allows for the use of simulated solar irradiance in the system. We hypothesize that enhanced electron transfer between the two materials will lead to a higher yield of evolved gaseous products. The separation of the excited electrons from their photo-generated holes extends the lifetime of the charge-separated state, leading to a higher probability of electron transfer to catalytically active surface sites on the material. A higher population of electrons at these active sites is expected to directly correlate to increased product evolution.

We hypothesize that changing the weight percent (wt%) of BP relative to a constant amount of Co@C₃N₄ will result in different ratios of products evolved. As CO₂ reduction is attributed to Co@C₃N₄ and proton reduction to BP, we expect to see increased H₂ production with increased loadings of BP. This will be highly valuable for large-scale implementations as the potential tunability of the ratio of products can lead to H₂/CO feedstocks for a variety of down-stream products.
2.3 Results and Discussion

2.3.1 Black Phosphorus Exfoliation

Previous studies were carried out by Hannah Bell to determine the appropriate solvent system for exfoliation of bulk BP. The ideal exfoliation results in uniform, thin sheets with large lateral dimensions. A 4:1 acetonitrile:triethanolamine solvent system was determined to be the best due to the lack of aggregation observed using scanning electron microscopy (SEM) but failed in respect to generating flakes with large lateral dimensions. A microwave exfoliation technique was employed in an effort to develop a more gentle exfoliation technique based on literature precedent. Small, polar molecules become intercalated between the sheets of the bulk BP, and the microwave irradiation causes these molecules to move upon excitation which separates the layers that are then more thoroughly exfoliated into large sheets using sonication. N-methyl-2-pyrrolidinone (NMP) was chosen due to its use in previous studies, as well as the planar ring structure that will fit easily between the sheets. NMP also has a very high boiling point of 204 °C, so it will not evaporate when subjected to microwave irradiation. If the molecules intercalated between the layers evaporate, the BP layers may get blown apart too rapidly. This would reduce the lateral dimensions of the flakes and lead to a much lower degree of uniformity in size. Encapsulation of the exfoliated flakes in NMP solvent limited the ability to probe the dimensions of the material and inhibited the catalytic ability of the material (Figure 2.4). This was ascribed to the inaccessibility of protons to the surface of the BP where catalysis takes place. A solvent switch by centrifugation and redispersion in methanol was unable to fully remove all NMP from the BP, and the high boiling point of NMP prevented it from fully evaporating during the normal dropcast procedure. As a result, no atomic force microscopy (AFM) was performed out of fear of solvent
coating the AFM tip. This would result in the loss of the atomically sharp tip and resolution and necessitate the replacement of the tip.

![Image](image.jpg)

**Figure 2.4.** Low magnification image of BP flakes exfoliated in NMP via microwave irradiation and sonication. The dark patches are residual solvent covering the exfoliated flakes.

Microwave exfoliation was attempted using acetonitrile rather than NMP due to both molecules having similar dipole moments, but acetonitrile has a lower boiling point which would result in significantly less solvent encapsulation. This was confirmed using SEM as a much higher resolution was achievable compared to BP exfoliated in NMP. To determine the thickness of the exfoliated flakes, AFM was used to scan over a specific area. It was found that the individual flakes consisted of approximately 10 layers, but significant streaking after the raised flakes on the surface complicated the analysis (**Figure 2.5**). These streaks arise as a function of the feedback loop used in the AFM. If the feedback loop is not appropriately set for the scanning speed, then a delay in the tip returning to the surface results in streaks after the raised sample areas.
2D Raman spectroscopy can also be used to determine the thickness of exfoliated flakes by comparing the ratio of the $A_g^1$ and $A_g^2$ vibrational modes. The $A_g^1$ vibrational mode lies nearly perpendicular to the BP sheet, and as the number of layers decreases, the prevalence of this vibrational mode decreases due to the reduced inter-sheet interaction. The $A_g^2$ vibrational mode lies in plane and parallel to the BP sheet and experiences a significantly smaller decrease in intensity as the number of layers in the exfoliated flakes decreases. Abellán and co-workers used this fact to create calibration curves using the ratios of the two vibrational modes to assign values to the known thickness of flakes. Ratios were found to range from 0.89 to 0.91, agreeing with the ~10-layer thickness found using AFM (Figure 2.6). Photocatalytic experiments using only exfoliated BP in MeCN showed no activity, which was believed was due to the band gap of BP not being energetic enough to supply the proper reducing power for proton reduction at the thickness of ~10 layers.
Figure 2.6. 2D Raman spectrum with numbers indicating the specific spots where displayed spectra (right) were collected. Bright spots on the 2D spectrum are a result of surface impurities and are not flakes.

2.3.2 Methyl Viologen Electron Transfer Studies

The ability of BP to transfer electrons to an acceptor is critical for the use of this material in combination with either molecular redox catalysts or in a photocatalytic heterojunction. Methyl viologen (MV$^{2+}$) has been used to measure the electron transfer capability of compounds and materials. MV$^{2+}$ is soluble in water, where it exists as a dicationic species with a reduction potential of $-0.45$ V vs NHE.$^{91}$ The reduction of MV$^{2+}$ to form a radical cation species can be monitored by UV-Vis absorbance, with two peaks at 395 and 603 nm.$^{92}$ The radical (and subsequent diradical) species are oxygen sensitive and are quenched upon exposure to, and oxidation in, air, thus care must be taken to ensure an anaerobic atmosphere when using these to monitor for electron transfer events.$^{93}$ The combination of BP and MV$^{2+}$ will ideally show electron transfer from the conduction band of BP to the LUMO of MV$^{2+}$, and to prevent MV$^{2+}$ light absorbance above 420 nm a cutoff filter is used. The addition of EDTA as a SED will enhance the potential for electron transfer from
BP by refilling the photogenerated hole and preventing recombination. Within 15 minutes, a maximum peak at 395 nm was observed indicating that electron transfer from BP to MV$^{2+}$ was occurring. However, we found that MV$^{2+}$ could be reduced by EDTA in the absence of BP. The combination of BP and MV$^{2+}$ in the absence of EDTA showed a slight peak at 395 nm with the use of a >420 nm cutoff filter, confirming the ability for the MeCN microwave exfoliated BP to transfer electrons directly to MV$^{2+}$ (Figure 2.7).

![Graph showing absorbance over time](image)

**Figure 2.7.** Reduction of MV$^{2+}$ by BP with no SED over time. A ≥ 420 nm filter was used on the solar light.

### 2.3.3 Black Phosphorus with Molecular Catalysts

The photocatalytic H$_2$ evolution capability of BP in the absence of any other catalytic species was studied as a control sample. The initial trials using a 4:1 acetonitrile: triethanolamine (MeCN:TEOA) solvent system showed no H$_2$ evolution over the course of a 4 hour photocatalytic experiment. Additions of water to increase available proton concentration did not yield any H$_2$. Aqueous EDTA solution was used to determine the impact of SED on H$_2$ evolution, because if the
SED is not able to fill the photogenerated hole in the valence band of the BP, then the probability of recombination remains high. Still, no H₂ was observed, and it was concluded that BP exfoliated via a microwave method in MeCN on its own was not capable of H₂ evolution in the absence of other catalytic materials.

The first catalyst explored for inclusion with BP through photocatalysis experiments was [Ni(bis(1,5-R’-diphospha-3,7-R”-diazacyclooctane)]²⁺ (NiP) (Figure 2.8). NiP has shown hydrogen evolution activity as both an electrocatalyst and photocatalyst with high Faradaic efficiency and turnover number. Additionally, the phosphonic acid groups on the outer sphere of the catalyst offers the potential for coordinating the molecular catalyst to the surface of the BP flakes. This coordination has a dual benefit, as the linked photosensitizer and catalyst should exhibit increased electron transfer ability while also providing the hypothesized benefits of BP surface passivation, specifically reduced BP degradation. NiP has exhibited a catalytic lifetime of approximately four hours in photocatalytic systems utilizing carbon quantum dots as the photosensitizer. This demonstrated ability to generate hydrogen in hybrid photocatalytic systems makes NiP a good candidate for application in systems containing BP. NiP was obtained by Dr. Christine Caputo, and the proton reduction properties of NiP were tested using the well-studied [Ru(bpy)₃]²⁺ photosensitizer (PS) with EDTA as an SED. Hydrogen evolution was observed in the test system, confirming the catalyst is redox active and the PS is able to reduce NiP. NiP was also tested for H₂ evolution in the absence of a photosensitizer; in this control experiment no hydrogen was detected. When NiP was combined with BP, no quantifiable H₂ evolution was detected over 4 hours of irradiation, but an increase in oxygen concentration was observed. The tube was wrapped in foil to prevent light exposure and allowed to sit overnight to determine if the oxygen present was due to a leak. Oxygen concentration (as determined by GC analysis) at 24
hours remained relatively constant compared to the 4-hour concentration indicating this oxygen was not due to a leak in the system, and it was hypothesized the system was oxidizing the water in the system. To take advantage of the abundance of H⁺ that would be present in the solution if water oxidation was occurring, subsequent additions of NiP were added to the tube. No H₂ evolution was observed following the addition of catalyst.

Figure 2.8. Structure of molecular catalyst NiP.

The exfoliated BP has demonstrated electron transfer capabilities with MV²⁺, and the NiP had shown catalytic activity with [Ru(bpy)₃]²⁺, but the combination of BP and NiP did not produce any gases. It was hypothesized that the difference between the conduction band of BP and the LUMO of NiP was too great for efficient electron transfer to occur, so MV²⁺ was used to provide an intermediate energy level in the electron transfer to NiP. The conduction band of the exfoliated BP is unknown, but MV²⁺ has a reduction potential of −0.45 V vs. NHE, and NiP has a reduction potential of −0.38 V vs. NHE.¹⁻⁹⁴ Since BP was able to transfer electrons to MV²⁺, a potential “cascade” of energy levels exists for the excited electrons to eventually be transferred to the NiP catalyst. It was found that TEOA will spontaneously reduce MV²⁺, so EDTA was used as the SED. A blue color indicative of MV²⁺ reduction was observed in all tubes regardless of NiP being present or not, but still no H₂ evolution was observed. The idea of “charging the system” was attempted,
where NiP was added to a BP/MV$^{2+}$ tube in aqueous EDTA after 1 hour of irradiation, but no H$_2$ was evolved over the following 15 hours. This may be due to the fact that proton reduction is a two-electron process, and the second reduction of NiP (−0.54 vs NHE) requires larger driving force than the reduction of MV$^{2+}$ (−0.45 vs NHE).$^{91,94}$ As a result, MV$^{2+}$ was removed from the system for all subsequent experiments.

In an effort to increase the collisional interactions leading to possible covalent attachment of the phosphoric acid groups of NiP with defects in the BP material, we shifted focus to increasing the mixing of catalyst and BP. Sonication was used to promote interactions between NiP and BP, and light was removed during this process by covering the sonicator in tin foil. This allowed for greater mixing of the samples while also inhibiting any potential degradation of the catalyst by light exposure. No H$_2$ evolution was observed, but the presence of methane was detected after sonication. The generation of methane was not attributed to any photocatalytic events, as methane was observed in the absence of both BP and NiP as well as in the absence of irradiation. We believe the methane to be a product of a mechanochemical transformation of acetonitrile, but no mechanism is suggested for this. Despite these attempts, we deemed this system of NiP with BP as a photosensitizer was not capable of carrying out photocatalytic H$_2$ evolution, and this approach was abandoned.

The catalytic ability of cobaloxime (Figure 2.9) with BP was tested to see if there was better catalyst compatibility between cobaloxime and BP. Brown crystals of cobaloxime were collected and combined with BP (at various concentrations) using TEOA as the SED, but again no quantifiable H$_2$ peak was observed.
Due to these failed trials, no further work was carried out to combining molecular catalysts with BP and the lab was shut down for several months due to the pandemic.

### 2.3.4 Black Phosphorus with C₃N₄

Following the precedent set by former graduate student in the Caputo group, Hannah Bell, liquid phase exfoliation of BP in 4:1 MeCN:TEOA was performed using probe and bath sonication to generate flakes with an approximate thickness of 5 layers as determined by 2D Raman spectroscopy. This exfoliated BP sample was unable to carry out proton reduction in a typical photocatalysis experiment. Single-site Co²⁺ active sites were loaded onto C₃N₄ using a microwave method previously described.⁷⁷ Co@C₃N₄ alone showed simultaneous proton and CO₂ reduction with gas production activities of 15 ± 1 μmol H₂ g⁻¹ h⁻¹ and 46 ± 3 μmol CO g⁻¹ h⁻¹. This corresponds to a H₂/CO syngas ratio of 0.3, but a higher evolution of H₂ is needed to generate the ideal ratio of 2 for solar fuel generation.

BP and Co@C₃N₄ were combined and sonicated together to form a heterojunction. This mixture was then subjected to simulated solar irradiation in a 4:1 MeCN:TEOA solvent system. We hypothesized that this combination would increase the H₂ production with increasing amounts of BP. Increasing the wt% of BP relative to a constant mass of Co@C₃N₄ resulted in increased H₂ production.
evolution, coupled with decreased CO evolution over the BP wt% range of 5 - 45% (Figure 2.10). The H\textsubscript{2}/CO syngas ratios were linearly correlated with the change in wt% BP, with an R\textsuperscript{2} value of 0.965 (Figure 2.11). This indicates the tunability of this heterojunction and makes this system attractive for large scale implementation because of the ability to select the ratio needed for any application.

The highest total gas production of 0.665 ± 0.146 μmol came from the sample with 20% loading of BP relative to Co@C\textsubscript{3}N\textsubscript{4}, and this system maintained a H\textsubscript{2}/CO syngas ratio of 2 over the course of a 4 hour experiment. All samples tested gave relatively constant syngas ratios over the course of the 4 hour experiments, no matter the BP loading. This allowed for the desired ratio of products to be generated continuously, avoiding the delay of gaseous product evolution that can be seen in other photocatalytic systems. Additionally, all samples remained active for 24 hours, showing the enhanced stability of BP when combined with C\textsubscript{3}N\textsubscript{4}.

Figure 2.10. H\textsubscript{2} and CO evolution after 4 h with varying wt % BP loading on Co@C\textsubscript{3}N\textsubscript{4} (2 mg in 4 mL MeCN/TEOA (4:1 v/v) with full spectrum simulated solar irradiation (AM 1.5G).
Figure 2.11. Linear increase in syngas ratio (H₂/CO) using different material compositions, from 0 to 45 wt % BP with Co@C₃N₄ (2 mg in 4 mL MeCN:TEOA 4:1 v/v) over 4 h simulated full solar spectrum irradiation (AM 1.5G).

Previous work by Feng and co-workers found that solvothermal deposition of CoCl₂ on BP resulted in the formation of CoP particles on the surface of the BP. The direct growth of CoP on the BP surface was performed by Feng and co-workers using a solvothermal method, which upon photocatalysis resulted in a large increase in H₂ evolution rate to 694 μmol H₂ g⁻¹ h⁻¹ compared to 95 μmol H₂ g⁻¹ h⁻¹ from mixing BP and CoP in solution. This gives potential to control H₂ evolution through the introduction of CoCl₂ rather than by increasing the amount of BP in the system. BP is the most expensive material in the system and contributes most to H₂ evolution, so having a second route to increase H₂ evolution that does not cause a large increase in total cost of the system is of significant interest.

Increased CoCl₂ concentrations in solution with the 20% BP/C₃N₄ heterojunction showed low CO activity of 14 ± 3 μmol CO g⁻¹ h⁻¹ using 0.2 μmol of CoCl₂, but this is significant because the BP/C₃N₄ system showed no CO evolution. This indicates that the addition of CoCl₂ in solution does indeed form catalytically active Co-sites on the material. It is unclear at this stage if it is deposited on BP or on C₃N₄. A massive increase in H₂ activity up to 693 ± 24 μmol H₂ g⁻¹ h⁻¹ was observed for this sample (Figure 2.12). This is a similar performance metric to the CoP/BP system.
and outperforming a comparable Pt/BP system with an activity of 368 μmol H\textsubscript{2} g\textsuperscript{-1} h\textsuperscript{-1}.\textsuperscript{65} This is notable, as the new system reported here does not contain a noble metal.

![Figure 2.12](image.png)

**Figure 2.12.** Photocatalytic generation of H\textsubscript{2} using BP\textsubscript{10%}/C\textsubscript{3}N\textsubscript{4} (2 mg in 4 mL MeCN:TEOA 4:1 v/v) with 0.01 to 0.40 μmol CoCl\textsubscript{2} mg\textsuperscript{-1} C\textsubscript{3}N\textsubscript{4} over 4 h simulated full solar spectrum irradiation (AM 1.5G).

The effects of light intensity and wavelength range were also studied to determine their effects on photocatalysis using the BP/Co@C\textsubscript{3}N\textsubscript{4} system. Samples of 20% BP/Co@C\textsubscript{3}N\textsubscript{4} were used as standard conditions in these tests due to the high gas evolution obtained and the desirable H\textsubscript{2}/CO syngas ratio produced. This system showed an approximate 70% decrease in total gas evolution when a > 400 nm long-pass filter was used (Figure 2.13). Removing higher energy light had a stronger effect on H\textsubscript{2} evolution than CO evolution, as the H\textsubscript{2}/CO syngas ratio decreased from 2 to 0.64 after 4 hours. This is likely due to the reduced amount of higher energy photons available to the system, reducing any light absorption from BP and reducing the amount of excited electrons available to transfer from the C\textsubscript{3}N\textsubscript{4} species to BP.

The effects of reduced total irradiation were studied using optical density filters (Figure 2.14). A 50% decrease in light intensity on the 20% BP/Co@C\textsubscript{3}N\textsubscript{4} system resulted in an
approximately 60% decrease in total gas evolved. A 68% decrease in light intensity led to an approximately 80% decrease in total gas evolved. This indicates that the system is not light limited and that the process is photocatalytic in nature, but it was shown in all cases that H₂ evolution is more greatly affected by changes in light than CO evolution.

Figure 2.13. Total gas evolution (H₂/CO) when irradiating BP₂₀%/Co@C₃N₄ (2 mg in 4 mL MeCN:TEOA 4:1 v/v) over 4 h with simulated full solar spectrum irradiation (AM 1.5G) and λ > 400 nm (using a longpass filter).

Figure 2.14. Total gas evolution (H₂/CO) when irradiating BP₂₀%/Co@C₃N₄ (2 mg in 4 mL MeCN:TEOA 4:1 v/v) over 4 h with simulated full solar spectrum irradiation (AM 1.5G) and neutral density filters (O.D. 0.3 and 0.5).
2.4 Conclusion

In this chapter, the exfoliation and photocatalytic capabilities of black phosphorus were discussed. Microwave exfoliation in acetonitrile was used to try and achieve thin, laterally large flakes that could not be achieved using sonication techniques. These flakes were analyzed and found to have an average thickness of 10 layers, as determined using a Raman spectroscopic analytic technique, resulting in a nanoflake material that maintains many of the properties of the bulk material. It was observed that BP was capable of transferring electrons to MV$^{2+}$ in the absence of UV light that can excite MV$^{2+}$, indicating that BP is capable of absorbing light to generate excited electrons. However, the smaller band gap in BP exfoliated this way resulted in no H$_2$ evolution from BP alone or in combination with the molecular catalysts NiP or cobaloxime. Even with the addition of MV$^{2+}$ to BP/molecular catalyst systems, no H$_2$ was evolved over the course of any experiments.

Photocatalytic systems utilizing BP and Co@C$_3$N$_4$ were able to simultaneously generate tunable amounts of H$_2$ and CO in one pot. By increasing the amount of BP in the BP/Co@C$_3$N$_4$ system, the amount of H$_2$ evolved subsequently increased, coupled with a decrease in CO evolution. This gave a H$_2$/CO syngas range of 1-5 after 4 hours, whereas Co@C$_3$N$_4$ on its own gave a syngas ratio of 1.2. The 20% BP/Co@C$_3$N$_4$ system showed the highest total gas evolution of 0.665 µmol syngas produced with an activity of 69 ± 15 µmol syngas g$^{-1}$ h$^{-1}$. Additions of CoCl$_2$ to the system resulted in large increases in H$_2$ evolution, indicating a second potential pathway to control H$_2$/CO syngas ratio besides changing the loading of BP.

2.5 Experimental Section
Microwave Exfoliation of BP

Materials: Black phosphorus was purchased from Smart Elements. 1-methyl-2-pyrrolidinone (NMP, 99.5%) was purchased from Sigma-Aldrich. Acetonitrile (MeCN, 99.9%) was purchased from Sigma-Aldrich.

BP Exfoliation: Bulk black phosphorus (SmartElements, 10 mg) was added to a mortar and pestle and wet ground for 10 minutes in 0.3 mL of the chosen solvent in a nitrogen atmosphere glovebox. The total volume was brought up to 1 mL and transferred to a quartz tube with a stir bar that fit inside a microwave reactor tube and placed in a CEM Corporation Discover SP microwave synthesizer. For NMP, a constant power of 140 W for 60 minutes was held, and a safety temperature of 200 °C was set. For MeCN, a constant power of 60 W for 60 minutes was held, and a safety temperature of 75 °C was set. The sample was transferred to a conical Teflon vial and bath sonicated in a Branson 2510 Ultrasonic Cleaner with chilling for 4 hours. The material was characterized by scanning electron microscopy (SEM) performed on a Tescan Lyra3 GMU FIB SEM. A drop of the exfoliated suspension was dropcast on a silicon chip and heated under vacuum, then attached to a metal stub with carbon paint prior to SEM analysis. Raman spectroscopy was performed using an NT-MDT NTEGRA Spectra microscope. The exfoliated sample was dropcast on a silicon chip and heated under vacuum to prepare the sample for Raman analysis.

BP and MV$^{2+}$

Materials: Black phosphorus was purchased from Smart Elements. Ethylenediaminetetraacetic (EDTA) acid was purchased from Aldrich. Methyl viologen (MV$^{2+}$) was purchased from Sigma.

Electron transfer study: In a cuvette, exfoliated BP (0.25 mL in MeCN, 0.25 mg) was added to an EDTA/MV$^{2+}$ stock solution (0.75 mL, 0.1 M EDTA, 0.45 mmol MV$^{2+}$) in a nitrogen atmosphere
glovebox. The cuvette was irradiated using a Xe lamp equipped with an AM 1.5G filter at a power of 100 mW cm$^{-2}$, and UV-Vis spectra were collected on a Cary 50 UV-Vis spectrophotometer at regular intervals.

**BP and Molecular Catalysts**

**Materials:** Black phosphorus was purchased from Smart Elements. NiP was obtained by Dr. Christine Caputo. Ru(bpy)$_3$Cl$_2$•6H$_2$O was obtained from prior synthesis by Dr. Ethan Jarvis. Ethylenediaminetetraacetic acid tetrasodium salt dihydrate (EDTA, 99%) was purchased from Acros Organic. Methanol (99.8%) was purchased from Fischer Scientific. Triethanolamine (TEOA, 97%) was obtained from Acros Organics. Methyl viologen chloride hydrate (MV$^{2+}$, 98%) was purchased from Acros Organic.

**Cobaloxime synthesis:** CoCl$_2$•6H$_2$O (1.0 g, 4.20 mmol) was dissolved in acetone (30 mL) in a 50 mL round-bottom flask, resulting in a blue solution. Dimethylglyoxime (0.98 g, 8.44 mmol) was added to the solution and stirred for 10 minutes, resulting in a dark green solution. The solution was vacuum filtered to remove undissolved materials, and the solution was allowed to stand overnight uncovered. Green crystals of CoCl$_2$(dmgH)(dmgH$_2$) (0.5088 g, 33.3%) were recovered from the solution. Previously prepared CoCl$_2$(dmgH)(dmgH$_2$) (0.5 g, 1.4 mmol) was dissolved in CH$_3$Cl (25 mL) in a 50 mL round-bottom flask. Pyridine (0.56 mL, 6.9 mmol) was added to the flask and allowed to stir for 10 minutes. Water (10 mL) was added and stirred vigorously for 60 minutes to mix the two layers together well. The chloroform layer was collected and washed three times with water (10 mL), and rotary evaporated down to ~5 mL. Brown crystals of the crude product precipitated upon addition of ethanol. The crude product was vacuum filtered and recrystallized from hot acetone, and brown crystals of [CoCl(dmgH)$_2$(pyridine)] were collected (0.1745 g, 30.7% yield).
**Exfoliation:** Bulk black phosphorus (SmartElements, 10 mg) was added to a mortar and pestle and wet ground for 10 minutes in 0.3 mL of MeCN in a nitrogen atmosphere glovebox. The total volume was brought up to 1 mL and transferred to a quartz tube with a stir bar that fit inside a microwave reactor tube and placed in a CEM Corporation Discover SP microwave synthesizer. A constant power of 60 W for 60 minutes was held, and a safety temperature of 75 °C was set. The sample was transferred to a conical Teflon vial and bath sonicated in a Branson 2510 Ultrasonic Cleaner with chilling for 4 hours.

**Photocatalysis:** In a general photocatalytic experiment, BP (1.00 mg; 1 mg mL\(^{-1}\), MeCN) was added as well as the desired catalyst (NiP: 30 nmol-3.725 µmol; cobaloxime: 200 nmol-1 µmol) and MV\(^{2+}\) (3.1 µmol in 0.1 M aqueous EDTA, 1 mL) if being used. The total volume of the tube was brought up to 4.0 mL with a mixture of MeCN and TEOA (4:1 v/v) or aqueous EDTA (0.1 M) depending on SED being used. A stir bar was added, and the tube was capped with a septum and sealed with parafilm. When sonication was used, the tubes were sonicated for 30 minutes in the dark in a sonicating bath with ice.

The sample was then irradiated using a Xe lamp equipped with an AM 1.5G filter at a power of 100 mW cm\(^{-2}\) for 4 h with constant stirring. The temperature of the cell containing the samples was maintained at 18 °C by a water chiller, which also functioned to filter out the IR radiation. 100 µL samples of the headspace were collected every hour to monitor gas evolution in the sample vials.

The headspace was analyzed by gas chromatography (GC) using an SRI model 8610C dual injector gas chromatograph with an 18’ HAYESEP-D column and a 3’ MS 5Å column, with simultaneous detection using FID and TCD detectors. The GC was programmed to hold 50 °C for 1 minute, ramp to 90 °C for 2 minutes, then hold at 90 °C for 2 minutes. H\(_2\) was analyzed on the
TCD detector, and CO was analyzed simultaneously on the FID detector. H₂ and CO concentrations were assessed by comparison of peak areas to a calibration curve of known concentration of these gases.

**BP/C₃N₄**

*Materials:* Black phosphorus was purchased from Smart Elements. Cobalt(II) chloride was obtained from Sigma-Aldrich. Triethanolamine (TEOA, 97%) was obtained from Acros Organics. Methanol (99.8%) was purchased from Fischer Scientific. Carbon nitride (C₃N₄) and single Co²⁺ sites on carbon nitride (Co@C₃N₄) were prepared using the microwave method and characterized as previously reported.

**BP Exfoliation:** Bulk black phosphorus (SmartElements, 10 mg) was added to a scintillation vial in an inert N₂ atmosphere glove box. A mixture of degassed acetonitrile and TEOA (10 mL, 4:1 v/v) was added to the vial and attached to a Hielscher UP100H ultrasonic processor with a MS3 sonotrode (100 W, 30 kHz) and the vial sealed around the probe using a rubber septum. The sample was probe sonicated for 7 h, then capped and sealed with tape before removal from the glovebox. The sample was further bath sonicated in a Branson 2510 Ultrasonic Cleaner for 24 h with a water chiller maintaining a constant 10 °C to prevent evaporation. The sample was then returned to the glovebox for use in photocatalytic experiments. The material was characterized by scanning electron microscopy (SEM) performed on a Tescan Lyra3 GMU FIB SEM. A drop of the exfoliated suspension was dropcast on a silicon chip and heated under vacuum, then attached to a metal stub with carbon paint prior to SEM analysis. Raman spectroscopy was performed using an NT-MDT NTEGRA Spectra microscope. The exfoliated sample was dropcast on a silicon chip and heated under vacuum to prepare the sample for Raman analysis. Exfoliation in methanol and
water followed the same general procedure, but bath sonication time increased to 56 h in water and decreased to 14 h in methanol.

**Photocatalysis**: Photocatalytic experiments were performed in triplicate. Each experiment was run in triplicate and gas chromatography of each experiment was measured independently. The error associated with the average gas production of the samples was found using the following equation:

\[
\sigma = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}
\]

In the event that any number of samples in the triplicate did not generate gas, those sample were removed from the set and the calculations proceeded with the non-zero values. In a general photocatalytic experiment, the specific C\textsubscript{3}N\textsubscript{4} species (2 mg) was added to a glass photocatalysis tube (7.9 mL). An amount of BP (0.02 – 1.00 mg; 1 mg mL\textsuperscript{-1}, MeCN:TEOA 4:1 v/v) was added as well as CoCl\textsubscript{2} (0.0026 M in MeCN) if used. The volume of the tube was brought up to a total volume of 4.0 mL with a mixture of MeCN and TEOA (4:1 v/v). A stir bar was added, and the tube was capped with a septum and sealed with parafilm. The tube was sonicated for 30 minutes in the dark in a sonicating bath with ice, then the headspace was purged with CO\textsubscript{2} (99.999%, Airgas) for 20 minutes.

The sample was then irradiated using a Xe lamp equipped with an AM 1.5G filter at a power of 100 mW cm\textsuperscript{-2} for 4 h with constant stirring. The temperature of the cell containing the samples was maintained at 18 °C by a water chiller, which also functioned to filter out the IR radiation. 100 µL samples of the headspace were collected every hour to monitor gas evolution in the sample vials.
The headspace was analyzed by gas chromatography (GC) using an SRI model 8610C dual injector gas chromatograph with an 18’ HAYESEP-D column and a 3’ MS 5Å column, with simultaneous detection using FID and TCD detectors. The GC was programmed to hold 50 ºC for 1 minute, ramp to 90 ºC for 2 minutes, then hold at 90 ºC for 2 minutes. H₂ was analyzed on the TCD detector, and CO was analyzed simultaneously on the FID detector. In some experiments, ND filters (0.3 O.D., 50 % transmission; 0.5 O.D., 31 % transmission) placed directly in front of the samples or a >400 nm long-pass filter was also used in addition to the AM 1.5G filter, which was placed next to the light source.
CHAPTER III

Oxidation of 4-Methylbenzyl Alcohol to 4-Methylbenzaldehyde

3.1 Background

Thus far, the reduction products of photocatalytic systems have been discussed, but this fails to take the oxidation half reaction into account, which is essential when considering a complete catalytic system. The use of sacrificial electron donors allows for specific studies into the reduction half reaction of photocatalytic systems, but these wasted molecules represent a great opportunity to increase the overall viability of these systems. For a substrate to be used in place of an SED, it must have a HOMO level thermodynamically aligned with the valence band of the semiconductor to allow for electron transfer. However, the value of using a substrate over an SED comes from the ability to derive value-added products from the oxidation of the substrate. Substrate oxidation is also used in various applications for air purification\textsuperscript{95–97} or dye degradation,\textsuperscript{98–100} where the focus of the photocatalytic system is on achieving a specific task, and not in the generation of value-added products. Due to the nature of this thesis, examples involving the generation of value-added organic products will be the focus of this section.

The target goal of photocatalytic oxidation is to convert less chemically useful molecules, whether that be due to a lack of reactivity or wide abundance, into more valuable intermediates. These intermediate molecules are called platform molecules, as they can be used to create a wide variety of products (Figure 3.1). One of the most common classes of platform molecule is an aldehyde, which is typically obtained by the oxidation of an alcohol (Figure 3.2). Aldehydes offer
a significantly more reactive carbon center for further chemical modification compared to alcohols, allowing for significant tunability in downstream products. A major advantage to using organic substrates in photocatalytic oxidation half reactions is that typical synthetic organic strategies require the use of large amounts of energy or harsh oxidants. By using a renewable energy source to power these reactions, the relatively gentle conditions of the photocatalytic approach can achieve remarkable results in a much greener way. In addition, heterogeneous catalysis has a distinct advantage over homogenous catalysis due to the need to separate out the oxidized substrates from the catalyst upon conversion. Homogenous catalysts based on ruthenium and iridium demonstrate high activity but pose significant difficulties in their application due to challenging product extraction. Physical separation of a solid from a liquid in a heterogeneous catalytic system allows for a much simpler isolation of the target product, and is a more scalable procedure as well. This has the potential for use on an industrial scale where the products of the oxidative reactions are the most valuable.

**Figure 3.1.** The well-studied platform molecule 5-Hydroxymethyl furfural (HMF) with some potential downstream products for polymers (red), biofuels (blue) and pharmaceuticals (yellow).
Figure 3.2. Proposed mechanism for oxidation of benzyl alcohol to benzaldehyde over photoactive In$_2$S$_3$ engineered with defects.$^{101}$

The idea for photochemical oxidative reactions were first proposed by Giacomo Ciamician in 1912 as an alternative to traditional synthetic measures that results in less waste.$^{104}$ These reactions did not involve any catalysts, but the same discovery that led to photocatalytic generation of H$_2$ also opened up the possibilities of organic substrate oxidation using photocatalysts.$^{28}$ However, a major issue that plagues this field of study is the lack of selectivity of the oxidative processes in aqueous media.$^{105}$

Shiraishi and Hirai observed this phenomenon when they attempted to oxidize benzene to phenol using TiO$_2$.$^{106}$ Low selectivity percentages of 8% and 6% were found using 100% and 58% anatase TiO$_2$, respectively, with a maximum 26% conversion of benzene being achieved with 100% anatase TiO$_2$. The researchers saw selectivity increase to a maximum of 83% upon the use of mesoporous TiO$_2$, while still dealing with a low 23% benzene conversion. A maximum 42%
conversion was achieved with increased irradiation time, and selectivity remained relatively constant at 81%.

Phenol is of great industrial interest due to the large scale production, typically from fossil fuels, for use in many products ranging from plastics to pharmaceuticals.\textsuperscript{107} Selectivity and yield of phenol from benzene oxidation has been improved using a variety of methods, including the use of precious metals such as gold or platinum on TiO\textsubscript{2},\textsuperscript{108–110} or through the use of other materials such as iron-loaded C\textsubscript{3}N\textsubscript{4} and various tungsten oxide nanoparticles.\textsuperscript{111–113} A maximum selectivity of phenol was achieved by Chen and co-workers using Fe-g-C\textsubscript{3}N\textsubscript{4} under visible light irradiation in a solvent mixture of acetonitrile, H\textsubscript{2}O, and H\textsubscript{2}O\textsubscript{2}. A maximum percent conversion of 50.8% was achieved by Tomita and co-workers using a Pt/WO\textsubscript{3} system under visible light irradiation in water.

Other common substrates for photocatalytic oxidation include alkanes and alcohols, as the C–C and C–H bonds in these molecules require high amounts of energy and harsh conditions to modify using typical organic synthetic strategies. Alkane oxidation can result in the introduction of an oxygen species, typically an aldehyde, into the carbon chain, thus providing a reactive handle for further modification. Alcohols are typically reduced to an aldehyde as well, providing the same ability to be more easily chemically modified. Recent advances in the partial oxidation of toluene show the potential for photocatalytic oxidation of the strong, inert sp\textsuperscript{3} hybridized C–H bond.\textsuperscript{102} Toluene can be oxidized to benzyl alcohol, benzaldehyde, benzoic acid, and benzyl benzoate, products that function as intermediates of a broad range of products including perfumes, pharmaceuticals, and preservatives.\textsuperscript{114} The typical commercial routes for the production of benzaldehyde from toluene involve chlorination of toluene with a subsequent saponification to produce the desired benzaldehyde.\textsuperscript{115} Benzoic acid production from toluene is also subjected to harsh conditions, in this case high temperatures of 165 °C in acetic acid with an overall low
conversion of less than 15%.\textsuperscript{114} TiO\textsubscript{2} with UV irradiation has been used to partially oxidize toluene to benzaldehyde with a selectivity of 65.3%,\textsuperscript{116} but was increased up to 89.1% upon additions of Ru on the TiO\textsubscript{2} surface.\textsuperscript{117} Other oxide materials including Bi\textsubscript{2}WO\textsubscript{6},\textsuperscript{118} and Bi\textsubscript{2}MoO\textsubscript{6}-Bi\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12}\textsuperscript{119} showed high selectivity percentages of 96% and 98.5% conversion to benzaldehyde respectively, which is a major advantage to be able to limit side products and target a single oxidative product.

One of the most common reactions performed in photocatalytic oxidation reactions is the conversion of benzyl alcohol to benzaldehyde. Much like the methods for oxidizing toluene, oxidation of alcohols to aldehydes typically relies on corrosive or toxic chemicals.\textsuperscript{120} The use of carbon nitride is advantageous over other photocatalysts, mostly metal oxides, due to the favorable photophysical properties of carbon nitride such as increased visible light absorption. Additionally, the use of these systems removes the need for harsh solvents or reaction conditions, as demonstrated by Zhou and co-workers, who were able to achieve a 52.2% conversion of benzyl alcohol to benzaldehyde with a 92.6% selectivity in trifluorotoluene at 60 °C.\textsuperscript{121} The researchers used a crystalline form of carbon nitride obtained by applying a melt-salt treatment on carbon nitride prepared by thermal polymerization of melamine. Carbon nitride synthesized from melamine or urea showed low conversion percentages but maintained relatively high selectivity towards benzaldehyde of ~66% and ~84%, respectively. The enhanced performance of the crystalline carbon nitride was attributed to the faster transfer and separation of charges in this form of the material, as well as an observed adsorption maximum of benzyl alcohol compared to the other forms of carbon nitride studied.

To increase the capabilities of more standard forms of carbon nitride, Kasap and co-workers used a hybrid photocatalytic system consisting of C\textsubscript{3}N\textsubscript{4} and a molecular nickel(II) bis(diphosphine) (NiP) catalyst.\textsuperscript{122} Under solar irradiation, the researchers found that the C\textsubscript{3}N\textsubscript{4}
functioned as the light harvesting material, transferring electrons to the NiP catalyst for proton reduction. The photogenerated holes at the surface were filled by oxidation of 4-methyl benzyl alcohol (4-MBA) to 4-methyl benzaldehyde (4-MBAd). The oxidation of 4-MBA also functioned as the source of protons used in the evolution of H₂ gas. The optimized system achieved a 66 ± 6% selective yield of 4-MBAd, and a 1:1 stoichiometry of H₂: 4-MBAd after 24 hours with yields of 21.3 ± 2.1 µmol and 19.8 ± 2.0 µmol respectively. It was concluded that the strength of the electron acceptor was the driving force for substrate oxidation, as a stronger driving force to separate electrons from their holes decreases the potential for recombination and allows the oxidative reactions to fill those holes preferentially. However, a disadvantage of this work was the demonstrated short lifetime of the NiP catalyst, which limited the maximum turnover of this system. The use of a molecular catalyst also leads to the previously discussed issue of efficient product isolation.

The use of two 2D materials to form a heterostructure has the distinct advantage of being fully and easily separable from the product matrix in a photocatalytic system. Wen and co-workers utilized this strategy by formation of a heterostructure between black phosphorus sheets with nickel nanoparticle active sites anchored on carbon nitride (Figure 3.3). Electron transfer between these materials is similar to what we observed, and was used to enhance the lifetime of the photogenerated holes. However, a key difference in their system was the placement of the catalytically active nickel nanoparticles on BP (BP@Ni). Electron transfer from C₃N₄ must occur before these metal active sites can accept electrons, potentially leading to a higher degree of recombination in the C₃N₄ material as it is the primary light absorber. When a 10% loading of BP@Ni on C₃N₄ was irradiated with simulated solar light using a 420 nm cutoff filter, a H₂ evolution rate of 2.1 mmol h⁻¹g⁻¹ was achieved when ethanol was used as a sacrificial electron
donor. When benzyl alcohol was used in place of ethanol, the rate decreased slightly to 1.31 mmol h$^{-1}$g$^{-1}$ over the first 4 hours and continued decreasing over time. After 10 hours of irradiation, a conversion yield of benzyl alcohol to benzaldehyde of 31.3% was achieved. A nearly 1:1 stoichiometric ratio of benzaldehyde to H$_2$ was also observed. The authors attribute these product yields to the enhanced charge separation observed in the system upon the addition of BP@Ni, as systems not containing this material showed very little photocatalytic activity.

Photoluminescence was used to determine the full effect that BP@Ni had on the charge separation in the system, and the researchers found that the C$_3$N$_4$/BP@Ni heterostructure showed a 62% quenching of the fluorescence intensity observed by C$_3$N$_4$ alone. The average lifetime of excited electrons in the C$_3$N$_4$/BP@Ni system increased to 7.48 ns from the 3.78 ns average observed by C$_3$N$_4$ alone. These results demonstrate the advantages of using a BP/C$_3$N$_4$ heterostructure for photocatalytic oxidative reactions that arise primarily as a result of the increased charge separation afforded by the heterojunction. Additionally, the materials are easily removed for facile isolation of a liquid phase product. The lack of extreme conditions and solvents is another valuable advantage that improves the potential for use of these systems for valuable organic product generation on an industrial scale.
3.2 Hypothesis

We hypothesized that the use of Co-loaded BP (Co@BP) in combination with Co@C₃N₄ could form a heterojunction capable of producing syngas at ratios comparable to what was observed with the BP/Co@C₃N₄ system, while also oxidizing 4-MBA to 4-MBAd. We anticipate that the addition of Co on BP will outperform bare BP in photocatalytic oxidation reactions. Simple photoreduction of Co²⁺ on the surface of BP is expected to yield Co@BP. The addition of Co on BP should result in an even larger increase in charge separation and lead to longer hole lifetimes, which will be crucial to drive the oxidation half-reaction. Further, the inclusion of catalytically active sites on both materials is expected to enhance the charge separation and prevent recombination. We do not expect 4-MBA to be oxidized as readily as TEOA, so the enhanced lifetime of the photogenerated holes should assist in boosting the percent conversion of 4-MBA.
We will also assess if Co@BP is capable of CO$_2$ reduction in addition to proton reduction. This may lead to the formation of lower H$_2$:CO ratios in these systems.

### 3.3 Results and Discussion

#### 3.3.1 4-MBA Oxidation with Bare BP

In order to establish a baseline of activity, the previously published BP/Co@C$_3$N$_4$ system was first studied to assess if oxidation of 4-MBA to 4-MBAd was possible. 4-MBA solution was added to a series of BP/Co@C$_3$N$_4$ samples with varying wt% loadings of BP. No H$_2$ evolution was observed over the course of 4 hours of simulated solar spectrum irradiation. With the use of TEOA as the SED, we previously found that BP exfoliation in the presence of TEOA increased the photocatalytic capabilities of the system likely due to increased surface interactions between the BP and TEOA. BP exfoliated in a 4-MBA solution in MeCN did result in H$_2$ evolution observed after 24 h of irradiation. It was generally found that lower wt% loadings of BP resulted in increased H$_2$ evolution, but the maximum evolved 0.21 µmol H$_2$ is significantly lower than the system with TEOA (Table 3.1).

**Table 3.1.** Comparison of H$_2$ production with different SEDs with BP/Co@C$_3$N$_4$.

<table>
<thead>
<tr>
<th>BP loading (mg)</th>
<th>Electron donor</th>
<th>H$_2$ (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>4-MBA</td>
<td>0.21$^a$</td>
</tr>
<tr>
<td>0.4</td>
<td>4-MBA</td>
<td>0.12$^a$</td>
</tr>
<tr>
<td>0.2</td>
<td>TEOA</td>
<td>0.23 ± 0.04$^b$</td>
</tr>
<tr>
<td>0.4</td>
<td>TEOA</td>
<td>0.45 ± 0.11$^b$</td>
</tr>
</tbody>
</table>

$^a$: values gathered after 24 h in N$_2$ atmosphere in singlicate. $^b$: values gathered after 4 h in CO$_2$ atmosphere in triplicate.
The formation and quantification of oxidation products was monitored using $^1$H nuclear magnetic resonance spectroscopy (NMR) by comparing the integration of the methylene peak of 4-MBA at 4.6 ppm to the aldehyde peak of 4-MBAd at 9.9 ppm.

The oxidation process of 4-MBA to 4-MBAd is the source of protons for the reductive evolution of H$_2$, so roughly equal amounts of both H$_2$ and 4-MBAd are expected. In addition, literature values indicate ranges of 15-20 µmol of 4-MBAd with ~20% conversion of 4-MBA to 4-MBAd over 24 h.$^{122}$ In our trials, no correlation between H$_2$ evolved and 4-MBAd present by $^1$H NMR spectroscopy was observed. We achieved a maximum value of 0.8 µmol 4-MBAd which translates to a conversion of less than 0.4%. The significantly lower than anticipated yield of 4-MBAd was attributed to the overall reduced catalytic activity of the system. We predicted that introduction of more catalytically active species into the system would increase the degree of charge separation and subsequently the lifetime of photogenerated holes, allowing for a higher degree of oxidation to occur.

Based on the previous success achieved by additions of CoCl$_2$ to the BP/C$_3$N$_4$ system, this same strategy was used with the replacement of TEOA with 4-MBA. After 24 hours of irradiation, only 0.049 µmol of H$_2$ was observed. Due to this small value and presumed reduced catalytic activity, the oxidation products were not analyzed. The active metal sites on C$_3$N$_4$ were changed to Pt (Pt@C$_3$N$_4$) in an effort to maximize H$_2$ evolution. After 24 h of irradiation, Pt@C$_3$N$_4$ alone produced 6.5 µmol H$_2$ and achieved a conversion of 4-MBA to 4-MBAd of 1.4%. The addition of 10% and 20% BP reduced the H$_2$ evolution to 4.0 and 4.5 µmol and gave 4-MBAd conversions of 0.1% and 0.7%, respectively. Increased loadings of BP gave similar H$_2$ evolution amounts but resulted in reduced percentage conversion. This was attributed to the starting concentration of 4-MBA in the photocatalytic experiments; it necessarily increased with increased BP loadings since
the BP was exfoliated with 4-MBA in solution. Similar levels of activity were seen in the systems with 30% – 50% BP indicating a similar oxidative activity is expected, but the percent conversions were significantly reduced due to the larger initial amounts of 4-MBA. The addition of CoCl₂ to the BP/Pt@C₃N₄ was studied in an attempt to increase the amount of catalytically active sites present in the system, with the aim to enhance charge separation and promote oxidation. Unfortunately, no significant increase in activity from the system was observed.

Atmosphere and solvent conditions were also tested to probe the oxidation capabilities of the system. In the presence of a CO₂ atmosphere, H₂ production by the BP/Pt@C₃N₄ system was reduced. The addition of CoCl₂ to the BP/Pt@C₃N₄ system under a CO₂ atmosphere resulted in more greatly decreased rates of H₂ evolution over 4 hours despite varied loadings of BP (Table 3.2). No CO evolution was observed at any loading of BP. Pt@C₃N₄ without BP in these conditions showed the highest 4-MBA conversion to 4-MBAd of 1.5%, with further additions of BP resulting in conversion percentages below 1% (Table 3.3). No significant change in percent conversion was observed as a function of BP loading.

**Table 3.2.** H₂ production and 4-MBA conversion percentages from BP/Pt@C₃N₄ with CoCl₂ additions in a CO₂ atmosphere after 4 h.

<table>
<thead>
<tr>
<th>BP loading (mg)</th>
<th>CoCl₂ (µmol)</th>
<th>H₂ (µmol)</th>
<th>% conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0</td>
<td>0.60</td>
<td>0.37</td>
</tr>
<tr>
<td>0.6</td>
<td>0.4</td>
<td>0.08</td>
<td>X³</td>
</tr>
<tr>
<td>0.6</td>
<td>0.8</td>
<td>0.03</td>
<td>X³</td>
</tr>
<tr>
<td>0.6</td>
<td>1.6</td>
<td>0.12</td>
<td>X³</td>
</tr>
</tbody>
</table>

³: no conversion determined due to low H₂ production. All data gathered in singlicate.
Table 3.3. H\textsubscript{2} production and 4-MBA conversion percentages from BP/Pt@C\textsubscript{3}N\textsubscript{4} in a CO\textsubscript{2} atmosphere after 4 h.

<table>
<thead>
<tr>
<th>BP loading (mg)</th>
<th>4-MBA loading (µmol)</th>
<th>H\textsubscript{2} (µmol)</th>
<th>% conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>200</td>
<td>0.10</td>
<td>1.6</td>
</tr>
<tr>
<td>0.2</td>
<td>200</td>
<td>0.13</td>
<td>1.4</td>
</tr>
<tr>
<td>0.4</td>
<td>400</td>
<td>0.40</td>
<td>0.6</td>
</tr>
<tr>
<td>0.6</td>
<td>600</td>
<td>0.60</td>
<td>0.4</td>
</tr>
<tr>
<td>0.8</td>
<td>800</td>
<td>0.62</td>
<td>0.4</td>
</tr>
<tr>
<td>1</td>
<td>1000</td>
<td>0.54</td>
<td>0.4</td>
</tr>
</tbody>
</table>

All data gathered in singlicate.

Water was added to the system with the goal of increasing the rate of 4-MBA oxidation to 4-MBA\textsubscript{d} by increasing the availability of protons. However, no H\textsubscript{2} evolution was observed under either a CO\textsubscript{2} or N\textsubscript{2} atmosphere when water was present in the system. The poor photocatalytic results obtained did not warrant further investigation as the oxidation production was too low and the focus of the work was to design a system capable of both reductive and oxidative product evolution.

3.3.2 4-MBA Oxidation with Co@BP

The poor catalytic activity observed with 4-MBA as a substrate was generally attributed to the increased rates of electron recombination due to the decreased rate of electron donation from 4-MBA compared to TEOA. Wen and co-workers demonstrated increased charge carrier separation by additions of Ni on BP which led to 4-MBA\textsubscript{d} conversion rates as high as 31\%.\textsuperscript{79} The effect of Co loaded on BP for the oxidation of 4-MBA to 4-MBA\textsubscript{d} was studied in an effort to improve upon the poor conversion seen with the BP/M@C\textsubscript{3}N\textsubscript{4} system.

Co@BP was synthesized using a microwave reduction method similar to the one used to form Co@C\textsubscript{3}N\textsubscript{4}. Briefly, BP (2 mg) was suspended in MeCN with CoCl\textsubscript{2} (20 µmol) and TEA (65
µL) and placed in a microwave reactor with stirring at 80 °C for 60 minutes. The solid material was recovered using centrifugation and rotary evaporation, then transferred to the glovebox where the sample was resuspended in MeCN to bring to a concentration of 1 mg mL⁻¹. The resulting Co@BP suspension showed no photocatalytic activity after 4 hours when combined with C₃N₄ or Pt@C₃N₄ with 4-MBA as the reducing substrate. Changing the solvent system from MeCN to H₂O had no effect on the activity of the system. Oxidation products were not analyzed by NMR spectroscopy due to the lack of gaseous products observed.

A second method for making Co@BP was implemented as a result of the lack of activity seen using the microwave method for Co@BP. A photoreduction of Co²⁺ on BP to form Co nanoparticles was performed using a blue LED in the presence of an MeCN/IPA solvent system, following a method previously reported for making BP@Ni. Briefly, the desired amount of exfoliated BP was suspended in a 3:1 MeCN:IPA (10 mL) mixture with CoCl₂ (1 mM) and stirred under blue LED irradiation for 30 minutes. The solid material was isolated by centrifugation and washed three times with EtOH before being re-dispersed in MeCN in a N₂ atmosphere glovebox. Literature precedent using a BP loading of 10% in a similar system produced optimal results for 4-MBA oxidation, so these conditions were tested with C₃N₄, Co@C₃N₄, and Pt@C₃N₄. The effects of using MeCN or H₂O as the solvent system were also tested (Table 3.4). A maximum H₂ evolution of 0.079 µmol after 4 h was achieved using a sample of Co@BP/Pt@C₃N₄ in MeCN, outperforming the Co@BP/Co@C₃N₄ and Co@BP/C₃N₄ systems in MeCN, which gave H₂ evolutions of 0.053 µmol and 0 µmol, respectively. MeCN proved to be the better solvent for the production of gaseous products compared to water, with Co@BP/C₃N₄ and Co@BP/Co@C₃N₄ systems in the presence of water producing 0.037 and 0.044 µmol H₂, respectively.

**Table 3.4.** Solvent effects on H₂ evolution using 0.2 mg Co@BP, 30 µmol 4-MBA, and various C₃N₄ species after 4 h.
No aldehyde peak was detected by NMR for any sample. All values gathered in singlicate.

Co@BP created using the photoreduction method proved to be more photocatalytically active than Co@BP made using the microwave method. However, NMR analysis of samples using photoreduced Co@BP in H₂O showed no peaks by NMR spectroscopy for 4-MBAd formation and only very small peaks for 4-MBA compared to previous experiments.

It was hypothesized that π-π stacking between the conjugated ring of 4-MBA and C₃N₄ or BP may result in the substrate being removed from the solution that was isolated for NMR analysis by adsorption to one or both material surfaces. To test this hypothesis, the solid materials were isolated after the photocatalytic experiment and washed with MeCN in an attempt to remove any 4-MBA or 4-MBAd. NMR spectroscopic analysis of the washed samples did not yield any additional peak intensity for 4-MBA or 4-MBAd.

### 3.4 Conclusion

The use of BP/M@C₃N₄ and Co@BP/M@C₃N₄ photocatalytic systems were tested for the oxidation of 4-MBA to 4-MBAd with simultaneous reduction of protons to H₂ or production of syngas. ¹H NMR spectroscopic analysis was used to determine the amount of 4-MBA generated over the course of the photocatalytic experiments by comparing the peak integration between the aldehyde proton and the methylene protons. This ratio and the starting concentration of 4-MBA were used to determine the final concentration of 4-MBAd. A maximum 4-MBA conversion of
0.7% was found using the BP/Pt@C₃N₄, which was significantly lower than the literature values of ~20% conversion. Pt@C₃N₄ alone achieved a 1.4% 4-MBA conversion, the highest value observed during these experiments. Two different methods for making Co@BP were tested to determine the optimal method to increase the percent conversion to 4-MBAd by increasing the population of catalytic sites to extend the lifetime of the photogenerated holes. No increase in catalytic conversion of 4-MBA was observed using Co@BP. Further attempts to oxidize 4-MBA to 4-MBAd were abandoned due to the low catalytic turnover observed and the work published by Wen and co-workers during the course of these experiments. It was determined that this work was not significantly different from the published work, and we decided to focus our efforts on selecting a different substrate for oxidation.

3.5 Experimental Section

Pt@C₃N₄

Materials: K₂PtCl₄ was purchased from Pressure Chemical. Ethylene glycol (99%) was purchased from Fischer Chemical. Carbon nitride (C₃N₄) was prepared using the tube furnace method as previously reported.⁷⁷

Synthesis: C₃N₄ (100 mg) was sonicated in ethylene glycol (16 mL) for 30 minutes. K₂PtCl₄ (4.3 mg, 2 wt% Pt) was added with stirring, and the mixture was refluxed at 150 °C for 2 h. The Pt@C₃N₄ was centrifuged and washed three times with water and ethanol. The isolated solid was dried in an oven overnight at 110 °C.
**Co@BP**

**Materials**: Black phosphorus was purchased from Smart Elements. Cobalt(II) chloride was obtained from Sigma-Aldrich. Acetonitrile (MeCN, 99.9%) was purchased from Sigma-Aldrich. Triethylamine (TEA, 99.5%) was purchased from Acros Organics. Isopropyl alcohol (IPA, 99%) was obtained from Pharmco.

**Microwave method**: Black phosphorus was exfoliated as described previously. In a microwave reaction tube in a N₂ glovebox, BP in MeCN (2 mg, 2 mL) and CoCl₂ (20 µmol) were combined with TEA (65 µL) and a stir bar, then capped and transferred to the reactor. The temperature was held at 80 °C for 60 minutes with a constant power of 20 W. The resulting solution was centrifuged to isolate the solid material and remove excess CoCl₂ before removing the solvent using a rotary evaporator. The isolated Co@BP was transferred back to the glovebox and re-dispersed in MeCN (1 mg mL⁻¹).

**Photoreduction method**: Black phosphorus was exfoliated as described previously. In a Schlenk tube in a N₂ atmosphere glovebox, BP in MeCN (1 mg, 1 mL) and IPA (2.5 mL) were combined, and the total volume was brought to 10 mL with MeCN. CoCl₂ was added to make a 1 mM solution in the Schlenk tube, and a stir bar was added. The Schlenk tube was removed from the glovebox and placed in front of a blue LED array designed by Nick Pierini and stirred for 30 minutes. The resulting solution was centrifuged and washed with EtOH three times, then dried and transferred back to the glovebox and re-dispersed in MeCN (1 mg, 1 mL).

**Photocatalysis**

**BP**: In a general photocatalytic experiment, the specific C₃N₄ species (2 mg) was added to a glass photocatalysis tube (7.9 mL). BP exfoliated as previously described with additions of 4-MBA
(0.1524 g, 1.24 mmol) added prior to sonication for certain reactions. An amount of BP (0.1 – 1.00 mg; 1 mg mL⁻¹, MeCN) was added as well as CoCl₂ (0.0026 M in MeCN) if used. 4-MBA was added (0.75 – 1.00 mL; 40 mM, MeCN) if the BP species used was not exfoliated with 4-MBA. The total volume of the tube was brought up to a total volume of 4.0 mL with MeCN or H₂O depending on the experiment. A stir bar was added, and the tube was capped with a septum and sealed with parafilm. The tube was sonicated for 30 minutes in the dark in a sonicating bath with ice, then the headspace was purged with CO₂ (99.999%, Airgas) for 20 minutes, if used.

The sample was irradiated, and the headspace was analyzed as previously described. Samples were centrifuged to remove solid material prior to ¹H NMR spectroscopic analysis, solvent was removed using a rotary evaporator and dissolved in CDCl₃. The organic liquid phase products were analyzed using a Bruker BioSpin 500 MHz NMR spectrometer and the ratio of the peak integrations for the characteristic aldehyde peak of 4-MBAd at ~9.9 ppm and the methylene peak of 4-MBA at ~4.63 ppm was used to determine the percent conversion to 4-MBAd. The following equation was used:

\[ \text{Conv. %} = \frac{2}{M} \times 100 \]

Where M is integration of the methylene peak when the aldehyde peak integration is set to 1. The 2 is because methylene integrates to 2 when aldehydes integrate to 1.

**Co@BP:** In a general photocatalytic experiment, the specific C₃N₄ species (2 mg) was added to a glass photocatalysis tube (7.9 mL). An amount of Co@BP (0.1 – 1.00 mg; 1 mg mL⁻¹, MeCN) prepared using the specified method was added as well as CoCl₂ (0.0026 M in MeCN) if used. 4-MBA was added (0.75 – 1.00 mL; 40 mM, MeCN) and the total volume of the tube was brought up to 4.0 mL with MeCN or H₂O depending on the experiment. A stir bar was added, and the tube
was capped with a septum and sealed with parafilm. The tube was sonicated for 30 minutes in the dark in a sonicating bath with ice, then the headspace was purged with CO\textsubscript{2} (99.999\%, Airgas) for 20 minutes if used.

The sample was irradiated, and the headspace was analyzed as previously described. Samples were centrifuged to remove solid material prior to \textsuperscript{1}H NMR spectroscopic analysis, solvent was removed using a rotary evaporator and dissolved in CDCl\textsubscript{3}. The organic liquid phase products were analyzed using a Bruker BioSpin 500 MHz NMR spectrometer and the ratio of the peak integrations for the characteristic 4-MBA\textsubscript{d} aldehyde peak at ~9.9 ppm and the 4-MBA methylene peak at ~4.63 ppm was used to determine the percent conversion to 4-MBA\textsubscript{d} using the equation above.
CHAPTER IV

Oxidation of Glucose to Value-Added Products

4.1 Background

Biomass and biomass-derived molecules are an excellent target for photocatalytic oxidation to value-added products as they are renewable, highly available, and comprised of different types of molecules that can be valorized to a wide range of products.\textsuperscript{124} In 2015, the EU had 8500 PJ y\textsuperscript{-1} of residual biomass, enough to power all of Italy and Belgium combined.\textsuperscript{125} Biomass can be valorized to form products ranging from hydrogen\textsuperscript{126–128} to biodiesel\textsuperscript{129,130} to 5-hydroxymethylfurfural (HMF),\textsuperscript{131–133} a major intermediate for many biochemicals. Glucose is one of the most common bioavailable molecules as it is a major component of many plant-based life forms, making it an ideal target to use in photocatalytic oxidation reactions. The main molecules that are targeted by researchers pursuing glucose oxidation are formate, gluconic acid, and glucaric acid, with other oxygenated carbonaceous products possible.

Formate is of particular interest due to being worth significantly more than glucose, as well as having a high volumetric energy density of 6.4 MJ L\textsuperscript{-1}.\textsuperscript{134} This energy density is over 3 times larger than H\textsubscript{2} at 200 bar, and formate has shown the ability to act as a hydrogen source for the modification of biomass-based platform molecules. The oxidation of glucose to formate proceeds by a complicated mechanism that is not yet fully understood, but researchers have proposed potential mechanistic pathways leading to the desired products. Sanwald and co-workers present a “current doubling” mechanism that involves glucose injecting electrons into the photogenerated holes on TiO\textsubscript{2}, thus creating radicals that lead to eventual ring opening and formation of a formate.
unit (Figure 4.1). Da Vià and co-workers proposed a ring-opened glucose molecule undergoing either α-scission with formate formed through hydrolysis to the C\textsubscript{n-1} aldose or through C–C-cleavage, with the latter the pathway expected in neutral solutions (Figure 4.2).

**Figure 4.1.** “Current doubling” mechanism for glucose oxidation to formate.

**Figure 4.2.** α-scission and oxidative decarboxylation pathways for glucose oxidation to formate.
As seen with previous photocatalytic oxidation studies, selectivity of products remains a challenge when using glucose. An interesting note about the other by-products of glucose oxidation is that they are nearly all valuable, either in terms of monetary value or as a platform molecule for higher order complex molecules. A lack of selectivity, however, muddies the potential for these systems to be used on larger scales.

Zhang and co-workers attempted to tackle this issue and targeted formation and quantification of three organic acid oxidation products: gluconic acid, glucaric acid, and formic acid. They employed an iron thioporphyrazine modified SnO$_2$ photocatalytic system in aqueous solution using atmospheric O$_2$ as the oxidant.$^{137}$ These researchers found that a maximum organic acid content of 52.2% was achieved using a 0.1% loading of the FePz(SBu)$_8$ catalyst on SnO$_2$ (Figure 4.3). This gave an overall glucose conversion of 34.2%, with the highest selectivity to gluconic acid at 32.9%, followed by glucaric acid at 12.9% and formic acid at 6.4% conversion, respectively.

Figure 4.3. Structures of gluconic and glucaric acid (left) and photocatalytic results (right) with reaction conditions: catalyst (20 mg), glucose (1 mmol L$^{-1}$, 50 mL, aq.), air flow rate of 0.4 L min$^{-1}$. $^{138}$

A maximum selectivity for formic acid was observed using P25 TiO$_2$ instead of SnO$_2$, but remained relatively low at 16.8% selectivity with a total organic acid content of 20.9%. $^{124}$ This is
of particular interest due to the strong potential for formate to serve as a source of liquid H₂ owing to the high energy density possessed by this molecule. The researchers were able to change the selectivity of the system by controlling the pH of the solution; more acidic conditions led to a significantly reduced glucose conversion with gluconic acid at a low selectivity being the only target product identified. Additions of base increased the glucose conversion percentage and gave a high total selectivity for gluconic and formic acid but resulted in no detectable glucaric acid concentration. In the absence of O₂, a significantly lower glucose conversion percentage was observed compared to the maximum 34.2%, but selectivity remained high for gluconic acid. Glucaric acid was more greatly affected by the lack of O₂, as the selectivity was diminished from 8.7% to 1.0%. In the absence of either light or SnO₂, only trace amounts of oxidation products were observed, indicating that this is indeed a photocatalytic system where the SnO₂ functions as the main light absorber.

Selectivity towards formate from glucose oxidation was studied by Da Vià and co-workers using various forms of TiO₂ in MeCN/H₂O solvent under visible or UVA irradiation.¹³⁵ Anatase, rutile, and P25 TiO₂ were used to determine the selectivity towards different organic products, including gluconic acid, arabinose, erythrose and glyceraldehyde, and formic acid. The largest glucose percent conversion of 42% was achieved only when using a low 2.8 mM concentration of glucose, and when this concentration was increased to 20 mM this value dropped to 5%, a roughly scalar decrease. P25 TiO₂ with visible irradiation resulted in a maximum formic acid selectivity of 48%, but the total 3.7% glucose conversion remains disappointingly low. Worth noting, however, is that the use of UVA irradiation with P25 TiO₂ resulted in a formic acid selectivity decrease to 22%. Anatase and rutile TiO₂ both performed better with UVA irradiation compared to visible irradiation, an undesirable characteristic when trying to design a photocatalytic system.
authors also explored the role of the solvent system and found significant decreases in total percent glucose conversion in the presence of pure water. This result was hypothesized to be due to increased singlet oxygen lifetimes in the presence of polar, aprotic solvents, but no further discussion was given.

Jin and co-workers also experimented with solvent conditions to increase the overall percent conversion of glucose to formate with high selectivity. These researchers included 0.06 M NaOH solution with P25 TiO$_2$ at 50 °C and irradiated the sample with visible light to achieve 79.6% conversion of glucose, but a relatively low formate selectivity of 14.2%. In the absence of NaOH, only a 9.7% glucose conversion was observed, a result that was attributed to the behavior of oxidative radicals in the presence of alkali. The increased presence of hydroxyl anions accelerates the production of active oxidative radicals, which in turn causes a “shield effect” that hinders both glucose adsorption and formic acid desorption. A major factor that limited the selectivity for formate was the temperature, as a large yield of lactic acid was observed. The researchers remarked that the conversion of glucose to lactic acid was approximately 74.28 kJ mol$^{-1}$, and the temperature increased to 50 °C as a result of irradiation which likely played a strong role in this process. Furthermore, the oxidation of glucose to formic acid is exothermic, making temperature control a crucial component of selectively producing formate from glucose; as such, increased lactic acid content was observed with increasing temperature (Figure 4.4). At 25 °C, glucose conversion dropped to just over 60%, but the formate selectivity increased to 23.4%. When the irradiation time was extended to 12 h, complete conversion of glucose with a 33.1% selectivity towards formate was achieved. The combination of low temperatures and low alkalinity solvents leading to full conversion of glucose with appreciable selectivity towards formate is a very promising result in the use of semiconducting materials for photocatalytic glucose oxidation.
Other materials have been used for glucose oxidation to value added chemicals. Zhang and co-workers used a C₃N₄/CoPz (cobalt tetra(2,3-bis(butylthio)maleonitrile)porphyrazine) composite material with aqueous H₂O₂ to perform selective photocatalytic oxidation of glucose to gluconic and glucaric acid. The C₃N₄/CoPz composite was made by soninating a dichloromethane solution of CoPz with C₃N₄ for 30 minutes followed by 12 hours of stirring, and the composite was isolated by distillation. Spectroscopic data of the C₃N₄/CoPz composite indicates the materials interact through π–π stacking. To enhance the adsorption of glucose on the surface of the C₃N₄/CoPz composite material, the samples were suspended in aqueous glucose solutions and stirred prior to the addition of H₂O₂. These mixtures were irradiated with a 300W Xe lamp. Interestingly, the researchers found that in the absence of catalyst, a 91.3% glucose conversion was achieved but with a low total selectivity for the desired acids (gluconic and glucaric acid) of 23%. C₃N₄ alone was able to increase the selectivity to 51.9%, but the C₃N₄/CoPz composite showed the highest selectivity at 79.4%. This maximum selectivity was observed with a 0.5 wt% CoPz content. Increased loadings of CoPz led to larger glucose conversion percentages,
coupled with decreased selectivity at a CoPz content of 2 wt%. The authors hypothesize that the reduction in selectivity with increased CoPz content was due to the increased presence of reactive species attacking the organic acids instead of the remaining glucose molecules, thus leading to over-oxidized products and the production of CO$_2$ due to the complete mineralization of glucose.

Adsorption studies utilizing UV-Vis spectroscopy to determine concentration of acid species in solution before and after soaking found that the C$_3$N$_4$/CoPz composite had a lower adsorption capacity for gluconic and glucaric acid compared to C$_3$N$_4$, which should help prevent the over-oxidation of the products as the target acids are less likely to remain on the surface of the catalyst once formed. The ability to increase the selectivity of C$_3$N$_4$, a stable and sustainable light absorbing material, by the addition of molecular catalysts inspires confidence that the use of the BP/C$_3$N$_4$ system may also be capable of glucose oxidation and might provide enhanced selectivity of products. The authors also showed the C$_3$N$_4$/CoPz composite to be recyclable over at least 5 cycles, a major boon when considering the implementations of this type of material in larger scale catalytic systems.

No studies involving the use of BP for photocatalytic oxidation of glucose have been reported to date. The use of BP has the potential for use in these types of applications due to the propensity for BP to form robust P–O bonds, which may assist in supporting the glucose substrate on the material surface increasing the likelihood for catalytic transformation. The proposed pathways for glucose oxidation typically involve the adsorption of glucose onto the catalytic surface through covalent bond formation by the hydroxyl groups. In the absence of other sources of oxygen, glucose is expected to preferentially bond to BP rather than the C$_3$N$_4$ in our system. Additionally, the proposed Type I heterojunction in the BP/C$_3$N$_4$ system should result in
photogenerated hole migration to BP, advantageously sequestering both the holes and substrate needed to perform the oxidation reaction in one material.

Previous work by Uekert et. al. proposed that the main issue affecting photocatalytic systems involving substrate oxidation is electron recombination, prohibiting both the reductive and oxidative capabilities of the TiO$_2$/Ni$_2$P system studied.$^{140}$ The heterojunction formed by the two materials in our work, as well as the presence of Co active sites on one or both materials, should help to remediate these issues and makes the choice of the BP/C$_3$N$_4$ photocatalytic system a viable and valuable one for simultaneous syngas generation and glucose oxidation to value added chemicals.

4.2 Hypothesis

We hypothesize the use of glucose as an oxidation substrate in the photocatalytic BP/C$_3$N$_4$ system will result in simultaneous reductive generation of syngas as well as oxidative formation of value-added products, specifically formate. The use of Co active sites on BP, C$_3$N$_4$, or both will help to alleviate the charge recombination issues that hampered other photocatalytic systems. Charge separation is expected to be the most important factor leading to optimized glucose oxidation as increased hole lifetime is expected to increase the likelihood for oxidation to occur. Due to the Type I heterojunction formed, oxidation is expected to occur at the BP surface due to the transfer of photogenerated holes from C$_3$N$_4$ to BP. We hypothesize an oxidation mechanism similar to the “current doubling” mechanism proposed by Sanwald and co-workers due to the known propensity for BP to form P–O bonds.$^{136}$ Higher loadings of BP are expected to result in a higher glucose conversion for these reasons. Overall gas production is anticipated to be lower.
compared to the system using TEOA due to the reduced rate of electron transfer from glucose compared to TEOA.

4.3 Results and Discussion

4.3.1 Formate Detection

Formate detection in aqueous solution is a challenge due to the extremely close boiling points of water and formic acid and the high solubility of formate salts. This makes the isolation of formate or formic acid from water a difficult process, resulting in the need for a method of detection that is capable of handling the complex sample matrix. In this work, low concentrations of formate in the range of $10^{-7} – 10^{-8}$ mol are expected, so the detection method must also have a limit of quantification suitable for these experiments. Further, the concentration of formate cannot be increased due to the difficulties of removing water from the sample matrix. The most analysis method for quantification of formate is ion chromatography, which allows selective isolation of formate from other anions in solution and can achieve quantification at very low concentrations. Ion chromatography was not used during the course of this work as the instrument was not available during the course of experimentation and we had to devise an alternate method for formate quantification.

A formate detection assay designed by Maeda and co-workers was investigated for use in these experiments. This assay employs UV-Vis spectroscopic monitoring of the signal of the Mn in KMnO$_4$ being reduced by formate anions. A signature UV-Vis absorption at 545 nm belonging to MnO$_4^{-1}$ decreases over time as MnO$_4^{-1}$ is reduced to MnO$_2$, and a calibration curve can be developed using this technique. Briefly, aqueous solutions of formic acid and KMnO$_4$ were
combined in a cuvette and brought to a total volume of 2 mL with water. The reaction was allowed to proceed for a specific amount of time before the UV-Vis spectrum was obtained for the sample. A major issue encountered using this technique was inconsistent timing between adding the components of the assay and collecting the UV-Vis spectrum. This changes the amount of MnO$_4^{-1}$ reduction that can be observed, as the reaction was observed to reach equilibrium in 20 minutes. However, repeated trials to generate the calibration curve showed a wide range of inconsistencies in the absorbance values even when samples were allowed to reach equilibrium. More consistent results were seen with higher concentrations of formate with spectra collected 30 seconds after the reaction began. Literature precedent supports the use of shorter time scales for more consistent UV-Vis measurements, but the increased concentration of formate generated a calibration curve that was not ideally suited to the ranges of formate concentration expected from the experiments. The calibration curve was made on the mM scale while data was collected and analyzed on that calibration curve in the µM range. The earlier inconsistencies observed with formate at low concentrations, as well as a scale-incompatible calibration curve, led to the abandonment of the KMnO$_4$ assay for formate detection.

$^1$H NMR spectroscopy was used to measure the concentration of formate in samples after photocatalysis with the use of an internal standard for quantification. tert-Butanol was used as the internal standard because the distinctive singlet peak at 1.24 ppm from the nine CH$_3$ protons did not overlap with the peaks of any other components in the system. A constant volume of a t-butanol stock solution in D$_2$O was added to filtered photocatalysis samples and placed in an NMR tube for analysis. Photocatalysis samples were filtered immediately after the final headspace sample was obtained and injected into the GC. By $^1$H NMR spectroscopy formate shows a single peak at ~8.45 ppm, and the ratio of the integration values for the two formate and t-butanol peaks can be
compared to determine the concentration of formate present. The difficulty in this method arises in the presence of water, as the peak for water dominates a significant portion of the spectrum. In fact, the formate peak baseline is affected by the water peak and a special baseline correction strategy had to be devised to flatten out the spectrum over this region to get consistent integration values. Consistency in baseline correction is also a major factor, as small changes in where the baseline integration points are chosen can have a significant effect on the final integration values. This method was chosen as the most appropriate technique for data analysis in our system, as standard methods for spectral interpretation and baseline correction could be implemented to ensure all spectra were treated identically.

4.3.2 Photocatalytic Oxidation

Initial experiments were performed using various M@C₃N₄ species to determine the effect of the catalytic species on glucose oxidation. Additionally, the differences between BP exfoliated via sonication and microwaving methods were explored. Trials were performed with an N₂ atmosphere to promote the thermodynamically favored reduction of protons to H₂. The majority of H₂ observed was produced during the sonication of the photocatalysis tubes prior to irradiation, with little evidence of photocatalytic H₂ evolution (Table 4.1). The oxidation products were analyzed using the UV-Vis assay method previously described, so the formate concentrations obtained were unreliable and not quantifiable.
Table 4.1. H$_2$ evolution from BP exfoliated two different ways with various C$_3$N$_4$ species and glucose.

<table>
<thead>
<tr>
<th>BP exfoliation method</th>
<th>C$_3$N$_4$ species</th>
<th>$t_0$ H$_2$ (µmol)</th>
<th>$t_4$ H$_2$ (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sonication</td>
<td>C$_3$N$_4$</td>
<td>0.400</td>
<td>0.439</td>
</tr>
<tr>
<td>Sonication</td>
<td>Co@C$_3$N$_4$</td>
<td>0.225</td>
<td>0.312</td>
</tr>
<tr>
<td>Sonication</td>
<td>Pt@C$_3$N$_4$</td>
<td>0.541</td>
<td>0.512</td>
</tr>
<tr>
<td>Microwave</td>
<td>C$_3$N$_4$</td>
<td>0.276</td>
<td>0.832</td>
</tr>
<tr>
<td>Microwave</td>
<td>Co@C$_3$N$_4$</td>
<td>0.219</td>
<td>0.303</td>
</tr>
</tbody>
</table>

50 µmol glucose, 2 mg C$_3$N$_4$ species, 0.4 mg BP. All values gathered in singlicate.

Co@BP redispersed in MeCN was combined with C$_3$N$_4$ and Pt@C$_3$N$_4$ for photocatalytic glucose oxidation. The only source of water in the tubes was from the glucose solution compared to the previous experiments that contained mostly water. These samples containing Co@BP showed no H$_2$ evolution after sonication, and only Co@BP/Pt@C$_3$N$_4$ showed photocatalytic H$_2$ production, reaching a maximum H$_2$ evolution of 1.09 µmol after 24 h. Co@BP/C$_3$N$_4$ showed no photocatalytic evolution of H$_2$. These trials were repeated with MeCN replaced by water, and no H$_2$ evolution was observed during sonication, indicating a mechanochemical reaction between bare BP and glucose may result in the generation of H$_2$. Maximum H$_2$ evolution of 0.96 µmol after 24 h was achieved using the Co@BP/Pt@C$_3$N$_4$ system, indicating that the amount of water present in the sample has little effect on H$_2$ evolution when using Pt@C$_3$N$_4$. However, increased water content leads to H$_2$ production using C$_3$N$_4$ and Co@C$_3$N$_4$, meaning that water likely plays a larger role in the oxidation of glucose when using materials loaded with a less active catalyst compared to Pt. The oxidation products were only analyzed using the UV-Vis assay method previously described, so the formate concentrations obtained were unreliable and not quantifiable.

The effects of Co@BP concentration for both H$_2$ production as well as glucose oxidation to formate were studied. Co@C$_3$N$_4$ was chosen as the M@C$_3$N$_4$ species for these experiments due to the previously observed activity with BP. The decreased catalytic capabilities compared to
Pt@C₃N₄ was justifiable in order to make use of a cheaper, more earth-abundant metal for catalysis. A maximum H₂ evolution after 4 h of 0.249 µmol was achieved in a 10% Co@BP/Co@C₃N₄ sample with a formate production of 0.168 µmol formate determined by NMR analysis (Figure 4.5), an overall glucose conversion to formate of 0.34%. Co@C₃N₄ alone produced 0.131 µmol of H₂ after 4 h with a formate production of 0.344 µmol and a conversion of 0.69%.

Surprisingly, in the absence of a CO₂ atmosphere, CO was detected for all samples with complete mineralization of glucose hypothesized as the source of the detected CO. The 10% Co@BP/Co@C₃N₄ sample resulted in 0.249 µmol of H₂ and 0.079 µmol of CO after 4 h, giving a syngas ratio of 3.15. Significantly reduced CO production of 0.005 µmol was observed by a sample of Co@C₃N₄ alone. These experiments were repeated with a CO₂ headspace which resulted in no photocatalytic activity observed over the course of a typical 4 h photocatalytic experiment. Co@BP was replaced with Ni@BP, and all loadings of Ni@BP in Ni@BP/Co@C₃N₄ samples showed ~10 times less gaseous products compared to equivalent Co@BP/Co@C₃N₄ systems (Table 4.2).

Table 4.2. Effects of BP species and loading on H₂ evolution and glucose percent conversion to formate.

<table>
<thead>
<tr>
<th>BP species</th>
<th>BP loading (mg)</th>
<th>H₂ (µmol)</th>
<th>% conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni@BP</td>
<td>0.1</td>
<td>0.031</td>
<td>0.23</td>
</tr>
<tr>
<td>Ni@BP</td>
<td>0.2</td>
<td>0.018</td>
<td>0.3</td>
</tr>
<tr>
<td>Ni@BP</td>
<td>0.4</td>
<td>0.011</td>
<td>0.22</td>
</tr>
<tr>
<td>Co@BP</td>
<td>0.1</td>
<td>0.055</td>
<td>0.74</td>
</tr>
<tr>
<td>Co@BP</td>
<td>0.2</td>
<td>0.096</td>
<td>0.46</td>
</tr>
<tr>
<td>Co@BP</td>
<td>0.4</td>
<td>0.057</td>
<td>0.59</td>
</tr>
</tbody>
</table>

2 mg Co@C₃N₄, 50 µmol glucose, H₂O. Analyzed after 4 h. All values gathered in singlicate.
Some of the hypothesized mechanisms for glucose oxidation to formate involve oxygen as the ultimate reductant. In our trials, no additional oxidants have been added and all experiments have been carried out in either N₂ or CO₂ atmospheres with negligible oxygen concentration in the sample tubes. We hypothesized that the inclusion of oxygen in the tubes would increase the oxidation of glucose while possibly limiting the evolution of gaseous products. The decrease in gaseous products is expected due to electron scavenging and formation of oxygen radical species. These radicals can be used in oxidative reactions, while the reduced number of excited electrons will subsequently reduce those available for proton or CO₂ reduction observed in these experiments. Direct comparisons of open and closed headspace samples containing 10% Co@BP
with C₃N₄ or Co@C₃N₄ were performed to determine the effects of exposure to air on the final concentration of formate after 4 h of irradiation. Both closed headspace systems outperformed their open headspace counterparts, likely due to the lack of oxygen present in solution (Table 4.3). These experiments were performed using deoxygenated solvents, and the catalytic processes occur in the solution phase, where atmospheric oxygen is largely inaccessible.

**Table 4.3.** Effect of open vs. oxygenated, closed system and C₃N₄ species on formate production.

<table>
<thead>
<tr>
<th>C₃N₄ species</th>
<th>Formate (µmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃N₄&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.037</td>
</tr>
<tr>
<td>Co@C₃N₄&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.029</td>
</tr>
<tr>
<td>C₃N₄&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.053</td>
</tr>
<tr>
<td>Co@C₃N₄&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.152</td>
</tr>
</tbody>
</table>

<sup>a</sup>: open system. <sup>b</sup>: oxygenated, closed system. 2 mg C₃N₄ species, 0.2 mg Co@BP, 50 µmol glucose. Analyzed after 4 h. All values gathered in singlicate.

A method for purposely oxygenating samples post-sonication was developed in order to introduce oxygen into the sample solution just before irradiation to minimize any potential negative impacts on BP from degradation. The oxygenated 10% Co@BP/Co@C₃N₄ sample generated 0.07 µmol H₂, the maximum amount of H₂ after 4 h from oxygenated Co@BP/Co@C₃N₄ systems ranging from 5% – 50% wt% loading of Co@BP in the sample. This is a significant decrease from the oxygen-free 10% Co@BP/Co@C₃N₄ sample, but the oxygenated system showed an increase in formate generation to 0.453 µmol compared to 0.168 µmol from the oxygen-free sample. The oxygenated 5% Co@BP/Co@C₃N₄ system produced the highest concentration of formate at 0.733 µmol, a glucose conversion percentage of 1.47%. This value is the maximum glucose conversion observed over the course of experimentation, indicating the importance of oxygen in the oxidation of glucose to formate.

The low glucose to formate conversion rates observed are a point of concern as these values are far from what has been reported in the literature. Previous experiments were conducted with
50 µmol of glucose in each tube, and the effects of lower glucose concentrations were studied using the oxygenated 10% Co@BP/Co@C₃N₄ system as the model system. Glucose loadings ranging from 1-10 µmol in the sample tube were tested and compared to the previous work with 50 µmol. The largest glucose conversion of 14.4% was achieved using 1 µmol glucose, with percent conversion of 3.9% and 3.4% for 5 µmol and 10 µmol of glucose, respectively (Table 4.4). Compared to samples with 50 µmol of glucose with a 0.91% conversion, these samples are more efficient in overall conversion but suffer from a lack of total formate formation, with all glucose loadings less than 50 µmol yielding significantly less formate. Varied Co@BP loadings decreased the formate concentration below the LOQ of NMR spectroscopic analysis.

Table 4.4. Effects of glucose loading on percent conversion using the 10% Co@BP/Co@C₃N₄ system.

<table>
<thead>
<tr>
<th>Glucose (µmol)</th>
<th>H₂ (µmol)</th>
<th>% conv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.029</td>
<td>14.4</td>
</tr>
<tr>
<td>5</td>
<td>0.042</td>
<td>3.9</td>
</tr>
<tr>
<td>10</td>
<td>0.092</td>
<td>3.4</td>
</tr>
</tbody>
</table>

2 mg CoC₃N₄, 0.2 mg Co@BP, H₂O. Analyzed after 4 h. All values gathered in singlicate.

4.4 Conclusion

The glucose oxidation capabilities of the Co@BP/M@C₃N₄ system were studied to determine the optimal conditions to maximize glucose oxidation to formate, a valuable chemical with the potential to serve as a source of liquid hydrogen storage for fuels. Sample conditions were found to be important in terms of what products were generated during irradiation, with increased concentrations of water leading to more catalytic activity. Oxygen was also found to have a significant impact on glucose oxidation, with increases in formate production observed when the samples were oxygenated. The maximum amount of formate generated after 4 h of irradiation was 0.733 µmol with an oxygenated solvent using 10% Co@BP/Co@C₃N₄ as the catalyst, but the
highest glucose percent conversion of 14.4% was achieved by a 1 µmol glucose loading in a 10% Co@BP/Co@C₃N₄ system. A lack of photocatalytic activity was observed in the presence of a CO₂ atmosphere, but CO was observed and hypothesized to be due to complete mineralization of glucose. The lack of efficient CO evolution led to highly inflated syngas ratios, with the lowest ratio achieved being 3.15 from an oxygen-free 10% Co@BP/Co@C₃N₄ sample.

More favorable glucose conversion percentages can be achieved by lowering the initial concentration of glucose in trials, but this has been shown to come at the price of reduce formate evolution. While efficiency of the system is of importance, the amount of formate that can be generated during these experiments is more valuable. Future efforts should be focused on increasing the efficiency of systems that show the highest rate of formate evolution.

4.5 Experimental Section

Photocatalytic Glucose Oxidation

Materials: Co@BP, C₃N₄, Co@C₃N₄, and Pt@C₃N₄ were synthesized as previously described. Acetonitrile (MeCN, 99.9%) was purchased from Sigma-Aldrich. Glucose was purchased from Sigma-Aldrich.

Photocatalysis: In a general photocatalytic experiment, the specific C₃N₄ species (2 mg) was added to a glass photocatalysis tube (7.9 mL). An amount of Co@BP (0.1 – 1.00 mg; 1 mg mL⁻¹, MeCN) prepared using the previously mentioned method was added. Glucose was added (0.01 – 0.50 mL; 1–50 µmol glucose, H₂O) and the total volume of the tube was brought up to 4.0 mL with MeCN or H₂O depending on the experiment. A stir bar was added, and the tube was capped with a septum.
and sealed with parafilm. The tube was sonicated for 30 minutes in the dark in a sonicating bath with ice, then the headspace was purged with CO$_2$ (99.999%, Airgas) for 20 minutes if used.

The sample was irradiated, and the headspace was analyzed as previously described. Solid materials in samples after photocatalysis were removed using a 0.22-micron syringe filter immediately after experimentation. Samples were analyzed using either the KMnO$_4$ assay or $^1$H NMR spectroscopic analysis as described below.

**KMnO$_4$ Assay**

**Materials:** KMnO$_4$ was obtained from Fisher Scientific. Formic acid (≥ 95%) was obtained from Sigma-Aldrich.

**Calibration Curve:** Aqueous KMnO$_4$ (1 mL, 1 mM) was combined with various concentrations of an aqueous formic acid solution (0.25-1 mL, 400 mM) with the total volume brought to 2 mL with water. The reaction was allowed to proceed for 30 seconds before a UV-Vis absorbance spectrum is collected and the peak absorbance value at 545 nm is recorded. The calibration curve is shown below.

![Calibration Curve](image.png)
**Sample Analysis:** Filtered photocatalysis samples (1 mL) are combined with aqueous KMnO₄ (1 mL, 1 mM). The reaction was allowed to proceed for 30 seconds before a UV-Vis absorbance spectrum is collected and the peak absorbance value at 545 nm is recorded. The value is compared to the calibration curve to determine the concentration in the aliquot, which is then scaled to find the concentration in the entire sample.

**¹H NMR Spectroscopic Analysis**

**Materials:** D₂O was obtained from Cambridge Isotope Laboratories. tert-Butanol (100%) was obtained from Fisher Scientific.

**Sample Analysis:** A stock standard solution of tert-butanol (47.8 µL, 500 µmol) was combined with D₂O (10 mL) in a scintillation vial and sealed with tape before being stored in a refrigerator. NMR samples were created with stock solution (0.2 mL, 10 µmol tert-butanol) and filtered photocatalysis samples (0.5 mL) in a quartz NMR tube and agitated to ensure complete mixture. Spectroscopic analysis was performed on a Bruker BioSpin 500 MHz NMR spectrometer. The tert-butanol peak was integrated to 90, and the resulting integration value of the formate peak gives the concentration of formate in the aliquot, which can be scaled up to determine the total production of formate in the sample as shown below:

\[
F = I \times \frac{V_t}{V_s}
\]

where \(F\) is the total formate production, \(I\) is the integration value of the formate peak when the integration of the t-butanol is set to 90, \(V_t\) is the experimental volume (4 mL), and \(V_s\) is the sample volume (0.5 mL).
CHAPTER V

Fundamental Insights into BP/C$_3$N$_4$ Heterojunction Electron Dynamics

5.1 Background

Transient absorption spectroscopy (TAS) is a relatively new analytical technique made possible with the development of ultrashort tunable lasers in the early 1990’s.\textsuperscript{142} In short, this spectroscopic technique works by using a laser pulse to excite a portion of the sample. Then, after a determined length of time, a probe light with a broad spectrum will be absorbed by the sample. The ground state absorption spectrum is subtracted from the excited state absorption spectrum to determine the spectrum resulting from the population of excited electrons at that specific time delay. By varying the time delay between the pump and the probe, a time-dependent profile of the excited electron population can be determined. A delay line is used to manually move a mirror along a track, causing the time the laser pulse takes to get to the sample to change (\textbf{Figure 5.1}). This is a particularly powerful technique to use when studying heterojunctions, as non-emissive electron transitions can be monitored using TAS that wouldn’t be caught using time-resolved fluorescence techniques. It can also be used to probe ultrafast, femtosecond electron behavior based on the type of laser being used and provides a very high degree of resolution due to the fine motor controls on the delay track that modulate the time delays. The lifetimes of the excited electrons are determined through the use of data fitting software based on the equation of the line that best fits the decay shapes shown by the experimentally gathered data. The decay curves are generated by compiling the absorbance at one wavelength that shows a significant feature in the spectrum into a single graph, showing how the absorbance changes over time.
Figure 5.1. An example of a TAS setup.\textsuperscript{142}

Sun and co-workers used TAS to investigate the ultrafast charge trapping on metal sites on titanium dioxide.\textsuperscript{143} Alternating layers of TiO\textsubscript{2} and metal sites, specifically W and Co, were deposited on glass films using a radio-frequency reactive magnetron sputtering technique. The films were then annealed at 500 °C for 2 hours. A 350 nm pump was used to excite the sample, which was then probed in the UV-Vis range. The researchers found that increased metal doping led to faster decay times, both in the fast component attributed to electron decay to defect states below the CB and in the slow component attributed to electron decay to deep-level trapping states near the center of the band gap. Co was found to result in a nearly two times faster electron decay compared to W regardless of the thickness of the deposited metal layer. The addition of metal particles on TiO\textsubscript{2} greatly changed the electronic properties of the semiconducting material, and the use of Co showing faster electron decay has promising potential for the work presented in this thesis. Interestingly, the authors determined that the metal particles exist as ions in between the layers of TiO\textsubscript{2} and not as oxides. Previous work on Co-loaded C\textsubscript{3}N\textsubscript{4} has shown that the presence of CoO\textsubscript{x} species on C\textsubscript{3}N\textsubscript{4} reduces the catalytic capabilities of the material,\textsuperscript{77} so efforts taken to
reduce the presence of oxides in these materials will also have a greater impact on tuning the electronic properties of the system.

To further understand the electron transfer capabilities of TiO$_2$ and how they may be affected by different factors, the kinetics of electron transfer between TiO$_2$ and a cobalt reduction catalyst (CoP) was studied by Reynal and co-workers.\textsuperscript{144} Three different systems, one including TiO$_2$ and CoP, one including TiO$_2$ and CoP with a sacrificial electron donor, and one including TiO$_2$ and CoP with a dye molecule (RuP). These allow for different electron transfer processes to be studied as a result of how these different components interact in the system (Figure 5.2). CoP was loaded directly onto the TiO$_2$ surface via a simple dipping method, and the dye sensitized TiO$_2$ films were obtained by soaking in aqueous RuP solution. Excitation of the sample was performed using 355 nm irradiation, and photo-excited electron decay was monitored at 900 nm while the decay of photogenerated holes was monitored at 460 nm. The researchers found that additions of TEOA as the sacrificial electron donor increased excited electron lifetimes in TiO$_2$ to 1 s, but the negligible H$_2$ evolution observed indicates that proton reduction occurs at an even slower rate than that. However, with additions of CoP into the system, electron recombination in TiO$_2$ is in competition with electron transfer to CoP, with the main factor for which process dominates being the intensity of irradiation. In cases of high flux, recombination within TiO$_2$ dominates due to the higher density of holes in the material, but in conditions similar to solar irradiation, transfer from TiO$_2$ to CoP is the dominant electron pathway. In combination with an efficient hole scavenger like TEOA, unwanted recombination can further be avoided. This study shows how electron dynamics of systems change as donor molecules fill the photogenerated holes and shows the importance of choosing a donor molecule that has an oxidizing potential that aligns with the valence band of the material that will have the photogenerated holes accumulating in it. These
lessons are crucial to keep in mind as these techniques will be applied to the BP/C₃N₄ system to determine potential pathways to increase the oxidative power of the system.

![Diagram](image.png)

**Figure 5.2.** Three different experimental setups to elucidate electron transfer kinetics in a TiO₂/CoP system.¹⁴⁴

Thus far, the ability for materials to be impacted by metal sites as well as the ability for materials to transfer electrons to catalysts have been discussed. However, the crux of this thesis work involves the heterojunction formed between BP and C₃N₄. The ability to probe the electronics occurring between two 2D materials is of great value in understanding the fundamental properties of the heterojunction present between the two materials. A study by Zhu and co-workers set out to answer this question by examining the electron kinetics between BP and C₃N₄ using time-resolved diffuse reflectance spectroscopy (TDR).⁸⁰ TDR was used as the researchers generated BP/C₃N₄ powdered samples through stirring desired amounts of each material together overnight and isolating the material via centrifugation. The samples were prepared by dispersing the powder in ethanol to make an ink that was deposited on a clean glass slide. The absorption of the BP, C₃N₄, and BP/C₃N₄ samples at 950 nm was monitored to determine the lifetimes of the electrons excited by a 400 nm or 780 nm pump. Two-exponential functions were used to fit the data to determine the short and long lifetimes of the electron decays. Each sample exhibited both short and long electron lifetimes that were then averaged together, with BP having an average lifetime of 0.8 ps using both a 400 nm and 780 nm pump. Only the short lifetime was detected due to the very fast
recombination observed in BP. C₃N₄ was not excited by the 780 nm pump, but the average lifetime with the 400 nm pump was found to be 101 ps. The short and long lifetimes of C₃N₄ were found to be 11 ps and 195 ps with populations of 51% and 49% respectively. These lifetimes changed to 73 ps and 44 ps for the BP/C₃N₄ system with 400 nm and 780 nm pump, but this is a remarkable increase over BP alone (0.8 ps and 0.8 ps). The researchers determined that P–N coordinate bonds between the two materials acting as electron trap sites to be the main reason for increased electron lifetimes with the 780 nm pump as the BP is the main light absorber in this system. Using the 400 nm visible light pump causes the C₃N₄ to function as the main light absorbing material and the Type I heterojunction formed between the two materials efficiently shuttle electrons to adjacent BP.

Xie and coworkers added isolated Pt single atoms as a co-catalyst on C₃N₄, and observed a large increase in H₂ production compared to bare C₃N₄.¹⁴⁵ These researchers found that a 0.16 wt% loading of Pt on C₃N₄ resulted in a turnover frequency as high as 775 h⁻¹ and used TAS to probe the origin of these improved photocatalytic results. The average excited state lifetimes were found to be 237 ± 9 and 433 ± 38 ps for C₃N₄ and Pt@C₃N₄, respectively. The increased lifetime of these excited states was attributed to the inclusion of Pt atoms allowing for longer charge carrier separation, thus resulting in a higher proportion of excited species participation in proton reduction. These single atom sites act as trap sites for the electrons, which slows down the rate of electron–hole recombination. This study also indicates the ability for TAS to be used to study the change in electron dynamics by modification of materials with metal active sites.

This is a critically important result for the application of these time resolved spectroscopic techniques to the work presented in this thesis. The presence of the heterojunction has been experimentally confirmed by measuring the photocatalytic properties of the system, so the
inclusion of metal active sites provides an additional option for electron transfer between the two materials. The previous studies of electron transfer from materials to catalysts in solution phase combined with studies focused on electron transfer between two materials lays a solid groundwork for the use of TAS to study the electron dynamics of the BP/Co@C₃N₄ system.

5.2 Hypothesis

We hypothesize that the use of TAS on the BP/C₃N₄ heterojunction will allow us to determine the lifetime of excited electrons in the system. We hypothesize that addition of cobalt active sites on one or both of the materials will change these lifetimes based on the rate of excited electrons transferring to the active metal sites. The understanding of the rates at which electrons are transferred in the heterojunction will allow for the system to be more intelligently tuned to produce certain gaseous products, while also giving insight into potential methods for increasing the rates of the oxidative half reaction using substrates other than TEOA. Comparisons of TAS spectra with both TEOA and glucose in the system will allow for the comparison of the oxidative abilities of both molecules in the photocatalytic system. We hypothesize that TEOA will prove to be a more effective reducing agent compared to glucose, but that by experimenting with different system components and ratios the effectiveness of glucose as a reducing agent can be optimized. The gaseous reduction products can also potentially be tuned based on the information gleaned from using TAS data, as the amount of time the excited electrons take to go to different metal active sites can be determined. This will allow for more intelligently designed future catalytic systems if the behavior of excited electron transfer can be understood at a fundamental level.
5.3 Results and Discussion

Experimentation using transient absorption spectroscopy was performed on every combination of BP and C\textsubscript{3}N\textsubscript{4} with and without metal doping, as well as electron donor, in order to determine how each component of the system impacts the lifetime of the charge separated state. Generally, two separate spectral features were observed: ground state bleaching centered at 480 nm, and stimulated absorption centered at 625 nm (Figure 5.3). A ground state bleaching is the result of the broad probe irradiation being absorbed by the sample before the pump hits the sample, resulting in a negative spectrum that “grows in” over time as the delay between pump and probe is increased. Stimulated absorption occurs when electrons are excited by the pump irradiation, then are excited a second time by the probe irradiation into a higher virtual excited state. Each of these spectral features demonstrated a short and a long electron lifetime. This data can be analyzed by monitoring a single wavelength over time or by monitoring slices of the entire absorption spectra at specific times (Figure 5.4). Preliminary data analysis is mostly focused on how these short and long lifetimes are affected by changing the components of the system. The use of BP in TAS is exceedingly complicated due to the difference in electronics based on the thickness of the flakes coupled with the thickness of the samples demonstrating a distribution of layers. Furthermore, the introduction of C\textsubscript{3}N\textsubscript{4} species as a second material in the system, as well as the fact that substrates can donate electrons to both materials, further complicates the analysis of data. As such, systems of this complexity are rarely studied.
Figure 5.3. 2D map of TAS data from BP/C₃N₄ showing the ground state bleaching (blue region) and the stimulated absorption (red region). Wavelength and time are displayed on the x and y axes, respectively. ΔA values are shown by the color scale to the left.

Figure 5.4. TAS data for BP/C₃N₄ at 625 nm (left) and at various times (right).

Analysis of BP species (BP and Co@BP) was conducted to determine the effect of Co loading on BP, as well as to determine how these materials interact with TEOA and glucose (Table 5.1). Measured excited state lifetimes at 480 nm for BP in the absence of any substrate were dominated by the short lifetime (0.328 ps, 96.92%), with a weighted average of 0.37 ps. The inclusion of either glucose or TEOA increased the long lifetime percentage (up to 52.34 and 21.35%, respectively) but resulted in just a small change to the weighted average lifetime (up to 0.59 and 0.44 ps, respectively). By contrast, at 625 nm, bare BP showed mostly long lifetimes (374 ps, 89.12%).
Table 5.1. TAS values comparing BP and Co@BP with the use of various oxidation substrates.

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength (nm)</th>
<th>τ1 (ps)</th>
<th>τ2 (ps)</th>
<th>Short %</th>
<th>Long %</th>
<th>Avg time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP</td>
<td>480</td>
<td>0.328</td>
<td>1.59</td>
<td>96.92</td>
<td>3.08</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>26.9</td>
<td>374</td>
<td>10.88</td>
<td>89.12</td>
<td>336.23</td>
</tr>
<tr>
<td>BP with glucose</td>
<td>480</td>
<td>0.295</td>
<td>0.864</td>
<td>47.66</td>
<td>52.34</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>54.2</td>
<td>121</td>
<td>47.57</td>
<td>52.43</td>
<td>89.23</td>
</tr>
<tr>
<td>BP with TEOA</td>
<td>480</td>
<td>0.2</td>
<td>1.34</td>
<td>78.65</td>
<td>21.35</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>0.894</td>
<td>184</td>
<td>16.33</td>
<td>83.67</td>
<td>154.09</td>
</tr>
<tr>
<td>Co@BP</td>
<td>480</td>
<td>0.171</td>
<td>0.977</td>
<td>99.27</td>
<td>0.73</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co@BP with glucose</td>
<td>480</td>
<td>0.184</td>
<td>0.805</td>
<td>62.46</td>
<td>37.54</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>74.8</td>
<td>440</td>
<td>48.99</td>
<td>51.01</td>
<td>261.09</td>
</tr>
<tr>
<td>Co@BP with TEOA</td>
<td>480</td>
<td>0.51</td>
<td>14.8</td>
<td>83.16</td>
<td>16.84</td>
<td>2.92</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>30</td>
<td>147</td>
<td>37.28</td>
<td>62.72</td>
<td>103.38</td>
</tr>
</tbody>
</table>

365 nm pump, 350 – 700 nm probe, pathlength 1 mm.

The inclusion of glucose caused a shift in the short lifetime (54.2 ps, 47.57%) and became more influential on the average lifetime of 89.23 ps when observing the 625 nm signal compared to BP alone (336.23 ps). Overall, the addition of substrates increased the average lifetimes when observing the signal at 625 nm compared to BP alone. It is unclear why this is occurring, but it is possible that as these substrates donate electrons to fill the holes in BP the new electrons are excited by the probe, thus reducing the total amount of photons available for the excited state electrons already in the system.

When using Co@BP, the average lifetime at 480 nm (0.18 ps) was significantly extended by the addition of glucose (261.09 ps) or TEOA (103.38 ps). The use of glucose resulted in a large increase in the proportion of electrons exhibiting long lifetime behavior (up from 0.73% to 37.54%), while the use of TEOA greatly enhanced the length of the long electron lifetime (up from 0.977 ps to 14.8 ps). This indicates that glucose more readily donates into Co@BP compared to BP, as Co@BP demonstrated both a shorter average lifetime and a larger portion of electrons exhibiting short electron lifetime behavior.
The opposite trend is seen with the use of TEOA with Co@BP. No spectral events were observed for Co@BP in the absence of substrates at 625 nm. The use of TEOA led to a shorter average electron lifetime compared to that observed in the presence of glucose (103.38 ps and 261.09 ps, respectively). In addition, both the short and long lifetime values were much longer with the use of glucose (74.8 ps and 440 ps) compared to TEOA (30 ps and 147 ps). This seems to agree with the model of electron transfer from glucose to Co@BP being more favorable than TEOA to Co@BP, as the longer lifetimes are hypothesized to be a result of electrons being trapped in the excited state due to the photogenerated holes being filled by the substrate.

Similar experiments were conducted with C₃N₄ and Co@C₃N₄. At 480 nm, both species of C₃N₄, whether in the presence of substrate or not, demonstrated very similar average electron lifetimes (Table 5.2). In general, Co@C₃N₄ species showed a higher percentage of long lifetime electrons compared to their C₃N₄ counterpart with the exception of these species with TEOA. At 625 nm, both C₃N₄ and Co@C₃N₄ showed very similar activity in the absence of any substrates (111.97 ps and 132.63 ps, respectively), but a slight increase in the percentage of electrons exhibiting a long lifetime for Co@C₃N₄ compared to C₃N₄ (42.29% and 36.60%, respectively). We hypothesize that electron transfer to the Co²⁺ active sites on the material which act as electron trap sites that increases the long lifetime. The use of glucose with both C₃N₄ species resulted in a significantly decreased average lifetime compared, through similar or slightly higher percentages of electrons exhibited longer lifetimes for Co@C₃N₄ and C₃N₄ respectively.
Table 5.2. TAS values comparing C$_3$N$_4$ and Co@C$_3$N$_4$ with the use of various oxidation substrates.

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength (nm)</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
<th>Short %</th>
<th>Long %</th>
<th>Avg time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$N$_4$</td>
<td>480</td>
<td>0.164</td>
<td>3.07</td>
<td>92.47</td>
<td>7.53</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>21.3</td>
<td>269</td>
<td>63.40</td>
<td>36.60</td>
<td>111.97</td>
</tr>
<tr>
<td>C$_3$N$_4$ with glucose</td>
<td>480</td>
<td>0.164</td>
<td>6.9</td>
<td>93.24</td>
<td>6.76</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>3.18</td>
<td>116</td>
<td>47.89</td>
<td>52.11</td>
<td>61.97</td>
</tr>
<tr>
<td>C$_3$N$_4$ with TEOA</td>
<td>480</td>
<td>0.176</td>
<td>1.72</td>
<td>78.20</td>
<td>21.80</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>33.4</td>
<td>310</td>
<td>34.22</td>
<td>65.78</td>
<td>215.35</td>
</tr>
<tr>
<td>Co@C$_3$N$_4$</td>
<td>480</td>
<td>0.164</td>
<td>2.57</td>
<td>84.73</td>
<td>15.27</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>30.5</td>
<td>272</td>
<td>57.71</td>
<td>42.29</td>
<td>132.63</td>
</tr>
<tr>
<td>Co@C$_3$N$_4$ with glucose</td>
<td>480</td>
<td>0.171</td>
<td>3.92</td>
<td>89.94</td>
<td>10.06</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>14.1</td>
<td>106</td>
<td>58.18</td>
<td>41.82</td>
<td>52.53</td>
</tr>
<tr>
<td>Co@C$_3$N$_4$ with TEOA</td>
<td>480</td>
<td>0.174</td>
<td>2.9</td>
<td>92.65</td>
<td>7.35</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>25.3</td>
<td>281</td>
<td>35.30</td>
<td>64.70</td>
<td>190.74</td>
</tr>
</tbody>
</table>

365 nm pump, 350 – 700 nm probe, pathlength 1 mm.

The use of TEOA with either C$_3$N$_4$ species resulted in longer average lifetimes than without substrate, confirming the ability for TEOA to efficiently donate electrons to the photogenerated holes in C$_3$N$_4$ materials. The decrease in average lifetime at 625 nm with the use of glucose compared to TEOA is an interesting result that is not yet fully understood. It is possible that the direction of electron flow could be counter to what we’ve assumed and instead electrons could transfer from the C$_3$N$_4$ species to glucose or other products in the solution, which would shorten the lifetime of these systems by removing excited electrons from the photoactive material. This would result in a smaller spectroscopic response from the probe. Further analytical testing of the organic products in solution may reveal reduced glucose-related products.

The electron lifetimes and distribution of electrons displaying each lifetime are expected to change when both BP and C$_3$N$_4$ species are present to form the photocatalytic heterojunction due to the high potential for increased charge carrier separation. In general, short lifetimes are
expected to dominate upon ground state bleaching observed at 480 nm in the presence of substrates. Additionally, hole transfer between C$_3$N$_4$ and BP species may be determined by these TAS studies by monitoring the behavior at 480 nm. The interaction of the substrates with the materials is not expected to be significantly different than when the materials are on their own, thus the kinetics of an individual material that aligns more closely with those of the full heterojunction is most likely the location of photogenerated holes.

Alternatively, excited electron transfer between the two materials may be determined by the electron dynamics measured upon stimulated adsorption at 625 nm. Using similar reasoning, the overlap of electron lifetimes and distribution may give insight into where excited electrons are being transferred. These observations are made with the knowledge that both materials are being excited by the 365 nm pump used on the sample, as demonstrated by the similar spectral features displayed by both materials alone.

In the BP/C$_3$N$_4$ system, the ground state bleaching at 480 nm was greatly affected by the inclusion of TEOA and glucose in the system. No significant change in time between analogous BP, C$_3$N$_4$, and BP/C$_3$N$_4$ systems was observed for this spectral feature, but a significant increase in the percentage of electrons exhibiting a short electron lifetime was observed upon the addition of substrates to the BP/C$_3$N$_4$ system (Table 5.3). In the absence of substrates, BP/C$_3$N$_4$ showed a significantly larger proportion of electrons with a longer lifetime compared to BP or C$_3$N$_4$ alone. No clear conclusions can be made on hole transfer occurring between the two materials as no correlation between the electron lifetimes of the BP/C$_3$N$_4$ system and analogous BP or C$_3$N$_4$ systems were determined.
Table 5.3. TAS values comparing BP/C₃N₄ with the use of various oxidation substrates.

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength (nm)</th>
<th>τ₁ (ps)</th>
<th>τ₂ (ps)</th>
<th>Short %</th>
<th>Long %</th>
<th>Avg time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP/C₃N₄</td>
<td>480</td>
<td>0.209</td>
<td>0.793</td>
<td>53.38</td>
<td>46.62</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>70.2</td>
<td>354</td>
<td>52.22</td>
<td>47.78</td>
<td>205.80</td>
</tr>
<tr>
<td>BP/C₃N₄ with glucose</td>
<td>480</td>
<td>0.426</td>
<td>2.81</td>
<td>82.08</td>
<td>17.92</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>32.5</td>
<td>217</td>
<td>33.23</td>
<td>66.77</td>
<td>155.68</td>
</tr>
<tr>
<td>BP/C₃N₄ with TEOA</td>
<td>480</td>
<td>0.527</td>
<td>3.28</td>
<td>92.60</td>
<td>7.40</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>57.3</td>
<td>395</td>
<td>43.78</td>
<td>56.22</td>
<td>247.15</td>
</tr>
</tbody>
</table>

365 nm pump, 350 – 700 nm probe, pathlength 1 mm.

In general, the stimulated absorption spectrum at 625 nm in the BP/C₃N₄ system showed an increased average electron lifetime with the use of substrates. Interestingly, the data indicates the electron dynamics in the BP/C₃N₄ system are strongly influenced by the specific substrate being used. When TEOA was used, the BP/C₃N₄ system displayed electron lifetimes and percentages more closely related to C₃N₄ with TEOA, while the BP/C₃N₄ system with glucose was more closely related to BP with glucose. We hypothesize that an interaction between BP and glucose is occurring that provides a greater catalytic driving force for hole transfer to BP. This could potentially be measured by isolating the BP material and using XPS to detect the formation of new phosphorus bonds, but isolating BP without exposing it to degrading conditions would prove challenging. In the absence of substrates in the BP/C₃N₄ system, no clear correlation between this data set and the data sets of BP or C₃N₄ are observed.

In the Co@BP/C₃N₄ system, the heterojunction in the absence of substrates exhibited a longer average lifetime than each material alone for the ground state bleaching at 480 nm (Table 5.4). With glucose included in the heterojunction system, the average electron lifetime and percent of electrons exhibiting short and long lifetimes correlated more closely with Co@BP with glucose than C₃N₄ with glucose. This indicates that glucose donates electrons more efficiently into Co@BP and that photogenerated holes are gathering in Co@BP when the heterojunction is used.
Comparing the bleaching at 480 nm between BP/C₃N₄ and Co@BP/C₃N₄, both in the presence of glucose, showed similar percentages of electrons with short or long lifetimes, but the average electron lifetime is significantly shorter for Co@BP/C₃N₄. We hypothesize that glucose more readily donates electrons into photogenerated holes in Co@BP compared to BP, as the shorter average lifetime indicates that the ground state holes are filled more quickly. This may be a result of a strong interaction between glucose and BP. For the spectral feature at 625 nm, no correlation between the studied Co@BP/C₃N₄ heterojunction and analogous Co@BP or C₃N₄ systems was observed.

Table 5.4. TAS values comparing Co@BP/C₃N₄ with the use of various oxidation substrates.

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength (nm)</th>
<th>τ₁ (ps)</th>
<th>τ₂ (ps)</th>
<th>Short %</th>
<th>Long %</th>
<th>Avg time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co@BP/C₃N₄</td>
<td>480</td>
<td>0.454</td>
<td>3.91</td>
<td>81.34</td>
<td>18.66</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>90.4</td>
<td>242</td>
<td>43.94</td>
<td>56.06</td>
<td>175.38</td>
</tr>
<tr>
<td>Co@BP/C₃N₄ with glucose</td>
<td>480</td>
<td>0.166</td>
<td>0.965</td>
<td>77.93</td>
<td>22.07</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>13.9</td>
<td>202</td>
<td>31.42</td>
<td>68.58</td>
<td>142.89</td>
</tr>
<tr>
<td>Co@BP/C₃N₄ with TEOA</td>
<td>480</td>
<td>0.518</td>
<td>2.37</td>
<td>90.18</td>
<td>9.82</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>45.1</td>
<td>418</td>
<td>45.42</td>
<td>54.58</td>
<td>248.62</td>
</tr>
</tbody>
</table>

365 nm pump, 350 – 700 nm probe, pathlength 1 mm.

As seen with the Co@BP/C₃N₄ system, the BP/Co@C₃N₄ system again showed longer average electron lifetimes at 480 nm both with and without the use of substrates (Table 5.5). This is likely due to the increased charge separation afforded by the heterojunction and may be indicative of an electron transfer occurring between the two materials. Percentages of electrons exhibiting short or long lifetimes are not closely related to the results observed with analogous BP or Co@C₃N₄ systems. The percentages observed in the heterojunction are more closely related to analogous BP systems than Co@C₃N₄ systems, but the values are not significantly correlated. At 625 nm, the BP/Co@C₃N₄ system with TEOA displayed nearly identical percentages and average electron lifetime to Co@C₃N₄ with TEOA, indicating that TEOA is likely donating electrons to
photogenerated holes in Co@C₃N₄. This trend of heterojunctions with TEOA behaving similarly to the analogous C₃N₄ systems with TEOA is likely due to the well-studied efficiency of electron donation from TEOA to photogenerated holes, as well as the likelihood that C₃N₄ species are absorbing pump irradiation more strongly than BP, leading to a larger concentration of photogenerated holes existing in C₃N₄ compared to BP. When a slower electron donating substrate is used, like glucose, a larger population of photogenerated holes exists in BP, which could be attributed to hole transfer from C₃N₄ to BP.

**Table 5.5.** TAS values comparing BP/Co@C₃N₄ with the use of various oxidation substrates.

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength (nm)</th>
<th>τ₁ (ps)</th>
<th>τ₂ (ps)</th>
<th>Short %</th>
<th>Long %</th>
<th>Avg time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP/Co@C₃N₄</td>
<td>480</td>
<td>0.408</td>
<td>1.51</td>
<td>79.47</td>
<td>20.53</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>70.7</td>
<td>405</td>
<td>43.96</td>
<td>56.04</td>
<td>258.05</td>
</tr>
<tr>
<td>BP/Co@C₃N₄ with glucose</td>
<td>480</td>
<td>0.181</td>
<td>0.852</td>
<td>18.16</td>
<td>81.84</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>43.5</td>
<td>344</td>
<td>40.07</td>
<td>59.93</td>
<td>223.60</td>
</tr>
<tr>
<td>BP/Co@C₃N₄ with TEOA</td>
<td>480</td>
<td>0.425</td>
<td>2.05</td>
<td>76.63</td>
<td>23.37</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>69.7</td>
<td>260</td>
<td>37.50</td>
<td>62.50</td>
<td>188.64</td>
</tr>
</tbody>
</table>

365 nm pump, 350 – 700 nm probe, pathlength 1 mm.

The final heterojunction tested was Co@BP/Co@C₃N₄ which showed an increase in the average electron lifetime in the absence of substrates compared to each material on their own at 480 nm (**Table 5.6**). Addition of glucose to the heterojunction resulted in a similar average electron lifetime when compared to analogous Co@BP or Co@C₃N₄ systems. A correlation between short and long lifetime percentages between the heterojunction and Co@BP was observed, in agreement with previously observed results. With TEOA, the heterojunction demonstrated an average electron lifetime between the values determined from each material separately with TEOA. Similarities in percentages were observed between Co@BP/Co@C₃N₄ and Co@BP, but with a large difference in average electron lifetime. At 625 nm, there was no observable correlation between electron lifetime or percent of electrons exhibiting short or long lifetime behavior.
Table 5.6. TAS values comparing Co@BP/Co@C₃N₄ with the use of various oxidation substrates.

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength (nm)</th>
<th>τ₁ (ps)</th>
<th>τ₂ (ps)</th>
<th>Short %</th>
<th>Long %</th>
<th>Avg time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co@BP/Co@C₃N₄</td>
<td>480</td>
<td>0.421</td>
<td>2.71</td>
<td>84.57</td>
<td>15.43</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>8.85</td>
<td>198</td>
<td>15.75</td>
<td>84.25</td>
<td>168.21</td>
</tr>
<tr>
<td>Co@BP/Co@C₃N₄ with glucose</td>
<td>480</td>
<td>0.164</td>
<td>0.632</td>
<td>54.24</td>
<td>45.76</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>20.6</td>
<td>206</td>
<td>36.06</td>
<td>63.94</td>
<td>139.14</td>
</tr>
<tr>
<td>Co@BP/Co@C₃N₄ with TEOA</td>
<td>480</td>
<td>0.454</td>
<td>1.31</td>
<td>78.10</td>
<td>21.90</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>35.4</td>
<td>223</td>
<td>32.79</td>
<td>67.21</td>
<td>161.49</td>
</tr>
</tbody>
</table>

365 nm pump, 350 – 700 nm probe, pathlength 1 mm.

With the inclusion of Co on BP in the Co@BP/Co@C₃N₄ system, all electron lifetimes either remained the same or decreased when compared to analogous BP/Co@C₃N₄ systems. However, a larger percentage of electrons in the Co@BP/Co@C₃N₄ system displayed long lifetimes. The true mechanism of electron transfer dynamics between the materials remains unclear as a result of these studies, but it is evident that the fundamental electronic behaviors of the BP/C₃N₄ heterojunction can be changed by the inclusion of Co active sites on one or both materials.

5.4 Conclusion

The electron dynamics in different BP and C₃N₄ species, with or without TEOA or glucose acting as oxidation substrates, were tested using transient absorption spectroscopy. Two different spectral features, specifically a ground state bleach at 480 nm and a stimulated absorption at 625 nm, were analyzed to determine the decay kinetics of electrons in the system. In general, it was found that the use of TEOA resulted in heterojunctions maintaining similar electron dynamics as the analogous C₃N₄ species with TEOA, and analogous BP species performed similarly to the heterojunction in the presence of glucose. A major focus of this work was to determine which system would promote glucose oxidation. It was found that Co@BP resulted in the longest average
electron lifetime (261 ps at 625 nm) in the presence of glucose. However, Co@BP is not likely to have a band gap appropriate for excitation by simulated solar spectrum thus won’t enable maximization of glucose oxidation. The heterojunction that displayed the longest average lifetime in the presence of glucose was BP/Co@C₃N₄ (223 at 625 nm). This system also has the advantage of a higher proportion of electrons displaying long lifetimes compared to Co@BP, indicating a longer average lifetime for photogenerated holes. This increases the likelihood of glucose oxidation to occur by donating electrons into these holes.

5.5 Experimental Section

Materials: C₃N₄ and Co@C₃N₄ were prepared as previously described. BP (Ch.2) and Co@BP (Ch. 3) were prepared as previously described. Acetonitrile (MeCN, 99.9%) was purchased from Sigma-Aldrich. Triethanolamine (TEOA, 97%) was obtained from Acros Organics. Glucose was purchased from Sigma-Aldrich. All chemicals were used without further purification.

Sample preparation: Aqueous solutions of the desired C₃N₄ species (0.2 mg mL⁻¹) were sonicated for 2 hours. The solids were allowed to settle, and the solution showed a distinct yellow tint. The supernatant was used for TAS analysis. BP and Co@BP (1 mg mL⁻¹) were used as prepared.

A constant ratio of the specific BP species and C₃N₄ species (1:5 v/v BP:C₃N₄) was added to a quartz cuvette (1 mm) in an Ar atmosphere glove box with a constant volume of 0.6 mL. If used, aqueous glucose (0.2 mL of a 0.1 M solution, 20 µmol) was added to a quartz cuvette (1 mm) and an appropriate amount of the desired BP species and C₃N₄ species were added to bring the total volume to 0.6 mL. If used, mixture of degassed acetonitrile and TEOA (0.2 mL, 4:1 MeCN:TEOA v/v) was added to a quartz cuvette (1 mm) and an appropriate amount of the desired
BP species and C₃N₄ species were added to bring the total volume to 0.6 mL. The samples were capped and removed from the glovebox, then sonicated for 30 minutes. The resulting suspensions were analyzed spectroscopically for absorption in the visible region using a Helios spectrometer.

**Spectroscopic measurements:** Transient absorption spectroscopy (TAS) was performed on a Helios spectrometer (Ultrafast Systems) using a commercial Ti:Sapphire laser system (SpectraPhysics, 800 nm, 100 fs, 3.5 mJ, 1 kHz). Pump pulses (365 nm) were generated using a commercial optical parametric amplifier (LightConversion). A portion of the fundamental laser was focused into a sapphire plate to produce continuous light in the visible region to serve as the probe. The pump and probe light sources were focused to overlap in time and space. An optical delay placed on the path of the probe beam afforded a dynamic range up to 3 ns and resolution as low as 100 fs. Time-resolved ΔA versus wavelength were chirp corrected and analyzed using Surface Xplorer software (UltraFast Systems). Equation fitting to determine decay times and amplitudes was performed using the same software. The equation used is shown below:

\[ \Delta A(\lambda, t) = A_0 + A_1(\lambda)e^{-\frac{t}{\tau_1}} + A_2(\lambda)e^{-\frac{t}{\tau_2}} \]

Short and long lifetime percentages were determined by normalizing the A₁ and A₂ values that correspond to the proportion of electrons with short and long lifetimes, respectively. The average time was determined by finding the sum of each lifetime multiplied by its corresponding normalized Aₙ value as shown below:

\[ \text{Average lifetime} = A_1 \ast \tau_1 + A_2 \ast \tau_2 \]
CHAPTER VI

Development of C$_3$N$_4$ Electrodes

6.1 Background

Semiconductors have been used as electrodes for their photocatalytic properties since the early 1970’s, but stability issues prevented major development of this field.\textsuperscript{147–149} The interest in using semiconductors in this way lies in the unique property of semiconductors to exhibit the photovoltaic effect. The photovoltaic effect was first discovered in 1839 by Edmond Becquerel during his experimentation with copper or silver halide salt electrodes dipped in electrolyte.\textsuperscript{150} He observed the production of a photocurrent upon exposure of this system to solar irradiation, which is called the photovoltaic effect. Semiconductors have a band gap corresponding to the energy difference between the valence and conduction bands of the material. Electrons populate the valence band in their relaxed state, and when irradiated by photons of sufficient energy, they can absorb the energy, are excited and populate the conduction band. These excited electrons are then able to pass through a collector or wire in a circuit, generating an observable current. The band gaps of semiconductors are unique to each specific material, and larger or smaller band gaps require photons with larger or smaller amounts of energy to excite the electrons. Additionally, the band gaps of semiconductors can be located at different energy levels, making some semiconductors more suitable for specific tasks (\textbf{Figure 6.1}). The amount of flexibility in choice of semiconductor makes this class of material interesting and widely studied.
Figure 6.1. Band gaps and energy alignments of many different semiconducting materials. Energy levels for various redox reactions are shown as dashed lines. In this figure, semiconductors to the right of the black line have an unfavorable band alignment for catalyzing CO\textsubscript{2} methanation.\textsuperscript{151}

While semiconductors on their own may possess the ability to perform photocatalytic reactions, charge recombination dominates and significantly decreased the efficiency of catalysis by the materials on their own. Catalysts can sometimes be directly attached to semiconductor surfaces to act as a thermodynamic sink to extract electrons and provide an active site for catalytic reduction processes to occur. TiO\textsubscript{2} is frequently used in these types of applications due to the ease of anchoring other molecules to the oxide bonds on the surface as well as the strong photovoltaic properties of TiO\textsubscript{2}. Han and co-workers used N-doped carbon dots to increase the charge separation in photogenerated charge carriers in TiO\textsubscript{2}.\textsuperscript{152} The N-CDs were anchored onto TiO\textsubscript{2} using a one-step hydrothermal method, which initiates the electron-trap effect. This results in a ~160\% increase in charge extraction due to the enhanced charge separation induced by the presence of the trap sites. A maximum photocurrent density of 3.09 mA cm\textsuperscript{-2} was achieved using AM 1.5G light in 1.0 M NaOH, and the authors also noted decreases in the impedance at both the TiO\textsubscript{2} photoanode and the interface of the electrode. This photocurrent density corresponds to a ~3 times increase in the photocurrent density of base TiO\textsubscript{2}. Ding and co-workers created a metal-
organic framework consisting of TiO$_2$ and Co$_3$O$_4$ to improve upon the photocurrent density of pure TiO$_2$ nanorods. The MOF was formed through the adsorption of Co-MOF (ZIF-67) on TiO$_2$ followed by annealing in air to obtain the final Co$_3$O$_4$/TiO$_2$ photoelectrodes (Figure 6.2). The maximum photocurrent density of 1.04 mA cm$^{-2}$ was achieved after the TiO$_2$ surfaces were immersed in an aqueous Co-MOF solution for 9 minutes. This photocurrent density was 1.65 times higher than pure TiO$_2$, which the authors attribute to a broadened optical response from the photoelectrode, as well as increased separation of photogenerated charge carriers. These electrodes also showed stability for photoelectrochemical water splitting over the course of 2 hours, indicating that the interactions between TiO$_2$ and Co$_3$O$_4$ help prevent the formation of oxide species that reduce the photocatalytic capabilities of the electrode. This simple method for enhancing the photoelectric response of cheap TiO$_2$ surfaces while maintaining the stability of the electrodes allows for economic and scalable generation of electrodes.

![Figure 6.2. Graphical preparation method of Co$_3$O$_4$/TiO$_2$ photoelectrodes.](image)

The addition of many types of materials to TiO$_2$ have been studied because of their ability to expand the wavelength range of the light that can be absorbed by the electrode. The use of a material for fabricating photoelectrochemical electrodes with broad visible light absorbance will
reduce the need for modification of electrode surfaces, thus increasing the ease of generating these surfaces. The easier these electrodes are to make, the easier it will be to implement them on a large scale to maximize their environmental benefits.

The use of C$_3$N$_4$ for photoelectrodes is of great interest due to the stability of the material as well as the broad visible light absorption it possesses.$^{72,73,80}$ Shalom and co-workers demonstrated the ability to grow highly ordered, uniform C$_3$N$_4$ layers on a variety of substrates, including glass, FTO glass, and TiO$_2$ (Figure 6.3).$^{154}$ A supramolecular complex between cyanuric acid and melamine was synthesized in water and isolated, with a thin layer of solid sandwiched between two layers of the target substrate. After heating to 550 $^\circ$C for 4 h, the samples were analyzed to confirm the conversion to C$_3$N$_4$ as well as determine the morphology of the surfaces formed. X-ray diffraction (XRD) and elemental analysis (EA) were performed on C$_3$N$_4$ material scratched off of the surface, and the researchers found that C$_3$N$_4$ grown on FTO was so tightly bound to the surface that not enough material could be isolated to perform these analyses. This was attributed to the presence of free hydroxyl and amine groups present in the supramolecular structure that are available to interact with the surfaces on which the films are grown. Current densities as high as 0.8 mA cm$^{-2}$ were observed from FTO-C$_3$N$_4$ in neutral media, indicative of the potential for C$_3$N$_4$ electrodes grown using a 1:1 cyanuric acid: melamine supramolecular complex to be used for efficient photoelectrochemical charge generation in mild conditions.
Qin and co-workers took a different approach to creating uniform C$_3$N$_4$ layers on various substrates for use as photoelectrodes.\textsuperscript{154} These researchers utilized a simple dipping method in hot, saturated thiourea solution to generate thin uniform layers on the desired substrate, with additional dipping generating increased film thickness. The optimal thickness based on maximum photocurrent response was found to be 39 µm which was obtained by three consecutive 1 s dips. These electrodes were placed in a test tube with melamine at the bottom before being wrapped tightly with aluminum foil and baked in a tube furnace at 500 °C for 2 h. The addition of melamine in the test tube increases the vapor pressure inside the tube when the melamine sublimes, and results in a tighter adhesion between the C$_3$N$_4$ and the FTO glass slide. Electrodes made using this method displayed photocurrent densities of 0.305 mA cm$^{-2}$ in neutral media and were more catalytically active in neutral conditions compared to alkaline media. The ability to perform water splitting in neutral conditions is extremely valuable, and the C$_3$N$_4$ electrodes made using this
method displayed impressively high Faradaic efficiencies of 55% and 52% for H₂ and O₂ respectively. These electrodes also demonstrated strong adhesion, as the C₃N₄ layer was resistant to sonication and applications of tape to remove the surface. Additions of melamine in the test tube resulted in stronger adhesion of C₃N₄ films compared to electrodes baked without melamine present. The combination of high efficiency towards water splitting as well as strong adhesion of the C₃N₄ surface to the FTO substrate makes these electrodes an excellent candidate for further study.

6.2 Results and Discussion

6.2.1 Purpose

The purpose of this work was to reproduce the method for the fabrication of C₃N₄ electrodes as described by Qin and co-workers. The combination of simple synthesis, strong adhesion, and high efficiency for simultaneous O₂ and H₂ generation made the thiourea dipping method the first procedure we elected to follow for C₃N₄ electrode fabrication. Electrodes made using previously prepared C₃N₄ will be attempted as well in order to establish a comparison for a baseline of photoelectrochemical activity.

6.2.2 C₃N₄ Paste

The structure or morphology of C₃N₄ has a strong impact on the catalytic abilities of the material. Being able to create C₃N₄ surfaces on an electrode substrate will allow for direct comparison of activity between our previously described C₃N₄ solution-based photocatalytic experiments and the C₃N₄ electrodes in photoelectrochemical experiments. The first attempt at making C₃N₄ electrodes involved directly dropping a prepared C₃N₄ paste directly onto a
conductive FTO glass slide and drying in an oven. After drying, the film was cracked and separated from the slide in the center of the circle formed by the dried C$_3$N$_4$. This was likely due to ethanol used to make the paste being trapped inside the paste and evaporating when placed in the oven, causing the film to separate from the surface. This disrupts the smooth surface and makes the electrode unstable, which is undesirable for photoelectrochemical experiments. Another drawback of this method was the applied surface was much too thick, which increased the likelihood of solvent becoming trapped beneath the surface which exacerbates the flaking issues.

To address these issues, a doctor blading method was used to ensure a thin layer of C$_3$N$_4$ was applied to the slide. The doctor blade method involves placing a slightly raised surface with an exposed area in the middle on a conductive glass slide. The paste is added to the exposed area and a razor blade is swiped keeping the edges along the raised surface to make a uniform layer of paste on the slide with the same thickness as the raised surface. This method was performed using Scotch tape, FTO glass slides (2.54 cm x 2.54 cm) and two different sizes of circles formed using a hole punch (with diameters of 0.8 cm and 1.27 cm).

Different drying methods were also tested. One slide of each circle size was dried in an oven and another slide of each was dried on the benchtop. All four of the electrode surfaces remained smooth and intact after drying and showed enhanced photocurrent response compared to bare FTO glass when analyzed using linear sweep voltammetry (LSV) (Figure 6.4). However, the surface was observed to flake off during the application of a potential to the electrode, and a reduction in photocurrent generation was observed as the C$_3$N$_4$ surface left the glass slide (this is seen on the subsequent sweeps to negative potentials).
Figure 6.4. LSV showing a peak from the doctor blade C$_3$N$_4$ electrode (blue line) compared to bare FTO (red line). The surface flaked off of FTO and gave a significantly reduced photocurrent response (green line).

The major issue with these trials is the lack of adhesion between the surface of the slide and the C$_3$N$_4$ material. This is likely due to the chemically inert C$_3$N$_4$ structure, where the silicon oxide bonds of the glass slide don’t interact strongly with C$_3$N$_4$ thus providing poor interaction to keep the film attached to the slide.

6.2.3 Dipping Methods

In an effort to anneal the C$_3$N$_4$ surfaces to the FTO glass slides, methods for direct growth of C$_3$N$_4$ on the slide were tested. We hypothesized that the process of converting starting material to C$_3$N$_4$ directly on the slide would allow for significantly enhanced adsorption between the two surfaces, enhancing the stability of the C$_3$N$_4$ film in electrolyte solution. The generation of a consistent electrode surface area is critically important, as the activity of the photoelectrode is directly related to the surface area. To compare electrodes from different experiments, identical
surface areas are required. Preliminary experiments using a dipping method reported by Qin and co-workers\textsuperscript{155} using a hot, saturated aqueous thiourea solution with a constant volume (5 mL) in a scintillation vial to reproducibly generate films of the same size by dipping the film until it contacted the bottom of the vial. When the room temperature slide contacts the solution, thiourea condenses on the surface in a uniform layer. This process can be repeated as many times as desired to generate films with different thicknesses, which in turn makes $C_3N_4$ electrodes with different degrees of thickness. These experiments were conducted with 3 consecutive dipping procedures with time between the dips to allow the thiourea film to fully dry on the glass slide surface. The dipped slides were baked in a tube furnace, and it was found that significant portions of the film left the surface of the glass slide. This was attributed to the increased thickness of thiourea deposited on the bottom of the glass slide resulting from the generation of nucleation sites created when the glass slide contacts the vial (Figure 6.5). In addition, literature reports indicate different photocurrent responses based on thickness of films, so differences in thickness within a single layer will elicit inconsistent results which is undesirable for photoelectrochemical systems.

![Figure 6.5](image.png)

**Figure 6.5.** Thiourea films on FTO glass featuring increased loadings of thiourea on the bottom of the slides due to contact with the bottom of the scintillation vial.

Lower concentrations of thiourea and larger volumes of saturated thiourea solution were used to prevent the issues described above. To generate consistent surface areas on the glass slides available for films, tape was placed on one end of the slide to create a 1 cm x 1 cm area. The slides were dipped past the exposed area onto the tape, and once the tape was removed Films made from
lower concentrations of thiourea gave consistent, thin layers deposited on the glass slide with less thiourea compared to the more saturated previous trials (Figure 6.6). Another issue with thicker layers of thiourea was encountered when the tape was removed from the slide. To ensure the entire exposed area of the slide was covered in thiourea, the slides were dipped to a depth that resulted in thiourea condensing on the tape. When the tape was removed, the layer on the glass slide occasionally broke off and left an uneven surface near the top of the electrode. The electrodes were baked in a 60 °C oven for 30 minutes prior to removing the tape in an effort to maintain electrodes with the desired thickness of thiourea film and a consistent surface area. This drying step had little impact on the ease of tape removal without disrupting the surface. Once the tape was removed from these slides, they were placed in a tube furnace and baked under a N2 flow to convert the thiourea to C3N4. After this process, we observed very little to no material remained on the glass slides.

![Figure 6.6. Thiourea films on FTO glass prior to baking into C3N4 made with A) low concentration of thiourea and B) saturated thiourea.](image)

The flow of nitrogen was considered to be problematic, as we thought it may contribute to the removal of volatilized starting materials in the tube furnace decreasing the propensity for deposition and growth of C3N4. To test this theory, electrodes made with the typical dipping method were baked in a muffle furnace using the same settings as the tube furnace but without a positive flow of N2 over the surfaces. The slides were placed in a ceramic boat and wrapped tightly
in aluminum foil, however, after baking no material was observed on the glass slide, but significant black deposits were observed to have formed on the top of the aluminum foil above each of the glass slides. We took this as confirmation that sublimation of volatilized starting material was occurring, and the flow of nitrogen in the tube furnace was likely displacing the sublimated material, preventing deposition of the intermediates back on to the glass slide.

These trials were repeated in the muffle furnace with a second clean slide placed on top of the slide with the thiourea layer on it. An intermediate in the conversion of thiourea to C$_3$N$_4$ sublimes at temperatures below the maximum temperature achieved during baking, and the second slide forming a “sandwich” was used to provide a surface for the material to deposit on. This method did not yield any material on either surface, but again showed sooty residue on the aluminum foil. In an effort to control the sublimation of the C$_3$N$_4$ or its precursor complex off the surface, samples using the typical dipping method were placed in the tube furnace set to ramp to a lower maximum temperature below the sublimation temperature of melamine of ~345 °C. Approximately half of the material on these glass slides sublimed off the surface, and the remaining material on the glass slides was discolored and showed no photocurrent response when tested (Figure 6.7).

![Figure 6.7](image.png)

**Figure 6.7.** C$_3$N$_4$ electrodes baked at 300 °C.
Communication with Dr. Sanjit Mondal, one of the co-authors of the literature report we were following, revealed that they used a test tube to help create C$_3$N$_4$ electrodes from thiourea. In this technique, the dipped slide is put inside a test tube with the dipped layer facing the opening. Up to three slides can be put in a single test tube. The test tube is then wrapped as tightly as possible with aluminum foil and put inside the tube furnace with the wrapped open end of the test tube facing the flow of N$_2$.

We attempted to employ this method and the slides were made using the typical dipping method and dried in a 60 °C oven prior to baking. One slide was found to be slightly tilted inside the tube furnace, and the surface on the half that was tilted down was removed while the raised half remained after baking (Figure 6.8). These slides showed an initial photocurrent response (Figure 6.9), but the material fell off the surface in one single intact sheet upon prolonged exposure to the electrolyte solution. However, the material that fell off the glass slide maintained its structure, a significant change compared to previous trials. Electrodes made with other methods would flake apart when they came off in the electrolyte solution. The material surface maintaining its structure indicates the potential for this method to develop strong C$_3$N$_4$ electrodes, should we figure out a way to tightly attach the films to the electrode surface.

![Figure 6.8. C$_3$N$_4$ electrodes baked inside a test tube. It is hypothesized that half the material left the glass slide due to the glass slide being physically tilted inside the tube furnace.](image)
Figure 6.9. LSV analysis of C₃N₄ electrodes baked inside a test tube in the tube furnace (green) compared to the doctor blade method (blue) and bare FTO glass (red). The tube method generated a high current response when exposed to simulated solar spectrum.

6.3 Conclusion

Many different methods for fabricating C₃N₄-coated electrodes were explored. Direct application of a prepared C₃N₄ paste resulted in smooth uniform surfaces that fell off the glass slide when placed in electrolyte solution. In an effort to make C₃N₄ surfaces with stronger adhesion to the glass slides, a hot saturated thiourea solution was used in a dipping method that deposited even layers of thiourea on the glass slides following a reported method by Qin and co-workers. These thiourea layers were baked at high temperatures to convert the thiourea to C₃N₄, and the resulting electrodes were tested using linear sweep voltammetry to determine the photoelectrochemical response of the electrodes. Unfortunately, inconsistent photocurrent response was observed due to the lack of adhesion between the C₃N₄ films and the glass slides. The use of a test tube for baking the slides showed promising results in terms of photocurrent
response and film integrity, but again showed poor adhesion to the glass slide. This technique merits further study to develop the best method for fabrication of C₃N₄ electrode surfaces.

6.4 Experimental Section

C₃N₄ Paste

Materials: C₃N₄ was prepared as previously reported in Chapter 2. Ethanol (100%) was obtained from Pharmco-AAPER.

Drop casting method: C₃N₄ (98.5 mg) was placed in a 25 mL Erlenmeyer flask and EtOH (2.5 mL) was added. The paste was sonicated for 20 minutes to maximize dispersion and create a homogenous texture. A single drop of the paste was placed in the center of a clean FTO conductive glass slide and dried in an oven at 125 °C overnight.

Doctor blading method: C₃N₄ (98.5 mg) was placed in a 25 mL Erlenmeyer flask and EtOH (2.5 mL) was added. The paste was sonicated for 20 minutes to maximize dispersion and create a homogenous texture. A circle of diameter 0.8 cm or 1.27 cm was punched in a piece of scotch tape and placed on a clean FTO conductive slide. A drop of the C₃N₄ paste was dropped in the circle, and a razorblade was dragged over the tape to spread out the paste. This process was repeated three times, then the films were dried either on the benchtop or in an oven at 125 °C overnight.

Dipping Methods

Materials: Thiourea was obtained from Baker Analyzed Reagents.

Method: A saturated aqueous thiourea solution (0.9 g/mL, 20 mL) was heated to ~70 °C while stirring. Clean FTO conductive glass slides were taped to generate a consistent surface area if used. The slides were dipped in the solution for 1 s, and this process was repeated to generate the desired
number of layers on the slide. The slides were dried for 30 min at 60 °C if this step was used. The tape was removed if used, then the slides were baked in a tube furnace for 2 h at 500 °C or 300 °C with a 5 °C/min ramp. A second clean FTO slide was put on top of the thiourea layer prior to being placed in the tube furnace if the “sandwich” method was used.

**Photoelectrochemical Testing Methods**

**Materials:** KOH was obtained from VWR Analytical. Electrodes were prepared as previously described.

**Method:** Linear sweep voltammetry was performed using a prepared C₃N₄ electrode as the working electrode, a Pt wire mesh counter electrode, and a Ag⁺/AgCl reference electrode in a 0.1 M KOH electrolyte. The C₃N₄ electrode was oriented to face the quartz window of the photoelectrochemical cell. Simulated solar spectrum light was used, as previously described, to irradiate the photoelectrochemical setup. Linear sweep voltammetry was used to measure the corresponding photocurrent upon the application of a potential to the electrode with each of the different fabricated C₃N₄ electrodes being tested. The current response was measured upon an applied potential sweeping from 0 V to −1.3 V with a step size of 0.01 V and a scan rate of 0.1 V/s.
CHAPTER VII

Summary and Future Outlook

7.1 Reduction Half Reaction Outlook

The reductive capabilities of the BP/Co@C₃N₄ system have been well explored, displaying tunable ratios of evolved H₂ and CO as a function of increasing BP. Increased loadings of BP led to simultaneous increased H₂ and decreased CO production. One-pot production of syngas is a significant challenge in the field, and this system meets and exceeds that challenge by generating easily tunable ratios of syngas. This is a major step forward in the use of earth-abundant catalysts for syngas production.

An increase in H₂ evolution was also observed with the addition of CoCl₂, indicative of a potential second pathway for controlling the ratios of the gases evolved. BP is a relatively expensive material to purchase commercially due to the difficult synthesis required to prepare it, so the ability to tune the photocatalytic system using a cheaper material is very appealing. Additionally, CoCl₂ was added either as a solid or as an aliquot of a stock solution, which is a straightforward method that did not require any inert handling to enable control over the ratio of gases formed. The effect of changes in the loading of Co@C₃N₄ were not explored in the course of the experiments performed. We hypothesize that increased loading of Co@C₃N₄ with a constant BP loading will lead to an increased CO evolution coupled with a decreased H₂ evolution. This pathway would then allow even more tunability in the system.

One potential strategy to improve the BP/Co@C₃N₄ photocatalytic system could be to reduce the concentration of both materials linearly such that the same loading ratios are obtained.
The tubes during experimentation were observed to be very opaque, with light unable to penetrate deeply into the sample, meaning that the systems were not light limited. This was also shown to be the case experimentally through the use of the neutral density filters. By reducing the total concentration of material, and more specifically Co@C₃N₄, more of the sample can be exposed to irradiation at any given point in time. This would hypothetically increase the efficiency of the system by increasing total photon absorption since more of the sample would be able to absorb photons per unit time. The reduction of overall material loading in the experiments will also be beneficial by reducing the overall cost of the system.

A decrease in overall material loading may lead to a decrease in total evolution of gaseous products. Even if the ratios of evolved gases remained constant with a decrease in total material loading, a decrease in total gas evolution is highly undesirable. We do not anticipate that this will happen as a result of the decrease in total material loading since more of the sample should be irradiated at any given time, but a decrease in catalytically active sites has the potential to decrease the amount of photocatalysis that occurs. The quantum efficiency will become a key metric when evaluating the activity of the BP/Co@C₃N₄ heterojunction. A high quantum efficiency will mitigate the reduction in the number of active sites because the increase in irradiated sample will generate the same number of excited electrons available for catalytic processes.

7.2 Oxidation Half Reaction Outlook

The research described in this thesis just scratches the surface of the oxidative power of the Co@BP/Co@C₃N₄ system. The preliminary results herein were gathered using analytical techniques that were not optimal for quantification of the materials being produced. This work helped to show that the photocatalytic system described is capable of oxidizing glucose to formate.
The formate represents just the first and final steps of the oxidative process. Our metric for analysis of glucose conversion only took into account the formate produced. However, there are many potential molecular intermediates between glucose and formate, and the detection of these intermediates is likely to result in a significantly higher glucose conversion percentage. The difficulty lies in gaining access to the analytical techniques required to separate, identify, and quantify these molecules. Two of the most likely intermediates present in the solution phase are gluconic acid and glucaric acid. $^1$H NMR spectroscopic analysis of these compounds would be exceedingly difficult due to the overlapping of many peaks in the spectra of these intermediates. The use of ion chromatography (IC) may be capable of separating and detecting these species when ionized, in addition to the formate product, and may present an elegant solution to this problem. Gluconic and glucaric acid may not be separable using this technique, but by employing a refractive index detector it should allow for the identification and quantification of these value-added acids.

An IC instrument with a column and detector suitable for formate detection in aqueous conditions became available at UNH shortly before I left for Brookhaven National Lab. Initial experiments showed a strong response for formate when tested with a standard solution, but initial experiments showed a large number of peaks indicating that the photocatalytic samples were a very complex mixture. As a result, these chromatographs could not be easily interpreted, and significant work would have to be done to identify and quantify the various components of the mixture. Fortunately, a peak corresponding to formate was observed by IC. What is clear is that a full understanding of the sample makeup would be extremely beneficial to allowing a clearer understanding of this complex system. It would also allow a more accurate assessment of the overall glucose conversion rather than relying on formate generation as the only metric for which
to assess glucose conversion percentages. Future work on this project should begin here, where standard solutions of possible glucose oxidation products are tested by IC. Calibration curves can then be generated once the retention times are known to allow for quantification.

Another issue with the IC was significant overlapping of peaks. This makes it difficult to get proper peak integrations to determine accurate concentrations using this methodology. An improved separation of products in the column would allow for more well-separated peaks in the chromatograph. Separation of products can be improved by lengthening the column or decreasing the flow rate of eluent. Both of these strategies would provide the products more time to interact with the column, thus changing the retention times and allowing for more accurate quantification to occur. Another possibility would be to use a different column stationary phase, but that would require thoughtful analysis of all presumed products being formed. It is likely that IC is not the best analytic method for the oxidation products that are not anions. It is possible that IC in combination with high-performance liquid chromatography (HPLC) might be required for full evaluation of all products formed.

Another issue for future consideration when thinking about the application of this type of system on a larger scale is the challenge of separating the oxidation products.

7.3 Electron Dynamics Outlook

The lack of access to facilities that allow for these ultrafast electron dynamics studies makes it difficult to further this research beyond what is presented in this thesis. Continued studies into varying the material loadings in the samples should be conducted. We hypothesized that increased loadings of BP would cause more electrons to be transferred from C$_3$N$_4$ to BP, resulting
in the observed increase in H\textsubscript{2} production. This hypothesis could be tested by conducting TAS experiments with a constant amount of various C\textsubscript{3}N\textsubscript{4} species and a varying amount of BP. We anticipate seeing a decrease in the percent contribution from the electrons with longer lifetimes, as these electrons would be transferred to BP. This percent contribution is expected to decrease as BP loading increases, indicative of more electrons being transferred from the conduction band of the C\textsubscript{3}N\textsubscript{4} species to BP.

Another potentially valuable study would be to carry out the same TAS measurements, but in the presence of a CO\textsubscript{2} atmosphere. The new catalytic pathways opened by the presence of CO\textsubscript{2}, compared to the inert Ar atmosphere these trials were conducted in, could have a dramatic impact on the electron dynamics. We hypothesize that this would shorten the average lifetime in systems containing Co@C\textsubscript{3}N\textsubscript{4}, as there would be a driving force for electrons to go to the catalytically active Co\textsuperscript{2+} sites.

One potential issue with these proposed loading studies is that TAS is concentration dependent. Increased concentration leads to significant changes in the data obtained, as some absorption features become more or less prevalent based solely on concentration and not due to the actual electron dynamics in the system. It is possible that by increasing the BP loading, new features in the spectra could be observed that may obscure the actual electronic processes occurring. It is also possible that increased total material loading will lead to a reduction in light reaching the detector due to scattering. This would have a similar effect on the spectral data, as intensities overall will be lower and lead to artificially faster decays. The low absorbance values at extended electron lifetimes would be more strongly affected by light scattering due to the low photon count of these absorbance, thus eliminating spectral features that contain the information needed to paint a clear picture the electron dynamics in the system.
Future work using TAS in these systems will require consideration of these potential pitfalls to ensure that accurate and meaningful data is collected during the experiments.

### 7.4 Electrode Outlook

The methodology for fabrication of C$_3$N$_4$ electrodes is relatively well understood, though this technique still needs to be perfected. Dipping FTO glass slides in hot, saturated thiourea prior to baking inside a tightly wrapped test tube in a tube furnace does result in increased current density observed by LSV using partial C$_3$N$_4$ films and shows the promise of this technique. Future work with these electrodes would be to fine tune this method, and to quantify hydrogen production upon irradiation. One challenge with quantification of H$_2$ would be the large available headspace present in the photoelectrochemical cell used for irradiation of the electrode. The volume of H$_2$ produced would likely be low, leading to low overall concentration in the headspace. The cell used is significantly larger than the headspace used for photocatalytic experiments. This may lead to difficulty quantifying the H$_2$ by GC as it would likely require larger volume injections to increase the observed peak area. However, it has been shown that increased injection volume does not scale linearly with the increase in peak area, meaning new calibration curves would have to be established specifically for larger injection volumes. Perhaps this will not be an issue if the system is able to produce large amounts of H$_2$, but it should be considered when making use of this photoelectrochemical setup.

Another course of study with these C$_3$N$_4$ electrodes would be in the loading of metal active sites on the surfaces. This may prove difficult, as these loadings would most likely need to be performed following the electrode fabrication using the test tube method. A soaking strategy could
be used to deposit catalytically active sites on the surface of the electrode, but this seems an unlikely way to deposit single atom cobalt active sites as in our Co@C₃N₄ powdered materials.

Additionally, the relatively inert C₃N₄ surface will likely remain unreactive to covalent linking of other molecules to the surface. Evidence of the formation of P–N bonds between BP and C₃N₄ in previous studies indicate that phosphorus-based linkers could potentially be used to anchor molecules to the electrode surface. A close look at methods reported in literature for loading metals, molecules, or other materials onto C₃N₄ surfaces should be conducted prior to experimental attempts to modify the electrode surfaces. Care must be taken not to disrupt the adhesion of the C₃N₄ surface to the FTO glass, as any modified electrode surface would then be subjected to photoelectrochemical measurements while soaking in electrolyte. The structural integrity of these surfaces is critical to be able to properly utilize the additional catalytic sites that would be added to the C₃N₄ electrode.
References


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Appendix

Figure A.1. BP TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.2. BP with glucose TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.3. BP with TEOA TAS at specified time delays (top) and 625 nm (bottom). No spectral feature at 480 nm was detected.
Figure A.4. Co@BP TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.5. Co@BP with glucose TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.6. Co@BP with TEOA TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.7. C₃N₄ TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.8. C₃N₄ with glucose TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.9. C₃N₄ with TEOA TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.10. Co@C₃N₄ TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.11. Co@C₃N₄ with glucose TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.12. Co@C$_3$N$_4$ with TEOA TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.13. BP/C$_3$N$_4$ TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.14. BP/C$_3$N$_4$ with glucose TAS at specified time delays (top) and 625 nm (bottom). No spectral feature at 480 nm was detected.
Figure A.15. BP/C$_3$N$_4$ with TEOA TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.16. Co@BP/C$_3$N$_4$ TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.17. Co@BP/C$_3$N$_4$ with glucose TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.18. Co@BP/C₃N₄ with TEOA TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.19. BP/Co@C₃N₄ TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.20. BP/Co@C$_3$N$_4$ with glucose TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.21. BP/Co@C$_3$N$_4$ with TEOA TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.22. Co@BP/Co@C$_3$N$_4$ TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.23. Co@BP/Co@C$_3$N$_4$ with glucose TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).
Figure A.24. Co@BP/Co@C₃N₄ with TEOA TAS at specified time delays (top), decays at 480 nm (middle) and 625 nm (bottom).