Investigating Metal Oxide Nanoparticles as Photocatalysts for Carbon Dioxide Reduction Reactions

by

« Thomas Wood »

A thesis submitted in conformity with the requirements for the degree of Doctorate of Philosophy
Chemical Engineering and Applied Chemistry
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Abstract

Metal oxide nanoparticles were investigated for their application as photocatalysts for the gas-phase photocatalytic conversion of carbon dioxide to value-added chemicals and fuels. A multiphotoreactor catalyst screening system was developed to screen a broad set of nanoparticles for photocatalytic activity. Carbon-13 labelled carbon dioxide ($^{13}{\text{CO}}_2$) isotope tracing was carried out to discriminate whether the products arose from CO$_2$ conversion or from reactions involving residual carbon contamination. A set of metal oxide photocatalysts were investigated at temperatures ranging from 80 °C to 190 °C in atmospheres containing both H$_2$ and CO$_2$. A nanoparticle heterostructure composed of Cu sputtered into a mesoporous TiO$_2$ nanoparticle film was synthesized. These films showed evidence of increased hydrocarbon production under illumination, but no $^{13}$C labelled product was measured.
Hydroxylated indium sesquioxide (In$_2$O$_{3-x}$OH$_y$) nanoparticles were synthesized and investigated for the photocatalytic conversion of CO$_2$. It was found that In$_2$O$_{3-x}$OH$_y$ nanoparticles are capable of photocatalytically and thermally driving the reverse water gas shift (RWGS) reaction at temperatures above 130 °C. Both $^{13}$CO and trace $^{13}$CH$_4$ were measured. A strong relationship between the CO$_2$ adsorption capacity and the relative surface concentrations of surface defects, such as hydroxides and oxygen vacancies, and photocatalytic activity was established. It was found that there is strong dependence on illumination intensity and wavelength, suggesting that the improved activity under illumination is from light.

A combined computational and experimental study investigating the (111) surface and kinetics of the RWGS reaction over In$_2$O$_{3-x}$OH$_y$ was carried out. It was found that a surface site containing a surface hydroxide adjacent to a surface oxygen vacancy was capable of the heterolytic splitting of H$_2$ and the subsequent reduction of CO$_2$ into CO. This proposed mechanism is analogous to a surface frustrated Lewis pair (FLP) and this discovery represents the first time such a system is shown to be present on the surface of a photocatalyst. Kinetic measurements revealed a 1$^{st}$ order dependence on CO$_2$ in the dark and light, whereas a zero-order dependence was observed for H$_2$. These observations are consistent with the proposed mechanism from theory, which is similar to the Eley-Rideal mechanism.
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1.1 Setting the stage for Solar Fuels

Transitioning to sustainable energy technologies and abating carbon dioxide emissions are global challenges which, if not addressed by 2027, could lead to an irreversibly damaged climate.\cite{1,2} In December 2015, world leaders forged the Paris Climate Agreement outlining restrictions to CO$_2$ emissions to prevent a global mean temperature rise above 2$^\circ$C, compared to pre-industrial levels. This agreement also sets a goal of global carbon neutrality by 2100.\cite{3} Hence, there is now a global need for technologies which can mitigate CO$_2$ emissions.

A novel process that addresses CO$_2$ emissions is solar fuel production: fuel produced via the utilization of solar energy.\cite{4,5} This fuel can be regarded as a sustainable source of energy trapped in an easily stored and transportable form, e.g. methanol or methane, and thus allows the simple integration of a renewable fuel into existing infrastructure. Furthermore, these processes use CO$_2$ as the primary reagent, and thus can limit CO$_2$ concentrations in the atmosphere. Therefore, developing solar fuel generating technologies is vital for a sustainable carbon neutral society.

Solar fuel production utilizes solar energy to drive the chemical transformation of CO$_2$ and H$_2$O into industrially relevant products. Figure 1.1 presents a simplified example of a solar fuel production cycle, where CO$_2$ and H$_2$O, fed as a concentrated stream produced from CO$_2$ capture and sequestration, are converted into fuels and by-product O$_2$. Alternatively, a portion of the fuel product can act as energy storage and be used to generate power during the night, producing CO$_2$ and H$_2$O, which can be fed back into the solar fuels generators. In this way, solar fuels technologies provide a means of satisfying energy demands and abating CO$_2$ emissions.

By utilizing solar energy, solar fuel production represents a sustainable source of energy. The average solar energy bombardment across the Earth’s surface averages is $4.3 \times 10^{20}$ J per hour,
and this energy is sufficient to satisfy current and future energy needs. As Nocera et al. pointed out, 1% of the solar energy converted at 1% efficiency produces the equivalent to the global energy demand in 2001 (4.68 x 10^{20} J).\[6\] Furthermore, trapping solar energy in chemical bonds of hydrocarbon fuels represents a renewable fuel source that can be integrated into existing infrastructure. An artificial leaf, operating at 10% solar-to-chemical conversion efficiency, could theoretically produce methanol at rates of 3500 mmol g_{cat}^{-1} hr^{-1}; at this rate, a 151 L tank, equivalent to a full tank of an average sedan sized automobile, can be filled in 7 hours using 150 grams of photocatalyst covering roughly 10 m^{2} of land. State-of-the-art photoelectrochemical cells have already demonstrated solar-to-fuel efficiencies of 7%.\[7\] A system capable of converting CO_{2} directly to fuel could cause a paradigm shift in sustainable energy production.

Carbon-containing fuel using CO_{2} as a feedstock is critical for abating global CO_{2} emissions. At present, the global average atmospheric concentration of CO_{2} has surpassed 400 ppm, and is quickly approaching a threshold concentration of 440 ppm which would cause a rapid increase in global temperature.\[8\] While temporary relief is found using carbon capture and sequestration (CCS) technologies, these solutions are not sustainable or economical in the long run. Consuming CO_{2} via solar fuel production and utilizing solar energy as the driving force for the process, a net-zero carbon emission process can be achieved.\[9\] Consider the Canadian CO_{2} emissions from transportation sources, which was 170 Mt in 2011: using a basis of 6 hours of

![Figure 1.1: A carbon dioxide cycle which utilizes an artificial leaf catalyst to generate solar fuels (Adapted from Ref. 9)](image-url)
daily operation, a photocatalyst that absorbs wavelengths shorter than 500 nm and has a quantum efficiency of 30% can produce enough methanol from CO$_2$ to neutralize the Canadian transportation emissions utilizing using 0.14% of Canada’s land mass. Therefore, solar fuels processes can serve to mitigate the CO$_2$ emissions in order to achieve the reduced global CO$_2$ concentration.

A sustainable carbon-containing fuel cycle requires a net conversion of renewable energy (wind, solar, etc.) into the chemical energy content of the fuel. Solar fuel production can currently be carried out utilizing a combination of existing technologies, which has been demonstrated via the Sunfire Solar Fuels production plant.$^{[10]}$ This plant combines three sequential conversion systems to convert water and CO$_2$ into hydrocarbon fuels:

1. Solar photovoltaic arrays that convert solar energy to electrical energy,

2. Water electrolysis systems that produce molecular hydrogen (and co-product oxygen), and

3. Fischer-Tropsch synthesis reactors that hydrogenate CO$_2$ into hydrocarbon fuels.

The storage of solar energy as chemical energy is accomplished in this system by steps 1 and 2, producing hydrogen fuel, while step 3 incorporates the carbon from CO$_2$ to produce a hydrocarbon fuel. However, a significant research effort is underway to combine steps 1, 2 and 3 into a single process. For example, the artificial leaf compresses steps 1 and 2 by coating a solar photovoltaic cell with an electrocatalyst capable of splitting H$_2$O into O$_2$ and H$_2$.$^{[11]}$

The simplest process that combines these steps is heterogeneous catalysis technologies. A system based on heterogeneous photocatalysts could compress these three systems into a single step and accomplish a simple, cost-effective, and energy-efficient process. This is carried out when light is absorbed by the photocatalyst, and the light energy, which generates high energy electrons and holes, assists the chemical transformation of CO$_2$ and H$_2$O into higher energy products, such as CH$_3$OH and O$_2$. This thesis aims to investigate heterogeneous photocatalysts for converting CO$_2$ into hydrocarbons and/or CO. By doing so, this work aims to answer whether a photocatalyst can carry out this type of chemistry, and if so, can we gain insights into the composition of the
photocatalyst in order to develop new systems that can compete with the rate and scale of the leaf.

1.2 Solar Fuels at the University of Toronto

At the University of Toronto, the Solar Fuels Team (www.solarfuels.utoronto.ca) led by Professor Geoff A. Ozin, was assembled to develop and research materials for solar fuels generation. The focus of the project is the creation of nanomaterials that are capable of catalyzing light-assisted chemical transformations of CO₂. This author’s role in this collaborative effort is centered on the critical kinetic evaluation of a broad spectrum of nanomaterials to be used as gas-phase heterogeneous photocatalysts, which were produced by team members from the Departments of Chemistry, Chemical Engineering, Electrical Engineering, and Materials Science and Engineering at the U of T.

1.3 Thesis Objectives

Photo-effects on gas-phase CO₂ catalytic transformations are the main focus of this study. Photoreactors designed by the author for this purpose were used to (1) evaluate a large array of nanomaterials to identify key material properties which facilitate CO₂ transformations, and (2) to better understand the kinetics and mechanism associated with the new materials discovered showing such photocatalytic activity. The first objective is realized through the development of a multi-photoreactor testing system, the development of a flow photoreactor, and a collaborative cross-disciplinary effort to investigate materials. The second objective is addressed by the discovery and characterization of hydroxylated indium oxide nanoparticles, In₂O₃₋ₓ(OH)ᵧ.
1.4 Research Context for Gas-phase CO₂ Photocatalysis

The most direct approach to generate solar fuels uses heterogeneous photocatalysts. In this approach, solar fuel production proceeds in a single-pass “black box” photoreactor. Within the photoreactor, a photocatalyst absorbs solar irradiation and uses the contained energy to facilitate the conversion of CO₂ and H₂O into the desired products: in order to be a sustainable source of energy, this product must retain the solar energy within the chemical bonds of the product molecules. The advantage of this process is that: it minimizes system complexities; reduces the overall footprint of the process; and has improved economies of scale. Notably, at the time of writing, there are no photocatalysts capable of driving this process. Discovering a photocatalyst that enables the conversion of both CO₂ and H₂O represents a monumental development in sustainable energy technologies. Furthermore, the development of photocatalysts capable of converting CO₂ also represents a significant development since CO₂ is a very thermodynamically stable molecule and this step is known as the difficult part when transforming CO₂ and H₂O into a fuel in one step. Therefore, work is required to investigate and develop novel materials to drive this process.

Heterogeneous photocatalysts are mostly applied to water and air detoxification, and H₂O splitting.¹²,¹³ Typical photocatalytic reactions are carried out using UV light and wide-bandgap semiconductors. Detoxification reactions typically utilize TiO₂-based systems, which can generate oxygen radicals, or hydroxyl radicals that oxidize unwanted contaminants. Typically, these purification reactions are very energetically favourable. Conversely, the H₂O splitting as well as the CO₂ reduction reactions are thermodynamically unfavourable. These reactions are often assisted by the use of hole scavengers, compounds that rapidly oxidize in order to preserve the lifetimes of the excited electrons, or with advanced architectures such as Nocera’s artificial leaf.¹¹

The desired solar fuel reaction between CO₂ and H₂O to produce a fuel is a multi-electron process that is thermodynamically uphill. This means that the reaction products are thermodynamically less stable than the reactants. Currently, there are no known heterogeneous
photocatalyst based systems capable of capturing the solar energy in the products and thus it is of interest to discover materials or identify material properties that may make this possible.

Heterogeneous photocatalysis can be carried out in either the aqueous or gas phase with a solid catalyst. One of the most significant drawbacks of the aqueous phase approach is the low solubility of CO₂ in water and limited reaction temperatures. A gas phase system can be combined with highly concentrated streams of CO₂ and the reaction temperature can be increased to much higher temperatures, thereby driving reactions easier to perform in the gas phase. Additional advantages of gas phase processes as compared to the aqueous phase approach are easier scalability, lower cost at larger scales and seamless integration with existing petrochemical infrastructures. Therefore, the focus of this work is on the gas-phase heterogeneous catalyst system.

1.5 Research Context for Screening Photocatalysts

Currently, no existing photocatalyst can enable light-driven CO₂ reactions at industrially relevant rates. Over the past two decades, the field of solar fuels has grown rapidly, as shown in Figure 1.2 via the increase in publications in this field, and despite this growth, the rates of CO₂ reduction have remained stagnant. For example, while state-of-the-art water splitting photocatalysts are able to generate H₂ at approximately 1 mmol g⁻¹ hr⁻¹, which has improved from 50 μmol g⁻¹ hr⁻¹ observed in 1984, CO₂ reduction rates have remained at 1 μmol g⁻¹ hr⁻¹ under 1 sun of simulated solar irradiation. Therefore, significant research effort towards the development and discovery of CO₂ photocatalysts is necessary.

While heterogeneous photocatalysis is an established field, only recently has it been applied to CO₂ reactions. This author identified a series of challenges currently faced by the field with respect to heterogeneous photocatalysis: there is no model material on which to focus research and development; there are no standard methods for testing of the materials; the reported production rates are often low or demonstrate false positive results due to carbon
contaminations; and finally, the overall reaction has significant thermodynamic challenges. It should be noted that TiO$_2$ has undergone a significant amount of investigation as a CO$_2$ photocatalyst, but yet has not proven to be effective for this purpose. Further investigation was carried out by this author in Chapter 4.[15] The absence of a photocatalyst capable of enabling the CO$_2$ chemistry necessitates material discovery research. Identifying these photocatalysts can be achieved by carrying out a rigorous screening process. As stated above, the absence of a standard testing method can be mitigated by rigorously investigating samples, either reproducing those in literature or synthesizing new materials, under the same reaction conditions within the same reactor. Currently, there is no agreed upon standards for testing, such as the International Electrochemical Commission (IEC) test standards for photovoltaics.[21,22] This has led to false positive results, such as when CH$_4$ production was attributed to photocatalysis but was later revealed to originate solely from the heating from a hot light source.[23,24]

A second significant issue is the absence of $^{13}$CO$_2$ isotope tracing in many studies to confirm CO$_2$ activation. Nanoparticles are often contaminated with carbon residues leftover from solvents and precursors used to control the shape, size and distribution of these particles. Combining this with the often low hydrocarbon production rates of the synthesized nanoparticles, it is difficult to distinguish the source of the carbon, particularly at low rates. Since the natural abundance of $^{13}$C is only 1.1%, detection of products with a large amount of $^{13}$C, when using $^{13}$CO$_2$, proves that the

![Graph](image)

Figure 1.2: The increase in publications with the keyword “Solar Fuels” from 2000 to 2015 found via SciFinder Scholar.
activity is real. A careful study utilizing in-situ Fourier transform infrared (FTIR) spectroscopic measurements revealed that TiO$_2$ produced no $^{13}$C labelled hydrocarbons, which went against the majority of the field.$^{[25]}$

These issues were addressed herein through the development of a multi-photoreactor system. This system, described in Chapter 3, addresses these issues by providing a system capable of investigating a set of six samples under identical reaction conditions, a single sample under six varied reaction conditions, or any combination. The temperature of the samples is carefully controlled and monitored. Furthermore, $^{13}$CO$_2$ isotope tracing was carried out for the majority of the work. This provides a way to evaluate multiple candidate photocatalysts rapidly. It also allows the sample to rapidly be evaluated under a broad set of reaction conditions.

### 1.6 Research Context for Hydroxylated Indium Oxide Nanoparticles

In order to limit the number of materials tested, candidate materials, often semiconductor nanoparticles, can be selected based on the principles of photocatalysis applied in conceptually similar systems, such as water-splitting or organic degradation. Therefore, the materials chosen for this study should have the following properties: significantly long lifetimes of photogenerated electron and hole pairs; surface sites capable of oxidizing water; surface sites which selectively reduce carbon dioxide; surface proton conduction; visible light absorption; stability in reaction environments; resistance to photocorrosion; and low selectivity for product oxidation. While materials with these properties are known in the literature, for the most part, their ability to drive CO$_2$ chemistry remains unknown.

Indium sesquioxide (In$_2$O$_3$) is a semiconductor which possesses many of the properties listed above. However, most of the investigations involving reactions of CO$_2$ catalyzed by In$_2$O$_3$ are limited to computational studies$^{[26–29]}$ with no experimental support, except for a single study that shows In$_2$O$_3$ is capable of driving the reverse water gas shift (RWGS) reaction thermally at
temperatures above 300 °C. In contrast, this work aimed to investigate In$_2$O$_3$ as a CO$_2$ reduction photocatalyst.

Recent advances in photocatalyst research revealed that defects play an important role. Surface defects can act as trap states for photogenerated electrons and holes, and may influence the absorption of the semiconductor. In$_2$O$_3$ has a visible-light transition that is forbidden by symmetry, but at the nanoscale defects may be introduced that allow visible light absorption, electron and hole trapping sites, and may also create surface sites for CO$_2$ activation. Furthermore, the valence and conduction band positions line up to the redox potentials of H$_2$O oxidation and CO$_2$ reduction. The combination of these properties make In$_2$O$_3$ an interesting material to investigate as a CO$_2$ photocatalyst.

In this work, the author has identified that defect-laden In$_2$O$_3$ is capable of the light-assisted conversion of CO$_2$ to CO via the RWGS reaction. This reaction was investigated at a range of temperatures, irradiation conditions and verified with $^{13}$CO$_2$ isotope tracing. The breadth and depth of this investigation provides strong evidence that this material is a CO$_2$ reduction photocatalyst. It was identified, with a combined theoretical and experimental study, that the active site is the combination of a set of defects. This study, for the first time, identifies a surface site to have characteristics similar to a frustrated Lewis pair (FLP) that, among many reaction possibilities, is capable of driving thermal and light driven catalysis of CO$_2$ to CO. While additional work remains, this is a novel way of understanding the activity of photocatalysts as well as educating the research community on the design principles of CO$_2$ photocatalysts.

1.7 Thesis Outline

This thesis proceeds from an examination of the basics of photocatalysis to the experimental details of the photocatalytic testing equipment assembled and, finally, to the results of the photocatalytic studies. Chapter 2 is a literature review of the common concepts employed in photocatalysis. Chapter 3 describes the experimental methodologies, and includes a detailed
description of the photoreactors. Chapter 4 contains a review of results from the extensive photocatalyst screening and isolates three of these systems as case studies. A combination of Chapter 3 and 4 will be submitted as a future publication. Chapters 5 and 6 concern the discovery and investigations of \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \), a successful single phase catalyst. Chapter 5 addresses the characterization and photocatalytic testing results of \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \), and Chapter 6 addresses the kinetic rate measurements of \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \). The work in these chapters has been published in refereed journals, therefore these chapters contain reprints of the publications in manuscript form. These chapters contain their references, while the bibliography for the rest of the thesis is assembled at the end, Chapter 7 contains a summary and discussion of future directions for this work.
Chapter 2
Literature Review

2.1 Introduction to Photocatalysis

Photocatalysis has been a topic of research interest for over a century. The earliest work tried to understand the browning of white paint and it was revealed, through these investigations, that titania, TiO$_2$, degraded volatile organics. In 1937, Goodeve demonstrated the ability of TiO$_2$ to degrade organics under light.$^{[37,38]}$ Interest in applying photocatalysts for solar fuels began 35 years later, when, in 1972, Honda and Fujishima published their famous work on the photoelectrochemical splitting of H$_2$O using a TiO$_2$ electrode. This work propelled the scientific community toward photocatalytic H$_2$O splitting. To date the most successful application of photocatalysis remains to be the decomposition of unwanted organics and there has been significant improvement to H$_2$O splitting systems.$^{[39]}$ However, photocatalysts capable of direct CO$_2$ conversion have remained elusive. Nevertheless, this cumulative research effort has set the foundation for applying photocatalysts for solar fuel generation today.

This literature review summarizes a few key concepts pertaining to photocatalysis. For further reading, this author recommends reviews on the principles of photocatalysis,$^{[40–42]}$ as well as detailed reviews of surface phenomenon of photocatalysts.$^{[43–45]}$ In addition, there are many reviews which attempt to compare literature results of photocatalysts.$^{[20,46,47]}$ There is also a review of designs for artificial leaves.$^{[11]}$ Finally, there are several articles which attempt to highlight misconceptions in the field, and this author would like to take note of these.$^{[48,49]}$
2.2 Fundamentals of Photocatalysis

Photocatalysis, as defined by IUPAC, is the process of accelerating a chemical reaction through the action of light. This broad definition is the result of decades of research and controversy disputing whether this is indeed a “catalytic” process. The photocatalytic process is an interaction between light, a solid material and adsorbed reactant molecules that results in a chemical transformation. This “photo effect” can occur via a variety of pathways, and terminology (not always unambiguous) has evolved to describe these different mechanisms.

Firstly, the photocatalytic process may be divided into categories by the function of light. Two traditional archetypes that describe the interaction between light, a catalyst, C, a reactant, R, and a product, P, were introduced by Salomon, and show by equations (2-1) through (2-4) below.\(^5\)

Photogenerated catalysis:

\[
C_{\text{inactive}} \xrightarrow{hv} C_{\text{active}} \quad (2-1)
\]

\[
R \xrightarrow{C_{\text{active}}} P \quad (2-2)
\]

Catalyzed Photolysis:

\[
C \xrightarrow{hv} C^* \quad (2-3)
\]

\[
C^* + R \rightarrow P \quad (2-4)
\]

In this scheme, **photogenerated catalysis**, shown by equations (2-1) and (2-2), denotes the photo-activation of a catalyst whereby the absorption of light produces an active form of the catalyst capable of allowing multiple reaction turnovers for each photon absorbed. In this process each photon is considered to be catalytic. On the other hand, **catalyzed photolysis**, shown by equations (2-3) and (2-4), is the creation of active catalytic reaction intermediates by the light
absorption. In this process the photo-creation of the reaction intermediate occurs at most once per photon and each photon can thus be considered to be a reactant. The term photolysis in the above scheme originates from the application of photocatalysts for photodegradation or water splitting, which was derived from the Latin word *lysis* that means decomposition. In these reactions, reactants are broken down and the photon energy is also preserved in the products. The photon absorption event places the primary absorber in a higher energy state as the result of a charge re-distribution within the absorbing complex.

The photocatalytic process can be further divided by whether light initially interacts primarily with the reactant or the catalyst.[52] A **catalyzed photoreaction** describes the photoexcitation of an absorbed reactant molecule which reacts with the ground state of the catalyst. A **sensitized photoreaction** describes the photoexcitation of the catalyst in an excited state which interacts with the ground state of an absorbed reactant. An example of a sensitized photoreaction is the decomposition of hydrocarbons by photosensitized mercury vapour.[53]

Photoexcitation can affect chemical reactions. Obviously the excitation must last long enough for the desired chemical conversion event to take place. For sake of brevity, these can be divided into: Kinetics enhancements and conversion enhancements. Firstly, kinetics enhancements: The photoexcitation enables the reaction either by assisting a rate-limiting step or by opening a new pathway with intermediates which can only be accessed with photoexcitation. If the reverse of these processes are thermally reversible, then the thermal equilibrium conversion is not exceeded and the photon energy ends up as heat. Here the photoprocess only speeds up a thermally accessible reaction. Secondly, conversion enhancement: The photoexcitation enables a unique reaction mechanism which is irreversible thermally. An obvious example of this, and the focus of much materials research, involves macroscopic preservation of the photo-induced charge separation. In this case the overall mechanism is broken up early into a reduction half reaction with the electron-rich species produced and an oxidation half reaction with the electron poor species.

Photocatalysts can be even further categorized, based on architecture, into three main categories which produce this charge separation: molecular photocatalysts which are often metal complexes
or organic dyes; molecular assemblies which take the form of functionalized lipid layers; and semiconductors.[54,55] This work focuses on the application of semiconductors as photocatalysts, and the remainder of this review will describe the fundamental aspects of this process.

Simply put, photosynthesis and the solar fuels chemistries accomplish similar chemical transformations. Electron density is shifted in the oxygen atoms in CO\textsubscript{2} and H\textsubscript{2}O to atoms of lower electron affinity (C, H, e.g.) in "fuel" molecules - a reduction, while the oxygen is rejected in an oxidized state (O\textsubscript{2}, e.g.). The energy required for this process is stored thereby stored in the fuel and is released in the reverse processes (combustion, fuel cells, etc.). Thus, the initial charge separation, induced by the photon absorption event, is stored in these reaction products.

2.3 Semiconductor Photocatalysis

Semiconductor photocatalysts are used in heterogeneous photochemical reactions, and are appropriate for both gaseous and liquid phase reactions. The process of semiconductor photocatalysis can be described as either catalyzed photolysis or a sensitized photoreaction. In this work, for simplicity, the process will be referred to as photocatalysis, which conforms with the IUPAC definition of photocatalysts.[50] Semiconductor photocatalysis begins with the adsorption of light often summarized by reaction (2-5).

\[ C \quad \text{hv} > E_g \rightarrow e^- + h^+ \]  

(2-5)

In this case, a semiconductor photocatalyst, C, absorbs a photon of light, represented by hv, with energy greater than the bandgap energy, E\textsubscript{g}, generating an electron and hole pair, as shown in the left-hand side of Figure 2.1. An electron in the \textbf{valence band} (the highest occupied electron energy level in the semiconductor) is excited into the \textbf{conduction band} (the lowest unoccupied electron energy level) if the light incident to the material has energy greater than E\textsubscript{g}; the difference in energy between the conduction band minimum (CBM) and the valence band maximum (VBM). These photogenerated electrons have a reduction potential and the generated holes have an oxidative potential.
One possible pathway for photocatalysis is the acceptor/donor model. In order for this photocatalytic reaction to proceed, an electron donor molecule, $R_D$, must be oxidized. For this to occur thermodynamically, the oxidation potential of the valence band, must be greater than the oxidation potential for $(R_D/R_D^+)$. Simultaneously, an electron acceptor molecule, $R_A$, must be reduced. For this reaction to occur, the reduction potential of the conduction band must be less than the reduction potential for the reaction $(R_A/R_A^-)$. This set of redox reactions can be summarized by the following set of reactions:

$$R_A + e^- \rightarrow R_A^- \quad (2-6)$$

$$R_D + h^+ \rightarrow R_D^+ \quad (2-7)$$

$$R_D^+ + R_A^- \rightarrow P \quad (2-8)$$

After photoexcitation, there are several competing pathways for the photoexcited charge carriers. Figure 2.2 shows schematically the processes that occur.\textsuperscript{[52]} After photoexcitation, the photoexcited electrons relax to lower energy states in the valence band. These electrons then hop through the bulk structure. Electrons which migrate to the surface may be trapped in surface traps, and these surface trap states can then interact with surface species. Alternatively, the
charge carriers may undergo recombination. Retarding the recombination of electrons and holes is essential for photocatalysis since the average time scale for recombination ranges from a picosecond to a nanosecond, while a chemical reaction often occurs on a microsecond timescale. It should be noted that while the diagrams presented in Figure 2.2 are common throughout the literature, the process of photoexcitation and transport of the charge carriers are distinct but occur concurrently.

Figure 2.2: Diagram of electron processes occurring within a semiconductor photocatalyst.\[52\]

It should be reiterated that photogenerated e\(^{-}/h^{+}\) pairs exist as definite chemical species in and on the surface of the material. For example, in TiO\(_2\) the electrons are trapped on titanium atoms, in the crystal structure, reducing the oxidation state from Ti\(^{4+}\) to Ti\(^{3+}\), thus creating surface Lewis acid sites. This process is summarized in equations (2-9) and (2-10).\[45\]

Generation of electron hole pair: \[\text{TiO}_2 \xrightarrow{hv} e^{-} (Ti^{3+}) + h^{+}\] (2-9)

Charge transfer in TiO\(_2\) lattice: \[Ti^{3+} - O^{2-} \xrightarrow{hv} Ti^{4+} - O^{-}\] (2-10)

These activated surface states can act as oxidizing (O\(^{-}\)) and reducing (Ti\(^{3+}\)) centers which facilitate the dissociation of H\(_2\)O to produce H\(_2\) and O\(_2\). However, these trap states are often short lived. Surface hole traps, largely responsible for the generation of O\(_2\), often last 1-10 ps and the lifetime of these holes often correspond to the activity of the photocatalyst.\[56\]
2.4 Energetics of Photocatalytic Reactions

2.4.1 Thermal Catalysis Kinetics and Equilibrium

Catalysts enhance the rate of chemical reactions without being consumed in the process. Each chemical reaction is comprised of a series of elementary steps and each of these steps has an energy barrier that hinders the progress of the reaction. Generally, the energy barrier of a single step in the series is sufficiently great so that it limits the rate of the overall reaction, and this single step is referred to as the rate determining step (RDS). The reaction progresses until the equilibrium composition is achieved.

The achievable product composition is determined by the thermodynamics of the system. The standard Gibb’s free energy of a reaction, $\Delta G^0_{\text{rxn}}$, is equal to the difference in the standard free energy of formation of the products and the reactants, as shown in the reaction (2-12) and instantaneous reaction free energy at arbitrary (non-standard) conditions in equation 2-12'.

$$\Delta G^0_{\text{rxn}} = \sum G^0_{f,\text{products}} - \sum G^0_{f,\text{reactants}} \quad (2-12)$$

$$\Delta G_{\text{rxn}} = \sum G_{f,\text{products}} - \sum G_{f,\text{reactants}} \quad (2-12')$$

A chemical reaction can only proceed spontaneously when $\Delta G_{\text{rxn}}$ is less than 0, in other words, the driving force of the reaction is the difference in free energy of the products and reactants and the net reaction will stop (reach equilibrium) when $\Delta G_{\text{rxn}} = 0$. The equilibrium composition can be determined by the equilibrium constant, $K_{\text{eq}}$. For a given reaction (2-13), the equilibrium constant is equal to the ratio of the activities of the products and the reactants, as shown in reaction (2-14).

$$aA + bB \rightarrow cC + dD \quad (2-13)$$
\[ K_{eq} = \frac{a_c c^A d}{a_A a_B b^B} \] (2-14)

While some reactions have a large positive G, it is possible to change the free energy of the reaction by changing the reaction conditions. For example, the free energy of the reaction can be changed by increasing the temperature or changing the reaction composition according to equation (2-15).

\[ \Delta G_{rxn} = \Delta G_{rxn}^o + RT \ln(K) \] (2-15)

However, the majority of reactions desired for solar fuel production have a \( \Delta G_{rxn} \) that is much greater than 0, as listed in Table 2.3.1. These reactions cannot be driven to a useful conversion thermally. An additional input of energy is necessary.

Nature provides a source of inspiration through the process of photosynthesis. The overall photosynthesis process, equation (2-16), is a highly energetically unfavourable reaction, but due to the complex photochemical, photophysical, and biochemical processes in the chlorophyll, light energy is able to transform CO\(_2\) and H\(_2\)O into sugar.

\[ 6CO_2 + 12H_2O \xrightarrow{hv} C_6H_{12}O_6 + 6CO_2 + 12H_2O \quad \Delta G_{rxn} = 2880 \text{ kJ mol}^{-1} \] (2-16)

Despite the high energetic cost for photosynthesis, it occurs globally and at significant rates with an input of energy in the form of light. By utilizing solar energy, it may be possible to drive the valuable solar fuels reactions between CO\(_2\) and H\(_2\)O. These reactions are multi-step multi-electron processes, and the overall reactions are thermodynamically uphill as summarized in Table 2.1. One observation is that the majority of the energy is consumed in the process of splitting water into H\(_2\) and O\(_2\). Separating these processes and converting CO\(_2\) directly with H\(_2\) is much more energetically favourable. A summary of CO\(_2\) hydrogenation reactions, and their reaction enthalpies are listed below in Table 2.2.
Table 2.1: CO\(_2\) and Water Reactions

<table>
<thead>
<tr>
<th>Reaction Stoichiometry</th>
<th>(\Delta H_{298}^o) (kJ mol(^{-1}))</th>
<th>(\Delta G_{298}^o) (eV)</th>
<th>(\Delta G_{298}^o) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CO_2 \rightarrow CO + 1/2O_2)</td>
<td>283</td>
<td>1.6</td>
<td>257</td>
</tr>
<tr>
<td>(CO_2 + H_2O \rightarrow HCOOH + 1/2O_2)</td>
<td>255</td>
<td>1.428</td>
<td>270</td>
</tr>
<tr>
<td>(CO_2 + H_2O \rightarrow HCHO + O_2)</td>
<td>571</td>
<td>1.350</td>
<td>529</td>
</tr>
<tr>
<td>(CO_2 + 2H_2O \rightarrow CH_3OH + 3/2O_2)</td>
<td>727</td>
<td>1.119</td>
<td>702</td>
</tr>
<tr>
<td>(CO_2 + 2H_2O \rightarrow CH_4 + 2O_2)</td>
<td>890</td>
<td>1.037</td>
<td>818</td>
</tr>
<tr>
<td>(H_2O \rightarrow H_2 + 1/2O_2)</td>
<td>286</td>
<td>1.23</td>
<td>237</td>
</tr>
</tbody>
</table>

Table 2.2: CO\(_2\) Hydrogenation Reactions

<table>
<thead>
<tr>
<th>Reaction Stoichiometry</th>
<th>(\Delta H_{298}^o) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sabatier Reaction</td>
<td>(CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O) (g)</td>
</tr>
<tr>
<td>Bosch Reaction</td>
<td>(CO_2 + 2H_2 \rightarrow C + 2H_2O) (g)</td>
</tr>
<tr>
<td>Reverse Water Gas Shift (RWGS)</td>
<td>(CO_2 + H_2 \rightarrow CO + H_2O)</td>
</tr>
<tr>
<td>Methanol Synthesis</td>
<td>(CO_2 + 3H_2 \rightarrow CH_3OH + H_2O)</td>
</tr>
<tr>
<td>Dimethyl Ether Synthesis</td>
<td>(2CO_2 + 6H_2 \rightarrow CH_3OCH_3) (g)</td>
</tr>
<tr>
<td>Formic Acid Synthesis</td>
<td>(CO_2 + H_2 \rightarrow HCOOH) (g)</td>
</tr>
</tbody>
</table>
2.4.2 Thermodynamics of Photocatalysis

Photocatalysts facilitate both a reduction and oxidation reaction on its surface. While the overall reaction may be energetically unfavourable, each half of the redox reaction (reduction and oxidation) is energetically favourable. Figure 2.3 shows diagrammatically the Gibb’s energy of the reactions.

![Figure 2.3: Thermodynamics of a photocatalytic reaction (adapted from Ohtani)](image)

This interpretation of photocatalysis implies that it is fundamentally an electrochemical process. Just as electrochemistry is the study of surfaces and materials which are involved in a system with a coupled electrical and chemical transfer of energy, photocatalysis is the localized coupled electrical and chemical transformation on the surface of a photocatalyst as a result of light absorption. The coupled energy transfer occurs through a physical separation of the redox (reduction and oxidation) processes of a reaction. Simply put, if the two half reactions take place at distinct energy levels - separated by the photon absorption event - then the two half reactions could proceed thermally and the overall reaction can reach an acceptable conversion level.

An electrochemical process involves the separation of the electrical charge, which generates an electrical current external to the chemical transformations and provides the basis for the applications, such as batteries and fuel cells. Consider the reaction between hydrogen and oxygen to form water, shown in reaction (2-17).

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H_{298} = -286 \text{ kJ mol}^{-1} \quad (2-17)
\]
This reaction may be separated into its half-cell reactions (the coupled redox reactions), which are the reduction, equation (2-18), and oxidation reaction, equation (2-19), for the overall reaction.

Reduction: \[ \frac{1}{2} O_2 + 2e^- + 2H^+ \rightarrow H_2O \quad \Delta H_{298} = -286 \frac{kJ}{mol} \] (2-18)

Oxidation: \[ H_2 \rightarrow 2e^- + 2H^+ \quad \Delta H_{298} = 0 \frac{kJ}{mol} \] (2-19)

It is possible to separate these processes physically within an electrochemical cell, which includes a cathode (the reduction center), an electrolyte (an ionic conducting material), an anode (the oxidation center) and a current collector (electron transporting material).

The electrochemical process can occur in two ways; galvanically which is the spontaneous progression of the reaction or electrolytically which is a process driven by an externally provided current. In this case, the reaction can proceed galvanically since the overall driving force for the reaction, which is \( \Delta G_{rxn} \), is negative. When \( \Delta G_{rxn} \) is less than zero, it is energetically favourable for the reaction to proceed.

\[ \Delta G < 0 = \text{spontaneous}, \Delta G > 0 = \text{non–spontaneous} \] (2-20)

The reaction in equation (2-20) proceeds galvanically in a fuel cell when the product is water, which is energetically downhill from \( H_2 \) and \( O_2 \). Conversely, water can be split into \( H_2 \) and \( O_2 \) by adding energy to the system through an applied external potential to the cell, and this process is said to occur electrolytically. The redox reactions are coupled by simultaneous ion and electron transport which is driven by an electrochemical potential difference, \( E \), between the redox reactions. Equation (2-21) shows the relationship between \( \Delta G \) and \( E \).

\[ \Delta G = -nFE \] (2-21)
In equation (2-21), \( n \) equals the number of electrons and \( F \) is Faraday’s constant. Generating this electrochemical potential in semiconductors through light absorption may make it possible to drive the surface chemistry desired for solar fuel production.

### 2.5 Material Properties of Semiconductor Photocatalysts

Photocatalytic activity arises from a particular set of surface and bulk material properties. These properties must work in concert in order to convert light energy into chemical energy. Over the past decade, researchers have developed a strong foundation to guide the design of photocatalysts.\(^{58-60}\) Since the main focus of this work is on metal oxides, this section mainly discusses the material properties of metal oxide semiconductors. The author recommends a recent review, and the references therein, of non-oxide semiconductor photocatalysts.\(^{61}\)

#### 2.5.1 Bulk properties

Photocatalytic activity of semiconductors is influenced by several bulk material properties.\(^{40,62}\) These properties include, band gap energies, the relative positions of both the valence and conduction bands energy levels, crystal structure, charge carrier recombination rates, surface and bulk chemical states, and charge carrier mobility. Each of these material properties must be optimized by either modification of the chemical composition or morphology in order to facilitate photocatalytic activity.

The generic make-up of a metal oxide (MO) semiconductor has the form \( M_x O_y \). Here, \( M \) is a metal with a positive oxidation state and \( O \) represents oxygen with an oxidation state \(-2\), and the subscripts \( x \) and \( y \) denote the stoichiometric values that balance the charge of the material. In the event of a multi-valent metal cation, multiple configurations are possible. For example, \( Cu \) can exist as either \( CuO \) or \( Cu_2O \) and each of these compounds has distinct material properties.
The crystal structure of a compound also influences its photocatalytic activity. This is best demonstrated by the difference in photocatalytic activity between the different polymorphs of TiO$_2$. The rutile crystal structure often exhibits lower photocatalytic activity than the anatase polymorph.[63]

The movement of electrons and holes through the material are influenced by the chemical composition of the MO. A stoichiometric semiconductor without impurities is an intrinsic semiconductor, which means that charge carrier conduction proceeds via electron or hole movement. It is possible to modify the semiconductor such that this conduction rate or preferred charge carrier changes. For example, the charge carrier conduction can be modified by doping the material through anodic or cathodic substitutions. These impure semiconductors are called extrinsic semiconductors and can be separated into two types of semiconductors, n-type, which has negatively charged majority charge carries, the electrons, and p-type, which has positively charged majority charge carrier, the holes.

The defining feature of a semiconductor is the band gap energy, $E_g$. The band gap is a region in the electronic structure between the VCM and CBM where there are no available electron energy levels. This is a key property because it predicts the spectrum of solar light that the semiconductor will absorb. A relationship between light energy and $E_g$ can be established from the energy of light. The energy of light, $E$, at a specific wavelength, $\lambda$, is proportional to the frequency, $\nu$, by Plank’s constant $h$, as shown in equation (2-22).

$$E = h\nu$$  \hspace{1cm} (2-22)

The frequency of light, $\nu$, is proportional to the wavelength, $\lambda$ and the speed of light $c$, as shown in equation (2-23).

$$\nu = \frac{\lambda}{c}$$  \hspace{1cm} (2-23)

Incident light absorbed by a semiconductor produces excited state electrons. When light is absorbed by the semiconductor, a photogenerated pair of charged states is formed. These states are a photogenerated electron and hole, also referred to as the electron-hole pair and written as $e^-$.
Once generated, these electrons and holes relax to the VBM and CBM, respectively. An accepted theory in the photocatalysis literature suggests that the relative redox potentials of each half of the e/h\textsuperscript{+} can determine the type of electrochemical reactions the semiconductor can photocatalyze. Figure 2.4 shows the relative positions for the valence and conduction bands for a variety of semiconductors. When a semiconductor absorbs light, photogenerated pairs of electrons and holes are generated.

This figure shows a set of oxidation and reduction reactions for a set of semiconductors. The equilibrium potentials are averaged by the number of electrons required for the reaction. The author notes that none of the listed semiconductors have reduction potentials negative enough to directly reduce CO\textsubscript{2} into its reduced radical. However, it is common in the literature to make reference to this as the first step in the photocatalytic reduction of CO\textsubscript{2}. Furthermore, it is possible for the charge carriers to undergo a degenerate reaction with reduced or oxidized surface species.

![Figure 2.4: Semiconductor energy levels of conduction and valence bands and their position relative to several carbon dioxide reduction reactions\textsuperscript{[64]}](image-url)
Band gap engineering is the attempt to change the chemical make-up of a semiconductor in order to modify the size of $E_g$ and position of the CBM and VBM. This is often achieved through doping, where a fraction of the atoms within a semiconductor are substituted for another. These atomic replacements may occur on either the metal site, a cationic substitution, or the oxygen site, an anionic substitution. Furthermore, these substitutions can have similar charge, an isovalent substitution, or dissimilar charge, alioivalent substitution. These substitutions modify the electronic structure of a semiconductor.

The electronic structure of the semiconductor has a significant influence on its ability to drive photocatalytic reactions. A general trend that has emerged for semiconductor photocatalysts is the presence of transition metal cations with either $d^{10}$ (such as In$^{3+}$) or $d^0$ (such as Ti$^{4+}$) electronic configurations.$^{[65]}$ It has been proposed by Inuoe et al. that semiconductors with $d^{10}$ orbitals also have hybridized sp orbitals that allow mobile charge carriers.$^{[66]}$ Understanding the electronic structure provides a basis for intelligent material design and modification by doping.

The position of the VBM, CBM and $E_g$ can be modified by doping. A popular example is nitrogen doping of TiO$_2$ photocatalysts. TiO$_2$ has a band gap of 3.2 eV which corresponds to a wavelength of 387.5 nm. Since UV light makes up only 5% of the solar spectrum, there is an upper limit to the maximum production rate. In this case, substituting a small fraction of O atoms in the lattice with N atom introduces an electron deficiency without significantly disrupting the lattice structure. This was demonstrated by Hong et al., when they increased the absorption edge of TiO$_2$ to 500 nm by nitrogen doping.$^{[67]}$ This type of doping introduced discrete energy states in the valence band from the addition of N, and shifted the VBM comprised mainly of filled oxygen 2p$^6$ orbitals, while the CBM remained the same since it is determined by the empty metal 3d$^0$ orbitals. While this catalyst absorbed a broader spectrum of solar energy, the net benefit in photocatalytic activity is debatable, as the additional N sites in the lattice act as recombination centers, reducing the photocatalytic activity.
2.6 Surface Chemistry

Photocatalytic reactions occur over the surfaces of heterogeneous photocatalysts. The structure of the surface can greatly influence the reactivity and selectivity of a reaction. In order for a reaction to proceed on a surface, the reactants must adsorb onto the surface and undergo a series of chemical transformations. Furthermore, the products must desorb from the surface in order to free surface sites for additional reactants to adsorb. The relative strength of the adsorption energies of the reactants and products determines whether the reactants or products adhere onto or repelled from the surface. Whether the reactants adsorb, chemical transformations occur, or the products desorb, depend on the nature of the surface.

The interactions between molecules and the surface is described by the Langmuir-Hinshelwood (L-H) kinetic model. The L-H model assumes that the catalyst surface is comprised of equivalent sites, and that each reactant and product molecule occupies only a single site on the surface. These adsorbed species compete with each other until the surface is fully covered. Reactants in the gas-phase adsorb onto the surface according to equation (2-15) and (2-16). The reaction occurs between adsorbed surface species to produce a product and a vacant site, as shown in (2-17). Finally, the product desorbs into the gas phase and frees a surface site, as shown in (2-18).

\[
A_{(g)} + _- \leftrightarrow A_{(ads)} \quad (2-15)
\]

\[
B_{(g)} + _- \leftrightarrow B_{(ads)} \quad (2-16)
\]

\[
A_{(ads)} + B_{(ads)} \leftrightarrow C_{(ads)} + _- \quad (2-17)
\]

\[
C_{(ads)} \leftrightarrow C_{(g)} + _- \quad (2-18)
\]
Here, a surface site is indicated by `__`; and each species either occupies a surface site indicated by (ads), or is in the gas phase (g). The Eley-Rideal mechanism assumes that a reactant molecule reacts directly with a surface species, as shown in equations (2-19) and (2-20).

\[
A_{(g)} + _- \leftrightarrow A_{(ads)} \quad (2-19)
\]

\[
A_{(ads)} + B_{(g)} \leftrightarrow \text{products} + _-
\quad (2-20)
\]

Catalysts are defined by the reaction rate per number of surface sites. The number of molecules that react per site per second is referred is as the *turnover frequency* (TOF) and it provides a fair means of comparing catalysts on a per site basis. In general, a metal catalyst has a surface density of the order of magnitude of $10^{15}$ atoms cm$^{-2}$, and this places an upper limit on the site density by assuming that each surface atom is an effective site.$^{[69]}$ However, it is common to find that the surface structure or geometry has a significant influence of the activity of the catalyst. Therefore, understanding the nature of an active surface site is critical for designing catalysts.

The surface structure determines the nature of the active sites on the surface. The surface face is related to the crystal structure, but when a surface is created, it relaxes to the lowest energy configuration. This lowest energy surface can change depending on the environment or the size and shape of the particle. Regardless, this surface face greatly influences the activity of the catalyst. It was demonstrated by Somorjai et al. that the Cu (311) has high CO$_2$ activity while the Cu (100) surface is relatively inactive.$^{[70]}$ Furthermore, the geometry of the surface can also influence activation.$^{[71]}$ It was demonstrated that CO$_2$ is activated by edge sites of MgO crystals.$^{[72]}$ Clearly the size, shape, and orientation of lattice atoms at the surface influence the activity of a catalyst.

Semiconductors have surfaces covered with defects that influence the photocatalytic activity. Surfaces will have active sites that depend on the surface face, the concentration of defects, the geometry of the particles and relative acidity or basicity. The surfaces can also affect the electronic properties of the material, such as providing surface traps for photogenerated electrons
and holes. The following is a discussion on surface defects on metal oxide surfaces; surface defects that act as electron / hole traps; and sites with acid / base character.

### 2.6.1 Surface Oxygen Defects

Defects on metal oxide surfaces have attracted much attention with speculation over it’s role in photocatalysis. An important defect on metal oxide surfaces is the oxygen vacancy. This type of defect is described as a point defect, since this defect corresponds to a single atom removed from a pristine surface when making direct comparisons. Its role in improving reactivity is by exposing oxidized metal cations that become available to drive chemistry. However, these defects are often distributed across a surface. The abundance of oxygen vacancies can be influenced by doping the material or by exposing the material to a reducing environment. Conversely, a high temperature treatment in an oxygen-containing environment will often fully oxidize the material. While doping can influence the abundance of surface oxygen defects, they occur readily under reducing environments, which is typically the reaction environment. Surface oxygen defects have demonstrated influence over the activity of photocatalysts. The defected anatase TiO$_2$ (001) demonstrated significantly higher activity than the pristine surface, which is full oxidized. The presence of oxygen vacancies can also improve the uptake and activation of CO$_2$ on metal oxide surfaces.

### 2.6.2 Acidic and Basic Sites

Surface sites can have an acidic or basic character. The acidity and basicity of surface sites has been of interest for heterogeneous catalysis field for quite some time. A surface site that is either basic or acidic can have either Lewis or Brønsted character. A Lewis acid site can accept an electron pair and a Lewis base is a site that can donate an electron pair. Brønsted acid is based on proton activity: A Brønsted acid can donate protons and a Brønsted base accepts protons. A thorough review by Garcia et. al. describes the role of Lewis acid sites on a variety of
catalysts. Studies have shown that Lewis acids are good at activating CO$_2$, such as this work showing the activity of CO$_2$ on a variety of MgO surfaces.

2.7 Multi-component Systems

The stringent requirements for photocatalysis are often beyond the capability of a single-phase solid material. Heterostructures overcome these limitations by separating the desired processes into multiple components. A heterostructure is a solid material composed of multiple distinct chemical phases, each with a different chemical composition, throughout its body. In this section, heterostructures that form Z-schemes are discussed as well as a discussion on the application of co-catalysts.

The simplest heterostructure is a two-component system. While simple, it can provide key benefits. For one, this system can improve charge carrier separation and lifetimes. This can be achieved through a junction that creates either a Z-scheme or a Schottky barrier.

A Z-scheme is a photoexcitation process that results in charge carriers with extended lifetimes and enhanced redox potentials. In this process, a heterostructure between two semiconductors, for instance A and B, is formed such that the conduction band minimum (CBM) of A is slightly above the valence band maximum (VBM) of B. At such a junction, it is hypothesized that a photogenerated electron will hop from the CBM of A to the VBM of B, as shown in Figure 2.5. At the same time, the CBM of B has significantly more reduction potential, so that it is capable of driving the desired reactions that are beyond the ability of B. Furthermore, the oxidation potential of the holes generated in A are significantly more oxidizing than B, such that the holes generated in A oxidize the desired reaction. Both semiconductors in this case absorb visible light and the result is the ability to drive a reaction that could typically only be driven by wide band gap semiconductors. The second semiconductor in this case also absorbs light; however, the holes are consumed by the electrons generated from the first semiconductor, and so the life-times are prolonged.
The addition of co-catalysts can improve photocatalytic activity.\textsuperscript{[79]} This is made possible when a slow step in the reaction takes place over a co-catalyst capable of catalyzing that step by lowering its energy barrier. Then, intermediate species formed over the co-catalyst’s surface can migrate onto the surface of the photocatalyst through a spillover mechanism.\textsuperscript{[80–82]} The reverse is also possible, and this is known as reverse spillover. This is often observed between traditional catalysts and their metal oxide supports.\textsuperscript{[83]} Taking advantage of the spillover, photocatalysts can be combined with co-catalysts to expand the possible reaction products and increase the overall product formation rates.
There are many possible configurations for nanostructured heterostructures. Figure 2.7 shows a variety of proposed architectures that can be applied to solar fuel production. On the first row is a set of photocatalysts. These photocatalysts are arranged from simple to complex in order from left to right. The simplest photocatalyst is a single-component photocatalyst. Complexity is added with co-catalysts. These photocatalysts can also be paired with other semiconductors to improve charge separation. In the second row is a set of photoelectrocatalyst systems. In the bottom row is a set of theoretical artificial leaf architectures. These systems are the most similar to photosynthesis, since they create a charge separation across a membrane across which H⁺ diffuse and on both ends of the material, the redox coupled reactions are separated.

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<tr>
<th>PC</th>
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<th>VB</th>
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<tr>
<td>GRIMES</td>
<td>e⁻</td>
<td>H⁺</td>
</tr>
<tr>
<td>KIM, SEOK, CHOI</td>
<td>e⁻</td>
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<td>HONDA-FUJISHIMA</td>
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<td>NOCERA</td>
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Figure 2.7 shows a variety of possible heterostructure architectures that can be applied to solar fuel production - Grimes, Kim, Seok, Choi, Honda-Fujishima, Panasonic, Centi, J.C.A.P and Nocera.
2.8 Background on $\text{In}_2\text{O}_3$

Indium sesquioxide, $\text{In}_2\text{O}_3$, is a semiconductor of moderate technological importance. Its most commercial utilization is in the form of Sn-doped $\text{In}_2\text{O}_3$ (ITO) in flat-panel displays. When $\text{In}_2\text{O}_3$ is doped with a significant amount of Sn, 8–10%, it becomes a transparent conductive oxide (TCO): an oxide that is optically transparent to the visible spectrum and has high electrical conductivity. While a transparent material makes an impractical photocatalyst, these research efforts have provided insights into the electronic and material properties of $\text{In}_2\text{O}_3$.\textsuperscript{[87–90]}

Other applications were suggested for $\text{In}_2\text{O}_3$. These applications include use as a chemical sensor and as a methanol steam reforming catalyst. As a sensor, $\text{In}_2\text{O}_3$ acts a chemiresistor and molecules of interest are monitored through a change in resistance upon adsorption onto its surface. $\text{In}_2\text{O}_3$ is sensitive to oxidizers ($\text{O}_3$, $\text{NO}_x$), being able to detect $\text{O}_3$ at ppm concentrations, but relatively insensitive to reducing gases (CO, $\text{NH}_3$ and hydrocarbons). It was demonstrated that $\text{In}_2\text{O}_3$ was sensitive to CO at 500 ppm.\textsuperscript{[91]} While some groups have identified that $\text{In}_2\text{O}_3$ shows promise as a photocatalyst, little work has been carried out. As a methanol steam reforming catalyst, $\text{In}_2\text{O}_3$ showed promise with low CO selectivity. This is important since CO poisons the catalyst used in methanol fuel cells which requires methanol steam reforming catalysts to supply a stream of $\text{H}_2$. These findings suggest that $\text{In}_2\text{O}_3$ can both make use of light and interact with $\text{CO}_2$, and is thus a good candidate as a photocatalyst for solar fuel generation.

$\text{In}_2\text{O}_3$ is a post-transition metal oxide semiconductor. The abundance of In is roughly 0.21 ppm in the Earth’s crust, on the order of magnitude as mercury. The most prevalent crystal structure of the oxide is bixbyite, which is equivalent to the cubic structure with vacancies occupying a quarter of the oxygen lattice sites.

The band gap energy of $\text{In}_2\text{O}_3$ was somewhat controversial, with reports of both 3.75 eV and 2.93 eV.\textsuperscript{[28]} However, the effort of several research groups have determined that the fundamental $E_g$ is 2.93 eV.\textsuperscript{[92]} The transition at 2.93 eV is a forbidden transition, and that a direct transition occurs at 3.75 eV, explaining the discrepancy that arises from the result of experimental measurements of bulk $\text{In}_2\text{O}_3$, which has repeatedly produced an optical band edge at 3.7 eV.\textsuperscript{[93]}
However, these forbidden transitions can be triggered by disrupting the symmetry of the structure through surface defects and nanostructuring.

A significant amount of theoretical simulations have been carried out on In$_2$O$_3$. Ye et al. investigating the interaction of CO$_2$ with In$_2$O$_3$ surfaces.$^{[29,30,94,95]}$ It was found that CO$_2$ likely forms surface carbonate and bicarbonate species on the (110) surface, which are often cited as intermediate species for the hydrogenation of CO$_2$.\textsuperscript{[29]}

Experimental work was carried out in order to understand the surface under oxidizing or reducing environments. In-situ FTIR experiments were carried out by Bielz et al. indicating that CO reduces In$_2$O$_3$ to form CO$_2$ and that the reverse oxidation proceeds at a significantly slower rate.$^{[96]}$ Sield et al. also investigated In$_2$O$_3$ using FTIR, showing that the surface is reversibly oxidized with O$_2$.$^{[97]}$ It was also shown that Drude absorption peaks arise in the presence of H$_2$, indicating that H$_2$ acts as an electron donor and the donated electrons occupy states in the conduction band of In$_2$O$_3$.$^{[97]}$ Other work has also demonstrated the ability of H$_2$ to act as a donor, contributing to additional charge carriers in In$_2$O$_3$.\textsuperscript{[98]} The oxygen vacancies that form under these reducing environments have implications for photocatalysis. It was shown in one study that the oxygen vacancies improved the photoelectrochemical activity of In$_2$O$_3$.\textsuperscript{[99]}

Some work has been carried out on In$_2$O$_3$ as a photocatalyst.\textsuperscript{[100]} A Cu$_2$O/In$_2$O$_3$ heterostructure was synthesized by Wei et al. in order to improve the photodegradation of methylene blue, but it was found that In$_2$O$_3$ alone showed better activity. The lifetime of charge carriers in In$_2$O$_3$ was improved by synthesizing a heterostructure with C$_3$N$_4$ by Cao et al.$^{[101]}$ Nanocrystalline TiO$_2$-In$_2$O$_3$ powders were synthesized by Shchukin et al. that showed the ability to degrade chlorophenols.$^{[102,103]}$
Chapter 3
Experimental Methods

3.1 Photocatalytic Testing

A set of photoreactors was designed to evaluate the photocatalytic activity of nanomaterials. The aim of the design was to improve the state-of-the-art lab scale gas-phase photocatalyst testing systems. In order to realize this goal, these reactors were designed to satisfy a set of requirements: the ability to pass light to a sample; the ability to apply external heating and the careful control of this heating to maintain a specified temperature; the ability to control the gas-phase reactant gas composition; access to continuous pressure measurement; and the ability to accommodate a variety of nanoparticle samples. Photoreactor design is a work in progress, and while not ideal, the reactors created satisfied these requirements.

Two types of reactors were designed and manufactured in this work: a batch photoreactor and a flow photoreactor. Photocatalyst screening was carried out in the batch photoreactors due to their low photocatalytic activity of the photocatalysts. In batch operation, products accumulate over an 18 to 24 hr period, and so the concentration of products was likely to exceed the detection limits of the flame ionization detector (FID), which is roughly 1 ppm. Once a sample was identified as photocatalytically active, it was then investigated using the flow photoreactor in order to study the kinetics of the reaction.

The next two sections provide a description of the two major types of photoreactors: The first of those sections covers batch photoreactors and the following section explains the flow photoreactor. A third part describes the $^{13}$CO$_2$ isotope tracing, which distinguished our group from other research groups.
3.2 Batch photoreactor testing systems

Herein, the common aspects for the batch photoreactor systems are described in detail. Each batch photoreactor built from a stainless steel vessel is made of two major pieces: a base flange and a viewport flange. Figure 3.1 shows a schematic diagram of a single batch photoreactor. Figure 3.2 shows a schematic diagram of each of the components that comprise a photoreactor. Finally, Figure 3.3 shows photographs of a photoreactor used in this work.

Each reactor is designed to accommodate a 1” by 1” (6.45 cm$^2$) by 1/8” (0.3175 cm) “thin film” sample. Depending on the thickness of the sample, a stainless steel spacer can be fitted into the reactor in order to decrease the dead volume. Additionally, powder samples are accommodated using a stainless steel sample boat. The reactor gas volume, $V_R$, without sample or spacer is 12.5 cm$^3$, 11.5 cm$^3$ of which were in the illuminated zone shown in Figure 3.1. An additional 1.5 cm$^3$ of dead volume is the result of the pressure transducer and lines from the valves. This dead volume affected the sensitivity of the product since it effectively reduces the concentration. With the stainless steel spacer, the total reactor gas volume amounted to 6.5 cm$^3$. The spacer was used whenever the sample was supported on a borosilicate filter paper.

The viewport flange and base flange are connected through a compression seal. A compression seal is made between a fused silica window and a single Viton O-ring (size-077) seal fitted into a groove in the base flange of the reactor. Viton was selected because it can handle moderate reaction temperatures (an operating temperature range of -4$^\circ$ to 204$^\circ$C); good ability to contain H$_2$, He, and CO$_2$; low H$_2$ permeation rates; and resistance to corrosion by UV and ozone. This simple seal allows the reactor to maintain a pressure of 45 psi (3.06 atm) with less than a 1 psi (0.068 atm) leak over a 24-hour period, which was observed by continuous on-line pressure monitoring by an Omega PX309 pressure transducer.
Photoreactor heating is achieved through a custom fit MICA Flange Heater Band powered by an Omega CN616 6-zone temperature controller. The maximum operating temperature was restricted to 180 °C due to the temperature sensitive parts: the pressure transducer, Teflon sealant, and Viton O-ring. An adjustable 1/16” (1.5875 mm) thermocouple, inside the reactor, makes contact with the sample and provides the necessary temperature measurement to the temperature controller which ensures that the sample temperature remains constant even during illumination. This helps to prevent the possibility of confusing a thermal effect, where the activity arises from an increase in temperature, with a photo-effect, where the activity arises from or is enhanced by the presence of photoexcited electrons. During photocatalyst testing, the photoreactors operating temperature ranged from room temperature to 180 °C. The author notes that the light source alone often increases the sample temperature; for example, a 1000 W
Hortilux metal halide bulb, as used in this work, is capable of heating a sample in the batch photoreactor to approximately 80°C.

Figure 3.2: Schematic drawing of a batch photoreactor from the side, with each of the components within the reactor.

Figure 3.3: Photographs of the batch photoreactor. (Left) Side view of a vertically mounted batch photoreactor. (Right) Top view of a horizontally mounted batch photoreactor.
This additional heat was accounted for during the experiment design and execution. In order to distinguish between photocatalytically and thermally activated reactions, “dark” reactions were carried out in the absence of light at the same temperature as the illuminated temperature.

An Alcatel dry pump was used to evacuate the reactors and samples lines to an ultimate pressure of 10 mtorr (1.4x10^{-5} atm) before reactions and before sampling. This oil-free pump was used to avoid contamination of any high vapour pressure carbon residues from oil lubricants.

### 3.2.1 Multi-photoreactor Material Screening System

A multi-photoreactor system was designed and built to rapidly screen photocatalyst samples. The objective of this system was flexibility, cost effectiveness, and capacity for screening multiple materials simultaneously. This system is made up of six batch photoreactors, as described above, surrounding a 1000 W Hortilux Blue metal halide bulb. Figure 3.4 shows a photograph and an illustration depicting the reactor orientation around the lamp. The metal halide bulb provided approximately 800 W/m^2 (which is approximately equivalent to 0.8 suns) and the spectral distribution closely mimics the sun, as shown in Figure 3.5. This bulb allows 360° illumination and minimal UV radiation at a fraction of the cost of a typical Newport Xe lamp system.

Figure 3.4: Photographs of the batch multi-photoreactor. (Left) Top view of the set of six photoreactors position around a metal halide bulb (Right) Schematic representation of the set of batch photoreactors surrounding a metal halide bulb.
Figure 3.5 shows a comparison of the spectral distribution of the metal halide bulb (solid line) and the solar spectrum (dashed line).
The standard testing protocol was carried out with the following procedure. After samples are installed into the photoreactors, the gas volume is evacuated by the Alcatel dry pump. Following a set evacuation time, the reactors were purged with the reactant gases H₂ (99.9995%) and CO₂ (99.999%) at a flow rate of 6 mL min⁻¹ through each reactor for an hour. The reaction stoichiometry was controlled by the ratio of the volumetric flow rates delivered by the set of Aalborg digital mass flow controllers. During the reactant purge, the reactors are heated to the desired set point temperature, if applicable. The reactor temperatures were controlled by an OMEGA CN616 6-Zone temperature controller. After an hour, the reactor outlet valves were sealed, and the reactors were pressurized with the reactant gas to 3.06 atm (45 psi). The pressure inside the reactor during reaction was monitored during the reaction using an Omega PX309 pressure transducer. Reactors were irradiated with a 1000 W Hortilux Blue metal halide bulb for a period of 16 hours. During experiments where the bulb was illuminated, the heating was provided in parallel to prevent the sample temperature from exceeding the maximum set temperature. Products were analyzed by a flame ionization detector (FID) and thermal conductivity detector (TCD) installed in a SRI-8610 Gas Chromatograph (GC) with a 3’ Mole Sieve 13X and 6’Hayeseep D column. Isotope tracing experiments were performed using $^{13}$CO₂ (99.9 atomic% Sigma Aldrich). In the event of an isotope tracing experiment, reactors are only purged with H₂ gas or a H₂/Ar mixture. Following the purge, the reactor outlet valves are sealed and $^{13}$CO₂ is injected into the reactor. Isotope product gases were measured using an Agilent 7890A gas chromatographic mass spectrometer (GC-MS) installed with a 60 m GS-Carbonplot column that separated gas compounds to the mass spectrometer.

The production rates for the photocatalyst screening experiments were simple time averages of the concentration of product, $C_p$, measured over a reaction time, $t$, in batch operation.

The reaction rate, $R$, is defined as the differential change in the moles of a component A, $n_A$, with respect to the reaction time, $t$, as shown in equation (3-1). When the gas volume of the reactor, $V_R$, is fixed, then $R$ is proportional to the concentration of component A, $C_A$.

$$ R = \frac{dn_A}{dt} = V_R \frac{dC_A}{dt} $$  \hspace{1cm} (3-1)
Component A in this case refers to the reaction component of interest. In the case that $R$ is the production rate of a product, such as the production of CO, then the rate is positive. When $R$ represents the depletion of a reactant, such as the consumption of CO$_2$, then the rate is negative.

In order to compare rates across a range of samples, a basis for comparison is necessary. There are many possible ways, such as surface area of the catalyst or number of surface sites. For the initial screening phase, wherein it is desirable to quickly test a large number of nanostructured materials for their photocatalytic activity, the mass of catalyst, $m_{\text{cat}}$, is used as a basis to calculate the specific rates, $r$. This basis was chosen for its simplicity for determining this value experimentally, which is a time constraint when comparing dozens of samples. The specific rate per unit mass of catalyst, $r_M$, is equal to $R$ divided by the mass of catalyst, $m_{\text{cat}}$, as show in the equation (3-2).

$$r_M = \frac{R}{m_{\text{cat}}} = V_R \frac{dC_A}{dt}$$  \hspace{1cm} (3-2)

The preferred means for comparing the activity of two photocatalysts is on the basis of molecules converted per photon absorbed.$^{[104]}$ This preferred rate is the internal quantum efficiency (IQE), $Y$, which is the number of molecules formed divided by the number of photons absorbed by the semiconductor, as shown in equation (3-3).

$$Y = \frac{\text{moles of product}}{\text{moles of photons} \times s}$$  \hspace{1cm} (3-3)

While this is the preferred means to compare two photocatalysts, it is rather difficult to determine experimentally. To calculate the IQE, it is necessary to measure the number of photons incident onto the surface of the photocatalyst as well as the fraction of these incident photons that are absorbed by the photocatalyst. This measurement is complicated by the reflection from the support the catalyst is loaded on to, shadowing effects, the thickness of the photocatalyst film, and light scattering. These may be determined experimentally. For example, absorption depth can be extrapolated by comparing samples of uniform thickness. However, it is typical to use the apparent quantum efficiency (APE) which only counts incident light, so it does not account for
the specific reactor geometry and sample morphology. This value is provided due to its experimental simplicity.

For the purposes of material screening studies, it is adequate to use a simplified specific rate on a catalyst mass basis, as shown in equation (3-1). Since the rates are often low, the reaction conditions do not change. Therefore, a specific time averaged rate, \( r_{M,avg} \), can be used and this is proportional to the difference in \( C \) and \( t \), as shown in equation (3-4).

\[
r_{M,avg} = \frac{V_R}{m_{cat}} \frac{\Delta C_A}{\Delta t}
\]

Note, that this methodology applies to the rates calculated using the dual arc lamp system presented in Section 3.2. If the reaction conditions do not change significantly over time, then the average rate is a good measure of the reaction rate. At low conversions, the reactant concentrations are nearly constant, in line with this expectation. However, if the reaction rate depends on product concentrations, then the instantaneous rate will change substantially with time as the product builds up, thus making this average a poor representation of the rate at the initial conditions.

### 3.2.2 Dual Arc Lamp Photoreactor System

The “Dual Arc Lamp” photoreactor system is a set of two batch photoreactors that are each illuminated by a Newport 300W Xenon Arc Lamp. Figure 3.7 shows the flow diagram of the Dual Arc Lamp system. These reactors are distinct from the multi-photoreactors due to the light source that provides additional experimental options. The Xe lamp allows for variations in the power output and spectral distribution, with the use of filters. The filters used include the following: an AM1.5 filter, which replicates the solar spectrum at 1.5 atmospheres optical path, a KG3 Global Filter that is a low-pass filter that removes photons with a longer wavelength in the IR and above, and a 420 nm high pass filter that eliminates all UV.
This system was used to investigate the spectral dependencies on the production rate of CO by In$_2$O$_3$. In order to determine the influence of the spectral distribution and power on the activity of the photocatalyst a set of filters were fitted on the output of the Xe Arc Lamp. The spectral dependence of the photoactivity was investigated using a combination of AM1.5, 420 nm high-pass and 615 nm high-pass filters. Since each filter reduced the total power of the light, the beam was focused using collimating lenses to compensate for this loss and to maintain an illumination intensity of 100 mW cm$^{-2}$. The spectral distribution was measured with a StellarNet Inc spectrophotometer. The illumination power was measured by a Newport 91150V calibrated reference cell and meter.

Figure 3.7: Schematic showing the enhanced gas sampling capabilities in the current multi-reactor system
3.2.3 Fixed Bed Photocatalytic Reactor

A flow photoreactor was designed and built in order to study the nanoparticle semiconductors under flow conditions. A schematic diagram is shown in Figure 3.8, and a photograph is shown in Figure 3.9.

![Schematic diagram of the packed bed photoreactor](image)

**Figure 3.8 Schematic diagram of the packed bed photoreactor**

![Photograph of the packed bed photoreactor](image)

**Figure 3.9 Photograph of the packed bed photoreactor.**
Photocatalytic rate measurements were carried out in this custom designed flow photoreactor. The reactor is a borosilicate tube (3 mm outer diameter and 2.5 mm inner diameter) reactor packed with 10-30 mg (1 to 4 cm bed length) of nanoparticle photocatalyst powder. Quartz wool supported both ends of the fixed bed. The reactor was fastened within a custom fabricated stainless steel brace which suspends the reactor within a channel of a heated copper block, allowing heating from the sides and below. Heating was supplied from a heated copper block fixed below the fixed catalyst bed. The top of the reactor was exposed in order to allow light irradiation from a Newport 300 W Xe Lamp (at a distance of 4 cm and a light intensity of 2.2 suns). The reactor was purged with H₂ (99.9995%) and CO₂ (99.999%) at a flow rate of 10 mL min⁻¹ and a stoichiometric ratio of 1:1 (stoichiometric for reverse water gas shift reaction). The reactor temperatures were controlled by an OMEGA CN616 6-Zone temperature controller. A thermocouple was in contact with the top of the reactor so that the reactor maintained a constant temperature of 150 °C. Pressure indicators were installed at the inlet and the outlet of the reactor to monitor the pressure drop across the catalyst bed. The product gases in the outlet stream of the reactor were analyzed with an 8610 gas chromatograph (SRI) installed with a 10 Mol Sieve 5a column and a 60 HayeSep D column.

The production rates for the photocatalyst in the flow photoreactor were calculated using the following methodology. First, this reactor was assumed to mimic an ideal plug flow reactor (PFR), which contains the assumptions that the reactor operates isothermally and has uniform radial molar distribution. In the case of a PFR, the reaction rate, R, is defined as the differential change in the molar flowrate of a component A, \( \bar{n}_A \), divided by the reaction volume, \( V \), as shown in equation (3-5).

\[
R = \frac{d\bar{n}_A}{dV} = \nu \frac{dC_A}{dt}
\]  

(3-5)

Here, \( \nu \) is the volumetric flow rate. As with the batch photoreactor case, the specific rate is set on the bases per unit mass of catalyst, \( r_m \), is equal to \( R \) divided by the mass of catalyst, \( m_{cat} \), as shown in the equation (3-7).
\[ r_M = \frac{R}{m_{cat}} = V_R \frac{dC_A}{dt} \] 

These measurements were applied to the kinetic studies carried out in Chapter 6.

### 3.3 Isotope tracing experiments

Isotope tracing experiments were carried out in order to identify the source of an element in the measured gas products. The primary motivation behind this experiment was to determine whether carbon containing products originated from CO\(_2\) or from adventitious carbon sources. By introducing a gas with an artificially high abundance of a rare isotope, in this case with 99% \(^{13}\)CO\(_2\), the source of the products can be elucidated. Products with a high \(^{13}\)C-to-\(^{12}\)C ratio originate from the introduced CO\(_2\), since the natural abundance of \(^{13}\)C is only 1.1%. However, compounds with a low \(^{13}\)C-to-\(^{12}\)C ratio likely originate from an alternative source of carbon, such as carbon-containing ligands or solvents leftover from nanoparticle synthesis.

Isotope tracing with deuterium D\(_2\), hydrogen gas was also carried out. This experiment aimed to determine the H source of CH\(_4\) from a reaction gas mixture of H\(_2\) and CO\(_2\). Since D\(_2\) makes up only 0.15% of the naturally abundant H\(_2\), products with a significant amount of D\(_2\) likely originate from the introduced hydrogen.

During isotope tracing, standard batch photoreactor methodology is carried out with an isotope labelled CO\(_2\). The carbon products are measured using the GC-MS. Both the product and isotope distribution are identified with the GC-MS. In this work, the majority of the photocatalyst screening was carried out using \(^{13}\)CO\(_2\) as the reactant gas. While the GC and GC-MS were able to identify a large range of hydrocarbons, the primary products for the isotope tracing investigations were carbon monoxide and methane.

The relative fraction of an isotope in products was determined using GC-MS. The GC column separates polar compounds, such as hydrocarbons, using a capillary GS-Carbonplot column. As the compounds elute from the column, the MS ionizes the compound, breaking it into ionized fragments. The distribution of the mass of these fragments is characteristic for each compound,
and, when necessary, the MS can isolate a particular range of masses of interest to increase sensitivity. For example, if CO is a compound of interest, the MS can be configured to only detect masses 12 AMU, 13 AMU, 16 AMU, 28 AMU and 29 AMU.

Products may have a mixture of $^{12}$C and $^{13}$C, which occurs when both the source of carbon is both adventitious carbon and $^{13}$CO$_2$. In this case, the ratio of the $^{13}$C containing fragments to $^{12}$C determines whether or not $^{13}$CO$_2$ is converted. A benefit of using D$_2$ is that mass 21 AMU, $^{13}$CD$_4$, is only the product of D$_2$ and $^{13}$CO$_2$, as shown in equation (3-8) and (3-9):

\[
\text{Carbon Residues: } D_2 + ^{12}C \xrightarrow{hv} ^{12}CD_4 \quad (3-8)
\]

\[
\text{Carbon Dioxide Conversion: } D_2 + ^{13}CO_2 \xrightarrow{hv} ^{13}CD_4 \quad (3-9)
\]

Analysis of the mass fragmentation patterns determined whether CO$_2$ was activated. Consider, for example, the mass fragmentation pattern of methane. The fragmentation patterns for $^{12}$C and $^{13}$C are shown in Figure 3.10. The parent peak for the methane is H$_4$C$^+$, which is 16 AMU for $^{12}$CH$_4$ and 17 AMU for $^{13}$CH$_4$. Additional ion fragments can be formed in the electron impact (EI) in the MS and the distribution can be used to identify the compound. Presence of 17 AMU in quantities greater than 16 AMU would indicate that the carbon dioxide was activated in some way. This used H$_2$.

![Fragmentation patterns measured by GC/MS for various isotope compositions of methane. On the left is $^{13}$CH$_4$ and on the right is $^{12}$CH$_4$.](image-url)
A limitation to the isotope tracing technique is, unfortunately, MS detector sensitivity. The upper limit for detection is roughly 10 ppm, which is a concentration that many samples were not capable of producing over a 24 hr reaction period. Since isotope gases are fairly expensive to use, their use was restricted to batch reactions. As adventitious carbon was a prime concern, priority was given to $^{13}$CO$_2$ tracing experiments with H$_2$.

### 3.4 Material Characterization

#### 3.4.1 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was carried out on samples throughout this work. The purpose of these measurements was to understand the elemental composition, chemical states and electronic states of the sample. Each experiment varied depending on the nature of the sample and the scientific inquiry into its nature.

This is a non-destructive technique which uses high energy X-rays to remove electrons from core shell states within the atoms of the sample. When the X-rays have sufficient energy, the electrons are propelled with kinetic energy roughly equal to the difference between the binding energy and the energy of the X-ray. Since the binding energy of core shell electrons is characteristic for each element, as well as its electronic state, it is possible to understand the properties of the sample.

XPS was also used to provide information on the oxidation state of oxygen in the lattice of In$_2$O$_3$. This experiment was performed using a Perkin Elmer Phi 5500 ESCA spectrometer, which operated at ultrahigh vacuum chamber with a base pressure of $1\times10^{-9}$ Torr. The spectrometer’s source was an Al K $\alpha$ X-ray which operated at 15 kV and 27 A.
3.4.2 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy can provide information on the surfaces and adsorbed states of materials of interest. An infrared source bombards a sample with infrared radiation. Some gas phase and surface species absorb this light energy. Chemical bonds generally adsorb in this frequency range and the adsorption in this region is characteristic of different types of bonds.

In situ diffuse reflectance infrared spectroscopy (DRIFTS) measurements were conducted using a Harrick Praying Mantis diffuse reflectance chamber with a Harrick environmental chamber. Powdered nanocrystalline In$_2$O$_{3-x}$(OH)$_y$ was packed into the sample cup and installed into the sample chamber. A reference spectrum was obtained after the powder had been heated to 120 °C in H$_2$ flowing at 20 cm$^3$ min$^{-1}$ for an hour, so as to remove any water or absorbed species. In order to obtain a reference spectrum, the chamber/powder was cooled to room temperature, and He was flowed through the chamber at 20 cm$^3$ min$^{-1}$ for an hour. Light illumination passed through the ZeSe window on the Harrick environmental chamber via an optical fibre of 1 meter in length attached to a Newport 300 W Xe Lamp with a light intensity of 200 W m$^2$ at the end of the optical fibre.
Chapter 4
Fact or Fiction:
Results from Preliminary Screening
of Semiconductor Photocatalysts

4.1 Introduction

The discovery of functional photocatalysts is crucial for gas-phase solar fuel production. While photocatalytic water splitting has advanced over the past couple of decades, little improvement in CO₂ photocatalysts has been realized.\textsuperscript{[15]} The absence of an industrially relevant photocatalyst creates the need to discover new materials or to improve existing photocatalysts with rates on the order of 1 mmol g\textsubscript{cat}\textsuperscript{-1} hr\textsuperscript{-1}. Unfortunately, photocatalyst discovery is cumbersome due to the large number of possible nanomaterial compositions. The multi-photoreactor screening system expedites this photocatalyst discovery. This section includes a description of the methodology for photocatalyst testing, a summary of preliminary screening, and results from a select set of samples which are presented as case studies.

Each nanomaterial encompasses a unique set of characteristics, which vary by elemental compositions, physical orientation, material properties, and the combination of all of these characteristics in heterostructures. The most compelling photocatalysts are bi-phasic, or multi-phasic materials, which combine the properties of two or more materials. With this in mind, it’s clear that the number of potential photocatalyst samples increases with the number of elements, and range of physical dimensions and orientations. Ultimately, a large number of nanomaterials were synthesized and tested, the results of which a briefly mentioned herein. In order to tackle the monumental challenge of material testing, a testing philosophy was established.
The material testing philosophy is presented in Figure 4.1. The goal of this framework was to simplify the material evaluation process by reducing the criteria to three simple checks. The first check is whether or not any products are detected after a batch photoreaction under light. If there are products, then the rate of production is compared to the rate in the absence of light in order to establish a beneficial effect of light. Finally, $^{13}\text{CO}_2$ isotope tracing is carried out to confirm that $\text{CO}_2$ is the source of the C in the products. Once these checks are demonstrated, the sample undergoes advanced material characterization and optimization.
Samples were often selected based on literature precedents. If no product was measured it was discarded, and so the researchers would then investigate a new sample. In some cases, such as when a known thermal catalyst is deposited as a co-catalyst, the reaction conditions were varied in an attempt to improve activity. These changes to reaction conditions were often increases in reaction temperature or reducing pre-treatments.

4.2 Results and Discussion

Over the course of this work, a broad set of semiconductor heterostructures (over 300 samples) were investigated as potential CO$_2$ reduction photocatalysts. These materials ranged in chemical composition, shape, and size. For example, this author tested thin-films composed of alternating layers of CuO and Fe$_2$O$_3$ nanoparticles and then investigated the effect of varying the thickness of each component in the thin-film. Each system, while most commonly a bi-phasic composite, ultimately resulted in a dozens of samples in order to produce a labelled product above the detection limit of the GC. A summary of this work is presented in a table Appendix A1.1. While this work enabled the discovery that In$_2$O$_{3-x}$(OH)$_y$ is a photocatalyst, a majority of the samples were not functional.

The first case is a study on a Cu/TiO$_2$ photocatalyst. In this case, preliminary photocatalytic testing revealed that this material produced CH$_4$ under illumination; however, $^{13}$CO$_2$ isotope tracing demonstrated that this conclusion was misguided. The second case study is a study on Ru/TiO$_2$. In this case, the sample produced CH$_4$ that was confirmed using $^{13}$CO$_2$ isotope tracing. However, the production of CH$_4$ is attributed to thermal catalysis and not photocatalysis. The results of this study identified In$_2$O$_3$ as a potential photocatalyst for CO and CH$_4$ production.

In this chapter, the results of three case studies are discussed. The focus of these results are on the photocatalytic testing, since this was the focus of this PhD thesis. Material characterization
was limited in these cases, since, it should be obvious to the reader at this point, the conclusions of some of this work was that these materials are not actually photoactive.

4.2.1 Case Study: Cu/TiO₂ Photocatalysts

This study was an attempt to reproduce literature results indicating that a TiO₂ based photocatalyst is capable of converting CO₂. After a significant amount of work, it was the isotope tracing experiments that demonstrated that the measured products are not from CO₂ but from contamination. This result convinced this author and the Solar Fuels team to include isotope tracing as a standard test to investigate photocatalysts.

A heterostructure composed of Cu/TiO₂ was synthesized via a novel synthesis method and tested as a CO₂ photocatalyst. The synthesis method utilized sputter deposition to partially coat the inner surfaces of a mesoporous bi-phasic photocatalyst. The ability of this method to infiltrate the pores of the nanoparticle film can be attributed to the high energy of depositing species, which is typically greater than an order of magnitude compared with other depositing synthesis methods. The end result is a high surface area heterogeneous thin film that contains multiple metal/semiconductor junctions, that may enhance the photocatalytic activity of the sample. In this particular set of samples, TiO₂ was chosen since reports suggested that it is a CO₂ reduction photocatalyst. The co-catalyst Cu was selected to improve the photocatalytic activity of TiO₂. This material was then synthesized and underwent photocatalytic testing.

The bi-phasic photocatalyst is a TiO₂ nanoparticle film with Cu distributed throughout it. The TiO₂ nanoparticles are synthesized from a colloidal solution prepared by the hydrolysis of titanium isopropoxide, Ti(OCH(CH₃)₂)₄. The hydrolysis was carried out as follows: 18.75 mL of Ti(OCH(CH₃)₂)₄ (Sigma Aldrich) was added to a stirred mixture of 112.50 mL water and 0.711 mL of nitric acid (70 wt%, Fisher, ACS reagent). After 8 hours at 80 °C, it was cooled down to room temperature. The dried nanoparticle powders were confirmed to be pure anatase by powder
X-ray diffraction (PXRD) analysis using a Siemens D5000 diffractometer and Cu-Kα line X-ray source. Figure 4.1 shows the TEM images of the TiO₂ nanoparticles, which were measured using a Hitachi S-5200 operating at 2.0-30 kV. The size of the colloidal particles is 8-10 nm and the porosity of the film is roughly 30%.

![TEM image of TiO₂ nanoparticles](image)

Figure 4.1: TEM image of TiO₂ nanoparticles (dark grey).

The TiO₂ nanoparticle films were spin-coated from the TiO₂ colloidal dispersions onto fluorinated tin oxide (FTO) coated glass (~2.5 cm x 2.5 cm) using a Laurell Model WS-400B6NPP/LITE spin-coater. Immediately after the spin-coating, the films were annealed at 450 °C for 15 minutes. This produced a TiO₂ film with a thickness of approximately 100 nm. The spin-coating process was repeated to increase the film thickness, which ranges from 100 nm to 1000 nm.

The Cu was deposited within the mesoporous TiO₂ films via a custom-made sputtering system. This system uses radio frequency (RF) magnetron sputtering from a Cu target. The base pressure of the sputtering chamber was pumped down to 6.7 x 10⁻⁵ Pa (5 x 10⁻⁷ Torr) before Ar was introduced into the chamber at a flow rate of 20 cm³. The chamber pressure was set to 0.4 Pa (3 mTorr) during the deposition, which was carried out at room temperature. For all cases, the distance between the substrate and target was approximately 14 cm, and the film growth rate was
9 \times 10^{-2} \text{ m/s} for the Cu deposition. The sputtering process was terminated when the desired thickness, measured by an \textit{in situ} thickness monitor (SQM-242 from Sigma), had been deposited. An SEM image of a cross-section and top view of a selected sample is presented in Figure 4.2.

![SEM image](image.png)

**Figure 4.2:** SEM image of a cross-section of TiO$_2$ nanoparticle film with sputtered Cu.

Initial photocatalytic testing of the Cu/TiO$_2$ samples revealed an increase in hydrocarbon production when the reaction proceeds under illumination. This result was based on the simple and direct comparison between CH$_4$ production in the light (illuminated by a 1000W metal halide bulb) and dark at 80°C in an atmosphere containing H$_2$ and CO$_2$ (non-isotope labelled). The initial average rate of CH$_4$ production was $1.6 \mu\text{mol g}_{\text{cat}}^{-1} \text{ hr}^{-1}$ under those conditions over a 24-hour reaction period. This rate is within an order of magnitude to similar samples investigated in the literature, as shown in Figure 4.3.\textsuperscript{[110–112]} Lo et al. measured a CH$_4$ production rate of $1.455 \mu\text{mol g}_{\text{cat}}^{-1} \text{ hr}^{-1}$ for TiO$_2$.\textsuperscript{[112]} A composite with Cu and Pt co-catalysts on TiO$_2$ nanoparticles was synthesized by the Varghese \textit{et al.}, and they measured a CH$_4$ production rate of $6.38 \mu\text{mol g}_{\text{cat}}^{-1} \text{ hr}^{-1}$.\textsuperscript{[110]} Although it should be noted that $^{13}$CO$_2$ isotope tracing was not employed in their work, and in the Varghese’s work, the sample was supported in the reactor using carbon tape, which may have contributed to the CH$_4$ production rate.
In order to demonstrate the effectiveness of the Cu co-catalyst, a series of control tests were undertaken. These tests were photocatalytic rate measurements of a Cu/TiO\textsubscript{2} film, a pure TiO\textsubscript{2} film and a pure Cu film. These samples were tested at 80\textdegree{}C in the dark and under illumination in an atmosphere containing 4:1 H\textsubscript{2} and CO\textsubscript{2}. The TiO\textsubscript{2} nanoparticle film is the same base nanoparticle film that comprises the film. The Cu film produced in the sample manner as the Cu sputtered deposition, but in this case, the Cu is deposited directly onto an FTO coated substrate. The results of this control experiment are presented in Figure 4.4. These results show that the heterostructure produces hydrocarbons under illumination at a significantly greater rate than the individual components. Since the Cu/TiO\textsubscript{2} sample demonstrated believable photocatalytic activity based on the presented control experiments, it was selected to undergo further study.

The next step was to investigate the Cu distribution throughout the TiO\textsubscript{2} nanoparticle film. It was demonstrated by Liu et al. that the Cu dispersion on TiO\textsubscript{2} can greatly affect the photocatalytic activity\textsuperscript{[111]} It is possible that a small fraction of Cu/TiO\textsubscript{2} junctions within the entire sample made up the bulk of the activity; therefore, improving the synthesis methodology could improve the photocatalytic activity. In order to improve the Cu dispersion of the sputtered samples, the sputtering conditions were varied: specifically, the energy of the Ar plasma and the Ar partial pressure. It is hypothesized that as the kinetic energy of the Cu particles increases, so will their penetration depths within the TiO\textsubscript{2} nanoparticle film.

![Figure 4.4: Control experiments for Cu/TiO\textsubscript{2}, Cu and TiO\textsubscript{2} photocatalyst films.](image)
A set of Cu/TiO$_2$ photocatalysts was made under different sputter deposition conditions in order to improve the Cu infiltration throughout the sample. These samples were synthesized with the Ar plasma at 300W and 100W, and the chamber pressure during sputtering was set to 0.13 Pa (1 mtorr) and 2.67 Pa (20 mtorr). In total, four samples were synthesized: (1) 300W and 20 mtorr, (2) 300W and 1 mtorr, (3) 100W and 20 mtorr, and (4) 100W and 1 mtorr.

The Cu infiltration was characterized using X-ray photoelectron spectroscopy (XPS) depth profiling. The XPS analysis was performed using a Perkin Elmer Phi 5500 ESCA spectrometer in an ultrahigh vacuum chamber with base pressure of 1.33$\times$10$^{-7}$ Pa (1$\times$10$^{-9}$ Torr). The spectrometer used an Al K$\alpha$ X-ray source operating at 15 kV and 27 A. An Ar sputter beam penetrated through the sample for specified time intervals to enable sampling at incremental depths (roughly 0.4 nm), and this generated a depth profile. The result is shown in Figure 4.5.

By varying the sputtering conditions, it was found that the Cu concentration profile could be significantly affected by decreasing the chamber pressure during sputtering. Figure 4.5 shows the depth profiles of the four Cu/TiO$_2$ samples. The samples produced at high pressures (solid triangle at 20 mtorr and 300W, and hollow squares at 20 mtorr and 100W) show a significant Cu film of roughly 17 nm, that abruptly transitions into the TiO$_2$ film. Within the TiO$_2$ film, the concentration of Cu is low but consistent. The samples produced at lower pressures (hollow triangle at 1 mtorr and 300W and solid square at 1 mtorr and 100W) revealed a significantly smaller Cu film. Furthermore, the transition between the Cu and the TiO$_2$ film was gradual, indicating a greater likelihood of Cu/TiO$_2$ heterostructures within the film, and so, this material should demonstrate the greatest photocatalytic activity.
The Cu/TiO$_2$ films underwent photocatalytic testing in order to determine the effect of the sputter conditions on hydrocarbon production. The samples were investigated under various reaction atmospheres, including pure H$_2$, pure H$_2$O, and combinations of H$_2$, CO$_2$ and H$_2$O. The results show that hydrocarbon production was only possible in the presence of CO$_2$, and the sample with the best Cu/TiO$_2$ profile (100W, 1mtorr) also demonstrated the greatest hydrocarbon production. However, these results show that the hydrocarbon production is not clearly correlated with the presence of CO$_2$. Figure 4.6 shows a chronological progression of CH$_4$ production rates for the four Cu/TiO$_2$ samples in batch photoreactions at 80°C with reaction times of 24 hrs. It is clear that hydrocarbon production is greatest when H$_2$ is the only gas present in the reactor.

Figure 4.5: XPS depth profiling of Cu/TiO$_2$ films prepared with different sputtering conditions.
The results from this study generated concern over the source of the hydrocarbons. While the samples demonstrated a decrease in production chronologically, it is not likely that the nanomaterials may deactivate with time. Deactivation may be the result of changes in oxidation state of the metal species or the generation/suppression of surface defects. Another potential explanation is that the hydrocarbons produced were from carbon residues leftover from the nanoparticle synthesis or another adventitious carbon source. In order to investigate this further, photocatalytic testing was carried out using $^{13}$CO$_2$ isotope.

Isotope tracing experiments are commonly used in the field of catalysis to determine reaction pathways.$^{[113,114]}$ Typically, a rare isotope labelled reactant is introduced into the reactor and the destination of each atom can be determined by analysis via GC-MS. Other groups have combined in-situ DRIFTS measurements of TiO$_2$ with isotope tracing using $^{13}$CO$_2$ to measure the
photoactivity of TiO\textsubscript{2} photocatalysts. It was found that this material only produced carbon monoxide and only 1/8th of the carbon monoxide produced contained \textsuperscript{13}C\textsuperscript{[25]} This was an important finding since this conflicted with claims regarding methane production from TiO\textsubscript{2}, but was consistent with this author's work.

In order to carry out the isotope tracing measurements, CO\textsubscript{2} composed of 99\% \textsuperscript{13}C was used as the reactant gas. The products were then measured using GC-MS to identify whether the product molecules contained significant amounts of \textsuperscript{13}C. Since the natural abundance of \textsuperscript{13}C is only 1.1\%, if hydrocarbon products contains a significant amount of \textsuperscript{13}C it is very likely that the source of the carbon was from \textsuperscript{13}CO\textsubscript{2} and not from an adventitious carbon source.

The Cu/TiO\textsubscript{2} samples were subjected to \textsuperscript{13}CO\textsubscript{2} tracing experiments. Figure 4.7 shows the intensity of the methane ion fragments as they elute from the GC column. This measurement shows that mass 17 AMU, which represents the mass fragment \textsuperscript{13}CH\textsubscript{4}\textsuperscript{+}, is lower than both 15 AMU and 16 AMU at 2.6 minutes. Since this mass fragment is absent, it is clear that the CH\textsubscript{4} produced from photocatalytic testing does not originate from the CO\textsubscript{2} introduced into the reactor. Therefore, the hydrocarbons originated from a carbon source present within the sample.

Figure 4.7: GC/MS of CH\textsubscript{4} ion fragments produced by Cu/TiO\textsubscript{2}.
4.2.2 Case Study 2: Ru/TiO\textsubscript{2}

This case study is the attempt to add a known CO\textsubscript{2} methanation catalyst to a system in order to improve the photocatalytic activity of the material. This study shows that often the thermal activity dominates, and it shows the importance of measuring the photocatalyst temperature when using such co-catalysts.

A photocatalyst composite of Ru and TiO\textsubscript{2} nanoparticles was synthesized for preliminary photocatalyst screening. The addition of a Ru nanoparticle co-catalyst onto TiO\textsubscript{2} would increase the activity of CO\textsubscript{2}. Ru is a known CO\textsubscript{2} methanation catalyst.\textsuperscript{[24]} It was reported that photomethanation is achieved by carbidic surface carbon (Ru-C), which are highly reactive species which facilitate the hydrogenation of carbon.\textsuperscript{[23]} However, since Ru is a known thermal catalyst, it is likely that the light may affect the kinetics of the thermal reaction. Nevertheless, enhancement of a thermal process using light irradiation would be insightful for co-catalyst selection.

A set of Ru/TiO\textsubscript{2} films was synthesized. A mesoporous TiO\textsubscript{2} nanoparticle film was synthesized using the method described in section 4.2.1. The TiO\textsubscript{2} film was calcined at 450\textdegree C for 44 hrs prior to electrodeposition. The Ru catalyst was electrodeposited using 0.4 mM RuCl\textsubscript{3} in a solution of 0.25 M H\textsubscript{2}SO\textsubscript{4} and 0.5M ethylene glycol (EG). The electrodeposition was carried out at -0.256 V vs an Ag/AgCl electrode, with bubbling N\textsubscript{2}. The electrodeposition time was 20 minutes. This synthesis was carried about by Dr. Jonathon Moir based on a synthesis by Tsai et al.\textsuperscript{[115]} SEM images of the Ru/TiO\textsubscript{2} system is shown in Figure 4.8.

The Ru/TiO\textsubscript{2} films were tested for photocatalytic activity based on the framework described above. Initial testing revealed that these films produced CH\textsubscript{4} with rates on the order of 10 umol g\textsubscript{cat}\textsuperscript{-1} hr\textsuperscript{-1}. When isotope labeled experiments were carried out, it was found that the CH\textsubscript{4} produced was indeed a 13C-labelled methane product, as shown in the mass fragmentation of products and reference in Figure 4.9. The methane produced matches the 13CH\textsubscript{4} standard fragmentation patterns, and the peak elution time matches the elution time for methane standard.
Figure 4.8: SEM Images of Ru electrodeposited onto TiO$_2$ nanoparticle films.

Figure 4.9: Mass fragmentation pattern for CH$_4$ measurements normalized to the parent peak 17 AMU of (black solid) Ru electrodeposited on TiO$_2$ nanoparticles measured at 80 °C with light in H$_2$ and $^{13}$CO$_2$ and (striped) A measurement of $^{13}$CH$_4$ gas standard.
The film then underwent a series of control experiments to evaluate the effect of light on the overall activity. As shown by the results in Figure 4.10, the CH₄ production decreased in light, compared to dark reactions. This strongly suggests that the activity was the result of the thermal component, Ru metal nanoparticles, catalyzing this reaction.

![Figure 4.10: Comparison of CH₄ production rates of Ru/TiO₂ at 80°C in H₂ and CO₂. These experiments were carried out sequentially on the same sample with alternating dark to light.](image)

**4.2.3 Case Study 3: CH₄ Production from Indium Oxide based Semiconductors**

During preliminary screening, it was made apparent that In₂O₃ nanoparticles were capable of enhanced CO₂ conversion under light. The majority of the work focused on the production of CO and this work is described in detail in Chapters 5 and 6. However, it was also shown that the CO₂ was converted into CH₄, albeit at significantly lower rates. For example, no measurable amount of CH₄ was observed during flow measurements. Nevertheless, CH₄ was measured in the batch photoreactors enabling isotope tracing experiments. Herein is a report that is intended to determine the source of this trace product.
A series of batch photoreactions were carried out on the In$_2$O$_3$ nanoparticle films in order to determine the source of the CH$_4$. The synthesis and characterization of these nanoparticles are described in detail in Chapter 5. The reaction was carried out at temperatures ranging from 90°C to 150°C in atmospheres containing a 4:1 ratio of H$_2$ and $^{13}$CO$_2$, which is stoichiometric for the Sabatier reaction. The products were characterized by both GC and GC/MS after a reaction time of 24 hrs. The mass fragmentation pattern produced by GC/MS of the measured CH$_4$ is shown in Figure 4.11, and this result reveals that the CH$_4$ is a mixture of both $^{12}$CH$_4$ and $^{13}$CH$_4$. The ratio of $^{12}$C to $^{13}$C can be determined by fixing the proportions of the fragment ions to parent ion, $^{12}$CH$_4^+$ for $^{12}$CH$_4$ and $^{13}$CH$_4^+$ for $^{13}$CH$_4$. For example, by setting the ratio of $^{13}$CH$_4^+$ to $^{13}$CH$_3^+$ the same as the ratio of $^{12}$CH$_4^+$ to $^{12}$CH$_3^+$, the amount of $^{12}$CH$_4$ can be calculated. Based on these calculations, it was found that roughly 50% of the CH$_4$ produced contained $^{13}$C. Using this logic, the $^{13}$CH$_4$ production rates were calculated and are presented in Figure 4.12.

![Figure 4.11: Chronological progression of batch reactions of Cu/TiO$_2$ samples](image-url)
It was clear that some portion of the CH$_4$ produced was labelled with $^{13}$C; however, it is possible that the CO$_2$ reacted with the carbon residues or the $^{13}$C scrambled with the $^{12}$C. In order to provide additional evidence that CO$_2$ is converted into CH$_4$, an isotope labelled reaction between $^{13}$CH$_4$ and D$_2$ was carried out in the batch photoreactors.

The mass fragmentation patterns for CH$_4$ under the two different isotope conditions are presented in Figure 4.12. From these data, it is clear that $^{13}$CD$_4$ is produced, confirming that CH$_4$ is produced by In$_2$O$_3$ catalytically. However, there is still the matter of the carbon contamination and scrambling. For both reactions, the total amount of CH$_4$ produced is the same and at the same rate. Assuming fixed proportions of ion fragments to their parent peaks, it was found that 23% of the product was $^{13}$CD$_4$ when using D$_2$ and 43.5% was $^{13}$CH$_4$ when using H$_2$. This means that a significant amount of scrambling between D$_2$ and H$_2$ occurred on the surface (existing O-H etc on the surface of In$_2$O$_3$) and possibly hydrocarbon residues.

Figure 4.12: Temperature dependence on $^{13}$CH$_4$ production rates on In$_2$O$_{3-x}$(OH)$_y$ nanoparticles under illumination and under H$_2$ and $^{13}$CO$_2$ atmospheres.
Conclusions

A multi-photoreactor system was built and facilitated the material screening of a wide set of nanomaterials. The nanomaterials were subjected to 24 hr batch reactions in H₂ and CO₂. A methodology was used to determine which materials were worthwhile for in-depth investigation. Isotope tracing using $^{13}$CO₂ revealed the source of C in the carbon products.

It was found that a great majority of the nanomaterials either did not produce a hydrocarbon product or carbon product at a sufficient rate to be measured by GC or GC/MS. Furthermore, a
set of samples that did produce hydrocarbons was later confirmed to only decompose carbon containing contaminants. It was shown that rudimentary control experiments often lead to misleading conclusions. For example, in the case of Cu/TiO$_2$, the control experiments showed that both light and the composite heterostructure enhanced the rate of reaction, but the reaction was simply the conversion of carbon contamination. However, the control experiments are beneficial. In the case of the Ru/TiO$_2$ system, the production of $^{13}$CH$_4$ was enabled thermally. These results suggest that a single measurement is not sufficient to prove light enhancement for CO$_2$ conversion. Additionally, these results may indicate the difficulty in the field to reproduce the results of other work or to improve the photocatalytic rates over time. Many photocatalysts are likely published on preliminary findings, and follow-up studies never appear.

It was also found that In$_2$O$_3$ nanoparticles are capable of converting CO$_2$ into carbon containing products. Using isotope tracing, with both $^{13}$CO$_2$ and D$_2$, it was shown that the CH$_4$ produced is from the reactants introduced into the reactor. This material was subjected to detailed characterization and follow-up studies which are discussed in Chapter 5 and 6. Also, an additional publication can be found here.\cite{116}
Chapter 5
The Rational Design of a Single-Component Photocatalyst for Gas-Phase CO$_2$ Reduction Using Both UV and Visible Light

The following chapter is presented with the consent of all contributing authors. It is the publication: The Rational Design of a Single-Component Photocatalyst for Gas-Phase CO$_2$ Reduction Using Both UV and Visible Light

The authors are listed as followed: Laura B. Hoch,† Thomas E. Wood, † Paul G. O’Brien, Kristine Liao, Laura M. Reyes, Charles A. Mims and Geoffrey A. Ozin *

Both Laura Hoch and this author are the co-first authors of this work. This author contributed by designing the photocatalyst testing equipment, carrying out all of the activity measurements, designing experiments to validate activity, and interpretation of material characterization measurements. The indium sesquioxide, In$_2$O$_3$, nanoparticles were characterized using several different techniques. These techniques included XPS (X-ray photoelectron spectroscopy), XRD, TPD and transmission spectroscopy. By varying the synthesis conditions, namely the calcination of the indium hydroxide precursor, it was possible to vary the relative amount of defects. Samples were prepared using this knowledge and tested for photocatalytic activity to determine whether there is any dependence on defect chemistry. It was found that the sample with the most defects (the sample prepared with a 250°C calcination temperature) was the most active. This sample was further studied to confirm photocatalytic activity using isotope tracing experiments, sample loading, light intensity variation and wavelength variation studies.

This was a collaboration which included consultations with Geoff A. Ozin and Charles A. Mims. The XPS measurements were carried out by Dr. Kristine Liao. Dr. Paul O’Brien assisted with the spectroscopic measurements. This author was responsible for planning and carrying out all photocatalytic experiments. This included designing and building the reactors and testing systems. This also included developing the experimental protocol and data analysis. Laura Hoch carried out the synthesis of the nanoparticles.
5.1 Abstract

The solar-to-chemical energy conversion of greenhouse gas CO$_2$ into carbon-based fuels is a very important research challenge, with implications for both climate change and energy security. Herein we experimentally identify key attributes of hydroxylated indium oxide nanoparticles, In$_2$O$_{3-x}$(OH)$_y$, that function in concert to reduce CO$_2$ under solar simulated radiation. In$_2$O$_{3-x}$(OH)$_y$ nanoparticles are prepared with varying surface hydroxide and oxygen vacancy content to investigate the effects of these parameters on light-driven, gas-phase CO$_2$ reduction rates. By optimizing these parameters, CO$_2$ can be converted to CO, in the presence of H$_2$, at a rate as high as 0.60 μmol g$_{cat}^{-1}$ hr$^{-1}$ under 0.8 suns of simulated solar irradiation at 150°C. $^{13}$CO$_2$ isotope labeling experiments identify CO as the sole carbon product of CO$_2$ photocatalytic reduction. Significantly, the surface hydroxide and oxygen vacancy concentrations correlate well with the CO$_2$ adsorption capacity and CO production rate, suggesting both play a key role in the reaction mechanism. This advance provides insight towards the rational design and optimization of single-component gas-phase CO$_2$ reduction photocatalysts to be incorporated into current advanced systems for solar fuels generation.

5.2 Introduction

The emerging field of solar fuels centers on storing radiant solar energy in the form of chemicals that can be used as an alternative to fossil fuels. A major goal in this field is to realize an “artificial leaf” which is a material that converts light energy, in the form of solar photons, into chemical energy, using CO$_2$ as a feedstock to generate useful chemical species. Enabling this technology will allow the greenhouse gas, CO$_2$, emitted from energy production and manufacturing exhaust streams, to be converted into valuable products (such as solar fuels or chemical feed-stocks), thereby creating huge economic and environmental benefits by simultaneously addressing energy security and climate change issues. While the global research
effort with respect to the artificial leaf has focused on H$_2$O splitting, the photocatalytic reduction of CO$_2$ remains a significant challenge and thus the focus of our work.\textsuperscript{[1]} This artificial leaf can exist in multiple configurations, of which gas-phase photocatalysis has been identified as the most practical and economically feasible option for large-scale CO$_2$ reduction.\textsuperscript{[1]} Thus, the envisioned artificial leaf will be a multi-component system that intakes large quantities of gaseous CO$_2$ and pipes out large volumes of carbon-based fuels. Clearly, the key component of this artificial leaf system is a functional material that utilizes the energy from absorbed solar photons to drive the complex multi-electron and proton transfer reactions involved in reducing CO$_2$ to fuels. As a result, there is growing interest in synthesizing semiconductor nanomaterials, which have the surface, optical, and electronic properties that enable photocatalytic reduction of gas-phase CO$_2$ to generate solar fuels.\textsuperscript{[1–5]} However, despite the growing interest and investment in the field, there are few examples of successful gas-phase photocatalysts, particularly those active in the visible region of the solar spectrum, suggesting that new approaches to materials discovery are necessary.\textsuperscript{[6]}

A class of materials capable of photocatalytically reducing CO$_2$ are oxygen deficient metal oxides. These oxides can generate active catalytic sites and enhance both the visible absorption of light and the photocatalytic activity of the material.\textsuperscript{[7]} The most notable example of this is black titania, TiO$_{2-x}$H$_x$, which exhibits a substantial increase in light absorption and photoactivity for water splitting after hydrogen treatment.\textsuperscript{[8]} Another effective approach to increasing the photocatalytic activity of metal oxide nanomaterials is to improve the CO$_2$ capture capacity of the nanoparticle surface. Several groups have demonstrated that surface hydroxides can enhance the affinity of CO$_2$ for a photocatalytic surface which can have a significant effect on the photocatalytic activity and CO$_2$ reduction rates.\textsuperscript{[9–11]} Clearly, the surface, optical, and electronic properties of metal oxide nanoparticles must work in concert for photocatalytic reduction of CO$_2$ to occur; understanding this relationship is critical for the advancement towards a practical global-scale solar fuels technology.\textsuperscript{[6,10,12–15]}

Indium oxide is a material with surface, optical and electronic properties that make it a compelling CO$_2$ reduction photocatalyst. For example, its conduction band (CB) and valence
band (VB) positions on an energy band diagram straddle the H\textsubscript{2}O oxidation and CO\textsubscript{2} reduction half reaction energies required to drive artificial photosynthetic production of hydrocarbons and carbon monoxide.\cite{16,17} Furthermore, since In\textsubscript{2}O\textsubscript{3} has a direct “forbidden” band gap, the lowest-energy optical transition from the top of its VB to the bottom of its CB and vice-versa is forbidden by symmetry.\cite{18} This “forbidden” transition provides a built in mechanism for decreasing photo-excited electron-hole pair recombination rates and prolonging their lifetime, thereby greatly increasing their chances of carrying out useful surface chemistry.\cite{19} In addition to these beneficial optical and electronic properties, the surface properties of In\textsubscript{2}O\textsubscript{3} have garnered interest in the field of thermally driven heterogeneous catalysis. Sun et al. have demonstrated the high activity of In\textsubscript{2}O\textsubscript{3} towards the reverse water gas shift (RWGS) reaction at high temperatures, specifically citing CO\textsubscript{2} capture as a key factor in enhancing the activity.\cite{20} Ye et al. have suggested from computational modeling that surface oxygen vacancies could act as active sites to promote thermally driven methanol synthesis.\cite{21}

In this paper, hydroxylated indium oxide nanoparticles (In\textsubscript{2}O\textsubscript{3-\textit{x}}(OH)\textsubscript{\textit{y}}), populated with surface hydroxides and oxygen vacancies, are investigated as a gas-phase CO\textsubscript{2} reduction photocatalyst. We use a temperature-programmed thermal dehydration reaction to make In\textsubscript{2}O\textsubscript{3-\textit{x}}(OH)\textsubscript{\textit{y}} nanoparticles from In(OH)\textsubscript{3}. This simple and “green” fabrication method has numerous advantages including high atom economy, ease of scale-up, and negligible residual carbon contamination, which can block active sites and lower the overall gas-phase adsorption capacity and catalytic activity.\cite{22} Moreover, since it has been reported that the sample calcination temperature has an effect on the incident photon-to-electron conversion efficiency (IPCE) of In\textsubscript{2}O\textsubscript{3} films for photoelectrochemical water splitting\cite{23} as well as the photocatalytic degradation of dyes,\cite{24} we produce, characterize and evaluate the photocatalytic performance of In\textsubscript{2}O\textsubscript{3-\textit{x}}(OH)\textsubscript{\textit{y}} nanoparticles prepared \textit{via} thermal dehydration reactions at 250°C, 350°C, and 450°C, as well as crystalline In(OH)\textsubscript{3} nanoparticles prepared from the same precursor.

Although minimal amounts of organics are present in our synthesis, we still took precautions by using \textsuperscript{13}C-labelled CO\textsubscript{2} (\textsuperscript{13}CO\textsubscript{2}) as a reactant while testing the photocatalytic performance of these nanoparticles for CO\textsubscript{2} photocatalytic activity. Light-driven CO\textsubscript{2} conversion rates reported
in the literature are often low and the ubiquitous carbon contamination from carbon-containing precursors, organic solvents, and organic additives that are used to control the size and morphology of the nanostructure can create false positive results, calling into question the validity of previously reported photoactivity.\textsuperscript{[22]} In fact, until recently, few studies provided this type of evidence to support their claims; however, this practice is becoming increasingly more common due to wide recognition of the importance of these tests.\textsuperscript{[25]}

The overall reaction between CO\textsubscript{2} and H\textsubscript{2}O is highly endergonic, with the majority of the energy consumed in splitting water; but vast improvements in H\textsubscript{2}O splitting systems have opened the possibilities for a sustainable and economically competitive supply of H\textsubscript{2} as a reactant. Reactions with H\textsubscript{2} and CO\textsubscript{2} are thermodynamically favourable relative to those between H\textsubscript{2}O and CO\textsubscript{2}. Thus, H\textsubscript{2} generated separately via solar-driven water splitting can be used in the subsequent photocatalytic reduction of CO\textsubscript{2} - such as the one described herein - to maximize the potential of the harvested sunlight. Therefore, CO\textsubscript{2} reduction photocatalysts that operate in an H\textsubscript{2} environment at reasonably elevated temperatures provide valuable insights into CO\textsubscript{2} reduction mechanisms and also increase the opportunity for researchers to discover components for a scalable artificial leaf.

The majority of CO\textsubscript{2} reduction photocatalysts reported in the literature operate at room temperature or 80 °C for gas- and aqueous-phase reactions, respectively.\textsuperscript{[6,12]} A key insight presented in this study is that although a photocatalyst may show little or no activity at these low temperatures, by slightly elevating the reaction temperature, the material can be activated and function as an efficient CO\textsubscript{2} reduction photocatalyst. These moderate temperatures (110-170 °C) can easily be reached by using simple solar trough concentrators,\textsuperscript{[26]} meaning that no external energy input is required to heat the samples.

In this work, we report gas-phase photocatalytic conversion of \textsuperscript{13}CO\textsubscript{2} in the presence of H\textsubscript{2} to generate \textsuperscript{13}CO at a rate as high as 0.25 μmol g\textsubscript{cat}\textsuperscript{-1} hr\textsuperscript{-1} at 150°C under simulated solar illumination intensities of 2200 W m\textsuperscript{-2} on hydroxylated indium oxide nanoparticle films. We then perform the isotope tracing experiments with coupled gas chromatography mass spectrometry (GC-MS) analysis to confirm - with complete certainty - that the observed gaseous products
originating from CO$_2$ rather than adventitious carbon sources.$^{[27]}$ Furthermore, under only visible light irradiation ($\lambda > 420$ nm), we find that our indium oxide nanoparticles photocatalytically reduce $^{13}$CO$_2$ at a rate of 70 nmol g$_{cat}^{-1}$ hr$^{-1}$ at the same light intensity. Our results show that the combination of favourable optical and electronic properties with a judiciously tailored surface makes In$_2$O$_{3-x}$(OH)$_y$ nanoparticles an active photocatalyst for gas-phase CO$_2$ reduction. This provides valuable insight about key parameters for the composition selection, materials design and performance optimization of an artificial leaf suited for large-scale solar fuels production.

5.3 Results and Discussion

5.3.1 Characterization of hydroxylated In$_2$O$_{3-x}$(OH)$_y$ via temperature-controlled decomposition of In(OH)$_3$

Hydroxylated indium oxide nanoparticles were produced via a thermal dehydration of In(OH)$_3$ (Figure 5.1). As the transition from In(OH)$_3$ to In$_2$O$_{3-x}$(OH)$_y$ does not occur until approximately 210 °C, only samples heated above this temperature undergo dehydration to form indium oxide.$^{[28,29]}$ The transmission electron microscopy (TEM) images in Figure 5.1 illustrate the change in nanostructure morphology with increasing calcination temperature. The In(OH)$_3$ sample calcined at 185 °C (Figure 5.1a) consists of large porous sheet-like structures. As the calcination temperature is increased to 250 °C, the sheet-like structures decompose into clusters of fused nanoparticles approximately 5 nm in diameter (Figure 5.1b and 5.1f). The overall clusters are similar in size to the In(OH)$_3$ sheets, indicating that the observed porosity is likely a result of water molecules being released from the lattice as the In(OH)$_3$ decomposes. As the calcination temperature increases further to 350 °C (Figure 5.1c and 5.1g) and 450 °C (Figure 5.1d and 5.1h), the average particle size increases and overall porosity of the clusters decreases.

The high angle angular dark field (HAADF) HR-TEM images and the powder X-ray diffraction patterns in Figure 5.2a confirm that each sample consists of a single pure crystalline phase. The sample treated at 185 °C crystallizes to form pure cubic In(OH)$_3$, while all other samples form
pure bixbyite $\text{In}_2\text{O}_3$ with no observable $\text{In(OH)}_3$ crystalline phases. For clarity, the series of $\text{In}_2\text{O}_3$ samples prepared at the different calcination temperatures of 250 °C, 350 °C and 450 °C will be referred to as I-250, I-350, and I-450 respectively.

The optical properties of each sample were determined from the diffuse reflectance spectra shown in Figure 5.2b. As expected, the absorption edge of $\text{In}_2\text{O}_3-x\text{(OH)}_y$ is significantly red-shifted in comparison to $\text{In(OH)}_3$. These diffuse reflectance spectra were fitted with a modified Kubelka-Munk function$^{[30]}$ (Supplementary Figure A2.S1) to determine the optical band gaps of

Figure 5.1. Morphology, structure, and appearance of $\text{In}_2\text{O}_3-x\text{(OH)}_y$ and $\text{In(OH)}_3$ samples. (a-d) TEM micrograph of samples treated at 185 °C, 250 °C, 350 °C, and 450 °C, respectively. All scale bars are 40 nm. e) Photographs of each sample after calcination as well as the overall reaction scheme. (f-h) HRTEM-SAADF micrographs (left) and FFTs (right) of the $\text{In}_2\text{O}_3$ samples treated at 250 °C, 350 °C and 450 °C respectively. The zone axes indicated are (1,2,0), (1,0,0) and (2,2,1), respectively.
each sample, as indicated in Figure 5.2c. By correlating these with the valence band maxima and Fermi energy ($E_F$) data obtained from X-ray photoelectron spectroscopy (XPS), we can calculate the band alignment relative to the vacuum level (Figure 5.2c), which corresponds well to what has been reported in the literature.[18,31] These data confirm that the as-prepared In$_2$O$_{3-x}$(OH)$_y$ samples are n-type semiconductors and that all samples may have sufficient reducing power to photocatalytically drive gas-phase CO$_2$ reduction reactions.

### 5.3.2 Demonstration of photocatalytic activity using $^{13}$CO$_2$ labeling

In order to confirm the photocatalytic activity of the In$_2$O$_{3-x}$(OH)$_y$ samples, carbon-13 labelled carbon dioxide ($^{13}$CO$_2$) is used as a tracer molecule to identify products from the photocatalytic reaction in the presence or absence of irradiation. This is an important step that determines whether the carbon source of the products originates from CO$_2$ or from adventitious carbon contamination on the sample.[22] After 16 hours of reaction at 150 °C under both light (80 mW cm$^{-1}$ using a 1000 W metal halide bulb) and dark conditions, I-250 produced CH$_4$, CO, H$_2$O and trace amounts of higher chain hydrocarbons. It was found that CH$_4$ is produced at an average rate of 11 nmol g$_\text{cat}$$^{-1}$ hour$^{-1}$ under irradiation, and was produced even in the absence of irradiation. It was also observed that the CH$_4$ production rate decreased with subsequent batch reactions. The

![Figure 5.2](image_url)  
**Figure 5.2.** Physical characterization of In$_2$O$_{3-x}$(OH)$_y$ and In(OH)$_3$ samples. a) Powder X-ray diffraction patterns for each sample after calcination at the temperature indicated. b) Diffuse reflectance spectra of the as-prepared nanoparticle films used in the photocatalysis experiments. c) Band position diagram of each sample. The valence band (VB) and Fermi energy (EF) were measured using XPS and the band gap was calculated by fitting the reflectance spectra using K-M theory (see SI for more details on the fitting).
product ion-fragmentation pattern obtained using GC-MS (Supplementary Figure A.S2) shows that the intensity of the 16 AMU parent peak of $^{12}$CH$_4$ is significant, while the intensity of the 17 AMU parent peak of $^{13}$CH$_4$ is barely above noise level. This suggests CH$_4$ is produced by the decomposition or reaction of adventitious carbon on the surface and not from the CO$_2$ feedstock. In contrast, it was found that CO is unequivocally a product of CO$_2$ photocatalytic activity and is produced only under light irradiation at an average rate of 0.2 μmol g$_{cat}^{-1}$ hour$^{-1}$, with the highest rate so far observed in this study of 0.6 μmol g$_{cat}^{-1}$ hour$^{-1}$ with on-going studies aimed at further improving the rate. Figure 5.3a shows the relative intensities of the 28 AMU parent peak of $^{12}$CO and the 29 AMU parent peak of $^{13}$CO under both dark and light conditions. The absence of the 29 AMU peak in the dark and the significant increase in its intensity under irradiation demonstrates that the conversion of $^{13}$CO$_2$ to $^{13}$CO is light driven. This finding is further confirmed by a comparison of time dependent product formation. Figure 5.3b shows that CO production increases linearly with time only under irradiation, while CH$_4$ production remains at near baseline levels under both dark and light conditions.

5.3.3 Investigating the effects of sample calcination temperature, and reaction temperature on photocatalytic activity

Previous studies have indicated that sample calcination temperature can have a strong effect on the aqueous-phase photoelectrochemical performance of indium oxide nanostructures.$^{[23,24]}$ In order to determine if the calcination temperature also affects the photocatalytic performance in the gas-phase, we measured the CO production rates under light and dark conditions for In$_2$O$_3$. $\chi$(OH)$_\chi$ samples calcined at different temperatures - I-250, I-350 and I-450 - as well as for an
In(OH)$_3$ control sample. The CO production rates under 80 mW cm$^{-1}$ of irradiation using a 1000 W metal halide lamp at a range of reaction temperatures are shown for each sample in Figure 5.3.
5.3c. In general, CO production rates increase with increasing reaction temperature, reaching a maximum at 150 °C, and then decline as the temperature is increased further. Moreover, indium oxide samples calcined at a lower temperature correspond to a higher CO production rate, where photocatalytic CO₂ reduction at 150 °C for sample I-250 is roughly twice that of I-350 and approximately an order of magnitude greater than that of I-450. The In(OH)₃ sample produces almost no CO at any temperature. The effect of irradiation on CO production rates for each sample at different reaction temperatures is also shown in Supplementary Figure A2.S3. As expected, all samples produced very little amounts of CO under dark conditions, demonstrating that the observed gas phase CO₂ reduction is a light-driven process (Supplementary Figure A2.S4).

5.3.4 Investigating the effect of light intensity and spectral distribution on photocatalytic activity

In order to determine the effect of light intensity on the CO production rate, an I-250 sample was irradiated with a Newport 300 W Xe Lamp fitted with an AM1.5 filter to simulate the solar spectrum. The photocatalytic activity of the sample was tested at 150 °C under varying light intensities from 0.8 to 2.2 suns. Figure 5.3d shows a linear increase in CO production rate with increasing light intensity, which further confirms that the CO₂ to CO conversion is a light-driven reaction. A single sample was used for the duration of these measurements demonstrating the robustness of this photocatalyst.

The spectral dependence of CO production was also investigated (Supplementary Figure A2.S4). A single I-250 film was irradiated with a Newport 300W Xe Lamp, fitted with either an AM1.5 filter or an AM1.5 filter combined with either a 420 nm or a 615 nm high-pass filter. The light intensity was set to 1700 Wm⁻², using a focusing lens to adjust the intensity and a calibrated reference cell to measure the output. When the I-250 sample was initially irradiated with the AM1.5 filtered light, a CO production rate of 0.20 μmol g⁻¹ cat⁻¹ hour⁻¹ was observed. The second run - with the additional 420 nm high pass filter that cut off all wavelengths with energy greater
than 420 nm - produced CO at a rate of 70 nmol g\text{cat}^{-1} \text{ hour}^{-1}. No CO was detected when a 615 nm high-pass filter was used. Finally, a repeat of the initial measurement using only the AM1.5 filter was conducted, reproducing the rate of 0.20 μmol g\text{cat}^{-1} \text{ hour}^{-1}. These results demonstrate that not only is the I-250 capable of converting gaseous CO\textsubscript{2} to CO using only visible light, which correlates well with the diffuse reflectance measurements, but also that In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} is stable under these reaction conditions and can reproduce the results even after being irradiated continuously for 4 days.

5.3.5 Characterization of surface hydroxides and oxygen vacancies

In order to further understand the effects of calcination temperature on the photocatalytic activity, XPS measurements were conducted. Figure 5.4a shows that the In3d\textsubscript{5/2} core level peak shifts to a lower binding energy as the calcination temperature is increased, indicating an increase in charge density around the In atoms as a result of the removal of OH groups. The O1s core level spectra in Figure 5.4b shows a sharp contrast between In(OH)\textsubscript{3} and In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} samples. There is a ~2.5 eV shift to lower binding energy of the main O1s peak from 532.7 eV for In(OH)\textsubscript{3} to 530.2 eV for I-450. Additionally, a shoulder peak appears in the O1s core level peak of the In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} samples, indicating that there is more than one chemical state of oxygen present in the structure. Indeed, the O1s peak for the In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} samples can be de-convoluted into three distinct peaks: the main oxide peak at 530.3 eV and two additional peaks at 531.7 eV and 532.5 eV (Figure 5.4c-e). The peak at 531.7 eV indicates the presence of oxygen vacancies in the structure.\textsuperscript{[32,33]} This peak is shifted to a higher binding energy relative to the main oxide peak. This is a result of the change in O interaction with an In center that is more reduced in character because it is surrounded by less than six O atoms due to the oxygen vacancies. The peak at 532.5 eV has been attributed to surface OH groups\textsuperscript{[32]} and agrees well with the O1s spectra for the pure In(OH)\textsubscript{3} peak. From these plots in Figure 5.4c-e, it is clear that the shoulder peak - with contributions from both vacancies and surface hydroxides - decreases with increasing calcination temperature. XPS measurements were also conducted on samples exposed to reaction conditions and results indicate a slight change in the shoulder peak of the O1s spectra. Current
on-going research aims to investigate this material in-situ to determine how the surface may change during reaction.

The hydroxide content of the samples was investigated further by both FT-IR-ATR and thermogravimetric measurements. The intensity of the OH stretches in the FT-IR-ATR spectra (Supplementary Figure A2.S5) decreases with increasing calcination temperature, illustrating that samples treated at higher temperatures have lower hydroxide contents. In order to establish the extent of hydroxide loss during synthesis, each In$_2$O$_{3-x}$(OH)$_y$ sample was synthesized in-situ inside a thermogravimetric analyzer, and the weight loss observed was attributed to hydroxide condensation to form bridging oxides. Supplementary Figure A2.S6 shows the weight loss of each sample after calcination under air flow for 3 hrs. It is clear that lower calcination temperatures correspond to less overall weight loss and result in stabilization at a higher relative weight. By comparing these plots to the theoretical maximum weight loss when all hydroxides are converted to bridging oxides, it is apparent that I-450 should have almost no hydroxides left. I-250 and I-350 on the other hand, have additional weight above the theoretical value, which we attribute to the retained hydroxyl groups. From these data and BET surface area described below, we estimate that the surface hydroxide coverage is on the order of 6 µmol m$^{-2}$ for I-250 and 3 µmol m$^{-2}$ for I-350. It is expected that the combination of both hydroxide groups and oxygen vacancies is a key feature of our functioning In$_2$O$_{3-x}$(OH)$_y$ nanoparticle photocatalysts and that both of these entities are present and work in concert at active sites.

### 5.3.6 Correlation of CO$_2$ capture capacity with observed photocatalytic rates

To clarify the observed trend in CO production rates between In$_2$O$_{3-x}$(OH)$_y$ samples, the CO$_2$ capture capacity was determined for each sample at 150 °C, the reaction temperature at which the highest CO production rates for all samples were observed. Furthermore, in order to more accurately compare the CO$_2$ capture capacity and the photoactivity, both are normalized to the surface area of each sample, determined using the Brunauer-Emmett-Teller (BET) method. The
surface areas for the In(OH)$_3$, I-250, and I-350 were remarkably similar at 124.7 m$^2$g$^{-1}$, 125.0 m$^2$g$^{-1}$, and 129.6 m$^2$g$^{-1}$ respectively. Only I-450 had a significantly lower surface area at 90.0 m$^2$g$^{-1}$, which is likely a result of some nanoparticle sintering at the higher calcination temperature. Figure 5.5 shows the surface-area-normalized CO$_2$ capture capacities for each sample plotted together with their corresponding CO production rates. There is a notable strong correlation between CO$_2$ reduction rates and the normalized CO$_2$ capture capacity.

5.3.7 Designing a surface for CO$_2$ photocatalytic activity

The affinity of a photocatalyst’s surface for CO$_2$ has been identified in this study, as well as in others,\cite{9-11} as a critical factor influencing photocatalytic activity. As Figure 5.5 demonstrates, the CO$_2$ capture capacity of the In$_2$O$_{3-x}$(OH)$_y$ nanoparticles corresponds very well with photo-reactivity, indicating that CO$_2$ adsorption plays an important role in the light-driven reaction. Intuitively, CO$_2$ molecules must be able to approach and interact with the surface for a sufficient amount of residence time in order for electron transfer to occur. Surface hydroxides have a known affinity for the Lewis-acidic CO$_2$.\cite{34} This could explain the strong positive correlation between CO$_2$ capture capacity and hydroxide content. However, while the In(OH)$_3$ control sample has the highest hydroxide content and a similar surface area to that of I-250, it also had a significantly lower CO$_2$ capture capacity. This indicates that surface hydroxides alone are not sufficient to facilitate CO$_2$ capture and photocatalytic reduction of CO$_2$.

In addition to hydroxides, the surface of the In$_2$O$_{3-x}$(OH)$_y$ nanoparticles is also populated with oxygen vacancies. The presence of these oxygen vacancies in the In$_2$O$_{3-x}$(OH)$_y$ samples is supported by both the de-convolution of the XPS O1s core level peaks (Figure 5.4c-e) as well as the n-type position of the Fermi-levels relative to the conduction bands (Figure 5.2c), which is typically a result of non-stoichiometry. It is apparent from both figures that I-250 has the largest peak associated with oxygen vacancies as well as the highest Fermi energy, implying a higher abundance of vacancies compared to the other temperature-treated In$_2$O$_{3-x}$(OH)$_y$ samples. The
increase in oxygen vacancies for I-250 may result from the natural increase in surface defect sites as the particle size decreases. Surface oxygen vacancies may also arise from the crystal structure of In$_2$O$_3$. The cubic In$_2$O$_{3-x}$(OH)$_y$ samples have a bixbyite structure, which can be understood as the CaF$_2$-type lattice with 25% of the tetrahedral anion sites vacant. This additional space in the bixbyite structure may result in more dynamic flexibility, especially at the nanoparticle surface, allowing for more atomic mobility in the lattice; indeed In$_2$O$_3$ is a known solid ionic and protonic conductor. Additionally, these intrinsic oxygen vacancies may increase the stability of the vacant surface sites, allowing the material to remain stable under reaction conditions. By contrast the stoichiometric In(OH)$_3$ with its perovskite structure does not have a significant concentration of surface oxygen vacancies. The implied necessary combination of surface hydroxides and oxygen vacancies could provide an explanation for the stark difference in CO$_2$ capture capacity and photocatalytic activity of In(OH)$_3$ and I-250.

Surface oxygen vacancies may also form due to interactions between surface oxygen sites and H$_2$ or CO under reaction conditions. In$_2$O$_3$ has been investigated experimentally$^{36,37}$ and theoretically$^{21,38}$ in order to determine surface oxygen vacancy formation under reducing environments (H$_2$ or CO) and oxidizing environments (O$_2$, CO$_2$ or H$_2$O). Surface oxygen vacancies are generated in H$_2$ environments at temperatures greater than 125 °C.$^{36}$ The In$_2$O$_{3-x}$(OH)$_y$ were investigated for temperature dependence under a H$_2$ atmosphere. It is found that the CO production increases significantly at temperatures greater than 130 °C. Figure 5.3c shows the temperature dependence of CO$_2$ reduction. Very little CO is observed at 110 °C (sample I-250 is the only sample to produce a significant amount of CO at 110 °C). However, at reaction temperatures above 130 °C, CO production under light irradiation is significant. This indicates that the surface vacancies may be necessary for the reaction to occur photocatalytically and that these vacancies are generated by the reduction of the surface by H$_2$, as shown in Equation 5-1:

$$H_2 + [O]_{lattice} \Rightarrow H_2O + [ \ ]_{lattice} \quad (1)$$
A maximum CO production rate is observed at a reaction temperature of 150 °C. At 170 °C the reaction rates decrease for all samples, which may be due to oxidation of CO by lattice oxygen on the In$_2$O$_{3-x}$(OH)$_y$ surface as shown in Equation 5-2.\textsuperscript{[37]}

\[ CO + [O]_{lattice} \Rightarrow CO_2 + [\quad]_{lattice} \] (5-2)

An alternative explanation for the observed dependence on temperature trend is the adsorption and desorption of molecules at the surface. At higher temperatures, product molecules such as H$_2$O, which can block active sites, may desorb enabling more turnovers at these active sites. Since it is observed that In$_2$O$_{3-x}$OH$_y$ samples achieve a maximum efficiency at 150 °C, this may indicate that 150 °C is a “sweet spot,” combining efficient CO$_2$ adsorption and efficient CO and H$_2$O desorption.

It is also possible that the reaction proceeds between CO$_2$ and the surface oxygen vacancies, produced in Equation 5-1 to produce CO through a surface oxidation reaction. However, pre-reducing the sample in H$_2$ at elevated temperature followed by a batch reaction in CO$_2$ yielded no trace of CO under irradiation. Thus it is believed that the observed reaction is the reverse water gas shift (RWGS) reaction as shown in Equation 5-3.

\[ CO_2 + H_2 \Rightarrow CO + H_2O \] (5-3)

While we have observed H$_2$O as a product, an exact reaction stoichiometry was difficult to quantify to complete a mass balance for the proposed RWGS reaction due to uncertainties created by the strong interaction of water with the tubing connecting the reactors to the GC and GC-MS.
5.4 Conclusion

A functional single component CO₂ reduction photocatalyst must have surface, optical, and electronic properties working in concert for photocatalytic reduction of CO₂ to occur in the gas phase. In this study, the In₂O₃-x(OH)ₓ nanoparticles demonstrate activity for the photocatalytic reduction of CO₂ in the presence of H₂ at temperatures as low as 130 °C using both ultraviolet and visible light. Our work strongly suggests that the observed activity of In₂O₃-x(OH)ₓ samples is associated with surface populations of oxygen vacancies and hydroxides, which may act in concert as active sites for CO₂ adsorption and charge transfer under simulated solar irradiation.

We have produced a series of nanostructured In₂O₃-x(OH)ₓ materials via a temperature controlled thermal dehydration of In(OH)₃. Using ¹³CO₂ as a tracer molecule, strong light and temperature-dependent photocatalytic reduction of gaseous ¹³CO₂ to ¹³CO is confirmed in the presence of H₂. The surface hydroxide and oxygen vacancy content strongly correlates with both an increase in ¹³CO₂ capture capacity and an increase in photocatalytic activity for ¹³CO production. By combining the favorable surface, electronic and optical properties of nanostructured In₂O₃-x(OH)ₓ with the bixybite crystal structure and its enhanced CO₂ capture capabilities, we have demonstrated a combination of key components to be considered in the discovery, optimization, and scaling of new and efficient gas-phase CO₂ reduction photocatalysts for solar fuels production.

5.5 Experimental Section

Synthesis of In₂O₃-x(OH)ₓ nanoparticles: An In(OH)₃ precursor was synthesized and subsequently dehydrated into In₂O₃ nanoparticles following a modified version of a previously published procedure. All chemicals were used as received without any further purification. In
a typical synthesis 3.6 g (16.2 mmol) of indium(III) chloride (Sigma Aldrich, 98%) was dissolved in 72 mL of a 3:1 solution of anhydrous ethanol (Commercial Alcohols) and deionized, nanopure water (resistivity 18.2 MΩ cm). In a separate beaker, a 3:1 mixture of ethanol and ammonium hydroxide was prepared by combining 18 mL of aqueous ammonium hydroxide (Caledon, 28-30% adjusted to 25 wt% with deionized water) and 54 mL of anhydrous ethanol. The solutions were rapidly combined, resulting in the immediate formation of a white precipitate. To control the particle size, the resulting suspension was immediately immersed in a pre-heated oil bath at 80°C and stirred for 10 min. The suspension was then removed from the oil bath and allowed to cool to room temperature. The precipitate was separated via centrifugation and washed 3 times with deionized water. The precipitate was sonicated between washings to ensure adequate removal of any trapped impurities and then dried overnight at 80°C in a vacuum oven. The dried precursor powder was finely ground with a mortar and pestle and calcined for 3 hours in air at 185°C, 250°C, 350°C, and 450°C. Samples were prepared by drop casting these precursor powders from an aqueous dispersion onto 1”x1” binder free borosilicate glass microfiber filters (Whatman, GF/F, 0.7 µm).

Physical Characterization: Powder X-ray diffraction (PXRD) was performed on a Bruker D2-Phaser X-ray diffractometer, using Cu Kα radiation at 30 kV. Nitrogen Brunauer-Emmet-Teller (BET) adsorption isotherms were obtained at 77 K using a Quantachrome Autosorb-1-C. Sample morphology was determined using a JEOL-2010 high resolution transmission electron microscope (HR-TEM). Fourier transform infrared spectroscopy (FT-IR) was performed using a Perkin Elmer Spectrum-One FT-IR fitted with a universal attenuated total reflectance (ATR) sampling accessory with a diamond coated zinc selenide window. Diffuse reflectance of the samples was measured using a Lambda 1050 UV/VIS/NIR spectrometer from Perkin Elmer and an integrating sphere with a diameter of 150mm.

Sample weight loss during the calcination process was determined by placing ~10 mg of uncalcined indium hydroxide precursor in a TA Instruments Q500 thermogravimetric analyzer, jumping to the set temperature of either 250°C, 350°C, or 450°C and holding for 3 hours under a flow of compressed air. The sample weight was determined using the built-in ATI CAHN C-34
microbalance. The film morphology and thickness was characterized by scanning electron microscopy using a QUANTA FEG 250 ESEM. The borosilicate glass microfiber filters were used as a substrate to provide increased surface area as well as mechanical stability. Supplementary Figure S7 shows SEM micrographs of a typical In$_2$O$_3$ sample on the filter. Supplementary Figure S7a shows a cross-section of the film, indicating its thickness is approximately 50 µm. The magnified image shown in Supplementary Figure S7b indicates that the as-prepared sample maintains its high porosity, an important factor for gas-phase reactions.

X-ray photoelectron spectroscopy (XPS) was performed using a Perkin Elmer Phi 5500 ESCA spectrometer in an ultrahigh vacuum chamber with base pressure of 1x10$^{-9}$ Torr. The spectrometer uses an Al Kα X-ray source operating at 15 kV and 27 A. The samples used in XPS analyses were prepared by drop-casting aqueous dispersions onto p-doped Si(100) wafers in the case of the In$_2$O$_3$ samples and fluorine-doped tin oxide substrate in the case of the In(OH)$_3$ sample. All data analyses were carried out using the Multipak fitting program and the binding energies were referenced to the NIST-XPS database and the Handbook of X-ray Photoelectron Spectroscopy.$^{[40,41]}$

**Gas-phase Photocatalytic Measurements:** Gas-phase photocatalytic rate measurements were conducted in a custom fabricated 1.5mL stainless steel batch reactor with a fused silica view port sealed with Viton O-rings. The reactors were evacuated using an Alcatel dry pump prior to being purged with the reactant gases H$_2$ (99.9995%) and CO$_2$ (99.999%) at a flow rate of 6mL/min and a stoichiometry of either 4:1 (stoichiometric for Sabatier reaction) or 1:1 (stoichiometric for reverse water gas shift reaction). During purging, the reactors were sealed once they had been heated to the desired temperature. The reactor temperatures were controlled by an OMEGA CN616 6-Zone temperature controller combined with a thermocouple placed in contact with the sample. The pressure inside the reactor was monitored during the reaction using an Omega PX309 pressure transducer during the reaction. Reactors were irradiated with a 1000W Hortilux Blue metal halide bulb (the spectral output is shown in Supplementary Figure A2.S8) for a period of 16 hours. Product gases were analyzed with a flame ionization detector (FID) and
thermal conductivity detector (TCD) installed in a SRI-8610 Gas Chromatograph (GC) with a 3’ Mole Sieve 13a and 6’ Haysep D column.

Isotope tracing experiments were performed using $^{13}$CO$_2$ (99.9 atomic % Sigma Aldrich). The reactors were evacuated prior to being injected with $^{13}$CO$_2$ followed by H$_2$. Isotope product gases were measured using an Agilent 7890A gas chromatographic mass spectrometer (GC-MS) with a 60m GS-Carbonplot column fed to the mass spectrometer.

The spectral dependence of the photoactivity of the In$_2$O$_3$ nanoparticles was investigated using a Newport 300W Xe Lamp (the spectral output is shown in Supplementary Figure 8) fitted with a combination of AM1.5, 420nm high-pass, and 615nm highpass filters. Since each filter reduced the total irradiation intensity, the beam was focused using collimating lenses to maintain an irradiation intensity of 100mw/cm$^2$. The spectral output was measured with a StellarNet Inc spectrophotometer. Irradiation intensity is measured by a Newport 91150V calibrated reference cell and meter.

**CO$_2$ Capture Capacity:** The CO$_2$ capture capacity of each sample was measured by thermogravimetric analysis (TGA) with a TA Instruments Q500 thermogravimetric analyzer. A desorption step was first carried out under N$_2$ flow at a rate of 100 mL/min and a temperature ramp of 10°C/min up to 150°C and holding the temperature at 150°C for 3 hours. To measure the amount of CO$_2$ adsorption, the gas was then switched to 100% dry CO$_2$ flow at 100 mL/min and the temperature was maintained at 150°C for 10 hours. The weight gain observed during this adsorption step was used to calculate the CO$_2$ capture capacity of the sample. Desorption of CO$_2$ was performed by switching the gas flow back to N$_2$ flow for 5 hours while keeping the temperature at 150°C.
5.6 Acknowledgements

L. B. Hoch and T. E. Wood contributed equally to this work. This author was responsible for development of experiments, building and running photoreactors, measuring rates, and interpreting results of both the material characterization and rate measurements. G. A. Ozin is Government of Canada Tier 1 Canada Research Chair in Materials Chemistry and Nanochemistry. The strong and sustained financial support of this solar fuels research project by the Ontario Ministry of Research and Innovation (MRI), the Ontario Ministry of Economic Development and Innovation (MEDI), the Natural Sciences and Engineering Council of Canada (NSERC) and the University of Toronto are deeply appreciated. We are also grateful for the help of Dr. Miguel Yacaman and Eduardo Larios at the University of Texas at San Antonio for conducting the HR-TEM measurements and Dr. Benoit Mahler for assistance and helpful discussion regarding the HR-TEM analysis.
Chapter 6
Illuminating CO$_2$ Reduction: Investigating the Role of Surface Hydroxides and Oxygen Vacancies on Nanocrystalline In$_2$O$_{3-x}$(OH)$_y$

The following chapter is presented with the consent of all contributing authors. It is the publication: Illuminating the CO$_2$ Reduction: Investigating the Role of Surface Hydroxide and Oxygen Vacancies on Nanocrystalline In$_2$O$_{3-x}$(OH)$_y$.

Kulbir Kaur Ghuman$^{a,†}$, Thomas E. Wood$^{b,†}$, Laura B. Hoch$^c$, Charles A. Mims$^b$, Geoffrey A. Ozin$^c$ and Chandra Veer Singh$^a$

Both Kulbir Ghuman and this author are co-first authors on this work. This work was inspired by the work carried out in Chapter 5, and this author used insights from this work to guide the development of questions answered by the work described herein. The theoretical work, carried out by post doctorate fellow Kulbir Ghuman under the advisement of Professor Chandra Singh in collaboration with myself, aimed to understand the influence of surface hydroxide groups and oxygen vacancies on the surface interactions between CO$_2$ and In$_2$O$_3$ surfaces. A set of (111) In$_2$O$_3$ surfaces was simulated: a pristine surface with no surface defects, oxygen deficient surfaces with specific surface oxygen vacancies, and hydroxide groups adjacent to oxygen vacancies. It was found, generally, that CO$_2$ does not strongly absorb onto the surface of (111) In$_2$O$_3$, regardless of the type of defect or the placement of the surface defect. However, when the same surfaces were investigated in the presence of H$_2$, an active site capable of dissociation CO$_2$ is formed on the site containing both oxygen vacancies and surface hydroxides. The H$_2$ splits heterolytically, at sites where a surface hydroxide is adjacent to an oxygen vacancy, creating a hydride and hydroxide. The hydride / hydroxide pair attracts a CO$_2$ molecule. The CO$_2$ dissociates to form CO and H$_2$O. This surface site is analogous to a frustrated lewis pair (FLP) type chemistry which is a sterically hindered Lewis acid and base site.
The experimental work in this study was carried out by this author. This work consists of several kinetic studies and in-situ DRIFTS measurements on the hydroxylated $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ nanoparticles. The kinetic studies measured the dependence of the CO production rate on the partial pressure of $\text{H}_2$, $\text{CO}_2$, and the total volumetric flow rate. It was found that $\text{H}_2\text{O}$ inhibits the reaction, and this finding was used to reveal that there is a first order dependence on $\text{CO}_2$ and no dependence on $\text{H}_2$ on the CO production rate. This observation is consistent with the reaction proposed by theory which suggests that a $\text{CO}_2$ molecule reacts directly with an absorbed surface molecule which can be described as an Eley-Rideal mechanism.

6.1 Abstract

Designing catalytic nanostructures that can thermochemically or photochemically convert gaseous carbon dioxide into carbon based fuels is a significant challenge, which requires a keen understanding of the chemistry of reactants, intermediates and products on surfaces. In this context, it has recently been reported that the reverse water gas shift reaction (RWGS), whereby carbon dioxide is reduced to carbon monoxide and water, $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$, can be catalysed by hydroxylated indium oxide nanocrystals, denoted $\text{In}_2\text{O}_{3-x}(\text{OH})_y$, more readily in the light than in the dark. The surface hydroxide groups and oxygen vacancies on $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ were both shown to assist this reaction. While this advance provided a first step towards the rational design and optimization of a single-component gas-phase $\text{CO}_2$ reduction catalyst for solar fuels generation, the precise role of the hydroxide groups and oxygen vacancies in facilitating the reaction on $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ nanocrystals has not been resolved. In the work reported herein, for the first time we present in situ spectroscopic and kinetic observations, complemented by density functional theory analysis, that together provide mechanistic information into the surface reaction chemistry responsible for the thermochemical and photochemical RWGS reaction. Specifically, we demonstrate photochemical $\text{CO}_2$ reduction at a rate of 150 $\mu\text{mol g}_{\text{cat}}^{-1} \text{hour}^{-1}$ and propose a reaction mechanism whereby a surface active site of $\text{In}_2\text{O}_{3-x}(\text{OH})_y$, composed of a Lewis base hydroxide adjacent to a Lewis base indium,
together with an oxygen vacancy, assists the adsorption and heterolytic dissociation of
H₂ that enables the dissociation and reaction of CO₂ to form CO and H₂O as products.
This mechanism, which has its analogue in molecular frustrated Lewis pair (FLP)
chemistry and catalysis of CO₂ and H₂, is supported by preliminary kinetic
investigations. The results of this study emphasize the importance of engineering the
surfaces of nanostructures to facilitate gas-phase thermochemical and photochemical
carbon dioxide reduction reactions to energy rich fuels at technologically significant
rates.

6.2 Introduction

A global paradigm shift is currently underway where the greenhouse gas CO₂ is regarded
as chemical feedstock for a carbon neutral sustainable energy economy.[117–119] This has
led to the pursuit of new technologies, which aim to capture light energy in the form of
chemical energy through the generation of solar fuels from CO₂.[4,120,121] As a result, there
is growing interest in the research community to discover and study materials that can use
light energy efficiently to activate gaseous CO₂ into different carbon based chemical
products.[59,122] Careful investigation of CO₂ activation on surfaces may provide insight
for designing materials that will power these solar fuel technologies in the future.

Indium sesquioxide (In₂O₃) is increasingly capturing the attention of researchers as a
potential photocatalyst due to its favourable optical, electronic and surface properties.[123–
127] Recently, our group has demonstrated light-assisted, gas-phase photoreduction of CO₂
to CO over hydroxylated In₂O₃₋ₓ(OH)ₙ nanocrystals at rates as high as 15 μmol g⁻¹ h⁻¹
in H₂ atmospheres at 150°C via the reverse water gas shift (rWGS) reaction.[60] The high
photoactivity was attributed to surface hydroxide groups and oxygen vacancies, whose
relative concentration correlated well with the CO₂ adsorption capacity and CO
production rate. This remarkable observation suggested that both surface hydroxide
groups and oxygen vacancies play a vital role in the reaction mechanism; however, their
function was unclear at the time.[60] Thus, it became apparent that a fundamental
understanding of the function of the hydroxide groups and oxygen vacancies on the surface of In$_2$O$_{3-x}$(OH)$_y$ nanocrystals will prove to be pivotal for the rational design of advanced catalysts for the photoreduction of CO$_2$ in the future. Motivated by this challenge, we describe herein a combined spectroscopic, kinetic and density functional theory study designed to provide an insight into the effect of surface hydroxide groups and oxygen vacancies on the RWGS reaction mechanism. The combined experimental and theoretical results support a mechanism in which CO$_2$ is adsorbed on the In$_2$O$_{3-x}$(OH)$_y$ surface at an active site, which arises from the heterolytic splitting of H$_2$ on adjacent hydroxide and indium sites which are next to a surface oxygen vacancy. Proton and hydride transfer to adsorbed CO$_2$ subsequently leads to the production of CO and H$_2$O with concomitant regeneration of the hydroxides and oxygen vacancies.

6.3 Methodology

6.3.1 Computational model

All the spin-polarized calculations were performed by the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approximation (GGA) and the Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) ultra-soft pseudopotentials implemented in the Quantum Espresso software.$^{[128–130]}$ Kinetic energy cut-offs of 50 and 200 Ry were used for the wavefunctions and charge density, respectively and the self-consistent field convergence criterion was set to $1E^{-6}$ Ry. Each system was relaxed with variable cell size using conjugate gradient minimization until the magnitude of the residual Hellman-Feynman force on each atom was less than $1E^{-3}$ Ry/Bohr. Based on experimental evidence, density functional theory (DFT) calculations were conducted for the (111) surface in the present study. Notably, this surface is also the most abundant crystal face from a thermodynamic equilibrium perspective.$^{[131]}$ To model the In$_2$O$_3$ (111) surface, a 4-layer slab having 160 atoms was used, in which a vacuum layer of ~20Å was applied. The modelled system was a continuous layer, roughly 11.5 Å in thickness, which
represents a nanofilm, and captures the behaviour of non-edge nanocrystal regions which form the majority of surface area. In all calculations, the bottom two layers were frozen at their equilibrium bulk positions, whereas the top two layers together with the adsorbates were allowed to relax. Because of the large size of the supercell, Brillouin zone integrations were performed using the gamma k-point only. The complicated surface with low symmetry is shown in Figure 6.1E, while a side view of the supercell is shown in Figure 6.1D. Bader charge analyses were performed for pristine and defected In$_2$O$_3$ (111) surfaces with and without CO$_2$ adsorption.[132,133] Transition states (TS) along a minimum energy reaction path (MEP) were determined using the climbing image nudged elastic-band (CI-NEB) method with 11 images.[134–136]

6.3.2 Material synthesis and characterization

Nanocrystalline In$_2$O$_{3-x}$(OH)$_y$ powder used in this work was synthesised by thermal treatment of In(OH)$_3$ nanocrystals at 250°C for 3 hours. A detailed description of the synthesis of the In(OH)$_3$ precursors and characterization of the In$_2$O$_{3-x}$(OH)$_y$ is outlined in a previous work.[60] The nanocrystals morphology was determined using a JEOL-2010 high resolution transmission electron microscope (HR-TEM). Powder X-ray diffraction (PXRD) was performed on a Bruker D2-Phaser X-ray diffractometer, using Cu Kα radiation at 30 kV.

6.3.3 Photocatalytic measurements and surface characterization

The gas-phase photocatalytic rate measurements were carried out in a fixed-bed flow reactor. A borosilicate tube (3 mm outer diameter and 2.5 mm inner diameter) was packed with 20 mg (1 cm catalyst bed length) of In$_2$O$_{3-x}$(OH)$_y$ nanocrystal powder, with quartz wool as support at both ends. The tubular reactor was heated by conduction using a heated copper block. The reactor was fastened within a custom fabricated stainless steel
brace which suspends the reactor within a channel of a heated copper block, allowing heating from the sides and below. The top of the reactor was exposed allowing light irradiation from a Newport 300 W Xe lamp at a distance of 2 cm, with a light intensity of 100 W cm\(^{-2}\). Reaction gas mixtures were composed of H\(_2\) (99.9995%), CO\(_2\) (99.999%) and an inert He (99.9999%). In order to stimulate different reaction conditions, either the total volumetric flow rate was varied ranging from 5 to 15 mL/min, or each gas was

Figure 6.1. (A) Low-resolution TEM image indicating the overall morphology and porosity of the nanocrystalline In\(_2\)O\(_{3-x}\)(OH)\(_y\) sample. (B) Dark field HR-STEM image of the In\(_2\)O\(_{3-x}\)(OH)\(_y\) sample illustrating the presence of (111) planes. The FFT inset corresponds to the (1-10) zone axis. (C) A representation of the In\(_2\)O\(_3\) crystal structure oriented along the (1-10) zone axis with cuts along the (1 1 1) and (11-1) planes. (D) Side view of bixbyite In\(_2\)O\(_3\) supercell with (111) orientation. (E) The upper surface structure of (111) terminated In\(_2\)O\(_3\). Surface In atoms (marked In\#; where \# = 1 to 7) and O atoms (marked O\#; where \# = 1 to 9) shown in (E) are considered for adsorption of various adsorbents. Red balls represent O atoms while blue balls represent In atoms.
varied while maintaining a constant flow rate. The reactor temperatures were controlled by an OMEGA CN616 6-Zone temperature controller combined with a thermocouple placed at the top of the catalyst bed within the reactor. Pressure indicators were installed at the inlet and the outlet of the reactor to monitor the pressure drop across the catalyst bed. The heating program increased the set point with 10°C temperature intervals, with a specific temperature maintained for a 40-minute time interval before increasing it to the next set point with a ramp rate of 1°C min⁻¹. The product gases in the outlet stream of the reactor were analysed with an 8610 gas chromatograph (SRI) installed with a 1’ Mol Sieve 5a column and a 6’ Haysep D column.

In-situ diffuse reflectance infrared spectroscopy (DRIFTS) measurements were conducted using a Harrick Praying Mantis diffuse reflectance chamber with a Harrick environmental chamber. Powdered nanocrystalline In₂O₃-x(OH)ₓ was packed into the sample cup and installed into the sample chamber. A reference spectrum was obtained after the powder had been heated to 120°C in H₂ flowing at 20 cm³ min⁻¹ for 1 hour, so as to remove any water or absorbed species. In order to obtain a reference spectrum, the chamber/powder was cooled to room temperature, and He was flowed through the chamber at 20 cm³ min⁻¹ for an hour. Light irradiation was passed through the ZeSe window on the Harrick environmental chamber via an optical fibre of 1 meter in length attached to a Newport 300 W Xe Lamp with a light intensity of 200 W/m² at the end of the optical fibre.

6.3.4 Results and discussion

We selected the most active sample of the nanocrystalline catalyst from our previous study and conducted its morphological characterization.¹² The TEM image in Figure 6.1A shows the overall morphology of the sample, indicating its porous nanocrystalline nature and high surface area, both necessary parameters for an active catalyst. The dark field HR-STEM image (Figure 6.1B) illustrates the high crystallinity of the In₂O₃-x(OH)ₓ sample. The fast Fourier transform (FFT) of the image, shown in the inset, corresponds to
the (1-10) zone axis and allows for identification of the (111) surfaces indicated in the figure. The simulated structure used for DFT calculations is shown in Figure 6.1D. It corresponds well with the experimental observations (Figure 6.1A-C), and is focused solely on (111) surface of indium sesquioxide.

6.3.5 Temperature dependence of CO production

In our previous work, the production rates of CO, measured in batch photoreactors for both thermochemical and photothermal conditions on In$_2$O$_3$-$_x$(OH)$_y$ nanocrystals increased with temperature but the study was limited to a maximum operating temperature of 170°C.[60] Expanding upon our investigation of this material, the temperature dependence of the thermochemical and photochemical production of CO from CO$_2$ and H$_2$ on In$_2$O$_3$-$_x$(OH)$_y$ nanocrystals was investigated in a flow reactor under various flowing gas atmospheres and in the dark and light, with the results shown in Figure 6.2A. The In$_2$O$_{3-x}$(OH)$_y$ nanocrystals selected for this study were the nanocrystals with the highest CO$_2$ capture capacity and CO photocatalytic production from our previous study. The reaction was carried out in a flow reactor which is capable of higher

![Figure 6.2. (A) Temperature dependence of CO production for In$_2$O$_{3-x}$(OH)$_y$ nanoparticle catalysts under flowing H$_2$ and CO$_2$. (B) Pseudo-Arrhenius plots drawn from temperature dependent measurements](image)
temperatures than previously possible in the batch photoreactors. However, while heating to 300°C is possible, the catalyst did not appear to be stable in our work at temperatures above 200°C, which limited investigations to temperatures up to 190°C.

Under light irradiation and flowing \( \text{H}_2 \) and \( \text{CO}_2 \), reasonable photoactivity of 15.4 µmol \( \text{g}_{\text{cat}}^{-1} \text{ hour}^{-1} \) is demonstrated at temperatures as low as 150°C, which increases to 153 µmol \( \text{g}_{\text{cat}}^{-1} \text{ hour}^{-1} \) at 190°C. In the dark, while measurable CO production was not observed until 165°C, it increases to 35.7 µmol \( \text{g}_{\text{cat}}^{-1} \text{ hour}^{-1} \) at 190°C under flowing \( \text{H}_2 \) and \( \text{CO}_2 \) conditions. Assuming that the apparent reaction rate constant, \( k \), is proportional to the CO production rate, a pseudo-Arrhenius plot was prepared to estimate the apparent activation energy of both the thermochemical and photochemical reactions, as shown in Figure 6.2B. The apparent activation energy of the photochemical RWGS reaction was estimated to be 86 kJ mol\(^{-1}\) while for the thermochemical reaction, it was estimated to be 107 kJ mol\(^{-1}\). This difference between light and dark activation energies amounts to 0.26 eV, which results in an observed 4-fold increase in reaction rate due to photoactivation. Previous studies reported activation energies of 40 kJ mol\(^{-1}\) or less for photocatalytic reactions, where it was suggested this barrier arose from a physical step involving the adsorption or desorption of reactants or products; however, in this study, the estimated activation energy is above 80 kJ mol\(^{-1}\), suggesting a chemical reaction step may be the rate determining step.\(^{[135,137]}\) While it is not clear what the photochemical activation energy represents in terms of chemical reaction steps, a lower photochemical activation energy compared to the thermochemical one is consistent with previous reports and will be the subject of future investigations.\(^{[138,139]}\)

6.3.6 Kinetic Investigations

In order to gain insight into the reaction pathway we conducted kinetic measurements through the variation of key reaction parameters. These dependences were investigated both in presence and absence of light. The CO production rate was measured in the flow reactor, while varying (1) the flow rates for \( \text{CO}_2 \) and an inert diluent (He), (2) the flow
rates for $H_2$ and an inert diluent (He) and (3) the total reactant flow rate, also characterized as a space velocity (volumetric flow rate divided by reactor volume). The temperature was chosen as 190°C for this particular study because of (i) the high CO production rate and (ii) the stability of $In_2O_{3-x}(OH)_y$ nanocrystals over a 10-hour reaction period under light reaction conditions, as shown in Figure A3.S1 contained in the Supporting Information.

Assuming that the reaction follows basic power law kinetics, the rate of CO production, $r_{CO}$, (rate per mass of catalyst) can be related to the partial pressure of each reactant and product as:

$$r_{CO} = k_1 p_{H_2}^\alpha p_{CO_2}^\beta p_{H_2O}^{\gamma} p_{CO}^\delta$$  \hspace{1cm} (6-1)$$

In expression (6-1), $k_1$ is the rate constant; $p_i$ is the partial pressure of reactant $i$; $\alpha$, $\beta$, $\gamma$, and $\delta$ are the reaction orders of $H_2$, $CO_2$, $H_2O$, $CO$, respectively.

First, the dependence of the CO production rate on the space velocity was investigated. The space velocity, at constant inlet compositions, was varied under both light and dark conditions. As shown in Figure 6.3A, the CO production rate decreases with decreasing space velocity under both light and dark conditions. This observed behaviour is consistent with a reaction product inhibiting the rate of reaction, since lower space velocity (longer gas residence time) allows a build-up of higher product concentrations. This hypothesis was tested using a simple plug flow reactor model and by assuming, once again, a power law kinetic expression and low conversion of the reactants. Here, we use a rate law which has a first order inhibition by one of the products, $H_2O$ in this case, i.e.

$$r_{CO} = k_0 p_{H_2O}^{-1}$$  \hspace{1cm} (6-2)$$
In expression (6-2), $k_0$ is a rate coefficient for a given condition where the partial pressures of CO$_2$ and H$_2$ remain constant. A detailed description of this analysis is included in the Supplementary Information. The resulting expression, equation (6-3), predicts that the CO production rate is proportional to the half power of the relevant kinetic parameters, as observed:

$$F_{CO} = (2m_{cat}k_0(F_{TOT}/P_{TOT}))^{1/2} \quad (6-3)$$

In expression (6-3), $F_{CO}$ (nmol hr$^{-1}$) is the molar flow rate of CO, $m_{cat}(g)$ is the weight of catalyst in the fixed bed, and $F_{TOT}$, the total molar flow rate, is proportional to the total volumetric flow rate (space velocity). When compared to the observed CO production rate plotted against the space velocity (see Figure 6.3A), it is clear that under both dark and light condition, the reaction is inhibited by the products. Since it is expected that H$_2$O can inhibit the reaction by blocking oxygen vacancies and/or hydroxide groups on the In$_2$O$_{3-x}$(OH)$_y$ surface, further investigations were carried out under both batch and flow reaction conditions to test this hypothesis. It was found that when H$_2$O is introduced into the reactor in the inlet stream, the CO
production is significantly suppressed. Since the reaction conversion is far from equilibrium conversion (H₂ and CO₂ concentrations are little changed), it is clear that this result arises from inhibition by the water product. This result provides strong support for the RWGS reaction mechanism proposed by theoretical calculations, as detailed later in Section 6.3.8.

The effective order of the reaction for CO₂ is determined by measuring the reaction rate while varying the partial pressure of CO₂ and keeping the total flow rate and H₂ partial pressure constant. Figure 6.3B shows that the CO production rate, under both light and dark conditions, depends on the half power of the CO₂ partial pressure. In equation (6-3), the kinetic CO₂ dependence is contained in the rate coefficient, k₀. The product inhibition raises the intrinsic CO₂ dependence to the 1/2 power; hence, the intrinsic CO₂ dependence is first order, i.e.:

\[ r_{co} = k' p_{co_2} p_{H_2O}^{-1} \]  \hspace{1cm} (6-4)

The similar behaviour under light and dark conditions indicates that fundamental reaction mechanisms under photochemical and thermochemical conditions are similar. This type of rate law produces an observed half order dependence on CO₂; therefore, based on our analysis the reaction has a first order dependence on the partial pressure of CO₂.

The effective order of reaction for H₂ is determined by measuring the reaction rate while varying the partial pressure of H₂ and keeping the total flow rate and the CO₂ partial pressure constant. Figure 3C shows that the CO production rate, under dark reaction conditions, has almost no dependence on the H₂ partial pressure. However, under light conditions, there appears to be a slight dependence (to the one-third power) of the CO production on the H₂ partial pressure. This subtle difference may provide some insight into the effect of light on the mechanism. A deeper examination of this effect will be the subject of a future study. Nevertheless, this result provides additional support to the RWGS reaction mechanism proposed in later in Section 6.3.8.
6.3.7 Experimental DRIFTS Data

In order to gain further insight on the reaction pathway, in-situ DRIFTS measurements are carried out on the In$_{2}$O$_{3-x}$(OH)$_{y}$ nanocrystals to identify the presence and/or absence of surface species under reaction conditions. Prior to the spectroscopic studies, the In$_{2}$O$_{3-x}$(OH)$_{y}$ nanocrystal powder is heated in the environmental chamber to 130°C under flowing H$_{2}$ to remove any water or surface organics as well as to replicate pre-treatments that the sample may be subjected to prior to catalytic measurements. After pre-treatment, the reference spectrum is taken under flowing He at room temperature shown in Supplementary Figure A3.S3.

The surface make-up of carbon species is investigated by flowing CO$_{2}$ at 10 cm$^{3}$ min$^{-1}$ at various temperatures from room temperature to 150°C which is shown by the series of DRIFTS spectra in Figure 6.4A. The spectral region of interest lies within 1000 to 1800 cm$^{-1}$, which is characteristic of the stretching modes for carbon-based species. A bicarbonate species is identified by comparing the measured and fingerprint stretching modes (in brackets): the δ(OH) observed at 1224 cm$^{-1}$ (1220 cm$^{-1}$), the asymmetric stretch ν$_{as}$(CO$_{3}$) observed at 1630 cm$^{-1}$ (1655 cm$^{-1}$) and the symmetric stretch ν$_{s}$(CO$_{3}$) observed at 1406 cm$^{-1}$ (1405 cm$^{-1}$).$^{[140]}$ The bicarbonate peaks have the highest intensity at room temperature and decrease with increasing temperature. Since these peaks change in unison, it suggests that they represent the same species. The presence of this species is consistent with theoretical calculations, which predict a loosely bound bicarbonate species on the oxygen vacancy surface and is expected from other theoretical studies that show it is energetically favourable on this surface.$^{[130]}$

Additional carbon species are observed at all temperatures in the measured range. A carbonate species is identified by comparing the measured and fingerprint stretching modes (in brackets): the asymmetric carbonate stretch ν$_{as}$(CO$_{3}$) observed at 1546 cm$^{-1}$ (1550 cm$^{-1}$) and the symmetric carbonate stretch ν$_{s}$(CO$_{3}$) observed at 1320 cm$^{-1}$ (1309 cm$^{-1}$). A formate species is also observed, with lower signal intensities, by comparing the measured and fingerprint stretching modes (in brackets): 1590 cm$^{-1}$ (1567 cm$^{-1}$) 1406 cm$^{-1}$ (1377 cm$^{-1}$) and 1367 cm$^{-1}$ (1366 cm$^{-1}$).
In order to observe the relative strength of adsorption of the surface carbon species, the In$_2$O$_{3-x}$(OH)$_y$ nanocrystal powder is cooled to room temperature under flowing CO$_2$ (10 cm$^3$ min$^{-1}$) after which the flowing gas is exchanged with flowing He (10 cm$^3$ min$^{-1}$) which is shown by the series of DRIFTS spectra in Figure 6.4B. Within 14 minutes it is observed that the intensity for all surface carbon species decreases, most of which is the bicarbonate species, where the fingerprint mode for the bicarbonate $\delta$(OH) disappears. Further investigation by heating to 150°C under flowing He (10 cm$^3$ min$^{-1}$) continues the trend of decreasing intensity, however, no single species appears to stand out as more strongly adsorbed than another.

Figure 6.4. In-situ DRIFTS spectra of In$_2$O$_{3-x}$(OH)$_y$ nanocrystals under various atmospheres and temperatures. (A) Spectra measured during a temperature ramp from room temperature to 150°C under flowing CO$_2$. (B) Time dependent spectra measured during a He flush at room temperature following flowing CO$_2$. 
6.3.8 Fundamental RWGS mechanism from DFT calculations

In order to gain an atomic scale understanding of the fundamental reaction pathway of the RWGS reaction on \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \), in-depth theoretical calculations were performed. We first describe the overall reaction mechanism deduced from DFT simulations, by analysing active sites for different crystal surfaces described below. Thereafter, we evaluate reaction pathways and activation energy barriers for key steps in the overall reaction. Experimental observations supporting the theoretically proposed mechanism are further discussed in Section 6.3.6. In Figure 6.5, we show the fundamental reaction mechanism for the RWGS reaction over \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \) obtained through DFT simulations by studying the interaction of \( \text{CO}_2 \) and \( \text{H}_2 \) with pristine and hydroxylated and oxygen vacancy containing surfaces (Figure 6.6).

We begin with the study of the oxygen deficient surface, considering 9 possible oxygen vacancy sites labelled as O1 to O9 shown in Figure 6.1E. It was found that the vacancy formation at all sites is endothermic in nature (vacancy formation energies are tabulated in Table A3.S2 of Supporting Information). The theoretical results identified the O1 vacancy (O1-vac) site to be the most favourable owing to its smallest formation energy, while the O4 vacancy (O4-vac) site was determined as the least favourable. These observations are consistent with previous understanding.\(^{[27]}\) The optimized \( \text{In}_2\text{O}_{3-x} \) surface (having O4-vac) is shown in Figure 6.6C. In order to mimic experimental conditions where surface hydroxide groups were present, one lattice oxygen from the \( \text{In}_2\text{O}_3 (111) \) surface was then substituted by an OH group (Stage I, Figure 6.5). For this analysis, two possible sites for OH were considered, corresponding to the most favourable oxygen vacancy site (O1-vac) and the least favourable one (O4-vac). DFT computations showed that OH binds very strongly to the In atom near either of O1-vac and O4-vac sites, with seemingly little difference between the binding energies at two sites (-2.76 eV at the O4-vac site and -2.71 eV at the O1-vac site). Furthermore, the nature of bonding showed that OH was bound terminally with In for both sites. Figure 6.6E shows the optimized configuration of the resultant hydroxylated \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \) surface having O4-vac substituted by an OH group. In this process, the neighboring In of the O4 site that bonded
with OH showed a slight increase in its positive charge, indicating the transfer of its excess electrons to O of OH. However, the other neighboring In of the O4 site, without an OH group, showed a slight decrease in its usual positive charge with respect to the lattice O. This unique spatial arrangement of atoms created by replacing lattice O with OH in proximity to In, results in the formation of Lewis acid-base pairs on the surface of In$_2$O$_{3-x}$(OH)$_y$ and is probably responsible for activating and dissociating H$_2$ heterolytically, as discussed below. The transfer of excess surface electrons from In to the O of the OH is further evident from the molecular orbital description illustrated in Figure A3.S5 contained in the Supporting Information. Here it can be seen that the excess charge present in the highest occupied molecular orbital (HOMO) of the In$_2$O$_{3-x}$ surface (Figure A3.S5B) due to the oxygen vacancy becomes neutralized in the presence of the OH group (Figure A3.S5C). The theoretical calculations also indicated that the least favorable oxygen vacancy site (O4-vac) produced strong OH binding suggesting that less favorable sites for oxygen vacancies on In$_2$O$_3$ may be able to bind surface hydroxides readily in search for a more stable configuration.

The role of the H$_2$ molecule was investigated next (stages II and III in Figure 6.5), by studying its adsorption on the In$_2$O$_{3-x}$(OH)$_y$ surface having OH substituting lattice oxygen at the least (O4-vac) and the most (O1-vac) stable oxygen vacancy sites. The results showed that H$_2$ becomes adsorbed molecularly on both sites exothermally. The surface having OH substitution to O4-vac site was found to be particularly interesting wherein H$_2$ undergoes endothermic heterolytic splitting (see Supporting Information Table A3.S5), during the absorption process. This results in proton binding to the surface O of the OH group and a hydride binding to the adjacent In site leading to formation of new In-H and H-OH bonds. The relaxed structure for the hydrogenated In$_2$O$_{3-x}$(OH)$_y$ surface is shown in Figure 6.6G. Bader charge analysis reveals that the Lewis acidic In and Lewis basic O of the OH sites at the surface possess charges of +1.66e and −1.50e respectively, and generate a strong electric field on the outer surface that polarizes the H$_2$ molecule as it approaches the surface. This is evident from Bader charges for H in stage II of Figure 6.5, (−0.34e and +0.39e), which suggest strong polarization of the H–H bond leading to the stabilization of structure. This charge analysis thus favours the heterolytic dissociative
adsorption of H₂ on the In₂O₃ₓ(OH)ᵧ surface. Because H is more electronegative than In the H atom of the H₂ molecule nearest to the In atom accepts the excess charge from Lewis acid In and thereafter attains a negative effective charge of -0.36e, forming what can be best described as a hydride. On the other hand, as O is more electronegative than H, the other H atom of the H₂ molecule loses its electrons to the Lewis base O of the OH and attains a positive effective charge of +0.74e, thereby forming what is in essence a proton. The newly formed In-H and H-OH bonds have lengths of 1.80 Å and 1.01 Å respectively, with the stable H-OH structure (Figure 6.6G) having bond angle (106.8°) similar to that of water. Overall, our analysis shows that the formation of Lewis acid-base pairs may account for the heterolytic dissociation of H₂ on the In₂O₃ₓ(OH)ᵧ surface.

In order to investigate the role of surface hydroxides and oxygen vacancies on the CO₂ reduction reaction, we conducted an analysis for CO₂ absorption on pristine In₂O₃ (Figure 6.6B), In₂O₃₋ₓ (Figure 6.6D) and In₂O₃₋ₓ(OH)ᵧ (Figure 6.6F) surfaces. Again, multiple
Figure 6.6. Side and top view of optimized configurations for (A) pristine (111) \( \text{In}_2\text{O}_3 \) surface, (B) adsorbed \( \text{CO}_2 \) on pristine surface, (C) \( \text{In}_2\text{O}_3 \) surface with O vacancy (O4-vac) defect \( (\text{In}_2\text{O}_{3-x}) \), (D) \( \text{In}_2\text{O}_{3-x} \) surface with absorbed \( \text{CO}_2 \) molecule, (E) \( \text{In}_2\text{O}_{3-x} \) surface with OH in place of O4 site \( (\text{In}_2\text{O}_{3-x}(\text{OH})_y) \), (F) \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \) surface with absorbed \( \text{CO}_2 \) molecule, (G) hydrogenated \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \) surface, and (H) \( \text{CO}_2 \) reduction on hydrogenated \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \) surface. Surface In, O, H and C atoms participating in the reaction are highlighted in light blue, red, dark blue and green, respectively. All other In and O atoms are represented by big and small grey balls, respectively. Side view represents bond lengths and bond angles while top view represents Bader charges of atoms participating in \( \text{CO}_2 \) reduction reaction.
unique adsorption sites (on either the In or O atoms) of the pristine (111) surface, as shown in Figure. 6.1E, were considered. None of the In sites labelled as In1 to In7 showed any appreciable chemical reactivity for CO₂ adsorption, whereas most of the O sites were able to interact with CO₂ when it was placed close to the surface atoms. This is as expected due to the higher electronegativity of surface O atoms, which can share charge with the C atom as opposed to In surface atoms. CO₂ gets adsorbed on the O5 site (Figure 6.6B) with negative ΔH_{ads}. Upon CO₂ adsorption, the charge on the nearest surface O atom increases, while the two O atoms in the CO₂ molecule experience corresponding decreases in effective charge. This results in a bending of the CO₂ molecule. Nonetheless, the adsorption energies of CO₂ on the pristine In₂O₃ surface were found to be extremely weak (Table A3.S1 in Supporting Information), suggesting the improbability of CO₂ reduction on In₂O₃ catalysts without surface hydroxides and oxygen vacancies.

The CO₂ adsorption on the In₂O₃-x surface was investigated. A careful analysis of multiple CO₂ placement strategies, over the least and most favourable vacancy sites showed that the only O vacant site that demonstrated some level of interaction with CO₂ was the one having the least favorable O vacancy, O4-vac (binding energies are tabulated in Table A3.S3 in Supporting Information). Interaction of CO₂ with the In₂O₃-x surface having O4-vac leads to bending of the molecule (bond angle 130.8°) and elongation of carbon-oxygen bonds to 1.21 Å and 1.30 Å (Figure 6.6D). CO₂ interaction with this site as compared to the O1-vac site is likely due to the availability of relatively higher energy surface electrons.

Subsequently, we investigated CO₂ adsorption on the In₂O₃-x(OH)_y surfaces with O1-vac and O4-vac oxygen vacancies. DFT computations showed that only the In₂O₃-x(OH)_y surface with the O4-vac and a vertical orientation of CO₂ produce a slightly negative adsorption energy (see Supporting Information Table A3.S4). The bond angle of the initially linear CO₂ molecule becomes 125.2° and the two C-O bond lengths increase to 1.25 Å and 1.29Å, respectively, as shown in Figure. 6.6F. It was found that the O of CO₂ interacts with surface In atoms when it is adsorbed at the O4-vac site having OH bonded
Figure 6.7. Highest occupied molecular orbital (HOMO) of the (111) terminated \( \text{In}_2\text{O}_{3-x} \text{(OH)}_y + \text{2H}^* \) surface and lowest unoccupied molecular orbital (LUMO) of \( \text{CO}_2 \) molecule. Red, light blue, dark blue and green balls represent O, In, H and C atoms, respectively.
to its neighboring In. Bader charge analysis shows that the oxygen of CO\(_2\) gets attracted towards excess electrons created by the O vacancy, whereas the oxygen atom of the OH molecule acts as an electrophile and shares electrons with the C atom. This leads to a decrease in electrons on the oxygens of CO\(_2\), which further enables them to interact with surface In atoms. The energetically favored state of CO\(_2\) interacting with In\(_2\)O\(_{3-x}\)(OH)\(_y\) in the ground state can be described as a tri-dentate form of adsorbed CO\(_2\) (Figure 6.6F). On the other hand, the configurations that showed weak interaction of CO\(_2\) with In\(_2\)O\(_3\) at the O5 site and In\(_2\)O\(_{3-x}\) at the O4-vac site, had both O and C atoms of CO\(_2\) interacting with the surface (In, O) atoms to generate a bi-dentate carbonate-like species as shown in Figures. 6.6B and 6.6D, respectively.

Lastly, the adsorption of CO\(_2\) on the In\(_2\)O\(_{3-x}\)(OH)\(_y\) surface in the presence of H\(_2\) was studied (stages IV and V in Figure 6.5). This simulation most closely resembles the RWGS experimental conditions reported above. \(\Delta H_{ads}\) calculations for multiple configurations of CO\(_2\) placement, showed that a CO\(_2\) molecule cannot be stably adsorbed on the hydrogenated In\(_2\)O\(_{3-x}\)(OH)\(_y\) surface with OH substituting the O1 site.

On the other hand, the hydrogenated In\(_2\)O\(_{3-x}\)(OH)\(_y\) surface with OH in place of the O4 site produced negative \(\Delta H_{ads}\) as well as the bending of CO\(_2\) for most of the configurations we considered. The most interesting configuration that leads to the bending as well as dissociation of the CO\(_2\) molecule is the one where CO\(_2\) was inserted in the In-H bond, shown in stage IV of Figure 6.5. Here, both O and C atoms of CO\(_2\) interact with the surface (In, O and H) atoms to generate a bi-dentate species (Figure 6.6H). This initial configuration made the structure highly unstable because of repulsion between the proton and the electrophilic C and the hydride and nucleophilic O of CO\(_2\). This configuration first leads to formation of a formate-like complex which finally dissociates into CO and H\(_2\)O, (stage V, Figure 6.5) exothermically. The newly formed H\(_2\)O molecule has O-H bond lengths of 1.08 and 0.98 Å and a bond angle of 109.4°, which is in fact very close to that of water in its ground state. The initially released CO molecule has a C-O bond length slightly higher (0.012 Å) than it has in its ground state. Bader charge analysis showed that the hydride formed after heterolytic splitting of H\(_2\) lost its negative charge after the CO\(_2\) adsorption. Furthermore, the two H atoms which originally were formed
due to heterolytic dissociation of the H₂ molecule and had become strongly oppositely charged hydride and proton, now both displayed positive charges of +0.66e and +0.99e as part of the newly formed H₂O molecule (Figure 6.6H). The C and O atoms of the released CO were found to possess roughly equal positive (+1.80e) and negative (-1.81e) effective charges, respectively, maintaining overall charge neutrality. The dissociative chemisorption of CO₂ can be further understood from Figure. 6.7 where the orbital interaction between the LUMO of CO₂ and the HOMO of the In₂O₃₋ₓ(OH)ₓ surface with dissociated H₂ is shown. The HOMO of the surface consists of not only surface oxygen atoms but also the orbitals from the nucleophilic hydride with a symmetry that matches the LUMO of CO₂, which is an anti-bonding σ* orbital. Charge transfer from the surface to CO₂ occurs due to this HOMO-LUMO overlap, leading to the dissociation of CO₂.

In order to evaluate the minimum energy pathway for the reaction and get a sense of the relative activation energy barriers faced during dissociation of H₂ and CO₂ molecules, CI-NEB calculations were performed. In order to capture the energetics of the molecular diffusion and adsorption process, the molecules were initially placed at a sufficient

Figure 6.8. Reaction pathway and energy barrier of (A) H₂ dissociation on In₂O₃₋ₓOHₓ and (B) CO₂ dissociation on In₂O₃₋ₓOHₓ + 2H* surfaces, from Climbing Image Nudged Elastic Band (CI-NEB) method. Red, light blue, dark blue and green balls represent O, In, H and C atoms, respectively.
distance (~3.5 Å) above the surface. These calculations showed that H₂ dissociation on In₂O₃₋ₓ(OH)ₓ surface is endothermic with an activation energy barrier of 0.66 eV (see Figure 6.8A). It can be seen from the figure that H-H bond breaking from the initial state (IS) to the transition state (TS) mainly contributes to the activation energy barrier of H₂ dissociation.

The exothermic dissociation of CO₂ on the hydrogenated In₂O₃₋ₓ(OH)ₓ surface has an activation barrier of 1.03 eV along with an additional activation barrier of 0.77 eV. In Figure 8B, IS1 shows the initial state with an undistorted CO₂ molecule. IS2 shows a secondary state higher in energy than the first in which the geometry of the CO₂ molecule is slightly distorted. The small barrier in this transformation corresponds to the energy required for orientation and distortion from the linear geometry of CO₂ molecule as it approaches the surface. Further, the high activation energy barrier of CO₂ dissociation suggests that this is the difficult step in the reaction mechanism and thus the rate determining step. This is consistent with first order dependence of the production rate on the partial pressure of CO₂ deduced from experimental observations.

To summarize the theoretical observations, this extensive DFT analysis has demonstrated that a In₂O₃₋ₓ(OH)ₓ surface containing both Lewis base hydroxide groups and Lewis acid indium sites together with oxygen vacancies can heterolytically dissociate H₂ to form a hydride bonded to In and a protonic O-H surface site. In the second step (Eq. 6-6), CO₂ adsorbs at an active site comprised of an oxygen vacancy, which subsequently desorb from the surface.

6.3.9 Reverse Water gas shift reaction on In₂O₃₋ₓ(OH)ₓ

The mechanism we propose for the RWGS reaction on the (111) surface of In₂O₃₋ₓ(OH)ₓ can be described by a series of reaction steps as follows: In the first step (Eq. 6-5), H₂ undergoes heterolytic dissociation into a hydridic In-H and a protonic O-H surface site. In the second step (Eq. 6-6), CO₂ adsorbs at an active site comprised of an oxygen vacancy,
an indium hydride and a proton on a hydroxide group that causes CO$_2$ to dissociate to CO with the concomitant formation of H$_2$O. This is followed by desorption of the reaction products CO and H$_2$O, represented by reaction (Eq. 6-7) and (Eq. 6-8):

\[
\begin{align*}
H_2(g) & \rightarrow O - H + In - H \quad \text{(6-5)} \\
CO_2(g) + O - H + In - H & \rightarrow CO^*_\text{(ads)} + H_2O^*_\text{(ads)} \quad \text{(6-6)} \\
CO^*_\text{(ads)} & \rightarrow CO(g) \quad \text{(6-7)} \\
H_2O^*_\text{(ads)} & \leftrightarrow H_2O(g) \quad \text{(6-8)}
\end{align*}
\]

In the overall reaction, oxygen vacancies and hydroxide groups are not consumed; instead they work synergistically to assist in the production of an active site that facilitates the heterolytic splitting of H$_2$, which is then capable of promoting the dissociation of CO$_2$ into CO. In this reaction scheme, gas phase CO$_2$ reacts directly with a preformed hydrogenated active site, instead of first adsorbing on an adjacent surface site and forming a reaction intermediate which subsequently reacts.

This type of reaction can be described using classical Eley-Rideal type kinetics, where a gas phase species reacts directly with an adsorbed species. For this type of kinetic scheme, it is generally observed that there is a first order dependence of the gas phase reacting species on the overall rate of reaction. Based on the experimental kinetic investigations, it is observed that the reaction order with respect to CO$_2$ is one half. The space velocity dependence and preliminary DFT analysis of CO$_2$ adsorption in presence of H$_2$O revealed that it is likely that a reaction product is inhibiting, which is most likely H$_2$O, since it can block CO$_2$ adsorption at surface active hydroxyl and oxygen vacancy sites.$^{[141]}$ In this case, it was demonstrated previously that a first order dependence on CO$_2$ is possible with an inhibiting reaction product. Therefore, the experimental results are consistent with the theoretically derived mechanism.

**In-situ** DRIFTS analysis was conducted to observe surface carbon species in an attempt to identify reactant, intermediate and product species under various reaction conditions. Bicarbonate, carbonate and formate groups were identified on the surface; however, it is not clear if they are bystander species, if they are involved in CO$_2$
adsorption, or if they are an intermediate species. The DFT analysis predicted that the adsorbed CO$_2$ surface species are weakly bonded to the surface. The relative strength of adsorption can be evaluated by flushing the chamber with flowing He (at 10 cm$^3$ min$^{-1}$) at room temperature after flowing CO$_2$ (at 10 cm$^3$ min$^{-1}$). The time dependent removal of adsorbed CO$_2$ species upon the switch from flowing CO$_2$ to He is shown in the DRIFT spectra in Figure 4B. Within 15 minutes, there is a significant decrease among the peaks identified as being a bicarbonate-like species. In our previous study, it was established that In$_2$O$_{3-x}$(OH)$_y$ adsorbed CO$_2$, suggesting that the more strongly adsorbed species is a possibly captured as a carbonate or formate and not as a bicarbonate.$^{[60]}

The collected experimental and theoretical results of this study demonstrate that the thermochemical and photochemical RWGS reaction depends on the concentration of available surface hydroxide groups and oxygen vacancies.

The DFT calculations also showed the dependence of the CO$_2$ reduction reaction on active sites present on the surface. Thus, CO$_2$ was not able to dissociate on an In$_2$O$_{3-x}$(OH)$_y$ surface alone. However, it does dissociate on In$_2$O$_{3-x}$(OH)$_y$ in the presence of hydrides and protons formed from heterolytic dissociation of H$_2$ and this happens favourably, with a small energy barrier, when CO$_2$ is present in close proximity to the hydrogenated In$_2$O$_{3-x}$(OH)$_y$ surface. Further, no dissociation of CO$_2$ was observed in the absence of surface hydrides even if O vacancies and OH groups are present and CO$_2$ is in vicinity of these defects.

6.3.10 Frustrated Lewis Pair Surfaces

Frustrated Lewis pairs (FLPs) are obtained when a main group Lewis acid and Lewis base are combined without forming a “classical” Lewis acid-base adduct but instead leave the acidity and basicity unquenched due to the steric bulk of their substituents. The FLP remained a chemical curiosity until Stephan and co-workers discovered their unique reactivity.$^{[142]}$ They found that FLPs were able to activate small molecules, where the
unquenched nature of such Lewis pairs results in the observation of unusual and important chemical reactivity.\textsuperscript{[143]}

Especially worth mentioning in the context of the mechanism described in this paper, are the observations that molecular FLPs can induce the heterolytic cleavage of H\textsubscript{2}, reversible binding and release of CO\textsubscript{2}, and reduction of CO\textsubscript{2}, for example to CO.\textsuperscript{[144]} These FLPs represent the only non-transition metal based systems known for this type of hydrogen activation and reaction chemistry.

What we find especially fascinating is the analogous relationship of the reactivity of molecular FLPs with H\textsubscript{2} and CO\textsubscript{2} to similar kinds of surface chemical reactions that we have discovered in the work described herein for In\textsubscript{2}O\textsubscript{3-\textit{x}}(OH)\textsubscript{\textit{y}} nanomaterials with H\textsubscript{2} and CO\textsubscript{2}. Like molecular FLPs, In\textsubscript{2}O\textsubscript{3-\textit{x}}(OH)\textsubscript{\textit{y}} also has main group Lewis acid-base proximal sites, the terminal hydroxide acts as a Lewis base and the indium acts as Lewis acid (as shown in steps II and III in Figure 6.5), a connection which bodes well for the future development of a new class of “FLP heterogeneous catalysts” that, among many reaction possibilities, could enable efficient gas-phase hydrogenation chemistry of CO\textsubscript{2} to fuels and chemicals.

6.3.11 Conclusions

This work represents the first combined experimental and theoretical attempt to understand the mechanism of the RWGS reaction on the surface of In\textsubscript{2}O\textsubscript{3-\textit{x}}(OH)\textsubscript{\textit{y}} nanocrystals in the dark and light. The collected findings provide a valuable insight into the role, that surface hydroxide groups and oxygen vacancies play, in the thermochemical and photochemical activation of H\textsubscript{2} and CO\textsubscript{2} reactants to form CO and H\textsubscript{2}O products. The relationship between heterolytic dissociation of H\textsubscript{2} and reduction of CO\textsubscript{2} on molecular FLPs and our similar observations on the surface of In\textsubscript{2}O\textsubscript{3-\textit{x}}(OH)\textsubscript{\textit{y}} nanocrystals may herald the birth of the new field of FLP heterogeneous catalysis. Based on the results and with the insight gained from this work, it should prove possible to design new nanostructured materials and improve upon existing ones through rational chemistry control of the
composition, size, shape, surface and assembly of nanomaterials and thereby improve the conversion efficiency of CO\textsubscript{2} reduction to energy rich fuels. To fully understand the function of light on the RWGS reaction, further experimental and theoretical studies are currently under way.

6.3.12 Acknowledgements

GAO is Government of Canada Research Chair in Materials Chemistry and Nanochemistry. This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC), the University of Toronto, Ontario Ministry of Research and Innovation (MRI) and the Ontario Ministry of Economic Development and Innovation (MEDI). Computations were performed at SciNet\textsuperscript{28} and Calcul Quebec consortia under the auspices of Compute Canada. SciNet is funded by the Canada Foundation for Innovation, the Government of Ontario, Ontario Research Fund - Research Excellence, and the University of Toronto. The authors gratefully acknowledge the strong and sustained support of all the above organizations. Critical reading and appraisal of this manuscript and insightful discussions with Professors Douglas Stephan and Robert Morris are also deeply appreciated.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/
Chapter 7
Conclusions and Future Work

7.1 Conclusions:

This work sought to investigate semiconductor nanomaterials as photocatalysts for CO$_2$ conversion. It began with the design and construction of a multi-photocatalyst screening system, which is capable of testing six samples in parallel. Dozens of nanoparticle semiconductor materials were tested for thermal and light driven CO$_2$ chemistry, with H$_2$ or H$_2$O as the co-reactant. It was shown that a significant number of semiconductors demonstrate no CO$_2$ conversion; the samples did not show a significant number of hydrocarbons or CO products after 18 hours in an atmosphere of H$_2$ and CO$_2$ under illumination of 1 sun at temperatures ranging from room temperature to 190°C.

A set of Cu/TiO$_2$ nanoparticle heterostructures was synthesized. This set of samples produced hydrocarbons after batch reactions from H$_2$ and CO$_2$, and, based on preliminary control experiments, there appeared to be activity under illumination. However, it was revealed through $^{13}$CO$_2$ tracing experiments that hydrocarbon production was the result of adventitious carbon decomposition. A set of Ru/TiO$_2$ nanoparticles heterostructures were also synthesized. In this study, the material produced labelled $^{13}$CH$_4$ after a tracing experiment; however, this product is attributed to the well-known Ru catalyst facilitating this reaction thermally. This work was an attempt to reproduce results often cited in literature and it demonstrates the importance of isotope tracing when evaluating the performance of catalysts.

A set of In$_2$O$_3$ nanoparticle samples were synthesized. It was discovered that In$_{2}$O$_{3-x}$(OH)$_{y}$ nanoparticles were capable of converting CO$_2$ into CO via the reverse water gas shift reaction,
and detailed work was carried out to understand the mechanism. It was found that hydroxylated indium oxide nanoparticles, $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ produced both CO and CH$_4$. This conclusion is the result from $^{13}\text{CO}_2$ isotope tracing. Furthermore, CO production was enhanced by light by demonstrating a dependence on wavelength and light intensity. It was also determined that the photocatalytic activity corresponded to the relative abundance of defects, oxygen vacancies and hydroxides. This was modelled using the (100) surface of In$_2$O$_3$, and the interaction between H$_2$ and CO$_2$ was simulated on a pristine and defected surface. It was found that the CO$_2$ dissociated into CO over a specific surface site. This surface site contained a hydroxide adjacent to an oxygen vacancy, dubbed a surface frustrated Lewis pair, SFLP.

### 7.2 Future work:

#### 7.2.1 Investigating surface FLPs

The current work has proposed a unique reaction mechanism involving an FLP on the surface of $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ under H$_2$ atmospheres. It is possible that this surface frustrated Lewis acid pair assists the cleavage of the C-O bond in CO$_2$. The core of this mechanism is the FLP surface site analog, which contains a hydroxide adjacent to an In-H, sterically separated by an oxygen vacancy. This site is believed to form by the heterolytic splitting of H$_2$. If true, this reaction mechanism expands the currently thinking of surface metal oxide catalysis, by identifying a key site that combines oxygen vacancies and hydroxides. While these defects are known to exist on the surfaces of metal oxides, this is the first time a combination of defects synergistically facilitates a reaction. However, in order to confirm this mechanism, stronger material characterization methods are required to identify the existence of this site.
In order to investigate this surface site, one can make use of *in-situ* FTIR. Using this system, it is possible to control the atmosphere and temperature of the samples while simultaneously gathering information on the surface species. Using this technique, it may be possible to observe the surface FLP. First, the sample would be investigated under inert atmospheres at room temperature and 150°C. Then, the sample would be exposed to H₂ under the same conditions. In this case, there will be an attempt to observe a simultaneous increase in In-H and O-H which would form. However, it is also possible that there are multiple pathways for H₂ dissociation on the surface.

### 7.2.2 On-going work with In₂O₃ₓ(OH)ₙ:

Recent reports have shown that at higher operating pressures (4-5 atm) and elevated temperature, an In₂O₃ based catalyst was capable of producing methanol from H₂ and CO₂. In order to improve the industrial significance of this catalyst, it is recommended to investigate the In₂O₃ nanoparticles under similar conditions. In order to carry out this experiment, the flow reactor system requires upgrades to accommodate the higher pressures.

Furthermore, the nanoparticles may require some support material. The effect of supports on the performance of catalysts has been well documented. Regarding the practical use of studying nanoparticles, significant pressure gradients often arise across a nanoparticle bed, which can be as high as 5 atm. Higher steady state operating pressures imply a much greater inlet pressure. One method is to use In₂O₃ nanorods, which do not develop any pressure gradient in the flow reactor. These nanoparticles were tested and reported by Le He et al.[116]

Additional work is also required to ensure the catalyst activity at higher temperatures. During this work, it was observed that the nanoparticles decrease in activity above 200°C. Increasing the temperature above 200°C greatly increases the CO production rate to above 1 mmol g⁻¹ hr⁻¹. At
300°C, the production rate rapidly decreases. This also made it difficult to observe enhancements due to light since the rate continuously decreased over time.

7.2.3 Test Other photocatalysts:

The photocatalyst screening system is currently continuing to evaluate semiconductors for photocatalytic conversion of CO$_2$. At the time of writing, there is no other system in the world that has the capability to screen multiple photocatalysts this quickly. This system is currently being used by students in the Solar Fuels research cluster in order to discover new photocatalysts or to rapidly determine the effect of modifications to known photocatalysts. Using the methodology prescribed in this thesis, researchers are still able to rapidly evaluate materials for potential use as a photocatalyst for CO$_2$ conversion. Since the screening uses $^{13}$CO$_2$ isotope tracing, conversion of CO$_2$ into products cannot be confused with the conversion of carbon contaminants.
Bibliography


A.1: Table of Tested Samples

A set of semiconductor samples were tested in the batch photoreactors for activity. The results from these tests are listed in Table A1.1. While this table does not present an exhaustive list of the tested samples, it does show a representative list of the type of samples that were tested. A majority of the samples did not produce a significant amount of product, and many that did produce enough product were not labelled with $^{13}$C product. In Table A1.1, n.o. represents no observed product and b.d. represents below detection limit.
<table>
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<th>Photocatalyst</th>
<th>Co-catalyst</th>
<th>Reaction Temperature (°C)</th>
<th>Products</th>
<th>Average Rate (umol/ g&lt;sub&gt;cat&lt;/sub&gt; hrs)</th>
<th>&lt;sup&gt;13&lt;/sup&gt;C Labelled?</th>
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<td>1.6</td>
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A.2: Supplementary Information for Chapter 5

The Rational Design of a Single-Component Photocatalyst for Gas-Phase CO\textsubscript{2} Reduction Using Both UV and Visible Light

Laura B. Hoch, Thomas E. Wood, Paul G. O’Brien, Kristine Liao, Laura M. Reyes, Charles A. Mims and Geoffrey A. Ozin *

Figure A2.S1. Estimation of the electronic band gap of the In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} and In(OH)\textsubscript{3} powders using a modified Kubelka-Munk function. Specifically, \((F(R)*h\nu)^n\) is plotted as a function of photon energy for samples (a) In(OH)\textsubscript{3}, (b) I-250, (c) I-350 and (d) I-450 where \(F(R) = (1 - R)^2 / 2R\). R is the diffuse reflectance of the films loaded onto the borosilicate supports and n was set to 1/2 for the In(OH)\textsubscript{3} film and 3/2 for the In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} films. The linear portion of the plot was extrapolated and its intercept with the abscissa provided the band-gap estimate.
Figure A2.S2. GC-MS fragmentation of CH₄ produced from ^13^CO₂ isotope tracing measurements of I-250 plotted in contrast to a ^12^CH₄ standard. This result confirms that methane does not originate from the carbon dioxide introduced into the reactor and is therefore likely a result of adventitious carbon contamination on the surface of the sample.
Figure A2.S3. CO production dependence on the presence of light and reaction temperature: CO production in the presence and absence of light and at temperatures ranging from 110 °C to 170 °C measured for samples (a) I-250, (b) I-350, and (c) I-450.
Figure A2.S4. (a) Effect of spectral profile on CO production rate for a single I-250 film under irradiation from a Newport 300 W Xe Lamp fitted with a combination of AM1.5, 420 nm high pass, or 615 nm high pass filters. (b) Comparison of the estimated absorption spectrum of an I-250 sample film with the emission spectra of the Xe lamp equipped with different filters.
Figure A2.S5. FT-IR-ATR spectra of In(OH)$_3$, I-250, I-350 and I-450 films used in photocatalytic reactions.
Figure A2.S6. TGA weight loss plots mimicking the calcination process for I-250, I-350 and I-450. The black line at -16.28 % corresponds to the maximum theoretical weight loss based on stoichiometry.
Figure A2.S7. CO production dependence on sample loading. A series of I-250 samples with different loadings were prepared on borosilicate glass microfiber filters and tested for CO production at 150 °C under 0.8 suns of simulated solar irradiation. Based on this data a loading of 20 mg was selected for all photocatalytic measurements as it maximizes light absorption per sample weight.
Figure A2.S8. Cross-sectional SEM micrographs of a typical In$_2$O$_{3-x}$(OH)$_y$ film deposited on borosilicate glass microfiber filter used in catalysis testing. (a) Low magnification image showing the average film thickness is ~50 µm. (b) High magnification image showing the porosity and high surface area of In$_2$O$_{3-x}$(OH)$_y$. 
Figure A2.S9. A comparison between the spectral distributions of the 1000 W Hortilux metal halide bulb, a 300 W Xe lamp with an AM 1.5 filter and solar irradiance.
A.3: Supplementary Information for Chapter 6

**Illuminating CO₂ Reduction: Investigating the Role of Surface Hydroxides and Oxygen Vacancies on Nanocrystalline In₂O₃-x(OH)₉**

Kulbir Kaur Ghuman⁴⁺, Thomas E. Wood⁹⁺, Laura B. Hoch⁵, Charles A. Mims⁶, Geoffrey A. Ozin⁷ and Chandra Veer Singh⁸

The photochemical and photothermal rate law based on the mass of catalyst depends on the reaction temperatures, the pressures, the concentrations of all active species, the light (spectral distribution and intensity), and the catalyst surface, which is given by:

\[
r_{CO} \left( \frac{\mu mol}{g_{cat} hrs} \right) = k(T) \cdot f(C_{H}, C_{CO}, C_{H,O}, C_{CO}, I(\lambda), etc) \quad (A3-1)
\]

In this equation \( r_{CO} \) is the rate of production of CO, \( k \) is the rate constant, \( C_i \) is the concentration of species \( i \), and \( I \) is the light intensity. In order to assess the effect of product inhibition (in this case H₂O) while all other parameters are held constant, assume that the rate law for the photocatalyst can be rewritten as:

\[
r_{CO} \left( \frac{\mu mol}{g_{cat} hrs} \right) = K \left( C_{H}, C_{CO} \right) \cdot C_{H,O}^{n} \quad (A3-2)
\]

In this equation \( K' \) is the rate coefficient which is a combined rate expression at a particular reaction conditions for all parameters except H₂O. Since the conversion is so low in our experiments the concentrations of reactants can be treated as constant. The result is the H₂O...
dependence is cast as a power law expression. For this test case, we use $n = -1$ (as predicted for simple site hogging in Langmuir-Hinshelwood kinetics). Also, for each "mole" of this reaction ($\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$) that occurs, one mole of H$_2$O will be produced along with one moles of CO. Finally, the plug flow (no axial mixing) reactor can be modelled as a continuously moving series of differential batch reactors. Therefore, the differential mass balance for plug flow reactor is given by:

$$dF_x = r_{\text{cat}} dm_{\text{cat}} \quad (A3-3)$$

Here $F_x$ is the molar flow rate of products (water) and the equation balances the differential change in product flow rate passing over a differential amount of catalyst. The product builds up as the gas contacts the catalyst charge. Substituting our rate expression and rearranging:

$$dF_x = K' * C_{\text{H}_2\text{O}}^{-1} * dm_{\text{cat}} \quad (A3-4)$$

In the flowing fluid, $C_{\text{H}_2\text{O}}^{-1}$ can be written $q/F_X$ where $q$ is the volumetric flow rate of the gas. With this substitution, we can write:

$$\int F_x dF_x = \int K' * q * dm_{\text{cat}} \quad (A3-5)$$

Integrating equation (A3-5) gives us the following:
\[ 0.5F_x^2 = K' * q * m_{\text{cat}} \]  \hspace{1cm} (A3-6)

Rearranging for \( F_x \), which in this case is CO since it is the measured quantity, we get the following expression:

\[ F_{CO} = 1.414 \left( m_{\text{cat}} * K' * q \right)^{0.5} \]  \hspace{1cm} (A3-7)

Equation (A3-7) tells us that a reaction the follows power law kinetics with a negative first order inhibiting reactant, the molar flow rate of CO (as well as the production rate of CO) will depend on the flow rate (and space velocity which is the total volumetric flow rate divided by the reactor volume) to the half power. Additionally, if we consider the rate coefficient, defined in equation (A3-2) to be proportional to the rate constant and partial pressure of the reactants, we can get the following expression:

\[ K' = k p_{CO_2}^\alpha p_{H_2}^\beta \]  \hspace{1cm} (A3-8)

Substituting (A3-8) into (A3-7) gives us the following:

\[ F_{CO} = 1.414 \left( m_{\text{cat}} * k * p_{CO_2}^\alpha * p_{H_2}^\beta * q \right)^{0.5} \]  \hspace{1cm} (A3-9)
Equation (A3-9) is an expression that relates the molar flow rate of CO (as well as the production rate of CO) to the partial pressures of CO$_2$ and H$_2$. In this case, an intrinsic first order dependence of either the reactants would result in an observed half order dependence.

Fig A3.S1. Demonstration of stable CO production over a 10 hour period by In$_2$O$_{3-x}$(OH)$_y$ nanoparticles at 190$^\circ$C under flowing H$_2$ and CO$_2$ (1:1) at two total volumetric flow rates.
Fig A3.S2. CO production rate over In$_2$O$_{3-x}$(OH)$_y$ nanoparticles in a batch photoreactor at 150°C under dry and wet atmospheres of H$_2$ and CO$_2$ at 1:1 over 16 hours of reaction under light irradiation by a 300 W Xe lamp.
Figure A3.S3. Background spectra of In$_2$O$_{3-x}$(OH)$_x$ used for DRIFTS measurements in flowing He at RT.
The adsorption energy of an adsorbate on the various surfaces considered in this study was calculated as:

\[ \Delta H_{\text{ads}} = E_{\text{tot}} - E_{\text{bare}} - E_{\text{ad}}, \quad (A3-10) \]

where, \( E_{\text{tot}} \) (\( E_{\text{bare}} \)) are the energy of the slab with (without) adsorbate and \( E_{\text{ad}} \) is the energy of the isolated adsorbate species calculated in the same supercell. Hence, a negative \( \Delta H_{\text{ads}} \) indicates stable adsorption whereas a positive value indicates instability.

Interaction of CO\(_2\) with pristine In\(_2\)O\(_3\) (111) surface was first investigated by placing it on top of multiple unique adsorption sites (on either In or O atoms) at various distances from the surface ranging between 1 to 3Å. Table S1 below shows the corresponding adsorption energies.
Table A3.1: CO\textsubscript{2} adsorption energies on pristine (111) In\textsubscript{2}O\textsubscript{3} surface

<table>
<thead>
<tr>
<th>On In site</th>
<th>Adsorption energy, ΔH\textsubscript{ads} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In1</td>
<td>0.093</td>
</tr>
<tr>
<td>In2</td>
<td>0.088</td>
</tr>
<tr>
<td>In3</td>
<td>0.018</td>
</tr>
<tr>
<td>In4</td>
<td>0.186</td>
</tr>
<tr>
<td>In5</td>
<td>0.095</td>
</tr>
<tr>
<td>In6</td>
<td>0.218</td>
</tr>
<tr>
<td>In7</td>
<td>0.130</td>
</tr>
<tr>
<td>On O site</td>
<td>Adsorption energy, ΔH\textsubscript{ads} (eV)</td>
</tr>
<tr>
<td>O1</td>
<td>0.272</td>
</tr>
<tr>
<td>O2</td>
<td>0.159</td>
</tr>
<tr>
<td>O3</td>
<td>0.178</td>
</tr>
<tr>
<td>O4</td>
<td>0.090</td>
</tr>
<tr>
<td>O5</td>
<td>-0.073</td>
</tr>
<tr>
<td>O6</td>
<td>0.176</td>
</tr>
<tr>
<td>O7</td>
<td>-0.008</td>
</tr>
<tr>
<td>O8</td>
<td>-0.009</td>
</tr>
<tr>
<td>O9</td>
<td>0.197</td>
</tr>
</tbody>
</table>
Further, in order to investigate the role of surface hydroxyls and oxygen vacancies on the CO₂ reduction reaction, an analysis was conducted for CO₂ absorption on the In₂O₃ surface with O vacancy defects (In₂O₃-x) and the In₂O₃ surface with O vacancy and OH defects (In₂O₃-x(OH)ₓ). For creating O vacancy in pristine In₂O₃ surface various O atoms were removed and corresponding formation energies were calculated using equation,

\[ E_{\text{vac}} = E(\text{cell}_{\text{vac}}) + \frac{1}{2}E(\text{O}_2) - E(\text{cell}), \]  \hspace{1cm} (A3-11)

where, \( E_{\text{vac}} \) is O-vacancy formation energy, \( E(\text{cell}_{\text{vac}}) \) is total energies of the optimized supercell with an O-vacancy defect, \( E(\text{cell}) \) is the total energies of the optimized supercell without an O-vacancy defect and \( E(\text{O}_2) \) is the total energy for the ground state of an optimized oxygen molecule in the gas phase calculated with the same supercell size and method. The \( E_{\text{vac}} \) for various oxygen vacancy defects given in Table S2 below, shows that the O1 site is most favored to form a vacancy with the lowest formation energy while the O4 site possess the highest formation energy and hence is the least favored vacancy.
Table A3.2. Oxygen vacancy formation energies

<table>
<thead>
<tr>
<th>O atom removed to create vacancy defects</th>
<th>Vacancy formation energy, $\Delta E_{\text{vac}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1 (lowest $E_{\text{vac}}$)</td>
<td>1.194</td>
</tr>
<tr>
<td>O2</td>
<td>1.197</td>
</tr>
<tr>
<td>O3</td>
<td>1.773</td>
</tr>
<tr>
<td>O4 (highest $E_{\text{vac}}$)</td>
<td>1.956</td>
</tr>
<tr>
<td>O5</td>
<td>1.615</td>
</tr>
<tr>
<td>O6</td>
<td>1.758</td>
</tr>
<tr>
<td>O7</td>
<td>1.558</td>
</tr>
<tr>
<td>O8</td>
<td>1.436</td>
</tr>
<tr>
<td>O9</td>
<td>1.655</td>
</tr>
</tbody>
</table>

These results agree with the results reported by A.Walsh [1]. As explained therein, the factors influencing the favorability of vacancy formation are the coordination number (a decrease in coordination from the bulk value results in a lower cost for removal) and the coordination number of surrounding In atoms (the cost of breaking a bond with a highly coordinated In atom is lower). The O4 site has In atoms with much lower coordination (4-fold) than the In atoms surrounding O1 site (6-fold). Hence, the In atoms around O4 are less willing to lose the O atom, another degree of coordination, and its corresponding charge stability which makes this site less favorable to vacancy formation.
It is found that placing CO\textsubscript{2} molecules both horizontally (O-C-O bonds parallel to the surface) as well as vertically (O-C-O bonds perpendicular to the surface) on top of the least (O1-vac) and most (O4-vac) favorable vacancy sites of In\textsubscript{2}O\textsubscript{3-x} (Table S3) and In\textsubscript{2}O\textsubscript{3-x(OH)}\textsubscript{y} (Table S4) surfaces, showed marginal interaction with the surface.

<table>
<thead>
<tr>
<th>O vacancy position</th>
<th>Adsorption Energy, ΔH\textsubscript{ads} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>On most favourable O vacancy (O1) site</td>
<td></td>
</tr>
<tr>
<td>O1 (horizontal)</td>
<td>0.167</td>
</tr>
<tr>
<td>O1 (vertical)</td>
<td>0.045</td>
</tr>
<tr>
<td>On least favorable O vacancy (O4) site</td>
<td></td>
</tr>
<tr>
<td>O4 (horizontal)</td>
<td>0.092</td>
</tr>
<tr>
<td>O4 (vertical)</td>
<td>0.903</td>
</tr>
</tbody>
</table>
Table A3.4. CO$_2$ adsorption energies on In$_2$O$_{3-x}$OH$_x$

<table>
<thead>
<tr>
<th>CO$_2$ adsorption position</th>
<th>Adsorption Energy, $\Delta$Hads (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>On most stable OH adsorption site</td>
<td></td>
</tr>
<tr>
<td>O1 horizontal</td>
<td>0.265</td>
</tr>
<tr>
<td>O1 vertical</td>
<td>0.175</td>
</tr>
<tr>
<td>On least stable OH adsorption site</td>
<td></td>
</tr>
<tr>
<td>O4 horizontal</td>
<td>0.172</td>
</tr>
<tr>
<td>O4 vertical</td>
<td>-0.072</td>
</tr>
</tbody>
</table>

Furthermore, molecular adsorption of H$_2$ on the In$_2$O$_{3-x}$(OH)$_x$ surface having highest and the lowest formation energy is investigated by placing H$_2$ very near to the surface horizontally (i.e. H-H bond parallel to the surface) as well as vertically (i.e. H-H bond perpendicular to the surface). The adsorption energies of various configurations of H$_2$ are tabulated in Table S5.

Table A3.S5. H$_2$ adsorption energies on In$_2$O$_{3-x}$OH$_x$

<table>
<thead>
<tr>
<th>H$_2$ adsorption position</th>
<th>Adsorption Energy, $\Delta$Hads (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>On least stable OH adsorption site</td>
<td></td>
</tr>
<tr>
<td>O-I horizontal</td>
<td>-0.18</td>
</tr>
<tr>
<td>O-I vertical</td>
<td>-0.15</td>
</tr>
<tr>
<td>On most stable OH adsorption site</td>
<td></td>
</tr>
<tr>
<td>O-IV horizontal</td>
<td>0.24</td>
</tr>
<tr>
<td>O-IV vertical</td>
<td>-0.23</td>
</tr>
</tbody>
</table>
Figure A3.S4. Adsorption of vertically oriented $\text{H}_2$ over $\text{In}_2\text{O}_{3-x}\text{OH}_y$ surface having O4-vac substituted by OH molecule. The $\text{H}_2$ molecule rotates, forming bonds with an In atom adjacent to the O4-vac and the O atom of OH. Eventually the $\text{H}_2$ molecule undergoes heterolytic dissociation and OH is converted to $\text{H}_2\text{O}$.

The difference in stability for different orientations suggests that the angle of adsorbate approach is crucial in allowing it to overcome surface geometrical constraints so that it can access the atoms and charge that it needs for stable adsorption. Further, the description of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for pristine (111) $\text{In}_2\text{O}_3$ surface, O4-vac ($\text{In}_2\text{O}_{3-x}$) surface, and a surface having O4-vac substituted by OH ($\text{In}_2\text{O}_3 \cdot x(\text{OH})_y$), is represented in Figure. S5 A, B and C respectively. For pristine (111) $\text{In}_2\text{O}_3$ surface,
HOMO is associated with surface O atoms, while LUMO is delocalized around the In sites (Figure. S5A). However, for O4 deficient In$_2$O$_3$ surface, the HOMO (Figure. S5B) is not only associated with surface O atoms but it is also highly delocalized over neighboring In atoms, which make OH substitution at O vacant site favorable leading to stable In$_2$O$_{3-x}$(OH)$_y$ surface shown in Figure. S5C.
Figure A3.S5. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of ground state, (111) terminated (a) In$_2$O$_3$, (b) In$_2$O$_{3-x}$ and (c) In$_2$O$_{3-x}$(OH)$_y$ surfaces. Red, light blue and dark blue balls represent O, In and H atoms, respectively.
References