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SEMICONDUCTOR PHOTOELECTRODES FOR PHOTOCATALYTIC ENERGY CONVERSION & SEMICONDUCTOR NANORODS FOR SOLID STATE LIGHTING

A Thesis in

Materials Science and Engineering

by

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ABSTRACT

Energy is the currency of the physical world; it is what allows us to perform any action. The development of denser and more usable forms of energy has supported the emergence of our technological civilization. From animal labor to the industrial revolution to the use of fossil fuels, the progressive acquisition of more powerful sources of energy has enabled humanity to increase agricultural and industrial productivity, and to raise the standards of living for all.

Our current dependence on fossil fuels stems from their relative abundance and ease of use; however, as has become undoubtfully apparent over the past decades, this dependence has taken an immense toll on the planet and the ecosystem. For this reason and because of the accelerating depletion of these nonrenewable resources, there exists a compelling need to advance alternative sources of energy. Ultimately, most sources of energy available on Earth originate from a single main source, namely, solar energy. Winds arise from the uneven heating of the planet's surface; biomass is created by the conversion of solar energy into organic molecules; even fossil fuels are the concentrated traces of ancient biological systems that once derived their sustenance from sunlight. Solar energy is the most abundant source of energy accessible to humankind, but it is variable and affected by climatic, seasonal, and diurnal intermittency. These limitations make it inadequate to fulfill the growing and delocalized energy needs of our society. A possible option to circumvent these disadvantages would be to store solar energy for when it is unavailable or insufficient to meet the consumer demand. One solution to achieve this goal is to convert solar radiation into chemical energy that can be stored for later use. In a manner similar to biological photosynthesis, it is possible to use semiconductors to harness the power of the Sun for storing sunlight into chemical energy. Photocatalytic semiconductors have the potential to convert abundant chemical substances such as water into fuels such as molecular hydrogen, which can be stored and utilized in internal combustion engines or in fuel cells, with the key benefit that the only by-product of this reaction is water. This process is carbon neutral and, if scalable, could

reduce our reliance on fossil fuels by accelerating the deployment of renewable energy into the electric grid and into the transportation sector.

In this thesis we have develop a high-throughput method to search for photocatalytic semiconductors using ab-initio DFT calculations and materials databases. The resulting candidates are screened by considering their band gap, band edges, abundance, toxicity, and synthesizability. Refined computational calculations are performed on the resulting candidates to improve the prediction of the band gaps (the Hubbard U correction). This search which initiated with a pool of over 66,000 materials was narrowed down to 68 candidates out of which 14 were successfully synthesized and characterized based on their optical, chemical, electrochemical and photocatalytic properties. Much of this work is dedicated to the synthetic pathways taken to produce these materials and the characterization of its optical properties. We were able to identify, synthesize, and validate 9 photocatalytic materials. Out of these materials, four are previously known water splitting photocatalysts, suggesting that our screening criteria are a valid way of approaching the problem. Three of these nine materials – NaInO₂, SrIn₂O₄ and PbTiO₂ – have been previously screened as potential candidates for water splitting, and we were able to validate this result experimentally. Three previously screened plumbates – Ca₂PbO₄, Ba₂PbO₄ and Cu₂PbO₂ – have never been experimentally validated as photocatalysts, even though they have been screened in multiple occasions. One of our materials, Na₃Fe₅O₉, has been determined as a good photoelectrode for the production of hydrogen but is thermodynamically not suitable for producing oxygen while being a potential candidate for hydrogen evolution. $Nb_2Co_4O_9$ is the most promising material obtained from our search as it has never been described as a potential candidate computationally or experimentally and has been determined to be a successful photocatalyst for water splitting. These results demonstrate the importance of coupling experimental and computational results. It also demonstrates a viable path for the discovery of novel photocatalytic materials that could ultimately provide renewable fuels from solar energy.

The second part of this thesis relates to the development of optoelectronic materials utilizing nanoparticle semiconductors. Lighting has become a commodity of the modern world that has allowed human activity and productivity to go past that established by natural daylight. This important aspect of our lives, accounts for 16-20% of all energy use worldwide. As we further increase our development in this world, more and more people will require the use of lighting to allow for improved lives. It is thus important that we transition away from the use of inefficient lightbulbs like incandescent lights and instead transition to the most efficient lighting system that we know of so far, solid state lighting. Solid state lighting is done using semiconductors in light emitting diode (LED) devices. These LEDS are 7 times more efficient than incandescent light and could contribute significantly in the reduction of energy we devote to lighting worldwide.

In this thesis, we propose the use of quantum nanorods to further improve solid state lighting. Quantum nanorods of particular compounds such as selenides and sulfides are susceptible to chemical modifications, through a process called cation exchange, where the intrinsic anion structure of the particle, the morphology, the shape and size of the particle are retained while the native cations of the particle are swapped for those of another element. This process through careful tailored conditions can create distinct regions in these nanoparticles with different chemical compositions, creating heterostructures in the nanoparticle. The formation of heterostructures at such scales we can create the formation of quantized systems such as quantum wells that are capable of emitting and absorbing lights at very particular frequencies with very high efficiencies.

Using this high level of colloidal chemistry, we suggest the study of the possible quantum systems we can synthesize to develop optoelectronic devices. Though the use of computational studies and experimental values of bandgaps and band edge positions of possible cation exchange products in nanorod particles, we were able to design 42 new quantum well nanostructures that could be of use in applications such as: Solid state lighting, lasers, photocatalysts and solar panels. Additionally, we propose troubleshooting approaches to modify the injection rates of carriers by modifying the well barriers to increase efficiency. Lastly, we propose a plan of action for the development and testing of a basic system and how to observe quantum confinement in the structure. These nanoparticle systems could ultimately be use for solid state lighting, flexible displays and solar panels, and could also enable high efficiency multijunction photocatalysts and photovoltaics.

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Chapter 1

Semiconductors to Convert Solar Energy into Chemical Fuels.

Introduction

Solar energy is virtually all around us, or at least it is during half of the day, when the Sun is out. Currently the amount of energy hitting the Earth in one hour in the form of solar radiation is roughly 10,000 times more than the global energy consumption.^{1–3} This means that solar energy has the potential to sustain the global energy demand in the long run. The global implementation of renewable energy as a primary source of power faces multiple challenges, but by far, the central problem plaguing the conversion of the global economy to renewable energy is its variability. Even if we could produce enough energy with renewable resources such as solar and wind, these resources are inherently intermittent. Our current world demands an instantaneous power delivery, and thus, the incorporation of these resources is a complex problem. As seen in Figure 1(a) and (b), the total and peak production solar energy peaks during the middle of the day, which is a mismatched by the peak load at around 19:00. This means that the most abundant source of energy, is incompatible with consumption requirements. This is also worsened by the fact that these numbers are averaged through the whole state of California, and the actual graphs of these sources in real time and locally fluctuates massively, particularly in regions of the world where cloud coverage is far more prevalent.

This chaotic system also currently imposes severe stresses on the electrical grid, as the sudden drop in power needs to be currently compensated by other sources of energy such as fossil fuels or nuclear power that can be freely controlled.⁴ The spontaneous ramping up and down of traditional power plants is grave problem, as these

systems are not designed to take the stress of ramping up and down many times a day and can cause premature wear and tear on the systems.



Figure 1-1: Energy production and mismatch energy production for a typical day in summer. 5

There exist several mitigation strategies to the issue of variability and intermittency of renewable energy some of which are (1) the diversification of renewable energies, to compensate for the baseloads that cannot be safely accounted for utilizing solar and wind⁶, and (2) the implementation of wide-reaching energy networks so that the energy production through vast areas can be stable and the fluctuating variations in renewable energies can be balanced out — these projects are sometimes called supersmart grids, super grids or megagrids.⁷ Alternatively, the ability to store these sources of energy so that they can be utilized when the energy supply is interrupted, or during times where the supply is not plentiful like at night or during long periods of cloud and snow coverage.

Currently the most efficient energy storage technology we have at our disposal is pumped-storage hydropower with roughly 70-87% efficiency^{8,9}. The main caveats being that not all places can utilize this technology and that it cannot power all portable electronic devices and electric transportation vehicles. Advances in battery technology have come a long way in recent decades, but we are reaching thermodynamic limits^{10,11}

of current chemical systems, that make the technologies' figures of merit, power density and energy density, lag behind the simplest answer, chemical fuels (see Figure 1-2).^{12–15}



Figure 1-2: Simplified Ragone plot for the various energy storage systems¹⁵

Chemical fuels have the advantage of portability, high energy density and high power density — not to mention the undeniable advantage imparted by the already existing world infrastructure for liquid fuels in powerplants and in the transportation sector, which is another major contributor to global warming, accounting for over 20%¹⁶ of global energy demand mainly in the form of fossil fuels. The main concern regarding our excessive reliance on chemical fuels is that they do not come from a renewable cycle and have caused undeniable disruption to the atmosphere, troposphere, seas and soil. This has all begun to change in recent decades with advancements in the formation of close loop fuels such as, hydrogen, syngas and various liquid carbon-based fuels and their production through electrolyzers, photoelectrochemical, photocatalytic, photoelectrocatalytic, and other catalytic processes. Using nothing but water and/or waste CO₂ and renewable sources of energy such as electricity derived from renewables like sunlight, the scientific community has been able to mimic the natural process of photosynthesis. The development of artificial photosynthesis and the recycling of waste or universally abundant chemical feedstocks into useful sources of stored energy has been hailed as the holy grail of energy research, but a low efficiency conversion, corrosion and instability of materials, as well as the use of rare earth elements or noble metals in these systems, has made them impractical for large scale commercial applications. The production of the most basic fuel, hydrogen, could potentially advance the technological development to these systems, increasing the chances that these materials become economically viable for the production of solar fuels.

The production of hydrogen at an industrial scale has primarily relied on steam reforming or coal gasification reactions, where fossil fuels or coal react with water vapor to produce carbon monoxide and hydrogen gas respectively. The chemical reaction typically proceed through the following steps:

 $CH_4 + H_2O \rightarrow CO + 3H_2$

 $3C + O_2 + H_2O \rightarrow H_2 + 3CO$

These chemical reactions account for over 90% of the production of hydrogen worldwide.¹⁷ This is concerning as the advantage of using hydrogen as a fuel is that it does not produce greenhouse gases. Through this process we are not eliminating the production of greenhouse gases and we are also inquiring on energy costs to generate this reaction at high temperatures. Recent research focuses on alleviating this problem by resorting to water splitting by means of photocatalysis, electrocatalysis, photoelectrochemistry, thermocatalysis and surface plasmon resonance.¹⁷

Thermolisis/Thermocatalysis

Probably the simplest method to split water into its constituent elements is though thermolysis, where water is heated to temperatures above 2,000°C, leading to its partial dissociation into hydrogen and oxygen. Due to thermal constraints, this approach is not a economical way to produce hydrogen from water. To use thermal energy more efficiently, thermochemical water splitting can be proposed as an alternative method of hydrogen production. Thermochemical water splitting relies on a set of chemical reactions at high temperatures (500-2000°C) to produce hydrogen. The system uses a series of chemical reaction intermediates where materials are utilized, recreated and reused in a closed loop to create hydrogen and consuming only water.¹⁸ These technologies may entail anywhere from 2 steps to most commonly 4 or more steps to generate hydrogen. To illustrate how the process works, we will discuss a simple two-step process, though these processes tend to be less attractive due to the high temperatures required. In this process a low valent metal oxide is heated to temperatures between 1700-3000°C to reduce the metal oxide to a lower valent metal oxide or to the metal itself. This process releases oxygen. Next the material is reacted with water, to oxidize the metal oxide or metal back to its original oxidation state, which in the process evolves hydrogen. The cycle is repeated continuously. Several metal oxide redox pairs are known such as ZnO/Zn and SnO₂/SnO.¹⁹

Photocatalysis

Another approach to splitting water is to utilize solar energy. Taking into consideration that the potential for water splitting requires 1.23 eV, this means that light corresponding to a wavelength of 1008 nm can theoretically be used to perform this separation. Solar energy of wavelength of 1008nm or shorter encompasses almost 70% of all solar radiation emitted by the Sun, including the visible and part of the close infrared spectrum. Unfortunately, water does not have large absorption in these wavelengths and thus, it usually takes exposures of UV or shorter wavelength to photolytically perform this reaction. This is not of large interest as only a small portion of the incident light of the sun is in these wavelengths and most get blocked by the atmosphere.

In order to perform photocatalytic water splitting, semiconductors are usually used under certain operating conditions. The conduction band of the material needs to lie at a potential less than 0.0 V, the reduction potential for H^+/H_2 vs. the normal hydrogen electrode (NHE), to perform the reduction of hydrogen, while the valence band needs to be at a potential higher than the oxidation potential for oxygen (O₂/H₂O) at 1.23 eV (See Figure 1-3).²⁰



Figure 1-3: Semiconductor band alignment for water splitting.

Semiconductors, that have a bandgap larger than 1.23 eV and have bands straddling the water's redox reactions, when irradiated with light can produce electronhole pairs that can participate the adequate redox reactions necessary to split water. One of the main downsides with this reaction and these materials is that electron-hole pairs can recombine in the material before performing the reactions, which leads to multielectron processes (Figure 1-4) that reduces the efficiency of the overall reaction drastically. This is the system that we will develop in this work and discuss further in the next section.



Figure 1-4: Electron hole pair pathways in semiconductor/electrolyte systems

Electrocatalysis

Electrocatalysis of water is the dissociation of water through an electrochemical process using hydrogen and oxygen evolution catalysts. In this reaction a potential greater than the redox potential of water is applied to an anode and cathodes in contact with an electrolyte, which causes hydrogen and oxygen to be evolved respectively. The standard materials to perform the oxygen evolution reaction (OER) under low overpotentials has been with noble metals such as, iridium and ruthenium. The use of platinum has also been explored but has shown less activity for this reaction than Ir and Ru. The production of nanoparticles of these metals have shown to improve substantially the activity of the electrocatalysis.²¹ The state of the art catalyst for the hydrogen evolution reaction (HER) is platinum. Due to its low overpotential, platinum is still considered one of the best electrocatalysts for the HER reaction.²² Due to the high cost and scarcity of these materials that consist of noble metals it makes the use of these catalyst impractical and unthinkable for large scale operations.

Photoelectrochemical systems

At first photoelectrochemical (PEC) and photocatalytic water splitting might seem like the same category, but as said by Wagner and Somorajai, "We use the term photocatalytic to describe processes, thermodynamically either uphill or downhill, in which both oxidation and reduction take place on a single illuminated catalytically active material. In photoelectrochemical reactions, on the other hand, the reduction and the oxidation of liquid- or gas-phase species occur on different surfaces requiring net flows of charge between these surfaces in both the solid phase and the liquid or gas phase.".²³ This is to say that charge carrier separation and electronic transport play a large role in photoelectrochemical water splitting, but some of the materials used in the photocatalytic category are the core of these setups for hydrogen production.

Honda and Fujishima discovered the first photoelectrochemical material system that used of titanium dioxide as the photoanode and platinum as a counter electrode.²⁴ In

this process, the charge-separation step, which is typically referred to as the 'Z-scheme' migration by analogy to photosynthesis (see Figure 1-5), contributes to enhancing the photocatalytic activity.²⁵



Figure 1-5: Schematic TiO_2/Pt photoelectrochemical system analogous to Honda and Fujishima's²⁶ setup.

Surface plasmon resonance

Yet another way of using light to split water is utilizing surface plasmon resonance (SPR). SPR is the phenomenon where charge density oscillations are confined to metallic nanoparticles due to the resonance of electromagnetic waves with the conducting electrons (See Figure 1-6).²⁷



Figure **1-6**: Surface plasmon resonance on a metal nanoparticle induced by an electromagnetic wave.

This effect causes intense light scattering, plasmon absorption peaks, and enhancement of local electromagnetic fields. Plasmonic nanostructures typically occur in metallic nanoparticles such as, Au, Ag and Cu and poses broadly tunable optical properties that are characteristic to each material. These properties are highly sensitive to size, shape and the dielectric medium of their immediate environment. This tunability and high absorption of electromagnetic radiation holds great promise for their incorporation into solar energy technologies in particular since their absorption can be modulated from the near infrared to the visible spectrum.²⁸ The SPR's interaction with the free electrons in the metal can cause the electrons to loose phase coherence and turn them into hot electrons and hot holes (See Figure 1-6) capable of performing vast chemical reactions to particles in their proximity.

Though it has been shown that water splitting can occur in bare metal nanoparticles by direct electron transfer, this only occurs when a particular resonant mode of the nanoparticle is excited by a specific wavelength that allows energetic and spatial overlap between the oscillating electron density of the nanoparticle and the antibonding orbitals of water.²⁹ Furthermore due to the short time that the hot electrons are available for, this drastically limits the efficiency of the nanoparticles as water splitting candidates.

Principles of Photocatalytic Water Splitting

Unlike metals, semiconductors do not have a continuous distribution of energy states that electrons and holes can occupy. The region where electrons and holes have no stationary states is known as the bandgap. The bandgap is between the valence band maximum (VBM) and the conduction band minimum (CBM). An electron can be excited beyond the VBM through the absorption of photons with energies greater than or equal to the energy difference of the bandgap. This process known as photoexcitation elevates the electron into the CB while leaving behind a hole in the VB. This newly created electronhole pair has an array of options it can undergo. The electron can recombine with the hole through radiative and non-radiative processes; the electron and hole can be separated and migrate to the surface where it can again recombine or it can participate in electrochemical reactions with molecules adsorbed to the surface of the semiconductor from the gas phase or solution it is in contact with. The latter possibility is what we are mostly interested in when we are talking about photocatalysis and water splitting. A separated electron or hole can participate in redox reactions if the energy of the electron and hole is thermodynamically favorable. The donation of an electron can be done to an electron acceptor so as to reduce the species; while a hole can accept an electron from an electron donor and oxidize said species (see Figure 1-3).

The ability of an electron-hole pair to be transmitted to an adsorbed species on the surface of the semiconductor is thermodynamically limited by the band edge position of the semiconductor with respect to the oxidizing and reducing species' redox potential. In order for an electron to be injected into an acceptor the energy level of the semiconductor's conduction band needs to be above (more negative than) the acceptor's potential. In order for an electron to be donated to the semiconductor's vacant hole by the donating species, the valence band of the semiconductor needs to be below (more positive than) the relevant energy level of the donor.

Unfortunately, there exist several alternative pathways for excited electron-hole pairs. Among such pathways we have mentioned before are the radiative and non-radiative recombination of these charge carriers be it in the surface or in the bulk, as shown in Figure 1-3. Either of these processes degrade the performance of our photocatalyst as some charge carriers do not participate in the desired electrochemical reactions. The exact mechanism for recombination of these charge carriers is beyond the scope of this thesis, nevertheless it is helpful to understand that these processes tend to happen in shorter time periods than charge transfer. Charge recombination processes can span time scales from 10⁻¹⁴ seconds for internal conversion from a singlet excited state to a triplet excited state to 10⁻³ seconds for phosphorescence; while chemical reactions in

the surface have time scales in the 10^{-10} to 10^{-5} seconds.³⁰ This means that recombination of the charge carriers is a competing mechanism that is must be avoided to increase reaction rates. One approach to prevent recombination is the efficient separation of the charge carriers and localization and isolation of these from each other.

To achieve the process of separating an electron-hole pair, typically an electric field (internal or external) needs to be present in the semiconductor. There are various ways in which we can induce an electric field in our semiconductor, the most intuitive one would be to impose a bias on one end of the semiconductor utilizing an external potential. Less intuitively we can apply an internal field through the creation of interfaces with other materials. When two materials come in contact, we obtain equilibrium when the Fermi energy levels of both materials are equal. For a solution, which is what we will be focusing on for the largest part of this work, the Fermi energy (E_F) of the solution is effectively equal to the redox potentials of the solvated species. This means that typically, for n-type semiconductors that come in contact with a solution that has a redox potential E_{redox} that is lower than the E_{F} there will be a net charge transfer from the semiconductor to the solution. This causes a net positive charge to build up in the region near the semiconductor's surface, called a space charge region, which results in a bending of the bands as the fermi level of the semiconductor drops and equilibrates with that of the solution. This charge transfer from the semiconductor to the solution causes a buildup of charge on the electrolyte side which establishes an electric double layer to compensate the space charge region (Figure 1-7).



Figure **1-7**: Band diagram of a semiconductor/electrolyte interface pre and post equilibrium.

This charge buildup at the surface of the semiconductor causes an internal electric field in the semiconductor that can separate the electrons and holes created by photoexcitation. The electrons would then be poured into the electrolyte and with the creation of the Schottky barrier would be able to "permanently" separate the charge carriers, thus extending the life of the electrons giving the charge more possibilities to react with the electrochemical species in solution. The same principle applies to a system where a metal and semiconductor meet, the charge transfer process is practically identical, and allows for electron and hole traps that can be used as co-catalysts.

As mentioned all throughout this section, the excited electron-hole pair can be used in electrochemical reactions on the surface of the semiconductor or when the electron and hole are transferred onto other materials such as catalysts to perform reactions. Thus, it is through this process that solar energy can be converted into chemical energy. This energy can therefore be used to perform chemical transformations and produce useful chemicals storing this energy in the chemical bonds which can later be used. This thesis focuses on the transformation of water molecules into oxygen and hydrogen gas which can be used as a fuel.

The process of electrolysis, the dissociation of water into its constituent elements, has a standard Gibbs free energy change (ΔG°) of 237 kJ/mol or 1.23 eV,³¹ which is dictated by the two redox potentials of the H₂/H₂O (0.0 V vs. NHE) and O₂/H₂O (1.23 V vs NHE) reactions occurring simultaneously in solution.

Oxidation: $2H_2O + 4h^+ \rightarrow 4H^+ + O_2$

Reduction: $2H^+ + 2e^- \rightarrow H_2$

Overall reaction: $2H_2O \rightarrow 2H_2 + O_2$

As I mentioned previously, in order for the semiconductor to be able to transfer the photogenerated charge carriers to chemical species, the bands of the semiconductor need to straddle the oxidation and redox potentials of the corresponding reactions, known as the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). This means that a photocatalyst that performs the complete reaction of overall water splitting must have a bandgap greater than 1.23 eV and the correct positions of the band edges mentioned previously. Nevertheless, this thermodynamic minimum is not a realistic energy minimum that we should be taking into consideration. There are kinetic limitations that need to be taken into account in order to produce the desired products in a realistic timeframe. These kinetic barriers mean that we would need to supply additional energy to the system by increasing the potential of the reaction for the reactions to take place at a faster rate, this added potential is known as an overpotential. The degree to which we need to supply an overpotential to produce our desired products at a desired rate is material dependent as the surface of each material can catalyze each reaction (OER or HER) to different degrees, thus reducing the amount of overpotential required. It is well know that the water oxidation reaction typically requires a higher overpotential than the proton reduction reaction.³² This is thought to be due to the more complex reaction pathway of oxygen evolution. This complexity is proportional to the number of electrons involved and the number of reactants that a reaction needs.³² The OER requires 4 electrons/holes per molecule of oxygen (O_2) evolved, as compared to the two electrons needed in the HER, which increases the complexity of the reaction pathway massively. The reaction pathway for this reaction is still up for debate and is likely to be somewhat material specific.

The use of semiconductors for such a reaction is also restricted by the availability of the solar energy spectrum and its corresponding intensities at each wavelength. It is known that the solar energy spectrum peaks at around 504 nm³³ or 2.46 eV, with a decay in power density as one would expect for a black body at around 6000 K. Semiconductor can only absorb, and therefor convert, the energy of photons that have an energy above or equal to its bandgap. This means that most well-known photocatalytic semiconductors such as TiO₂ with high bandgaps (E_g>3.0 eV) are not very effective at capturing most of the solar radiation, as they only absorb ultraviolet light, which accounts for <10% of the overall solar intensity on the surface of the Earth. In order for us to be able to most adequately absorb the solar spectrum, while being able to photocatalytically split water, a photocatalyst with a bandgap of around 2.26 eV would be ideal, which would lead to a conversion efficiency of around 11.2% (Figure 1-8).³⁴



Figure 1-8: Solar to hydrogen efficiency VS band gap.

This falls very short of the well know Shockley–Queisser limit of 30% for silicon³⁵ and the single photon absorber maximum power conversion efficiency for photocatalytic water splitting calculated by Hanna and Nozik of 31% ³⁶. Hanna and Nozik also provide us with the value of the bandgap of the material which would produce this maximum efficiency at 1.59 eV and a minimum of 1.5 eV for a single gap device.³⁶ This large difference in the maximum efficiency of conversion is largely due to the overpotentials needed to run the reactions. This efficiency is just barely acceptable for the target set by the Department of Energy for the cost of hydrogen per kilogram at \$2-\$4/kg, which would make it an economically viable rout for hydrogen production.³⁴

There are a couple of metrics we must define to understand efficiency in photocatalysis. The most basic, quantum yield (QY), is defined as the number of desired processes compared to the number of photons absorbed per unit time. In heterogenous photocatalysis apparent quantum yield or efficiency (AQE) is a more desirable metric, which is defined as the number of reacted electrons relative to the number of incident photons.³² Given that quantifying the actual number of absorbed electrons is particularly challenging for heterogenous particulate systems, due to losses in scattering, the use of the absolute light incident on a sample is far more useful.

AQE = number of electrons consumed by the water splitting reaction / number of incident photons x 100%

AQE = 2 x number of evolved H₂ molecules/ # of incident photons x 100%

AQE = 4 x number of evolved O₂ molecules/ # of incident photons x 100%

The other useful metric for us to compare efficiencies of catalysts in this field is known as the solar-to-hydrogen (STH) efficiency, which is more commonly used as a standard to compare efficiencies. It is a measure of the total amount of solar energy incident on a sample that is converted into potential chemical energy. It is defined as:

 $STH = output \ energy \ as \ H_2 \ gas/ \ energy \ of \ incident \ light = (rH_2 \ x \ \Delta G \ / \ P_{sun} \ x \ S \) \ x$ 100%

Here rH₂ is the rate of production of hydrogen (mmol/s), P_{sun} is the energy flux of the light incident on the sample (mW/cm²), S is the area of the reactor (cm²) and ΔG is the gain in Gibbs free energy for the reaction (J/mol), 237 kJ/mol for this system.

As I alluded to earlier, the efficiency of a photocatalytic system depends on the many paths that a photon and an electron hole pair can take in the system. The initial process that limits the ability of a semiconductor to convert light into energy is its ability to absorb light. When light hits the interface of a material is can either be reflected or it can be transmitted to the inside of the material. The light that penetrates the material can then travel through the solid where it has a probability of being absorbed by the material or, if the photon is not absorbed in the length of the material, it can be transmitted out. The intensity of the light through the material can be modeled with the Beer-Lambert law: $I(x) = I_0 e^{-ax}$ where "a" is the absorption coefficient, I_0 is the initial intensity of the light and "x" is the distance traveled by the light. We can therefore write an equation that relates the absorption of light by a semiconductor. A $(\lambda) = I(\lambda) - T(\lambda) - R(\lambda)$, where the absorption A is the difference between the incident light (I) and that which is reflected and transmitted (T) out of the material, all of which are dependent on the wavelength of light (λ). The second process that affects efficiency is charge separation. Once a photon is absorbed to create an electron hole pair, these charge carriers must diffuse to the surface for charge transfer to occur. During the process of diffusion or if the charges are not separated, the electrons and holes are capable of recombining through radiative or nonradiative processes and the possibility of charge transfer will be lost. Recombination can happen spontaneously, but it can also be mediated by bulk and surface defect states, that act as recombination centers. Interbrand or surface states are usually related to defects in the crystal. Thus, by increasing the crystallinity, we reduce the amount of defect sites, and thus decrease the probability of recombination.³⁷ Decreasing the size of the particles also decreases the diffusion distance these charge carriers need to traverse, thus enabling them to reach the surface before recombination. Other ways of reducing charge recombination include as mentioned previously, the imposition of an external electric field by imposing a potential on the material or by creating an interface with another material, such as a metal that can act as an electron trap and enhance the probability of conversion by both separating charge and aiding as a catalyst with lower overpotential. The last factor that affects the efficiency of a photocatalyst is the kinetics of the reaction that are happening on the surface. The faster these reactions happen the least amount of time is given for the electron hole pairs to recombine. If the reactions on the surface are slow, there will be charge accumulation at the surface of the semiconductor, which decreases the potential separating the charges in the bulk, thus inducing more charge recombination and decreasing efficiency. It is important to note that these systems are a complex combination of systems that would normally be studied separately, like a photovoltaic cell, a catalytic system and an electrochemical system. The combination and interplay of all these systems make photocatalytic systems incredibly complex.

Electrochemically, it is known that the total product formation rate for a reaction follows the equation. $r = I_0/nF \exp(anF(E_{cat}-E_0))/RT$ where n corresponds to the number of electrons involved in the reaction, F is Faraday's constant, E_{cat} and E_0 are the Fermi level of the catalyst and the redox potential of the solution, respectively, R is the universal gas constant and T is the absolute temperature. This equation tells us about the dependence of the kinetics to the number of electrons, the temperature and the applied overpotential (E_{cat} - E_0). As we apply a larger overpotential we can increase the rate of the reaction. These concepts as well as any other electrochemical insight can be applied to photocatalytic systems without too much alteration. The overpotential, as mentioned earlier, is an important criterion, which is not only dependent on the bandgap of the material. The photovoltage supplied by the photocatalyst when light impinges on its surface is dependent on several factors, such as light intensity, bandgap, the depletion layer, and potential losses that are expected at the surface and other interfaces.³⁸ As an example it is shown that the open circuit voltage for a crystalline silicon solar cell is only of around 0.738 V³⁹, when compared to its bandgap of 1.1 eV, it is clear that a significant portion (33%) of this potential is lost through the several processes in the semiconductor.

Computational Theoretical Background the Schrödinger Equation

In order to define the properties of any material, theoretically we only need to describe all of the quantum mechanical interactions of the particles in the system. In its simplest form, we need only to solve the time independent Schrödinger equation of the system:

$H\Psi = E\Psi$

where H is the Hamiltonian operator of the system, Ψ is the many-electron wavefunction, and *E* is the eigenenergy for the system. Though this equation may look simple, if we expand the Hamiltonian to explicitly show the many electron system the situation changes dramatically. This equation, shown below is far more complex, even after adding several simplifications like the Born-Oppenheimer approximation which treats the nuclei as fixed particles due to their overwhelmingly high mass compared to electrons, which would, in the frame of reference of the electrons, be slow enough not to react to the shift in electromagnetic fields caused by moving electrons.

$$\left[\frac{h^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N}V(r_i) + \sum_{i=1}^{N}\sum_{j<1}^{N}U(r_i,r_j)\right]\Psi = E\Psi$$

Here the terms of the equation refer to the kinetic energy of the electrons, the interaction between the electrons and the atomic nuclei, and the interaction between electrons, where $U(r_i, r_j)$ represents the electrostatic potential felt by an electron at position r_i and a second electron at position r_j , respectively. For this specific

Hamiltonian, Ψ corresponds to the electronic wave function, and is approximated in the Hartree approximation as the product of all individual wave functions, $\Psi=\Psi_1(r) \Psi_2(r)...$ $\Psi_N(r)$, which is a function of the spatial coordinates of all N electrons in our material, and E is the ground state, or lowest state of energy of our system. It is important to note that this equation a many body problem and has quickly become an intractable equation of 3N dimensional function, as each electron has 3-dimensions in space. As an example, the simplest hydrocarbon, methane would be a 30-dimensional problem same as with water, both containing 10 electrons. Solving the Schrödinger equation for any but the simplest system has become analytically unsolvable and is numerically very impractical.

It must be said that wave functions cannot be observed physically. What can be observed in a physical system is the charge density of a material via X-ray diffraction and other techniques. Fortunately, in quantum mechanics this can be approximated by the probability of finding an electron in a specific set of coordinates, or more accurately in a certain region of space. If we are to sum over all the electron probabilities of finding them in a specific region of space, this can closely be related to the electron density observed experimentally. For a many-electron Slater determinant, this is done through:

$$n(r) = 2\sum_{i} \Psi_{i}^{*}(r)\Psi_{i}(r)$$

where the probability of finding a single electron is the product of the complex conjugate of the wavefunction multiplied by the wave function: $\Psi^*(\mathbf{r}) \Psi(\mathbf{r})$. There is a factor of 2 prior to the summation to indicate Pauli's exclusion principle that states that every wavefunction can be occupied by two electrons of opposing spin. This physical quantity which is observable is representative of the state of the electrons in a material and can thus confer large amounts of information to us. Even more to our advantage, this quantity is only dependent on 3 dimensions, by the three spatial coordinates, orders of magnitudes simpler than any actual multi electron system.

Density Functional Theory

In order to utilize the electron density as a means of calculating materials properties, Kohn and Sham developed several theorems in the 1960's.^{40,41} The first of which states that the ground state of the Schrodinger's equation is a functional of the electron density of the material. This means that the energy, and all properties of a material, and the wave function are dependent on the electron density, which as we said before is a 3 dimensional variable that can now be used to solve Schrödinger's equation instead of the highly complex 3N variable equation resulting of a real system. The second theorem states that the electron density that minimizes the energy of the system will correspond to the electron density of the ground state energy. This means that since the energy is a functional of the electron density, E[n], by minimizing the functional form of the energy we could in theory find the ground state energy. That is if we know the form of the functional, which is usually approximated.

As we mentioned above the electron density can be written as the sum of the complex conjugate of the wave function and the wave function for each electron. Since the energy is a functional of these, the energy functional can be written as:

$$E[\{\Psi_i\}] = E_{known}[\{\Psi_i\}] + E_{XC}[\{\Psi_i\}],$$

where the $E_{known}[\{\Psi_i\}]$ includes all the contributions that we have mentioned previously.

$$E_{known}[\{\Psi_i\}] = -\frac{h^2}{m} \sum_i \int \Psi_i^* \nabla^2 \Psi_i d^3 r + \int V(r) n(r) d^3 r + \frac{e^2}{2} \int \int \frac{n(r)n(r')}{|r-r'|} d^3 r d^3 r' + E_{ion}$$

where the terms are respectively, the kinetic energy of the electrons, the coulomb interactions between electrons and nuclei, the coulomb interactions between pairs of electrons, and the coulomb interaction between nuclei. The term $E_{XC}[\{\Psi_i\}]$, corresponds to all the quantum mechanical effects.

Kohn and Sham developed the Kohn-Sham equations⁴⁰ which are very similar to our deconvolution of the Hamiltonian discussed earlier.

$$\left[\frac{h^2}{2m}\nabla^2 + V(r) + V_H(r) + V_{XC}(r)\right]\Psi_i(r) = \varepsilon_i\Psi_i(r)$$

The solution to these equations are those of a single electron wave function that depends only on the spatial variables, $\Psi_i(r)$. The first potential, V(r) described here, is in the known part of the energy functional depicted above and in the typical Hamiltonian, which depicts the interaction between electrons and the atomic nuclei. The second potential is called the Hartree potential and describes the interaction of an electron with the electron density. This potential is inherently flawed as it contains a self-interaction term, as the electron is interacting with an electron density that itself is part of. The correction for this "self-interaction" is part of the $V_{XC}(r)$, which defines the exchange and correlation contributions to the single electron, which is a functional derivative of the exchange correlation energy, defined as:

$$V_{XC}(r) = \frac{\delta E_{XC}(r)}{\delta n(r)}$$

It is apparent that this method requires a self-consistent cycle. In order to solve the Kohn-Sham equations so that we may find the electron density, we need to find the Hartree potential, which requires the electron density to be found, which in turn requires us to solve the Kohn-Sham equations, and so on.⁴² Specifically, the problem is solved as follows:

- 1. We first take a guess and assign a trial electron density
- 2. With this trial electron density, we solve for the Kohn-Sham equations to find the single-electron wave functions
- 3. Using the single electron wave functions, we calculate the product of the wave function with its complex conjugate to determine the electron density
- 4. We compare the initial and resulting electron densities. If the initial and final electron densities are different, we mix these densities and start again. Once these two last electron densities are close enough to a threshold, we stop the cycle. This
electron density is then equal to that of the ground state energy, and with it we can calculate the corresponding energy value.

Although we have discussed the algorithm for finding the minimum energy and electron density of a system, we have left out a way to determine an important parameter, the exchange correlation functional, E_{XC} . This functional specifies all of the quantum effects we have failed to take into account, like correlation and exchange interactions, and includes the self-interaction term mentioned previously. Though guaranteed to exist by the Hohenberg-Kohn theorem, its true form is unknown.⁴¹ The simplest approximation would be that derived by Hohenberg and Kohn, with the uniform electron gas approximation⁴⁰, also known as the local density approximation (LDA). In this approximation the local electron density at every point can be treated as a uniform electron gas, giving, for example, the exchange energy of the Thomas-Fermi-Dirac model:⁴³

$$E_{xc}^{LDA}[n(r)] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int n(r)^{\frac{4}{3}} dr$$

The correlation portion can also be estimated and it is typically based on the quantum Monte Carlo calculations on an electron gas, work done by Ceperley and Adler.⁴⁴This electron gas model is in fact incorrect for any real-world material but, surprisingly it has reasonable results for many systems. Additional estimates have been refined several times, with the best known class of functionals after the LDA being the generalized gradient approximation (GGA), and within this the most widely used is the Perdew–Burke–Ernzerhof functional (PBE). These class of functionals utilizes the local density information along with the gradient in the change of the electron density from one point to the next.

Bandgap Underestimation in DFT and the Hubbard U Correction

One of the limitations of the local and semilocal DFT approximations is the underestimation of the bandgaps of semiconductors.⁴⁵ This problem is well documented

and is mainly due to the self-interaction term that is not fully removed during calculations. As mentioned previously the Hartree potential describes the Coulomb interaction repulsion between an electron and the electron density of the system, which it is also part of:

$$V_h(r) = e^2 \int \frac{n(r)}{|r-r'|} d^3r'$$

Since the electrons are being repelled from one another with a greater force than what they would be without the interaction, occupied states are spread and the electron is delocalized and destabilized, which pushes its energy up. The unoccupied state on the other hand do not have any self-interacting terms, thus the energy levels of these are not pushed up, which effectively shortens the band gap of most materials to the point where some semiconductors are actually represented as metallic in nature. This problem is exacerbated in systems that are heavily correlated.⁴⁶ This means that local and semilocal DFT will not be accurate for predicting the properties of systems with overly localized electrons such as those where there are transition metals or actinides with partially filled "d" or "f" orbitals.^{47,48} This leads to local and semilocal approximation assigning an incorrect dⁿ⁻¹S¹ configuration instead of the real dⁿ⁻²s² electron configuration that leads to discrepancies in the cohesive energies of some materials.⁴² Systems like these tend to have a bandgap between suborbitals in the same orbital, caused by the crystal field splitting of the d or f orbitals. This crystal field causes the localization of the electrons into specific suborbital, causing the "Mott localization", the potential that inhibits the delocalization between suborbital is termed the "U". The band gap in these system can thus be expressed as a competition between the U potential and that of the transfer integral, t, between the sub bands in a localized system plus the addition of an additional term ,z, that is representative of the number of nearest neighbors and thus the tight binding model and the crystal field splitting, as expressed by Cococcioni:48

$$E_q = U - 2zt$$

In this model the energy of the system can be defined as:

$$E_{DFT+U} = E_{DFT} + E_U$$

Were the E_{DFT} is the energy of the system without the correction and E_U is the correction of the incorporated Hubbard potential. The simplest method for the formulation of the Hubbard U was formulated by Dudarev, et al., where its simplification comes through the neglect of the non-sphericity of the electronic interactions, and some differences among the exchange interactions. The simplified energy functional

$$E_u = \frac{U_{eff}^l}{2} \sum_l Tr \left[n^l (1 - n^l) \right],$$

where U_{eff}^{l} is the simplified U parameter including self-interaction potential and the exchange interaction term which accounts for Hund's rule on coupling, Tr indicates the trace of a matrix and n^{l} is the atomic orbital occupation matrix for the atomic site "l".

$$n^{l} = \sum_{k,v} f_{kv} \langle \Psi_{kv} | \Phi^{l} \rangle \langle \Phi^{l} | \Psi_{kv} \rangle,$$

where f_{kv} is the occupation of the Kohn-Sham state at that k-point and band v, which is determined by the Fermi-Dirac distribution, Ψ_{kv} is the Kohn-Sham orbital and Φ^l is the basis set for the atomic site "l". For a full description of the Hubbard U and its treatment, we refer the reader to the works of Himmetoglu⁴⁹ and Cococcioni^{48,49}.

All this to say that the U parameter adds a penalty in energy for states that are partially occupied, which decrease the delocalization of electrons and act as a correction on the self-interaction term. This method unlike more advanced DFT methods like hybrid functionals is moderately inexpensive to implement without much additional computational cost or time. This makes it a very tractable option to implement for high throughput calculations like the ones explored here, without requiring large amounts of time or computational resources and significantly improving the prediction of the materials properties such as their bandgaps.

High Throughput Computational and Experimental Screening of Semiconductor Photoelectrodes for Water Splitting

To enable the deployment of renewable energy into the electric grid and reduce the amount of carbon emissions by the transportation sectors, a high energy density and high power density form of energy storage is needed. It has been proposed that the transition to the "hydrogen economy" could be the solution to this problem.⁵⁰ Hydrogen also has the potential to decarbonize several other sectors including long-haul transportation, chemical production like ammonia, and the production of iron and steel.⁵¹ A sustainable closed loop, carbon-neutral way of producing hydrogen is thus highly desired. The discovery by Honda and Fujishima⁵², exemplifying how a semiconductor immersed in water could dissociate water into its constituent elements simply by shining light on it was revolutionary. This experiment set the example that the production of hydrogen could be achieved in a relatively simple method, and in a sustainable manner. The development of this field, photocatalysis, has had three main issues. The main issue is that the majority of materials that have been discovered to be capable of splitting water in this manner have a very large bandgap greater than 3 eV. This means that the percentage of the absorbed solar spectrum by these materials would only be that of UV light which accounts for less than 10% of the solar spectrum. Secondly it appears that those materials with a bandgap in the visible range that are capable of performing these kinds of reactions suffer from instabilities and tend to degrade while performing the reaction, likely due to self-oxidation by holes.³⁸ Lastly, and likely most importantly, the economic viability of these systems are not yet at the point for it to make financial sense for the world to adopt.³⁴ As Jaramillo, et al. mention in their paper³⁴, one of the most important factor for these systems to be able to achieve economic sense is to increase the absolute efficiency of the photocatalyst, the STH figure of merit, in order to make the mass production of hydrogen through photocatalysis viable. It is thus paramount for this endeavor that we find and develop materials that are capable of absorbing a higher percentage of solar energy in order to increase the efficiency of these systems. With this goal in mind we now propose a methodology to find these materials.

As discussed in the previous chapter, there are a few basic requirements that need to be met by a semiconductor for it to be capable of splitting water into hydrogen and oxygen. Firstly, as we just mentioned, the basic thermodynamic limitation is for these systems to be able to provide enough energy for the reaction to happen. Thus, we require a material that has a bandgap of at least 1.23 eV. Secondly, we must also have the band edges of our material be in the correct place, straddling the OER and HER potentials. Additionally, we require some overpotential for these reactions to take place. This overpotential has been estimated to be $\geq 0.5 V^{53}$ for driving the OER and HER, giving us a bandgap value for an ideal photocatalytic material of circa 1.8 eV. Finally, the material we utilize here must be stable. The term stability used here has two parts to it. Firstly, it is depicting that the material will not spontaneously decompose, meaning that the material is either kinetically trapped in the desired form or that it at the thermodynamically stable lowest portion of the phase diagram.⁵⁴ Secondly, the material should not react, corrode or dissolve in with water. This should be an obvious requirement, or else, the material we are working with would be useless for water splitting if it is not stable in water. Considering these fundamental requirements, we can search for a material that has all these properties.

The use of computational materials science has revolutionized the way we can search for materials. When before we would have had to go through thousands of papers and books in order to find potential candidates for any system, today we can search through databases filled with materials with computationally predicted properties. Thanks to these databases, computers can be used to search through thousands of materials for potential candidates and remove the burden from humans. Searches like these, known as high throughput screenings, can be facilitated and accomplished from a first principles perspective, and have been used in many applications thus far,^{55–59} from searching for ideal battery electrodes to searching for novel drugs for cancer treatment. A relatively recent initiative called the Materials Genome Initiative (MGI)⁶⁰ has been put in place to accelerate the discovery of materials for any application. This initiative envisions the accelerated discovery of materials through a collaborative effort among theory, computation and experiments. In this regard, the development of the Materials Project (MP)⁵⁹ (and other resources like this), a database of "all" known and theorized inorganic materials and some of their computed properties, is an instrumental key for the development of high throughput searches for many kind. The MP contains important

materials properties such as bandgap and formation energies, that can help us find ideal candidates for these searches. Previous computational screenings have been realized for the search of an ideal photocatalyst^{56,61–63} and have encountered two major common downfalls. The primary issue is the underestimation of the bandgaps of materials within conventional DFT calculations, though many attempts have been made to resolve or improve this issue. Secondly, the combination of experimental and theoretical work has been rare, so the screened candidates are rarely verified experimentally. This second limitation is highly important as it provides us with a way to verify and potentially improve the result by refining our screening criterion.

In this work, we have used the MP database as a prime resource for our high throughput search. We have developed an automated theoretical framework to determine the Hubbard U parameter for each material, for improved accuracy in bandgap prediction and further screening; and experimentally validate though synthesis, and characterization of optical, electrical and photocatalytic properties a list of 14 fully characterized materials out of a candidate pool of around 66,000 materials. Out of these 14 fully characterized materials, 9 have been determined to be photocatalytic and 4 of these have not been reported as experimentally functioning photocatalyst. The process of screening and the criteria used at every step is developed in the following section.

High throughput screening



Figure **1-9**: High throughput screening procedure scheme to predict photocatalysts. The screening criteria are on the right hand side, while the number of materials at each section is depicted in the "funnel" layers.⁴⁴

The computational screening was done utilizing the MP database that had roughly 66,000 materials with their respective DFT calculated energy above hull and bandgaps necessary for our calculations. Our fist criterion is the introduction of stability of our material. Regardless of the bandgap of the material, if the material is not thermodynamically stable, we are likely to be unable to use it for real life scenarios of water splitting. To make our lives easier, we selected materials with an energy above hull equal to zero. This can be translated as a $\Delta H_f < 0$, meaning that the formation of this

material is thermodynamically favorable from its constituent elements and they are stable against self-decomposition. Next, we determined the range we require for the acceptable bandgaps of the photocatalysts. As we have established previously, the ideal photocatalyst should have a bandgap of around 1.8 eV. Knowing that common DFT approximations can underestimate the bandgap of our material, and not wanting to have materials of too high or too low a bandgap, we chose to select a range of bandgaps from $0.7 < E_g < 2 \text{ eV}$. Using these two criteria, the number of candidate materials was decreased to 12,699. We then proceeded to calculate the band positions of our potential candidates, through an empirical method known as the geometric mean. This method utilized the bandgap of our material and the geometric mean of the electronegativity of each element in our compound to establish a value for the conduction and valence bands. It was estimated that the Fermi energy is located in the middle of our bandgap and the conduction and valence bands were calculated as follows: $E_{VB} = E_F - \chi/2$ and $E_{CB} = E_F + \chi/2$ $\chi/2$. Where E_{VB} is the valence band edge, E_F is the Fermi energy of our semiconductor, χ is the geometric Mulliken electronegativity and E_{CB} is the conduction band edge. We selected materials with a $E_{VB} > 0.8$ V vs NHE and $E_{CB} < 0.5$ V vs NHE, again in order to have some leeway between our calculations for both the bandgap and band edge positions and the actual values, we have not drawn a hard boundary on the exact limits for the thermodynamic requirements ($E_{VB} > 1.23 \text{ V} E_{CB} < 0 \text{ V}$ vs NHE). This filter left us with a pool of 2505 candidates. This list was further reduced by eliminating candidates that have highly toxic elements based on the LD_{50} scale. Materials having an LD_{50} greater than 250 mg/kg, materials with elements that are known to be radioactive, and materials with low Earth abundance (abundance less or equal to that of gold, $4.3 \times 10^{-7} \text{ wt\%})^{64}$ were not kept. The list of removed elements was As, Tc, Ru, Rh, Pd, Cd, Lu, Re, Os, Ir, Pt, Au, Hg, Tl, Po, At, Rn, lanthanide series, actinide series, and the last period of the periodic table. This reduced the candidates to 1998. To further narrow our search, these materials were crossreferenced through the Crystallography Open Database⁶⁵. This helped us identify some of the materials that had been previously reported as synthesized. This left us with a list of 452 candidates, though which we in the chemistry team did a manual search through these materials to identify which of these would be synthetically feasible. Factors such as

common oxidation states of the elements, coordination numbers and chemical precursors needed for the synthesis, and chemical intuition to predict materials that would be sensitive to air, water, etc., were taken into consideration to narrow down the list of candidates to 263 materials.

It is at this moment in the process where we addressed the previously mentioned concern with underestimation of the bandgap by semilocal DFT. We implement the Hubbard U parameter through the recently developed algorithm by Timrov et. al. for self consistently determining the Hubbard U parameter⁶⁶, which allowed us to calculate the bandgap of our materials with more accuracy. Since the calculation of the conduction band edges remains constant despite the changes in bandgap, we can plot these materials to determine which of these would be adequately positioned to phototactically split water, as depicted in Figure 1-10.



Figure **1-10**: Graphical representation of the band edge position of photocatalytic candidates. The ideal candidates are in the bottom right quadrant as these materials have

a bandgap larger than the overall water splitting reaction and have band edge positions that would allow for both OER and HER. The rainbow area depicts the bandgaps by with the minimum frequency of light needed to create an electron hole pair.⁴⁴

Based on this last figure we identified that there were 68 promising candidates for overall water splitting utilizing visible light. Most notably, some of these materials, such as the plumbates that will be talked about below, have not been experimentally determined to be photocatalytic materials.

Solid State Synthesis

Out of the 68 materials previously described, 14 materials were synthesized and characterized to determine phase purity via X-ray Diffraction (XRD) and via optical methods to characterize the bandgaps of these materials using Ultraviolet-Visible Spectroscopy (UV-Vis). 9 additional materials were also synthesized for this endeavor but were either not fully characterized or are chemical derivatives of the previous compounds and were made for future work. The results discussed here are mine. Additional information performed by other members of the collaborative team such as hydrogen production, flat band potential, and calculated parameters can be found in the Appendix.

Ba₃MnNb₂O₉

The synthesis of Ba₃MnNb₂O₉ in the literature is reportedly able to be made through simple solid-state methods.⁶⁶ Stoichiometric amounts of BaCO₃, MnO₂ and Nb₂O₅ are thoroughly mixed in a mortar and heated to 850°C for 20 hours, followed by remixing, and pressing of the resulting powder into pellets and sintering at 1350°C for 5 days with intermediate grinding and pelletizing.⁶⁶ Alternatively, this powder can be made through an aqueous solution route, where soluble salts of precursors are mixed in a solution and then dried and heated similarly than the previous methods, but reducing the final temperature to $1300^{\circ}C$.⁶⁷ The precursors chosen by Liu et. al. were barium acetate, (Ba(CH₃COO)₂, manganese (II) acetate tetrahydrate Mn(C₂H₃O₂)₂. 4H₂O), and niobium (V) chloride (NbCl₅).⁶⁶ Both approaches are relatively simple and similar, with the difference being that the aqueous method allows for a more intimate mixing of the precursors from the resulting powders, which theoretically should allow for easier diffusion of the corresponding thermodynamically stable phase in an easier manner. This is likely why the temperature for the final heating of the aqueous method is not as high as the solid-state method.

In this work Ba₃MnNb₂O₉ was synthesized in 1 g batches by adding BaCO₃ powder (Alfa Aesar, 99.95%), MnO₂ powder (Sigma-Aldrich, \geq 99%) and Nb₂O₅ powder (Sigma-Aldrich, 99.99%) in a 3:1:1 molar ratio respectively. The powder was ground using an agate mortar and pestle, pelletized using a hand press and added to an alumina boat. The sample was placed in a mullite tube furnace and heated in air to 400 °C at a rate of 5 °C/min and was dwelled at 400 °C for two hours before escalating the temperature to 800 °C at a rate of 5 °C/min, dwelling at 800°C for two hours. The sample was then heated to 1300°C at a rate of 5 °C/min and dwelling at 1300°C for 2 days. The sample was cooled to room temperature. Our synthetic method is very similar to the solid state reaction reported in the literature, with a change in the initial pelletizing of the powders and a reduction of the final temperature to 1300°C and a reduction of the overall time of calcination. These changes were implemented as it would cut down on the time of synthesis by initially heating to 1300°C, and not having to do intermittent grindings. Regardless of these changes, the resulting compound was analyzed via XRD and was shown to be phase pure via XRD as shown below.



Figure **1-11**: XRD scan of Ba₃MnNb₂O₉. Normalized experimental pattern shown in red and reference pattern (PDF 00-046-0998) shown in black.

In order to analyze the optical properties of this material, the sample was drop cast onto a glass slide. The sample was ground in a mortar with ethanol, and then drops of this suspension were placed on a glass slide and left to dry. Consecutive drops were added until a uniform, thick, and opaque film of the powders was observed (based on lack of light transmission through the film). A Perkin Elmer lambda 950 was used to measure diffuse reflectance spectra using a 150 mm integrating sphere collecting data from 250-2500 nm, taking 1 nm steps, and using a 4 nm slit width in diffuse reflection mode. The reference spectrum for total reflectance ("pure white") was measured against a Spectralon disc. A plot of the Kubelka-Munk function^{68–71}, raised to the power of ½ or 2 for indirect and direct semiconductors, respectively, vs. energy in nm was constructed to obtain the bandgaps. Bandgaps were calculated using the derivative of the Kubelka-Munk plot, finding the linear region in the onset of absorption from high to low energy, and extrapolating the region to the x intercept. The bandgap of the material was determined to be $E_g = 0.72 \text{ eV}$. This is unsurprising as the color of the material was a very dark hue of

purple, as can be seen in the inset of Figure 1-12, meaning that its bandgap is likely narrower than the visible range, 700nm – 400nm, which corresponds to energies of around 1.75 eV and 3.1 eV.





This means that unfortunately this material is not an adequate candidate for water splitting due to its low bandgap, regardless of its other properties. It must be noted that the predicted bandgap for this material was meant to be 1.7 and 3 eV according to DFT and DFT+U respectively (See appendix Table 1 for bandgap data). It is clearly an overestimation on either side, and this is likely due to the magnetic ordering of the material, that requires special considerations during calculations. Additionally, the creation of midgap states caused by fluctuations in the oxidation states of the Mn or Nb could be a root cause of this large discrepancy in the bandgap. Mn can easily achieve several oxidation states, and thus, this change in oxidation states caused by a photon could cause midgap states in the material, that would reduce the measured optical bandgap of this material. We were unable to find any reports in the literature of its bandgap so we were unable to corroborate this parameter.

BaCaFe₄O₈

The literature suggest that the formation of this metal oxide can be done through reacting nitric acid with stoichiometric quantities of barium nitrate, calcium carbonate and metallic iron, which would in turn form a mixture of nitrates.⁷² These would then be decomposed at 700°C. This mixture of oxides would then be heated in a platinum vessel at 1100°C for 5 hours, which leads to the formation of the compound without impurities.⁷² It is also mentioned that decomposition of the product appears at 1120°C.

We have determined that the synthesis of BaCaFe₄O₈ powder can proceed without the need for the initial step of reacting the mixtures with nitric acid. BaCaFe₄O₈ was synthesized in 1g batches by adding Ba(NO₃)₂ powder (Sigma-Aldrich, \geq 99%), CaCO₃ powder (Alfa Aesar, 99.99%), and FeO (Alfa Aesar, 99.95%) in a 1:1:4 molar ratio respectively. The powder was ground using an agate mortar and pestle, pelletized using a hand press and added to an alumina boat. The sample was placed in a Lindberg/Blue M tube furnace and heated in air to 400 °C at a rate of 5 °C/min and was dwelled at 400 °C for three hours before raising the temperature to 800 °C at a rate of 5 °C/min and then dwelling at 800 °C for 4 hours. The sample was then heated to 1100°C at a rate of 5 °C/min and dwelling at 1100°C for 2 days. The sample was cooled to room temperature. The sample was then reground, pelletized and heated to 1100 °C at 5 °C/min and dwelling at 1100 °C for 2 additional days. We must note that the slow heating rat is crucial with this prep as it prevents the volatilization and loss of Barium. If done too fast, this results in the desired phase, BaCaFe₄O₈ and a calcium iron oxide impurity (Ca₂Fe₂O₅) as seen below.



Figure **1-13**: XRD depicting BaCaFe₄O₈ and impurities of Ca₂FeO₅ prior to the regrinding and re-firing of the sample.

The additional grinding is also needed to increase the mixing of these elements. This procedure, though longer than the one cited in the literature does prevent the use of nitric acid, while still producing the desired pure phase by XRD, as seen below.



Figure **1-14**: XRD scan of BaCaFe₄O₈. Normalized experimental pattern shown in red and reference pattern (PDF 00-018-0147) shown in black. Impurities denoted by the blue labels.

In order to determine the optical properties of the material the diffuse reflectance measurement of this material was also determined. The resulting Tauc plot shown below shows a bandgap of 2.04 eV, which is still quite shy of the theorized 3.52 eV. The discrepancy of these values is once again likely due to the magnetic ordering and midgap states, previously described in Ba₃MnNb₂O₄. This can be noticed with a lot more clarity here, as the Tauc plot has several peaks inside the bandgap, denoting midgap states.



Figure 1-15: Tauc Plot of BaCaFe₄O₈ using the Kubelka-Munk function to the 1/2 power VS energy, used to determine the bandgap of the material.

This material has not been previously reported as a photocatalyst, nor could we determine if it could produce hydrogen in our experiments (See Table 1 in the appendix for data). We were unable to find any reports in the literature of its bandgap. This does not mean it is not capable of water splitting, simply that under our conditions we did not observe it to be. Some of the reasons for this could be large amounts of defects that could act as charge recombination sites, poor charge transfer to the surface, low surface area of the product, etc.

MgSb₂O₆

This compound is most commonly synthesized though wet chemical methods, where a sol of Sb₂O₅, H₂O₂ and water are added a stoichiometric solution of MgCl₂.⁷³ This solution is then heated until the solvent is evaporated. After the drying a pellet is pressed and the sample is heated to 1320K, or 1047°C, for 4 hours. It is also commonly synthesized as nanorods and nanoparticles, though colloidal methods.⁷⁴

We have determined that the synthesis of MgSb₂O₆ powder can be made by thoroughly grinding and mixing MgO powder (Alfa Aesar, 99+%) and Sb₂O₃ powder (Aldrich, \geq 99.9%) combined in a 1:1 molar ratio, pelletized, and heated at 5°C/min and held at 400°C and 800°C for two hours prior to heating to the final temperature of 1300°C for 48 hours in a Mullite tube furnace. The resulting XRD pattern is shown below. There is no need for any wet chemistry. It should be noted that it was shown that on occasion impurities can be found using this method, subsequent grindings and firings might be necessary.



Figure **1-16**: XRD scan of MgSb₂O₆. Normalized experimental pattern shown in red and reference pattern (PDF 04-007-4739) shown in black.

The determination of the optical properties of the material were made through a diffuse reflectance measurement. The resulting Tauc plot below shows a bandgap of 4.01 eV, which is very close to the value of 3.77 eV determined by DFT+U. We can see that this Tauc plot is quite trivial compared to some of the others in this thesis. This material is also one of only three materials that were determined to be direct bandgap materials in this study.



Figure **1-17**: Tauc Plot of MgSb₂O₆ using the Kubelka-Munk function to the 2 power VS energy, used to determine the bandgap of the material.

This material has not been previously reported as a photocatalyst, nor could we determine if it could produce hydrogen in our experiments (See Table 1 in the appendix for data). This does not mean it is not capable of water splitting, but we can see by the bandgap that the absorption of solar energy of this material would be in the UV portion of the spectrum, even above that of TiO_2 which is already a large bandgap semiconductor. This could make the materials very inefficient photocatalysis utilizing the solar spectrum, thus we might be unable to determine the minute quantities of hydrogen it does produce. Our band gap is a little short of the 4.3 eV⁷³ reported in previous literature, but it is still in good agreement.

Na₃Fe₅O₉

The literature states that this material can be synthesized as single crystals by firing a mixture of Na_2CO_3 and Fe_2O_3 at 1100°C for about two hours.⁷⁵ The literature also states that this compound is not stable at temperatures below 1029K where it decomposes into $Na_2Fe_2O_4$ ($NaFeO_2$) and Fe_2O_3 .⁷⁶ During our attempts at making this material, we saw that the process was not straightforward. We attempted a single crystal

approach to the synthesis of this through the molten compounds, which formed crystals, but not of the desired phase. Alternatively, the synthesis through powder synthesis was the most successful, but still showed significant impurities. The compound was never successfully made as a pure sample. Na₃Fe₅O₉ was synthesized in 1 g batches by adding Na₂CO₃ powder (EMD Chemicals, 99.9%) and Fe₂O₃ powder (Sigma-Aldrich) in a 3:5 molar ratio of Na₂CO₃:Fe₂O₃. The powder was ground using an agate mortar and pestle, pelletized using a hand press and added to an alumina boat. The sample was placed in a Lindberg/Blue M tube furnace and heated in air to 400 °C at a rate of 5 °C/min and was dwelled at 400 °C for two hours before escalating the temperature to 800 °C at a rate of 5 °C/min, dwelling at 1100°C for 2 days. The sample was cooled to room temperature



Figure 1-18: XRD scan of $Na_3Fe_5O_9$. Normalized experimental pattern shown in red and reference pattern (PDF 04-011-2582) shown in black. Peaks marked with an (*) correspond to $NaFe_3O_5$.

The final sample showed significant noise likely due to amorphous material in our sample. In addition to this, the material also showed impurities of the NaFe₃O₅ phase. In

previous runs, like in the attempts to make this material as single crystals, we did see the presence of the Na₂Fe₂O₄ phase, depicted as NaFeO₂, along with another sodium rich phase Na₂FeO₄.



Figure **1-19**: XRD pattern of Na₃Fe₅O₉ depicting impurities of NaFeO₂ and Na₂FeO₄ as side products of synthesis.

The determination of the optical properties of the material were made through diffuse reflectance measurement. The resulting Tauc plot shown below shows a bandgap of 0.77 eV, which is very far from the 2.64 eV determined by DFT+U. The discrepancy of these values is likely due to several factors. Once again, the magnetic ordering and midgap states can be observed in the Tauc plot like those previously described with magnetic materials. The Tauc plot has several peaks inside the bandgap, denoting midgap states. This can also be due to the impurities in our compound, which are not insignificant.



Figure **1-20**: Tauc Plot of $Na_3Fe_5O_9$ using the Kubelka-Munk function to the 1/2 power vs. energy, used to determine the bandgap of the material.

Nevertheless, this material could produce hydrogen through our experimental setup (See Table 1 in the appendix for data). Though the bandgap is not large enough to provide full water splitting, this material could be of potential use as a standalone HER catalyst. I was unable to find any reports in the literature of its bandgap, so I was unable to corroborate this value.

Nb₂Co₄O₉

This compound was reported to be synthesized through solid state reactions through the grinding and mixing of stoichiometric amounts of Co_3O_4 and Nb_2O_5 .⁷⁷ These are pelletized and heated in air at 1173K, 900°C, for 10 hours. The resulting sample was pulverized and pressed into pellets and heated to 1223K, 950°C, in air for 20 hours with intermediate grindings. It must be noted that the compound has been reported as an antiferromagnetic material, which as we have shown in the examples before, the magnetic ordering of these material will interfere with our ability to accurately describe the properties computationally.

Our method of synthesis is a bit more simplified than that reported in the literature. We have determined that the sample can be made by intimately grinding and pelletizing Nb₂O₅ powder (Sigma-Aldrich, 99.99%) and CoO powder (Research Organic/Inorganic Chemical Corp., 98%) in a 1:4 molar ratio using an agate mortar and pestle. The sample was added to an alumina boat and heated in air at 5°C/min and held at 400°C and 800°C for two hours prior to heating to 1300°C for 48 hours in a Mullite tube furnace. As shown below the this resulted in a phase pure sample by XRD.



Figure 1-21: XRD scan of Nb₂Co₄O₉. Normalized experimental pattern shown in red and reference pattern (PDF 00-038-1457) shown in black. Peaks marked with an (*) correspond to impurities.

The determination of the optical properties of the material were made through diffuse reflectance measurement. The resulting Tauc plot shown below shows a bandgap of 2.29 eV, which is far from the 3.46 eV determined by DFT+U. The discrepancy of these values is once again likely due to the magnetic ordering. Midgap states can be observed in the Tauc plot like those previously described with magnetic materials, but these are far more intense than those shown before. The change in oxidation number for

cobalt in this material could be another possibility for the midgap states, along with the d band splitting, which with the antiferromagnetic ordering could have energy levels inside the bandgap. The Tauc plot below shows several peaks inside the bandgap, denoting the midgap states.





The material was capable of producing hydrogen, and the bandgap and band alignment of the material do coincide with this material being capable of performing water splitting (See Table 1 in the appendix for data). That being said, with the number of mid gap states this material exhibits, it is quite impressive that the trap states aren't taking over the whole relaxation process inhibiting the production of hydrogen. This is an exciting material because it has not been reported as a water splitting photocatalyst, to my knowledge. I was unable to find any reports in the literature of its bandgap, so I was unable to corroborate this value.

PbTiO₃

The process of synthesizing $PbTiO_3$ is simple through solid state techniques of the mixture of metal oxides or carbonates. The mixture of PbO and TiO₂ heated to 375°C for

40hrs was the original method of described synthesis.⁷⁸ Several other methods of obtaining this materials have been described in an effort to obtain single crystals and nanoparticles that are defect free in order to study a multitude of promising properties of this material like its ferroelectric properties.^{79–82} We have determined that this material is easily and rapidly synthesized by grinding and pelletizing PbO powder (Alfa Aesar, 99.999%) and TiO₂ powder (Alfa Aesar, 99.9%) combined in a 1:1 molar ratio. The sample is then added to an alumina boat and heated in air at 5°C/min and held at 400°C and 800°C for two hours prior to heating to 900°C for 12 hours in a Lindberg/Blue M tube furnace. The resulting XRD pattern is shown below.



Figure **1-23**: XRD scan of PbTiO₃. Normalized experimental pattern shown in red and reference pattern (PDF 04-006-5418) shown in black.

The determination of the optical properties of the material were made through a diffuse reflectance measurement. The resulting Tauc plot shown below shows a bandgap of 2.69 eV, which is far from the 3.45 eV determined by DFT+U.



Figure 1-24: Tauc Plot of $PbTiO_3$ using the Kubelka-Munk function to the 1/2 power vs. energy, used to determine the bandgap of the material.

The material was capable of producing hydrogen, and the bandgap and band alignment of the material do coincide with this material being capable of performing water splitting (See Table 1 in the appendix for data). The literature has noted that this material has a bandgap between 3.2-3.4 eV^{83–85}, which is higher than what I determined. Our bandgap compares with another report on the literature of which claim a bandgap of 2.7 eV and a photocatalysis assessment⁸⁶, and as such is not as exciting, but it is still an important verifications that our methods are correct. This discrepancy in experimental bandgaps is likely due to impurities that are not perceptible by XRD or by the induction of defects in the material that lead to the creation of color centers. This material has a very slight yellowish tint, as opposed to it being purely white. The materials that exhibit the higher bandgaps are typically made through epitaxial methods as to get higher purities, while our methods are through solid state synthesis.

ZnFe₂O₄

This compound has been synthesized in the literature in many different ways through the use of polymer complex, microwave sintering, self-propagating combustion, sol-gel, to the simplest solid state reaction where ZnO and Fe₂O₃ are intimately ground, pelletized and calcined at 1200°C.⁸⁷ We have determined that the optimized synthesis can be done for our setup by grinding and pelletizing ZnO powder (Sigma Aldrich, \geq 99.0%) and Fe₂O₃ powder (Aldrich, catalyst grade) combined in a 1:1 molar ratio. The sample is then added to an alumina boat and heated in air at 5°C/min and held at 400°C and 800°C for two hours prior to heating to 900°C for 72 hours in a Lindberg/Blue M tube furnace. The resulting XRD pattern is shown below



Figure 1-25: XRD scan of $ZnFe_2O_4$. Normalized experimental pattern shown in red and reference pattern (PDF 04-002-2708) shown in black. Peaks marked with an (*) correspond to impurities.

The determination of the optical properties of the material were made through diffuse reflectance measurement. It must be noted that this material is only one of three materials to show a direct bandgap transition. The bandgap transitions were determined through the calculated band diagrams of each material. The resulting Tauc plot shown below shows a bandgap of 2.26 eV, which is far from the 3.60 eV determined by DFT+U. The discrepancy of these values is once again likely due to the magnetic

ordering. This material is known to possess an antiferromagnetic ordering which could cause these issues with the bandgap calculation. The change in oxidation number for iron in this material could be another possibility for the decreased bandgap, along with the d band splitting, which with the antiferromagnetic ordering could have energy levels inside the bandgap which would decrease the apparent bandgap in our measurements.



Figure **1-26**: Tauc Plot of $ZnFe_2O_4$ using the Kubelka-Munk function to the 2^{nd} power vs. energy, used to determine the bandgap of the material.

The material was capable of producing hydrogen , and the bandgap and band alignment of the material do coincide with this material being capable of performing water splitting (See Table 1 in the appendix for data). Our bandgap compares well with that reported in the literature of 1.9 eV and photocatalysis assessment is in line with that previously reported in the literature⁸⁷, and as such is not as exciting, but it is still and important verifications that our methods are accurate.

Ca₂PbO₄

This material has been described to be synthesizable through the mixture of CaCO₃ and PbO powders, finely ground ang heated in air at a temperature of 700-750°C for 6.5 hours.⁸⁸ We synthesized Ca₂PbO₄ in 1 g batches by adding CaCO₃ powder (Alfa Aesar, 99.99%) and PbO powder (Alfa Aesar, 99.999%) in a 2:1 molar ratio of CaCO₃: PbO. The powder was ground using an agate mortar and pestle, pelletized and added to an alumina boat. The sample was placed in a Lindberg/Blue M tube furnace and heated in air to 400 °C at a rate of 5 °C/min for two hours before escalating the temperature to 800 °C at a rate of 5 °C/min for 26 hours. The sample was cooled to room temperature. The resulting XRD pattern is shown below, showing phase purity by XRD.



Figure **1-27**: XRD scan of Ca₂PbO₄. Normalized experimental pattern shown in red and reference pattern (PDF 04-008-2917) shown in black.

The determination of the optical properties of the material were made through a diffuse reflectance measurement. The resulting Tauc plot shown below shows a bandgap of 2.94 eV, which is very close to the value of 2.47 eV determined by DFT+U. The Tauc

plot is simple compared to some of the rest that we have seen. This material was determined to have an indirect bandgap.



Figure **1-28**: Tauc Plot of Ca_2PbO_4 using the Kubelka-Munk function to the 1/2 power vs. energy, used to determine the bandgap of the material.

The material was capable of producing hydrogen, and the bandgap and band alignment of the material do coincide with this material being capable of performing water splitting (See Table 1 in the appendix for data). This material has not been previously reported experimentally to be a water splitting photocatalyst, but it has been screened previously by others as a potential candidate for water splitting.^{89,90}The screening studies determined a bandgap of 3.2 eV^{90} which is larger than the one we determined and predicted. This makes it clear that the coupling of experimental and theoretical works are fundamental for our advancement in the field.

Cu_2PbO_2

The literature states that this compound can be made through a solid state reaction of Cu_2O and PbO in a sealed quartz ampule.⁹¹ The sample is heated to 610°C for 260 hours. We determined that this material is more easily synthesized by thoroughly mixing Cu_2O powder (Fisher Scientific, 98.6%) and PbO powder (Alfa Aesar, 99.999%) combined in a 1:1 molar ratio. The sample was heated under argon flow to 450°C at a

rate of 2.5° C/min for two hours before heating to 700°C for 10 hours in a Lindberg/Blue M tube furnace. The original synthesis⁹¹ was attempted but the resulting powder was a mixture of Cu₂O and various lead oxides. It was determined that the sample required a very slow heating rate to prevent the loss of lead oxide and that the absence of air was fundamental for the formation of the compound. The XRD pattern of the resulting compound is shown below.



Figure **1-29**: XRD scan of Cu₂PbO₂. Normalized experimental pattern shown in red and reference pattern (PDF 04-010-7860) shown in black.

The determination of the optical properties of the material were made through diffuse reflectance measurement. The resulting Tauc plot shown below shows a bandgap of 1.59 eV, which is close to the value of 2.17 eV determined by DFT+U. The Tauc plot is simple compared to some of the rest that we have seen. This material was determined to have an indirect bandgap through its calculated band diagram.



Figure 1-30: Tauc Plot of Cu_2PbO_2 using the Kubelka-Munk function to the 1/2 power vs. energy, used to determine the bandgap of the material.

The material was capable of producing hydrogen in one of our conditions, and the bandgap and band alignment of the material do coincide with this material being capable of performing water splitting (See Table 1 in the appendix for data). This material has not been previously reported experimentally to be a water splitting photocatalyst, but it has been screened previously by others as a potential candidate for water splitting.^{90–92} The literature also cites that the bandgap of the material is of 1.7 eV⁹⁰, which is close to the one determined in our work.

Ba₂PbO₄

The material is known to be synthesized though solid state processes through the stoichiometric mixing of BaCO₃ and PbO or PbO₂ powders.⁹³ These powders are heated to 450°C for 12 hours and then ground and heated to 950°C for 12 hours. The sample is then ground and pelletized and calcined at 950°C for 24 hours. In this work Ba₂PbO₄ was synthesized in 1 g batches by adding BaCO₃ powder (Alfa Aesar, 99.95%) and PbO powder (Alfa Aesar, 99.999%) in a 2:1 molar ratio of BaCO₃: PbO. The powder was ground using an agate mortar and pestle, pelletized using a hand press and added to an

alumina boat. The sample was placed in a Lindberg/Blue M tube furnace and heated in air to 400 °C at a rate of 5 °C/min, was dwelled at 400 °C for two hours before escalating the temperature to 800 °C at a rate of 5 °C/min, dwelling at 800°C for 5 hours. The sample was then heated to 1100°C at a rate of 5 °C/min and dwelling at 1100°C for one day. The sample was cooled to room temperature. We must note that the PbO used to produce Ba₂PbO₄ had an orange color, likely due to either it being a mixture of the litharge polymorph which has been described as red to orange in color, and Massicot, which is typically yellow; or Pb₂O₃ impurities which are also orange in color. This second option could be reasonable as Pb₂O₃ is a mixture of Pb(II) and Pb(IV), meaning that this impurity of Pb(IV) could act as a nucleation site for the development of the phase we desire. This was necessary for this phase to form in high yield. The PbO of yellow origin was determined to not be suitable to produce the tetravalent lead in this compound. The resulting XRD pattern from this reaction is shown below. The use of PbO₂ had no issues in producing the desired phase.



Figure 1-31: XRD patterns of my attempts of synthesizing Ba_2PbO_4 through the use of different lead oxides. The figure depicts that yellow PbO (used in the bottom left corner) is unsuitable to produce the plumbate.

With this control experiment we can see that only the lead oxide precursors with Pb(IV) were capable of forming the material. Though not proven, it is likely that the orange color in PbO is due to Pb(IV) impurities that act as nucleation sites for the formation of the desired phase. The resulting XRD of our final product is shown below and shows phase purity by XRD.



Figure **1-32**: XRD scan of Ba₂PbO₄. Normalized experimental pattern shown in red and reference pattern (PDF 04-007-5957) shown in black.

The determination of the optical properties of the material were made through diffuse reflectance measurement. The resulting Tauc plot shown below shows a bandgap of 1.45 eV, which is not far off the 2.00 eV determined by DFT+U. The Tauc plot is simple and the bandgap can be obtained easily. This material was determined to have an indirect bandgap.





The material was capable of producing hydrogen in two of our conditions, and the bandgap allow for overall water splitting. That being said, the experimental band edges do suggest that this material should not be capable of producing oxygen as it is not straddling the OER (See Table 1 or Figure A-3 in the appendix for data). The experimental band edges do suggest a large overpotential for the HER, which could explain the ability for this material to produce hydrogen in more conditions than our other plumbates. This material has not been previously reported experimentally to be a water splitting photocatalyst, but it has been screened previously by others as a potential candidate for water splitting.^{90–92} They suggest a bandgap of 2.5 eV⁹², which is greater than our prediction or my optical determination. The literature also cites that the bandgap of the material is of 1.3 eV^{93} , which is close to the one determined in our work.

NaInO₂

The literature states that this material can be made through the through mixing and grinding of Na₂CO₃ and In₂O₃ in stoichiometric quantities. ⁹⁴ The powder is pelletized and heated to 1100° C in 24 hours and held at that temperature for 48 hours, after which it is cooled to room temperature in 6 hours. We synthesized NaInO₂ in 1g

batches by adding Na₂CO₃ powder (EMD Chemicals, 99.9%) and In₂O₃ powder (Alfa Aesar, 99.99%) in a 1:1 molar ratio respectively. The powder was ground using an agate mortar and pestle, pelletized using a hand press and added to an alumina boat. The sample was placed in a Lindberg/Blue M tube furnace and heated to 400 °C at a rate of 5 °C/min and was dwelled at 400 °C for two hours before escalating the temperature to 900 °C at a rate of 5 °C/min, dwelling at 900°C for 3 hours. The sample was cooled to room temperature. The resulting products XRD, shown below, shows the compound was made pure by XRD.



Figure **1-34**: XRD scan of NaInO₂. Normalized experimental pattern shown in red and reference pattern (PDF 04-008-3834) shown in black.

The determination of the optical properties of the material were made through diffuse reflectance measurement. The resulting Tauc plot shown below shows a bandgap of 3.85 eV, which is not far off the 4.22 eV determined by DFT+U. The Tauc plot is simple and the bandgap can be easily obtained. This material was determined to have an indirect bandgap.


Figure 1-35: Tauc Plot of NaInO₂ using the Kubelka-Munk function to the 1/2 power vs. energy, used to determine the bandgap of the material.

The material was capable of producing hydrogen, and the bandgap and band alignment allow for overall water splitting (See Table 1 in the appendix for data). The material's high bandgap and band edge positions should allow for photocatalysis but, the use of a photocatalyst like this is not recommended, as it would be less efficient at capturing solar radiation than the well-studied TiO2 which has a lower bandgap of 3.2 eV. The literature has shown that this material is photocatalytic and capable of full water splitting⁹⁵ and also cites that the bandgap of the material is of 3.9 eV⁹⁶, which is very similar to the one determined in our work.

CaIn₂O₄

It has been noted in the literature that this material can be made through the mixing of In_2O_3 and CaO or CaCO₃ powders intimately mixed and calcined at a temperature of 1400 °C for 24hours or at 880°C for 7 days.⁹⁷ We have synthesized CaIn₂O₄ in 1g batches by adding CaCO₃ powder (Alfa Aesar, 99.99%) and In₂O₃ powder (Alfa Aesar, 99.99%) in a 1:1 molar ratio. The powder was ground using an agate mortar and pestle, pelletized using a hand press and added to an alumina boat. The sample was

placed in a Lindberg/Blue M tube furnace and heated in air to 900 °C at a rate of 5 °C/min and was dwelled at 900°C for 12 hours before escalating the temperature to 1050°C at a rate of 5 °C/min and dwelling at 1050°C for 12 hours. The sample was cooled to room temperature. It must be noted that for CaIn₂O₄, our experimental pattern did not match the reference pattern from the corresponding CIF file, which referenced to a paper by Cruickshank, et al.⁹⁷ that described the CaIn₂O₄ crystal structures with a Pca2₁ or Pbcm crystal structure. My CaIn₂O₄ sample appeared to be isostructural to SrIn₂O₄, even though the XRD pattern matches patterns observed by several researchers including Cruickshank, et al. for CaIn₂O₄⁹⁷⁻¹⁰¹ who claim the CaIn₂O₄ structure is different from the srIn₂O₄ structure. ¹⁰² We generated the simulated XRD pattern for CaIn₂O₄ using the crystal structure of SrIn₂O₄ (space group Pnam), replacing Sr with Ca and using the experimentally determined lattice constants (*a* = 9.6781 Å, *b* = 11.2963 Å, and *c* = 3.2214 Å), shown below. This structure is consistent with Tang et al.⁹⁸



Figure **1-36**: XRD scan of CaIn₂O₄. Normalized experimental pattern shown in red and reference pattern (PDF 04-013-8519) for space group Pnam (as described above) shown in black.

The determination of the optical properties of the material were made through diffuse reflectance measurement. The resulting Tauc plot shown below shows a bandgap of 3.88 eV, which is not far off the 4.30 eV determined by DFT+U. This material was determined to have a direct bandgap.



Figure 1-37: Tauc Plot of $CaIn_2O_4$ using the Kubelka-Munk function to the 2^{nd} power vs. energy, used to determine the bandgap of the material.

The material was not capable of producing hydrogen even though the bandgap and band alignment should allow for overall water splitting (See Table 1 in the appendix for data). The literature has shown that this material is photocatalytic and capable of full water splitting¹⁰³ but has said that the solid state synthesis of this material is far less efficient at photocatalysis than those synthesized by solid combustion methods that produced nanoparticles.¹⁰² The author of that work¹⁰² suggests this is likely due to the low surface area and the large amount of defects produced though this method. The bandgap of the material is of 3.83 eV^{104} through nanocrystal synthesis, which is very similar to the one determined in our work. Others suggest this material has a bulk bandgap ranging from 2.48-2.7 eV depending on calcination conditions.¹⁰¹ The bandgap of the individual binary systems are 7.7 eV^{105} for CaO and 2.9-3.2 eV¹⁰⁶ for In₂O₃. It is unlikely that this material would thus have a bandgap below 3 eV. The material is clearly white with no undertones; thus, it is likely that its band gap is above the visible range and into the UV section of the electromagnetic spectrum.

SrIn₂O₄

This compound has been cited in the literature as being easily made through solid state reactions of SrO and In₂O₃ at 1200°C or by coprecipitation of the nitrates in oxalic acid ethanol solution and calcination at 1100°C.^{102,107} We have synthesized this compound identically as we synthesized CaIn₂O₄, in 1g batches by adding SrCO₃ powder (Alfa Aesar, 99.99%) and In₂O₃ powder (Alfa Aesar, 99.99%) in a 1:1 molar ratio. The powder was ground using an agate mortar and pestle, pelletized using a hand press and added to an alumina boat. The sample was placed in a Lindberg/Blue M tube furnace and heated in air to 900 °C at a rate of 5 °C/min and was dwelled at 900°C for 12 hours before escalating the temperature to 1050°C at a rate of 5 °C/min and dwelling at 1050°C for 12 hours. The sample was cooled to room temperature. The respective XRD shown below shows purity by XRD.



Figure **1-38**: XRD scan of SrIn₂O₄. Normalized experimental pattern shown in red and reference pattern (PDF 04-013-8519) shown in black.

The determination of the optical properties of the material were made through a diffuse reflectance measurement. The resulting Tauc plot shown below shows a bandgap

of 3.67 eV, which is not far off the 3.93 eV determined by DFT+U. This material was determined to have an indirect bandgap.



Figure **1-39**: Tauc Plot of $SrIn_2O_4$ using the Kubelka-Munk function to the 1/2 power VS energy, used to determine the bandgap of the material.

This material has been shown to be capable of water splitting photocatalysis and has a bandgap of 3.6 eV which is in line with what we determined.^{102,107,108} It is supposed to have a higher activity than $BaIn_2O_4$ but lower than $CaIn_2O_4$.^{102,103} This was not experimentally reproduced by our analysis likely due to the solid state synthesis of $CaIn_2O_4$ as discussed above. Our experiments showed that this compound was capable of producing hydrogen (See Table 1 in the appendix for data), which is in line with what we would expect as a previously known photocatalyst.

BaIn₂O₄

It has been established that the combustion synthesis and solid state synthesis of this material are possible.¹⁰⁹ The solid state reaction is typically done by intimately grinding and pelletizing stoichiometric amounts of BaCO₃ and In₂O₃ which are then calcined at 1000°C for 24 hours. We have synthesized this compound identically as we synthesized SrIn₂O₄ and CaIn₂O₄, in 1g batches by adding BaCO₃ powder (Alfa Aesar, 99.99%) and In₂O₃ powder (Alfa Aesar, 99.99%) in a 1:1 molar ratio. The powder was

ground using an agate mortar and pestle, pelletized using a hand press and added to an alumina boat. The sample was placed in a Lindberg/Blue M tube furnace and heated in air to 900 °C at a rate of 5 °C/min and was dwelled at 900°C for 12 hours before escalating the temperature to 1050°C at a rate of 5 °C/min and dwelling at 1050°C for 12 hours. The sample was cooled to room temperature. The XRD pattern shown below indicates phase purity.



Figure **1-40**: XRD scan of BaIn₂O₄. Normalized experimental pattern shown in red and reference pattern (PDF 04-013-8196) shown in black.

The determination of the optical properties of the material were made through a diffuse reflectance measurement. The resulting Tauc plot shown below shows a bandgap of 2.80 eV, which is not far off the 3.09 eV determined by DFT+U. This material was determined to have an indirect bandgap.



Figure 1-41: Tauc Plot of $BaIn_2O_4$ using the Kubelka-Munk function to the 1/2 power vs energy, used to determine the bandgap of the material.

This material has been shown to be capable of water splitting photocatalysis and has a bandgap of 3.2 eV which is larger than what we experimentally determined.^{102,108,109} This is likely due to contamination post synthesis. This can be seen in the inset of the Tauc plot posted above, where there is a slight yellow undertone for the sample in the center. Its activity is supposed to be the lowest among the other indates made here, $SrIn_2O_4$ and $CaIn_2O_4^{102,103}$, which could explain why we were unable to corroborate this material as a photocatalyst if too little hydrogen was being produced (See Table 1 in the appendix for data). Our discrepancy for the literature value of the bandgap could also be causing this issue, as imperceptible impurities could be decreasing the activity of the material as well as the bandgap. It is also possible that the same rationale for the CaIn₂O₄ applies here, where the solid state synthesis provides too little surface area and large defects that prevent photocatalysis.

Solid State Synthesis Post Screening

The materials depicted below were either attempts to synthesis materials for the high throughput screening of photocatalysts, or are chemical derivatives of the materials above. Chemical derivatives were made for work following up on the photocatalysts discussed above in order to gain more insight into their photocatalytic abilities.

Fe₂TeO₆

The literature states that this material can be easily formed by the solid-state reaction between Fe₂O₃ and TeO₂. ¹¹⁰ A stoichiometric amount of these precursors is ground and pelletized followed by calcination at 600°C for 12 hours, followed by 700°C for 12 hours and finally, at 750°C for 4 hours. We synthesized this product by grinding and pelletizing a stoichiometric mixture of Fe₂O₃ and TeO₂. The pellets were placed into an alumina crucible and calcined in air in a at 700°C for 48 hours inside a Lindberg/Blue M tube furnace. The XRD pattern below shows phase purity.



Figure 1-42: XRD scan of Fe_2TeO_6 . Normalized experimental pattern shown in red and reference pattern (PDF: 04-009-3444) shown in black.

The determination of the optical properties of the material were made through a diffuse reflectance measurement. The resulting Tauc plot shown below shows a bandgap of 2.80 eV, which is not far off the 3.09 eV determined by DFT+U. This material was determined to have an indirect bandgap.





The material has been reported to have a bandgap of roughly 1.7 eV, which is in line with what we determined. The materials was shown to produce small signs of hydrogen production through one of our tests but was shown to corrode under these conditions. Unfortunately, though its bandgap places it in perfect position for overall water splitting, corrosion makes it an unlikely candidate for water splitting.

$Ba_6Mn_5O_{16}$

This material has been known in the literature to be synthesizable by simple solid-state reactions between stoichiometric amounts of $BaCO_3$ and MnO_2 being thoroughly ground and fired at 900°C for 20 hours.¹¹¹ $Ba_6Mn_5O_{16}$ was synthesized here in 1g batches by adding $BaCO_3$

powder (Alfa Aesar, 99.95%), MnO₂ powder (Sigma-Aldrich, \geq 99%) in a 6:5 molar ratio respectively. The powder was ground using an agate mortar and pestle, pelletized using a hand press and added to an alumina boat. The sample was placed in a mullite tube furnace and heated in air to 400 °C at a rate of 5 °C/min and was dwelled at 400 °C for two hours before escalating the temperature to 800 °C at a rate of 5 °C/min, dwelling at 800°C for 2 hours. The sample was then heated to 1300°C at a rate of 5 °C/min and dwelling at 1300°C for 2 days. The sample was cooled to room temperature. The XRD pattern below shows phase purity.



Figure **1-44**: XRD scan of Ba₆Mn₅O₁₆. Normalized experimental pattern shown in red, reference pattern (PDF: 04-011-2378) shown in black and post electrochemical analysis is shown in blue.

It is clear from the XRD pattern that there is some degradation of the material from its photocurrent testing. I was unable to characterize the impurities in the degraded sample. This implies it is not a good candidate for photocatalysis under our conditions.



Figure 1-45: Tauc Plot of $Ba_6Mn_5O_{16}$ using the Kubelka-Munk function to the 1/2 power vs. energy, used to determine the bandgap of the material

The determination of the optical properties of the material were made through a diffuse reflectance measurement. We can see from the Tauc plot that the bandgap of this material would not be adequate for overall water splitting. That plus its instability during testing makes this material unsuitable for solar-electrolyte applications using our conditions. That being said, this material has been known to capable of the OER reaction though electrochemical methods in basic solutions.¹¹¹

ZnSb₂O₆

This material can be made through hydrothermal synthesis, combustion synthesis but simple solid state synthesis is also known.¹¹² The reaction can be made through mixing and grinding of ZnO and Sb₂O₃ in stoichiometric amounts, thoroughly mixed and heated to 600°C for 12 hours, followed by an increase in temperature to 900°C for 6 h both at heating rates of 4°C/min and cooled after reaction.¹¹² ZnSb₂O₆ was synthesized here in 0.6g batches by adding ZnO powder (Sigma Aldrich, \geq 99.0%), Sb₂O₃ powder (Sigma-Aldrich, \geq 99.9%) in a 1:1 molar ratio respectively. The powder was ground using an agate mortar and pestle, pelletized using a hand press and added to an alumina boat.

The sample was placed in a mullite tube furnace and heated in air to 600 °C at a rate of 5 °C/min and was dwelled at 600 °C for three hours before escalating the temperature to 900 °C at a rate of 5 °C/min, dwelling at 900°C for 12 hours. The sample was cooled to room temperature. The XRD pattern below shows phase purity.



Figure **1-46**: XRD scan of ZnSb₂O₆. Normalized experimental pattern shown in red and reference pattern (PDF: 00-038-0453) shown in black.

The determination of the optical properties of the material were made through a diffuse reflectance measurement. The resulting Tauc plot can be seen below.



Figure 1-47: Tauc Plot of $ZnSb_2O_6$ using the Kubelka-Munk function to the 2^{nd} power vs. energy, used to determine the bandgap of the material

The material has been shown to have a bandgap or around 3.35 eV.¹¹² This value us not far from the one we calculated from our Tauc plot, though ours is higher. This material has also been demonstrated to be a photocatalyst for the degradation of organic dyes¹¹², but has yet to be teste for overall water splitting. Given the bandgap of this material it is highly likely that it is capable of water splitting, but it's large bandgap makes it impractical. The previously mentioned paper was able to tune the bandgap of this material from 2.8-3.2 eV by nanosizing and doping this material with nitrogen¹¹², making this material more useful for solar applications as it's bandgap decreases.

MgIn₂O₄

Compared to the other indates seen so far, MgIn₂O₄ is more challenging to make. This material can be made through solid state reactions of MgCO₃ and In₂O₃, though the synthesis at 1100°C takes over 10 days. It is preferable to synthesize this material through the combustion synthesis method due to its faster reaction and enhanced purity of the resulting product.^{109,113} In this method, a solution of stoichiometric amounts of magnesium nitrate, indium nitrate ,and fuel (typically urea, or citric acid) are used in a 1:2:7 or 1:2:2.2 molar ratio respective of the fuel used. This solution is dissolved in deionized water, then dehydrated on a stirring plate by slow evaporation of the water. This forms a viscous foam that is then heated to 200°C, which spontaneously ignites the substance. The resulting white powder is further annealed at 1400°C. We synthesized this material by dissolving a stoichiometric mixture of the metal nitrates and citric acid in deionized water. The solution was dehydrated on a hotplate which when heated to 200°C resulted in a viscous gel that slowly turned into a white foam. This foam was collected, ground and pelletized and loaded into an alumina crucible. The sample was loaded into a mullite tube furnace and heated in air to 400 °C at a rate of 5 °C/min and was dwelled at 400 °C for two hours before escalating the temperature to 800 °C at a rate of 5 °C/min, dwelling at 1300°C for one day. The sample was cooled to room temperature. The XRD pattern below shows phase purity.



Figure **1-48**: XRD scan of MgIn₂O₄. Normalized experimental pattern shown in red and reference pattern (PDF: 01-073-2414) shown in black.

The determination of the optical properties of the material were made through a diffuse reflectance measurement. The resulting Tauc plot shown below shows a bandgap of 3.05 eV, which is close to the value reported in the literature of 3.1 eV.¹⁰⁹ This bandgap was also determined to be a direct bandgap via computational prediction of the band structure.



Figure **1-49**: Tauc Plot of $MgIn_2O_4$ using the Kubelka-Munk function to the 2^{nd} power vs. energy, used to determine the bandgap of the material.

The high bandgap of this material makes it an unlikely candidate for use in photocatalysis. Regardless, this material was synthesized to examine why alkali and alkaline earth metals mixed with p-block elements have been demonstrated to have significant photocatalytic properties as shown previously in this work. The study and understanding of these trends could bring about new insights that could help us find and possibly design novel photocatalysts.

$Cu_2Ta_4O_{11}$

There is only one synthesis of this material reported in the literature, to our knowledge. ¹¹⁴ This material has been reported to form via a flux synthesis, where Cu₂O and Ta₂O₅ nanoparticles were reacted in a CuCl flux.¹¹⁴ The Cu₂O nanoparticles were synthesized by mixing in a 1:1 molar ratio of CuSO₄·5H₂O and NaOH and reducing it with 0.1M ascorbic acid solution. The nanoparticles were washed and purified with deionized water and dried at 80°C. Ta₂O₅ nanoparticles were prepared from a 0.2 M solution of TaCl₅ in ethanol and the addition of concentrated HNO₃ whilst stirring for 6 hours and further drying. These were added in a 2:1:10 ratio of Cu₂O:Ta₂O₅:CuCl, the mixture was ground in a nitrogen glove box and calcined in an evacuated silica tube at 665°C for 1 hour. The reaction was quenched in air. The product was washed in ammonium hydroxide and deionized water to remove the flux. For our attempts we tried synthesizing these via simple solid state reactions and via nanoparticle precursors. For the solid state reactions, we attempted to ball mill the ground reactants in a 2:1:10 ratio of Cu₂O:Ta₂O₅:CuCl. These were then sealed in an evacuated tube to 21 mTorr and calcined in the furnace for 3 hours at 665°C. The product was quenched in air and washed with ammonium hydroxide and deionized water. Our nanoparticle synthesis of Cu₂O, and Ta_2O_5 as precursors to be used in a CuCl flux was attempted as follows. Cu₂O nanoparticles were prepared by using 8mL of a 0.01M CuSO₄ solution + 16 mL of a 0.1M sodium ascorbate + 8ml of a 0.01M CTAB solution. The solution was heated to 55°C while stirring for 5 min and 8mL of a 0.01M NaOH solution was added. This resulted in a change of color from yellow to black. A stoichiometric amount of TaCl₅ was used to prepare the Ta₂O₅ nanoparticles, by dissolving the compound in ethanol and adding nitric acid. The solution was stirred for 6 hours, and dried overnight at 80°C. The product, the Cu₂O nanoparticles and 0.08g of CuCl, corresponding to a double the flux quantity mentioned previously so that it would wet the whole product upon melting, was

ground and added to a quartz tube and sealed under vacuum to 12 mTorr. It was put in a in furnace at 200°C for 1 hour, followed by a heating to 450C for 1 hour and finally heating to 665°C for 1 hour. The tube was quenched in air, followed by washings with ammonium hydroxide and deionized water. The resultant products were both green in color.Both samples resulted in Ta₂O₅ and either CuO or Cu metal for the nanoparticle prep, with other phases of the Cu:Ta:O system mixed in. No evidence was found for the production of the desired phase as seen in figure 1-50.



Figure **1-50**: XRD scan of Cu₂Ta₄O₁₁. Normalized experimental pattern shown in red and reference pattern (PDF: 04-022-2061) shown in black. Stars correspond to β -Ta₂O₅, circles correspond to peaks of Cu₂O, the rest were not identified.

Though the compound was screened out as a potential candidate for photocatalysis, it was determined to suspended trying to make this material after several attempts were unsuccessful. This does not mean this material cannot be made, rather that further time investments would need to be made in order to be successful. Considering the infancy of our screening process, it is more important to pursue other avenues rather than continue the endeavor of synthesizing this material.

LiInO₂

The material LiInO₂ has been known to be easily made through solid state reactions of Li₂CO₃ and In₂O₃ at 1000°C for a few hours.^{95,115} I have nevertheless synthesized this material through the solid state reaction of Li₂CO₃ and In(NO₃)₃. We have synthesized LiInO₂ in 1g batches by adding Li₂CO₃ powder (Alfa Aesar, 99.99%) and In(NO₃)₃ powder (Alfa Aesar, 99.99%) in a 1:2 molar ratio. The powder was ground using an agate mortar and pestle, pelletized using a hand press and added to an alumina boat. It was observed that the addition of these two materials creates a reaction and produces a foam. This foam was left to dry and the sample was placed in a Lindberg/Blue M tube furnace and heated in air to 700 °C at a rate of 1 °C/min and was dwelled at 700°C for 4 hours before increasing the temperature to 950°C at a rate of 1 °C/min and dwelling at 950°C for 4 hours. The sample was cooled to room temperature. The slow temperature increase is due to the volatility of the reactants. The resulting material's XRD pattern, shown below, demonstrates phase purity based on XRD.



Figure **1-51**: XRD scan of LiInO₂. Normalized experimental pattern shown in red and reference pattern (PDF: 01-089-3853) shown in black.

The material is expected to have a high bandgap from its white color, similar to those of the previous inmates. It is reported that this material has a bandgap of around 4.2-4.3 eV.^{116,117} The high bandgap of this material makes it an unlikely candidate for use in photocatalysis. It has actually been reported that this material has photocatalytic water splitting capabilities, but it's performance lags behind of other indates $CaIn_2O_4 > SrIn_2O_4 >> NaInO_2 >> LiInO_2.^{95}$ Regardless, this material was synthesized to examine why alkali and alkaline earth metals mixed with p-block elements have been demonstrated to have significant photocatalytic properties as shown previously in this work. The study and understanding of these trends could bring about new insights that could help us find and possibly design novel photocatalysts.

KInO₂

KInO₂ has been shown to be made via flux of In₂O₃ in a KOH flux. ¹¹⁸ The reactants in 1:53.4 molar ratio of In₂O₃ to KOH are slowly heated in an alumina crucible to 700°C and cooled to room temperature.¹¹⁸ The crystals are isolated by dissolving the flux media in deionized water. The material is thought to be air sensitive and are stored in vacuum desiccators. I attempted the synthesis of this material though a flux synthesis by placing a 1:55 molar ratio of In2O3 to KOH in an alumina crucible and heating the reactants in a box furnace to 400°C for 30min followed by an increase in temperature to 700°C for 3 hours. The sample was then cooled to room temperature. It was found that further increasing the time of the reaction resulted in crusted KOH on the sides of the alumina crucible. The resulting solid was removed from the crucible and washed immediately with deionized water, dried and stored in a vial under argon flow. The XRD data, shown below, was taken the following day. It was found that the material was likely present as shown in Figure 1-52, but there were big signs of decomposition likely due to the sensitivity of the material to air.



Figure 1-52: XRD scan of KInO₂. Normalized experimental pattern shown in red and reference pattern (recreated from the crystal information provided by M. Bharathy et al.)¹¹⁸ shown in black. Additional peaks were not identified.

The unfortunate stability of this compound along with its high bandgap of 3.49 eV^{119} make it a non-viable candidate for photocatalysis. Regardless, this material was synthesized to examine why alkali and alkaline earth metals mixed with p-block elements have been demonstrated to have significant photocatalytic properties as shown previously in this work. The study and understanding of these trends could bring about new insights that could help us find and possibly design novel photocatalysts.

InSb₂S₄Br

The synthesis of this material and the Cl analogue has been reported once in the literature.¹²⁰ The material was reported to be made by the addition of In, SbBr₃, Sb and S in a 3:1:5:12 molar ratios.¹²⁰ The materials are loaded under nitrogen, sealed in a quartz tube under vacuum to $\sim 10^{-4}$ torr and heated to 450°C. This results in red needle crystals.

My attempts at making this material was through the addition of In, SbBr₃, Sb and S in a 3:1:5:12 molar ratios both in air and in an evacuated quartz ampule at ~20mTorr. It is important to note that SbBr₃ is a volatile, highly corrosive, deliquescent solid that melts at ~70°C, and therefore should be treated with care. The samples were heated to 450°C at a rate of 1°C/min and dwelled for 3 days. The temperature was lowered at 2°C/min to 350°C for 2 hours, then lowered again to 250°C again for two hours, and finally lowered to 200°C before cooling to room temperature. I was not able to make the compond.



Figure **1-53**: XRD scan of InSb₂S₄Br. Normalized experimental pattern shown in red and reference pattern (COD ID: 4001460) shown in black.

The resulting composition or compounds in our attempts were unable to be identified. Though we were able to make a material with red needle like crystals, as seen in Figure 1-52, it was surrounded by a black crystalline material. The attempt to isolate the red crystals was unsuccessful, and we could not determine if this process was able to successfully synthesis the material at least partly. Synthesis under more rigorous air free conditions will be necessary in the future.



Figure **1-54**: Synthesis attempt of InSb₂S₄Br shows red/orange crystals among a larger black mass. Red/orange crystals are consistent with experimental reports of the product.

Though the compound was screened out as a potential candidate for photocatalysis, it was determined to suspended trying to make this material after several attempts were unsuccessful. This does not mean this material cannot be made, rather that further time investments would need to be made in order to be successful. Considering the infancy of our screening process, it is more important to pursue other avenues rather than continue the endeavor of synthesizing this material.

InSb₂S₄Cl

There is, to our knowledge, one reported synthesis of this material and the Cl analogue in the literature.¹²⁰ The material is reported to be made by the addition of In, SbCl₃, Sb and S in 3:1:5:12 molar ratios. The materials are loaded under nitrogen, sealed in a quartz tube under vacuum to ~10⁻⁴torr and heated to 450°C. This results in red needle crystals. Our attempts at making this material was through the addition of In, SbCl₃, Sb and S in a 3:1:5:12 molar ratios both in air and in an evacuated quartz ampule at ~20mTorr. It is important to note that SbCl₃ is a volatile, highly corrosive, deliquescent solid that melts at ~50°C, and therefore should be treated with care. The samples were heated to 450°C at a rate of 1°C/min and dwelled for 3

days. The temperature was lowered at 2°C/min to 350°C for 2 hours, then lowered again to 250°C again for two hours, and finally lowered to 200°C before cooling to room temperature.



Figure **1-55**: XRD scan of InSb₂S₄Cl. Normalized experimental pattern shown in red and reference pattern (COD ID: 4001459) shown in black.

As mentioned previously, we were able to make traces of a material that looked like the crystal of our target, but we were unable to determine if this compound was partially made due to the large abundance of other crystals. The resulting composition or compounds in our attempts to make this were unable to be identified Though the compound was screened out as a potential candidate for photocatalysis, it was determined to suspended trying to make this material after several attempts were unsuccessful. This does not mean this material cannot be made, rather that further time investments would need to be made in order to be successful. Considering the infancy of our screening process, it is more important to pursue other avenues rather than continue the endeavor of synthesizing this material.

Conclusion and future directions

We were able to screen for, successfully synthesize and validate 9 photocatalytic materials. Out of these materials four are known full water splitting photocatalysts and show us that our selection criteria are a valid way of approaching the problem. Three of these nine materials – NaInO₂, SrIn₂O₄ and PbTiO₃ – have been previously screened as potential candidates for water splitting, and we were able to validate this result experimentally. Three previously screened plumbates $-Ca_2PbO_4$, Ba_2PbO_4 and Cu_2PbO_2 - have never been experimentally validated as photocatalysts, even though they have been screened in multiple occasions. Though not groundbreaking, these results are important as we have verified our own, as well as other's, screening criteria and it demonstrates the importance of coupling experimental and computational results. One of our materials, $Na_3Fe_5O_9$, has been determined as a good photoelectrode for the production of hydrogen but it is thermodynamically incapable of producing oxygen due to its low bandgap and band edge positions. This is nonetheless an important result as this has shown us that we can serendipitously find other important discoveries during our searches, such as this potentially good candidate for HER. Lastly, Nb₂Co₄O₉ is our most promising material in this trial as it has never been described as a potential candidate computationally or experimentally and has been determined to be a successful photocatalyst for water splitting. On the other hand, we were unable to successfully replicate the photocatalytic activity of $CaIn_2O_4$, which is a known photocatalyst. However, as was discussed before this has been reported in the literature as being likely due to our synthesis method along with the fact that some other experimental protocols utilize co-catalysts to aid in the water splitting reaction.

This project is still in its infancy. When this project began the Materials Project data base only consisted of around 66,000 materials, whilst now it has over 124,000 materials. This means that this project without even changing anything has twice the candidate pool to select and screen out candidates. It must be noted that one of the major

limitations in this work is our synthetic capabilities, that were artificially limited to materials that could be made relatively simply and efficiently in the lab, without the need of highly specialized equipment or conditions. It is possible that other materials, in particular some oxynitrides could be synthesized with slightly more advanced equipment, whilst still maintaining relative ease of synthesis.

Additionally, the loading of co-catalysts, such as platinum, to these screened candidates and new materials could be a possible avenue to explore. The addition of co-catalysts has been shown to increase the catalytic performance of many photocatalyst significantly. Though cocatalysts tend to be derived from noble metals such as platinum, rhodium and iridium, which are not earth abundant and would increase the manufacturing costs of these materials significantly.

Alternatively, a third avenue that could be approached would be to utilize a Z-scheme solar cell setup. In this setup two materials are chosen where one material is capable of the HER whilst the other is capable of the OER. This means that one material needs to be capable of straddling the OER and the other the HER, while being electrically connected directly or indirectly via wires to exchange charge carriers and maintain charge neutrality. The benefit to this setup is twofold. First, it can increase the efficiency of the STH conversion, by incorporating two materials with different bandgaps that can absorb different portions of the solar spectrum. Second it eliminates the requirement of a single material being good at both HER and OER. The disadvantages are also something to think about, as the growth of both materials in conjunction can be complicated and the connection of these two materials involves additional steps to the simple synthesis. This additional step could be detrimental to large scale adoption as increased complexity in manufacturing tends to be expensive, though the added efficiency in the system's STH could outweigh these added manufacturing costs.

Finally, an avenue we are currently pursuing is the further study of successful photocatalysts and some of the families that were effective water splitting candidates such as the plumbates and indates. Some preliminary computational results on our end have proposed that the mixture of alkali and alkaline earth metals with p-block elements in their oxide form creates significant dispersion in the conduction bands of materials.

This high dispersion is related to the mobility of the electron and could aid in charge separation, making these materials good candidates for photocatalysts.

Chapter 2

Designing complex nano-heterostructures for use in optoelectronics

Introduction to the use of quantum confined semiconductors in technology

The use of electricity for artificial lighting has been of high benefit to humankind. The world currently utilizes around 16-20% of all electrical energy to this purpose.¹²¹ It thus very important to increase the efficiency of these sources of light. State-of-the-art lighting technologies utilize light emitting diodes (LEDs). The most efficient of these systems utilize 85% less energy than incandescent light bulbs.¹²¹ This means they are almost 7 times (666.6%) more efficient than our previous technology. In this thesis we will not delve into the technical difficulties and problems of utilizing solid state lighting as opposed to incandescent light bulbs, such as increasing cost, low color rendering index (CRI), flickering, etc. because the industry has mostly resolved them and it is a general consensus that decreasing our energy consumption is a greater gain that any of these minor nuisances. The use of LEDs has also penetrated through to another major technological market that is on the rise of our energy demands. The displays for modern electronics as well as in the use of telecommunications; the use of solid state lighting is of utmost importance.

Increasing interest in semiconductor nanocrystals such as quantum dots have been thoroughly investigated for their use in technological photonic applications like LEDs, displays, sensors and lasers due in part to their low energy consumption, high color purity and their ability to render a high color gamut. Their photoluminescent (PL) properties have been used in recent years as phosphors in displays to down convert blue light LEDs to lower wavelength emissions to produce the backlighting in most LED displays. Recent advances in electroluminescence (EL) of these materials have gained traction for use in advanced display technologies, more efficient solid-state lighting and lasers.^{122–125} These properties along with the possible solution based processability through colloidal

chemistry give these technologies exciting technological possibilities. The potential solution based manufacture of large area and flexible devices is possible utilizing these technologies that rivals the efficiency and luminescence of organic light emitting diodes (OLEDs) the current state of the art technology.¹²³ Additional advantages such as longer lifetime, less sensitivity to oxygen environments, and more possibilities of bandgap engineering, gives these inorganic semiconductors an edge over OLED technologies.

These recent developments have been seen through the use of Quantum Dot PL and EL, which have narrower bandwidths of emission and lower turn on voltage than OLED technologies. The potential use of anisotropic particles like nanowires and nanorods; along with the exploitation of quantum confinement phenomenon could potentially improve device performance even more so. Thus, allowing us to increase energy efficiency and produce novel technologies such as foldable and stretchable electronics.

Principles of quantum confined semiconductor heterostructures

The principal property we look for in a semiconductor for use in optoelectronic devices is the material's bandgap. The bandgap of a material determines such properties as absorption and emission of light as a result of excited electronic states. During the last century the science of bandgap engineering has developed many ways of tailoring a material's bandgap through strain, solid solutions, doping, and most recently quantum confinement.¹²⁵ A quantum confined structure is one where the electrons or holes of a material are confined in one or more directions. The structures defined by quantum confinement are: Quantum wells (QW) where there is confinement in a single dimension, quantum wires when there is confinement in two directions, and finally, quantum dots (QD) when there is confinement in all three dimensions. Quantum confinement confers special properties to the electrons and holes in a material by quantizing the energy levels of that particle in a particular direction, see Figure 2-1.



Figure 2-1: Quantum confinement and its effect on density of states (DOS).

Quantum size effects become important when the restriction in a dimension is on the order of the de Broglie wavelength of a particle in the system:

$$\lambda_{deB} \approx rac{h}{\sqrt{mk_BT}}$$

Where "h" is planks constant, "m" is the effective mass of the particle in the material, k_B is Boltzmann's constant and T is the absolute temperature. This typically means that semiconductor structures of less than 10nm are required to observe quantum size effects.^{125,126} The most basic of these materials, the QW, is analogous to the finite quantum well examples know from quantum mechanics. This structure is typically found when there is a discontinuity in the conduction and valence bands of a material due to an interface of this material with another. This typically means that a thin (<10nm) section of a material is sandwiched between a larger material that has band edges that can straddle this material (see Figure 2-2).



Figure 2-2: Quantum well structure.

This quantum confinement inherently elevates the bandgap of our material by quantizing the energy of the holes and electrons. This gives scientists the ability to modify a material's native bulk bandgap and tailor it based on the confinement parameters (barrier heights, well size and any strain the structure feels). The second property this confinement provides is that it localizes and restricts the positions of charge carriers to the well. This will become important for radiative recombination. Lastly, the next main property that the confinement imparts is it makes the density of states (DOS) independent of energy as seen in Figure 2-1. The use of QWs is particularly important as there is no need for alloying in order to modify the bandgap of a material. This is significant because alloying increases the number of defects in a material compared to the simple binary compound. Secondly, as mentioned before, these wells can exhibit strain without acquiring defects as long as they are below the critical thickness of the material. This strain can increase or decrease the bandgap of a material. Compressive strain leads to an increase in bandgap, whilst tensile strain leads to a reduction in bandgap, thus, conferring additional bandgap tailoring. These same principles apply to the confinement of the particles in the other two remaining directions. The change in other dimensions changes primarily the DOS of the materials as seen in Figure 2-1.

The use of QW in LEDs and lasers is particularly beneficial due to the entrapment of electrons and holes within the wells. This creates an excellent overlap of the

wavefunctions of electrons and holes which aids in the recombination of carriers and thus the emission of light when compared to the bulk. This emission occurs after charge carriers are injected from the contacts and transported to the active region of the material and captured by the QW. The carriers then subsequently relax to the lowest confined levels emitting a photon. The reverse is also true: a photon of energy equal to or greater than that of the bandgap of the active region will be absorbed and create an electron hole pair. QW solar cells can thus also be utilized. In fact, there are advantages to the use for QW as solar cells. The power output from a solar cell is dependent on the product of the photocurrent (primarily determined by the fraction of light converted into charge carriers) and the voltage across the diode (primarily determined by the bandgap of the material and the p-n junction). These factors set our limits for single-junction solar cell efficiency. For QW solar cells, the voltage of the cell is determined not by the bandgap of the active region but by the bandgap of the barrier regions whilst the absorption is still dominated by the band edge of the QW. This can be seen in the single junction solar cell composed of GaAsP/InGaAs that had an efficiency of 28.3% under 535 suns of illumination.¹²¹ This is impressive because the highest efficiency single cell silicon device achieves around 25% and the efficiency of solar cells tends to deteriorate under such high concentrations due to high temperatures.

QWs have been amply used in technology. Curiously enough the second most used quantum systems are not the systems with an additional dimension being quantized, such as quantum rods and quantum wires, but instead the use of Quantum dots. QD have predated the use of single dimensional materials because of their ease of fabrication. These materials can be easily made through epitaxial methods as well as simple colloidal chemistry. The use of QD has had advantages over the use of traditional epitaxial QW because they once again have sharper energy spectrums, attributed to the quantized energy levels of these "artificial atoms". They have additionally pushed the envelope and have proven to be as efficient as the state-of-the-art OLED technologies. On the other hand, 1D materials are much harder to make, as they typically require templating or catalytic processes and there are limitations on the quality of such particles. Nevertheless, it is now, after QD technologies have appeared to have been close to limits of their efficiency that the ideas of using 1D materials have started to gain ground.¹²³ As mentioned previously the use of anisotropic nanostructures could potentially have advantages over the traditional use of QD. The main limitation that QD have is in the extraction of light from the structures. QD have been observed to achieve near to 90-100% internal quantum efficiency (IQE) but, as QD have randomly oriented transition dipoles, the light outcoupling efficiency also known as the external quantum efficiency (EQE) of these technologies has a maximum theoretical output of ca. 20%.¹²³ One of the main benefits that anisotropic light emitters can have is that the alignment of these materials and their transition dipoles there could be an increase in the EQE of these devices by a factor of 2.¹²³

Rod shaped nanocrystals have been used before as light emitters^{127–129}, solar cells¹³⁰, and even photocatalysts¹⁰⁰ of the materials previously seen in Chapter 1. Whilst the use of double heterostructures nanorods (DHNR) has been previously used,^{123,124,128} these structures do have disadvantages as they do not physically capture charge carriers as well as QW. This is detrimental in the recombination of the charge carriers as the overlap of the electron and hole wave functions is not as pronounced as with QW structures. This approach has been mostly done to alleviate the unbalanced injection in electron hole pairs due to uneven band alignments on either side, that can lead to charging and inefficiencies. The reported values for these DHNR at the EQE level are similar to those of the best QD reported, but whilst this is so, the values for the power efficiencies and current are surprisingly better than those of QD of similar wavelengths.¹²³



Figure **2-3**: DHNR band diagram example. ZnS and CuGaS2 as barriers of different heights for electrons and holes and CuInS2 as well material.

Cation exchange and the creation of heterojunctions

One synthetic way to create nanostructures with complex heterostructures is through the use of cation exchange.^{131–133} Cation exchange is a topotactic post synthetic modification process that replaces host ions in a structure with those of a different element. Though anion exchange is possible, the mobility of cations makes them easier to replace largely leaving the anion sublattice intact. This means that through this process we can generate many structures that are not typically accessible through direct synthesis of nanomaterials. The formation of II-IV, IV-VI and III-V semiconductors of previously inaccessible compositions have been accomplished.¹³⁴ Through the use of basic chemical and thermodynamic principles we can utilize the substitution and partial substitution of nanostructures to create complex heterostructures within a single nanoparticle, whilst maintaining shape, size and crystal structure.^{131–134} This type of chemical transformation has allowed the synthesis of bulk metastable phases in these nanoparticle systems.¹³⁴ Through partial cation exchange, the formation of doped and solid solution compositions is also achievable within soluble cation systems.¹³⁴ If cations of insoluble phases are utilized, phase segregated single or multi segmented heterostructures can be realized.¹³⁴ One item of particular importance is that the size of these domains can be easily tuned so that quantum confinement can be taken advantage of. This creation of segmented heterostructures is of interest for this work. The work by Steimle et. al.,¹³² has proven that the creation of complex mega libraries of compound semiconductor are possible. With the creation of these many possibilities, we are in one of the rare instances where our synthetic capabilities have exceeded our capacity to imagine the uses and possibilities of these systems. The exploitation and rational design of nanoparticles like these should be investigated for their potential use in photocatalytic and optoelectronic devices. It is through this work that I suggest steps towards creating uses and predictions for the optoelectronic properties of these materials.

In order for cation exchange to happen in a material the overall reaction of substituting a cation for another must be thermodynamically favorable (ΔG <0). For a divalent metal sulfide, the overall reaction is:

$$XS + Y^{2+} \rightarrow YS + X^{2+} \Delta G < 0$$

Here X and Y both represent a divalent metal ion. This reaction can be further split into its constituent components to determine the overall energetic favorability of this reaction utilizing the free energy of formation ΔG_f^0 of the respective solids and the standard reduction potentials E^0 of the metal ions.

$XS \rightleftharpoons X^0 + S^0$	$-(\Delta G_f^0)_{XS}$
$X \rightleftharpoons X^{2+} + 2e^-$	$-(E^0)_{X^{2+}}$
$YS \rightleftharpoons Y^0 + S^0$	$-(\Delta G_f^0)_{YS}$
$Y \rightleftharpoons Y^{2+} + 2e^{-}$	$-(E^0)_{Y^{2+}}$

Where the overall aqueous free energy for this reaction is thus the sum:

$$\Delta G_{reaction} = \left(\Delta G_f^0 \right)_{YS} - \left(\Delta G_f^0 \right)_{XS} - 2F[(E^0)_{Y^{2+}} - (E^0)_{X^{2+}}]$$

In the equation above F is Faraday's constant. Since most of these values can be found for most of our systems, this thermodynamic approximation can give us a good starting point to determine the possibility of cation exchange in a system. This is a very simple approximation as most of the cation exchange reactions are done on nanoparticle systems, for which the energetics of formation are highly dependent on surface energy, which are in turn affected by ligands present in solution, size of the nanoparticle, and the shape of the nanoparticle. Additionally, a lot of these cation exchange reactions are not done in aqueous solution and are accompanied by ligands which change the energetics of reduction potentials. Solvation and ligating environments in solution are of prime importance to these reactions and are an excellent way of manipulating these reactions to achieve our preferred outcomes. Through the use of Pearson's hard soft acid base (HSAB) theory, where the preferential interaction between hard-hard and soft-soft chemical species is preferred over hard-soft interactions, the preferential ligation of a particular cation can be exploited to "pull out" these cations from a structure and replace them with another.¹³⁴

Band alignment of possible basic heterostructures

In this work we will be proposing the use of roxbyite copper sulfide, $Cu_{1.8}S$, nanorods for their topotactic transformation into hetrerostructured nanorods using cation exchange to produce other sulfide compound semiconductors such as CdS, MnS, ZnS, CoS, CuInS₂, CuGaS₂ and Ag₂S. Table 2-1 and Figure 2-1 show the experimental values of the known bandgaps and band edge positions of these materials. It should be noted that we were unable to find the experimental band edge positions for CoS and thus have not included in this table. Table 2-2 and Figure 2-2 show the theoretically derived bandgaps and band edge positions based on DFT.

Table 2-1: Experimental bandgap and band edge positions relative to vacuum of possible cation exchange products^{135–141}

Material	Bandgap (eV)	Conduction Band position	Valence Band position
Ag ₂ S ¹⁴¹	1.00	-4.20	-5.24

CdS ¹⁴⁰	2.31	-4.34	-6.65
Cu _{1.8} S ¹³⁹	1.50	-3.50	-5.00
MnS ¹³⁸	1.80	-2.80	-4.60
ZnS ¹³⁷	3.60	-2.70	-6.50
CuInS ₂ ¹³⁸	1.50	-4.00	-5.50
CuGaS ₂ ^{135,136}	2.46	-3.96	-6.56

The bandgap calculations of the following materials were performed from first principles calculations. The self-consistent field calculations are performed at the Perdew-Burke-Ernzerhof (PBE)¹⁴² semilocal level of density-functional theory using the projected augmented wave (PAW)^{143,144} method implemented in the Vienna Ab-initio Simulation Package (VASP)¹⁴⁵. The plane-wave basis energy cutoff was set to 520 eV. Brillouin zones of the perovskites are sampled with gaussian smearings, with Γ -centered Monkhorst-Pack grid density of 0.04/Å. The atomic positions and the lattice vectors of the perovskite bulk structures are fully optimized to converge the total energy and force better than 1e⁻⁶ eV and 0.01 eV/Å respectively. I then also applied the hybrid Heyd-Scuseria-Ernzerhof functional (HSE06)¹⁴⁶ for improved descriptions of the bandgaps. The band edge positions were calculated through the geometric mean method mentioned in chapter 1.

Material	DFT Bandgap (eV)	Valence Band position	Conduction Band position
Ag₂S	1.82	-5.88	-4.06
CdS	2.14	-6.26	-4.12
CoS	1.26	-5.80	-4.54
Cu _{1.8} S	1.50	-5.84	-4.24
MnS	1.80	-5.71	-3.91
ZnS	3.20	-6.86	-3.66
CuInS ₂	1.50	-5.56	-4.06
CuGaS ₂	2.46	-6.08	-3.62

Table 2-2: Theoretical bandgap and band edge positions relative to vacuum of possible cation exchange products.
*Red represents a bandgap value obtained experimentally as the cell was to large to compute in a tractable manner. Green represents a bandgap value obtained experimentally, as the DFT calculation showed no bandgap.

In Figure 2-4 and Figure 2-5 we show these results in a graphical manner for easier visualization.



Figure **2-4**: Experimental bandgap and band edge position of sulfide semiconductors achievable via cation exchange.



Figure **2-5**: Theoretical bandgap and band edge position of sulfide semiconductors achievable via cation exchange.

It is interesting to compare the theoretical and experimental bandgap and band edge positions. There are clear discrepancies, such as the larger bandgap predicted by DFT than experimentally determined in Ag_2S , and the relative position of ZnS and MnS being further down in the theoretically. The discrepancies in the band edge positions are caused by the inability of the simple calculation we use, that utilizes the geometric mean of the electronegativity of the elements, to accurately portray the complexities of the surfaces that are present in a material. There is something to be said about utilizing the geometric mean to calculate the band edge positions in this way in that it intrinsically eliminates any surface contributions that might account for changes in the band position for real materials. Since we do not know the surface termination of our materials in the nanoparticles in this experiment, removing this variable allows us to make qualitative predictions for the positions of the band edges and will allow us to determine possible structures for these systems. Additionally, it has allowed us to place CoS in relative terms compared to the other materials in the system, which we were unable to place previously due to lack of experimental validation for the band edge positions. Though the exact positions are not captured, the overall trend is still maintained.

Utilizing the experimental bandgaps and band edge positions seen in Figure 2-1, it is easy to see that there are several possibilities to create prospects for heterostructures, in particular QW structures for their use in LEDs, photovoltaics, lasers, etc. These can be seen below in Figure 2-3.



Figure **2-6**: Possible QW from cation exchange sulfide semiconductors derived from experimental bandgaps and band edge postitions. Number in the strutures denotes the bandgap of the well material, thus referencing the minimum energy expected for absorbtion and emission of these systems.

If we were to consider the posible structures utilizing the theoretical calculations of bandgaps and band edge positions, we see that there are far more possibilities to create heterostructures. This additional heterostructures are due in part by the possibilities we add by being able to place CoS in the band diagrams along with the increase in possibilities due to the calculation of the band edge position that does not take into account the surface terminations. These are shown below in Figure 2-4.



Figure 2-7: Possible QW from cation exchange sulfide semiconductors derived from theoretical bandgaps and band edge postitions. Number in the strutures denotes the bandgap of the well material, thus referencing the minimum energy expected for absorbtion and emission of these systems.

The QW structures depicted in the figures above are only those of identical barriers of straddling band structures for both electrons and holes. There are more QW structures we could make if we were to confine only one of the structures, or if we were to use different barriers on each side. In this figure the bandgap of the central material is the minimum energy for the emission or absorption we would expect to get from these devices. As mentioned previously we would expect that the quantum confinement would elevate the energy of the electrons and holes in these structures, but these would depend on the thickness of the wells and the thickness of the barriers. Additionally, the effective mass of both electrons and holes in these materials would have to be known so that we may approximate a calculation. This is not the current purpose of this work; we are merely trying to exemplify the types of structures that could be achieved with these systems. These QW structures suggested above for the experimental set of data would have energies ranging from 1.0 eV to 1.8 eV without accounting for the quantum confinement in the wells or in the nanoparticle rods, which would undoubtedly confer some quantum confinement. This means that we could theoretically produce, by means of further confinement, nanoparticles that could span a reasonable section of the IR as well as the visible spectrum (1.7-3.7 eV). It is clear from this analysis that the active QW material for these devices are made out of 4 materials, Ag₂S, Cu_{1.8}S, CuInS₂ and MnS, some with different barrier materials. The theoretical model suggests at least 17 QW structures, out of which 5 are due to the addition of CoS to the mixture of possible compounds. The range of our energies these QW spans is also larger and more useful as we can have energies from 1.26 eV to 2.14 eV, further penetrating the visible spectrum. The fact that we can tune the barrier material gives us control over the degree of quantization of the quantum well, as lower barriers lower confinement. This tunability also gives us flexibility with regards to the potential barrier that each carrier is subjected too under a potential difference. This is beneficial as this can allow us to manage the amount of charge carriers being injected so that they are equal. It is typical for the injection of electrons to be done at a faster rate than hole injection, thus by increasing the energy barrier of electrons with respect to the holes, we can avoid charging of the device

and improves performance while maintain quantum confinment.¹²³ Some examples of the tweaking of the potential barriers of each charge carrier can be seen on Figure 2-4 below for structures compiled with the experimental band data and in Figure 2-5 some structures from the theoretical data.



Figure **2-8**: Experimental QW structures with different electron and hole barriers to prevent charging of device (DHNRs).



Figure **2-9**: Theoretical possible QW structures with different electron and hole barriers to prevent charging of device (DHNRs).

The total number of possible QW structures can be calculated using the tables below. Tables 2-3 shows if the bandgap of the material on the top row is capable of straddling the bandgap of the material on the left column. The top row becomes the barriers of the QW while the material on the left becomes the well material. The total number of combinations can be calculated by adding the total number of combinations of

99

the green(Y) for that row; this is essentially the permutation of the number of green boxes(Y). For example, the number of QWs that can be made with MnS as the well material, using the theoretical data, is 3. These are made by making two symmetrical QWs with barriers one of ZnS and one of CuGaS₂, the third one is made by making one barrier ZnS and the other CuGaS₂.

Table 2-3: Theoretical and experimental QW structures. Values depict if the material at the top can completely straddle the bandgap of material on the left. Top materials will form the QW barriers for the materials on the left.

	QW barrier materials								
QW to be straddled	Ag ₂ S	CdS	Cu _{1.8} S	MnS	ZnS	CuInS ₂	CuGaS ₂	Total #QW	
Ag ₂ S	N	N	N	N	Y	Y	Y	6	
CdS	Ν	Ν	N	N	Ν	N	Υ	1	
Cu _{1.8} S	N	N	N	N	Y	N	N	1	
MnS	Ν	Ν	N	N	Y	N	N	1	
ZnS	N	N	N	N	Y	N	N	1	
CuInS ₂	Ν	N	Ν	N	Y	N	Υ	3	
CuGaS ₂	N	N	N	N	N	N	N	0	

Experimental Straddin	g	
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Theoretical Straddling										
	QW barrier materials									
QW to be										
straddled	Ag ₂ S	CdS	CoS	Cu _{1.8} S	MnS	ZnS	CuInS ₂	CuGaS ₂	Total #QW	
Ag ₂ S	N	N	N	Ν	Ν	Y	N	Y	3	
CdS	Ν	N	N	N	N	Y	N	N	1	
CoS	Y	Y	N	Y	N	Y	N	Y	15	
Cu _{1.8} S	Y	Y	N	N	N	Y	N	Y	10	
MnS	N	N	N	N	N	Y	N	Y	3	
ZnS	Ν	N	N	N	N	N	Ν	N	0	
CuInS ₂	Ν	N	N	N	Y	Y	N	Y	6	
CuGaSa	N	N	N	N	N	N	N	N	0	

An additional advantage that the use of these nanorods confers is the ability to produce multiple quantum wells in a single rod. This could have two distinct advantages. Firstly, by adding sequential QW to the rods, the efficiency of these systems as emitters and as absorbers could increase. The possibility of making structures like these called multiple quantum wells (MQW) could enable us to make devices such as quantum cascade lasers and dual emission LEDs that make use of MQW structures.^{125,147} Secondly, the possibility of integrating into the same particle QWs with different bandgaps could potentially enable us to make dual or triple emitters/absorbers. Devices capable of emitting more than a single wavelength could be very useful in providing solid state lighting with white LEDs with greater efficiency and color rendering. Devices capable of absorbing different areas of the electromagnetic spectrum would make these systems nanosized multijunction solar cells, capable of greater efficiencies than traditional single junction solar cells. Some examples of these materials are shown below.



Figure **2-10**: Example of Theoretical possible MQW structures with different bandgaps. Number in the strutures denotes the bandgap of the well material, thus referencing the minimum energy expected for absorbtion and emission of these systems.

Though this work has been purely theoretical at the moment, we are optimistic that these systems have the capacity to be important to the photonic community due to their versatility in chemical composition, ease of synthesis and tunable bandgaps.

Future work

This work has been purely speculative as there has been no experimental confirmation that these specific material combinations are capable of PL or EL. The work by the Moonsub group^{123,124,127,128,148,149}, has demonstrated the capabilities of PL and EL of nanorod systems and have achieved working prototypes of these nanoparticle systems as working LEDs. This work gives us high hopes that the use of our larger library of materials could be used in optoelectronic systems. The initial trial of photoluminescence of a basic QW system utilizing these nanorod particles with heterostructures would be an ideal place to start. It is suggested that the synthesis of QW of Cu_{1.8}S or MnS (<10nm segments) surrounded by barriers of ZnS be the first material to be tested as the synthesis of this system appears to be straight forward.^{131,132} After confirming that this material is capable of PL and EL, the tunability of the bandgap can be confirmed by varying the size of the QW. By utilizing Cu_{1.8}S or MnS it is possible that we might be able to see the change in the EL clearly as it shifts from IR/Red or to red/yellow respectively.

Appendix

Additional Results

Table A-1: Reproduced from Xiong et al.⁴⁴ Compiled band gap, band edge, hydrogen evolution, and magnetic data collected computationally and experimentally. Hydrogen and oxygen evolution is recorded for two different test conditions: (i) 0.1 M oxalic acid (••) and (ii) 5% methanol in H2O (••). The cross symbol (×) indicates that the sample corrodes in the aqueous solution under acidic conditions.

		Space	Magnetic	Magnetic Hydrogen DFT (eV))	D	FT+U (e	Expt. (eV)			
		group	order	production	$\epsilon_{ m g}$	eE _{CB}	$eE_{\rm VB}$	$\epsilon_{ m g}$	<i>eE</i> _{CB}	eE_{VB}	$\epsilon_{ m g}$	$eE_{\rm FB}$
1	Ca₂PbO₄	Pbam	Ν	×●	1.48	-0.36	1.13	2.47	-0.79	1.68	2.94	-0.09
2	Ba_2PbO_4	I4/mmm	Ν	••	1.22	-0.10	1.12	2.00	-0.46	1.59	1.45	0.31
3	Cu_2PbO_2	C2/c	Ν	•0	0.65	0.60	1.25	2.17	-0.10	2.07	1.59	0.05
4	NaInO ₂	RĪm	Ν	••	1.91	-0.66	1.25	4.22	-1.76	2.46	3.85	0.24
5 <i>a</i>	$CaIn_2O_4$	Fd3m	Ν	_	2.00	-0.54	1.47	4.30	-1.63	_	_	_
5 <i>b</i>	$CaIn_2O_4$	Pnma	Ν	00	1.89	-0.48	1.41	4.10	-1.58	2.52	3.88	-0.67
6	$SrIn_2O_4$	Pnma	Ν	•0	1.81	-0.51	1.30	3.93	-1.51	2.42	3.67	0.13
7	BaIn ₂ O ₄	$P2_1/c$	Ν	×O	1.67	-0.31	1.36	3.09	-0.96	2.13	2.80	0.25
8	PbTiO ₃	P4mm	Ν	×	1.82	0.30	2.12	3.45	-0.46	3.00	3.65	1.27
9	MgSb ₂ O ₆	$P4_2/mnm$	Ν	00	1.04	1.37	2.40	3.77	0.06	3.83	4.00	-0.56
10	ZnFe ₂ O ₄	$Fd\bar{3}m$	Y	••	1.67	0.58	2.25	3.60	-0.38	3.22	2.26	-0.16
11	Na ₃ Fe ₅ O ₉	C2/c	Y	••	1.71	0.00	1.71	3.57	-0.93	2.64	0.77	0.09
12	Nb ₂ Co ₄ O ₉	$P\bar{3}c1$	Y	••	0.02	1.52	1.53	3.46	-0.21	3.26	2.29	-0.08
13	BaCaFe ₄ O ₈	$P\bar{3}1m$	Y	00	1.78	0.00	1.78	3.52	-0.87	2.65	2.04	-0.08
14	Ba ₃ MnNb ₂ O ₉	$P\bar{3}m1$	Y	00	1.74	-0.50	1.69	3.04	-0.70	2.34	0.72	-0.73



Figure A-1: Reproduced from Campbell et al.⁴⁴ Band alignment for nonmagnetic materials. Experimentally determined band alignment depicted in orange and simulated band alignment corresponding to DFT-U calculations is depicted in blue.⁴⁴



Figure A-2: Reproduced from Campbell et al.⁴⁴ Zoomed in version of Figure 1-10.

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