Functional Nanomaterials for Gas-Phase Heterogeneous Photocatalysis: Toward Efficient Solar Fuel Production

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Department of Chemistry
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Abstract

Harnessing abundant solar energy to facilitate the capture and conversion of greenhouse gas CO\textsubscript{2} into carbon-based fuels and chemical feedstocks represents a significant scientific challenge with implications for both climate change and sustainable energy production. Herein, we have demonstrated that highly defected indium oxide, In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y}, nanoparticles can function as effective gas-phase photocatalysts for CO\textsubscript{2} reduction to CO via the reverse water gas shift (RWGS) reaction. Significantly we have found that the presence of both oxygen vacancies and surface hydroxide groups are necessary to facilitate the reaction. Using transient absorption spectroscopy we demonstrated that these defects play a significant role in the excited state charge relaxation pathways, with higher defect concentrations resulting in longer excited state lifetimes, which is attributed to electron and hole trapping in oxygen vacancies and surface hydroxide groups, respectively. This supports the proposed surface Frustrated Lewis Pair (FLP) reaction mechanism, in which a surface active site composed of a Lewis acidic, coordinatively unsaturated indium atom, created by the presence of an oxygen vacancy, adjacent to a Lewis basic hydroxide, assists the adsorption and heterolytic dissociation of H\textsubscript{2}, which then enables the adsorption and reaction of CO\textsubscript{2} to form CO and H\textsubscript{2}O. Preliminary results indicate that photogenerated electron and hole localization in these defects enhances their Lewis acidity and
basicity, lowering the activation energy for the RWGS reaction under illumination. Finally, we demonstrated that by evenly dispersing In$_2$O$_{3-x}$(OH)$_y$ nanoparticles on vertically aligned silicon nanowires (SiNW), we can increase reaction rates by improving reflective losses and facilitating light trapping in the region of the solar spectrum where In$_2$O$_{3-x}$(OH)$_y$ absorbs. Further, by using the photothermal properties of the SiNWs, the light energy not absorbed by In$_2$O$_{3-x}$(OH)$_y$ can be converted into localized heat energy, removing the need for external heating and improving the overall energy efficiency of the process.
For Stephen Kass, who has been with me every step of the way.
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**Figure 5.** (a) CO production rate of different In$_2$O$_{3-x}$(OH)$_y$ samples under simulated sunlight irradiation. (b) O1s core level XPS spectra, Reproduced with permission from Dr. Le He.

**Figure 6.** Normalized transient absorption traces observed for S1, S3 and S5 at (a) 750 nm and (b) 500 nm. Reproduced with permission from Dr. Le He.
Figure 7. (a) Schematic illustration of the rate determination step in the RWGS reaction at In$_{2}$O$_{3}$-$x$(OH)$_{y}$ surfaces. (b) Schematic illustration of the difference in activation energy between the ground state FLP in dark and excited state FLP in light. Photoexcited electrons and holes trapped at surface sites enhance the conversion rate by lowering the activation energy. Reproduced with permission from Dr. Le He.

Chapter 6

Figure 1. (a) Cross-sectional SEM image of I-250/SiNW bi-layer sample (b) CO production rates under ~15 suns of illumination with no external heating. Adapted from Ref. 7 with permission from the PCCP Owner Societies.

Figure 2. Comparison of the powder X-ray diffraction patterns of as-prepared indium hydroxide nanoparticle precursor and the standard indium hydroxide precursors used in previous chapters. The vertical black lines correspond to a standard cubic In(OH)$_{3}$ diffraction pattern. The asterisks correspond to unidentified peaks that may be attributed to weakly crystalline InOOH phases.

Figure 3. Cross-sectional scanning electron microscope (SEM) images of In$_{2}$O$_{3}$-$x$(OH)$_{y}$/SiNW sample (a and c) and In$_{2}$O$_{3}$-$x$(OH)$_{y}$ on glass (b and d).

Figure 4. Cross-sectional scanning electron microscope (SEM) images with energy dispersive X-ray (EDX) mapping of In$_{2}$O$_{3}$-$x$(OH)$_{y}$ on SiNW and (b) In$_{2}$O$_{3}$-$x$(OH)$_{y}$ on glass, showing the distribution of silicon, indium, and oxygen within the two samples.

Figure 5. PXRD of the In$_{2}$O$_{3}$-$x$(OH)$_{y}$ films on SiNW and glass substrates. The vertical black lines correspond to a standard diffraction pattern for cubic bixbyite indium oxide (JCPDS 06-0416). Diffraction peaks for the silicon substrate are denoted with asterisks (*).

Figure 6. (a) GC-MS spectra at 29 amu of In$_{2}$O$_{3}$-$x$(OH)$_{y}$ on SiNW in both dark and light. (b) GC-MS spectra at 29 amu of In$_{2}$O$_{3}$-$x$(OH)$_{y}$ on glass in dark and light, as well as light with external heating to bring the temperature up to 150 °C. (c) $^{13}$CO production rates of In$_{2}$O$_{3}$-$x$(OH)$_{y}$ on SiNW in light and In$_{2}$O$_{3}$-$x$(OH)$_{y}$ on glass in light with external heating.
**Figure 7.** (a) Band diagram indicating the respective energy level offsets for the conduction band (CB) and valence band (VB) of Si and In$_2$O$_{3-x}$(OH)$_y$. (b) GC-MS spectra at 29 amu and (c) $^{13}$CO production rates of In$_2$O$_{3-x}$(OH)$_y$ on SiNW in light both with and without a 495 nm high-pass cut-off filter.

**Figure 8.** (a) UV-Vis-NIR reflectance spectra of In$_2$O$_{3-x}$(OH)$_y$ on SiNW and glass. Due to the transparency of the In$_2$O$_{3-x}$(OH)$_y$/glass film, a second reflectance spectrum is also shown in which the transmission is blocked by covering the back of the sample film with a 100% reflectance standard. For comparison, the reflectance spectrum of bare SiNWs is also shown. (b) Photographs of the In$_2$O$_{3-x}$(OH)$_y$ films on SiNW (left) and glass (right). (c and d) Photographs of the sample films inside the reactor under the same light intensity: (c) In$_2$O$_{3-x}$(OH)$_y$ on SiNW (d) In$_2$O$_{3-x}$(OH)$_y$ on glass.
Chapter 1
Introduction and Background

1.1 Scientific Motivation

For the past several decades the global emissions of carbon dioxide (CO$_2$) have been steadily increasing, raising serious concerns about climate change.$^1$ In 2012 alone, 3.5 billion tons of CO$_2$ were released from the combustion of fossil fuels.$^2$ To compound this issue, global energy demand is expected to increase dramatically, scaling with both population increases as well as enhanced standards of living throughout the world.$^3$$^4$ While there is no shortage of fossil based carbon reserves,$^3$ if we were to satisfy this projected energy demand with fossil based energy alone, the consequences on the environment could be severe.$^3$$^–$$^5$ It is therefore imperative to switch to alternative, more sustainable ways to generate energy from naturally abundant and renewable sources. By far, solar energy has the highest theoretical potential of all the Earth’s renewable energy resources.$^6$ More energy from the sun hits the earth’s surface in 3 hr than the entire (28 TW) projected global energy demand for 2050.$^4$$^7$ Harnessing even a small fraction of this incident solar energy would represent huge step forward in realizing a sustainable energy future. However, an important challenge associated with utilizing renewable energy sources, such as solar, is the inherent intermittent nature of natural energy sources.$^7$$^–$$^9$ It is therefore vital to be able to store this energy so that it can be released when needed.$^8$$^–$$^10$

The emerging field of solar fuels seeks to address this issue by storing radiant solar energy in chemical bonds, which can then be released on demand and act as a drop-in replacement for traditional fossil fuels.$^5$$^7$$^10$$–$$^13$ This concept is often described as an “artificial leaf,” essentially a material, or combination of materials, that can convert light energy in the form of solar photons into chemical energy, using water and/or CO$_2$ as a feedstock to generate useful chemical species. Enabling this technology would 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 feedstocks), thereby creating significant economic and environmental benefits.$^{12,14}$

To this end, we set out to design and synthesize materials capable of using sunlight energy to reduce CO$_2$ to more valuable chemical species. We also sought to understand more deeply how
and why such materials work as photocatalysts in order to create a set of design parameters for what makes an efficient photocatalyst possible. While a viable solar fuels technology is still many years away, our hope is that this work will help enable the scientific community to create better, more efficient photocatalytic materials that can make large-scale solar fuel production possible.

1.2 Heterogeneous Photocatalysis for Solar Fuel Production

In a 1912 article entitled “The Photochemistry of the Future,” the renowned Italian photochemist Giacomo Ciamician set out a scientific challenge: to harness solar energy via photochemical reactions that “master the photochemical processes that hitherto have been the guarded secret of the plants.” He further went on to point out that this ‘artificial photosynthesis’ should inherently “bear even more abundant fruit than nature, for nature is not in a hurry and mankind is.” Indeed, natural photosynthesis is inherently inefficient. Even under optimal conditions, terrestrial plants can capture and convert less than 1% of the incident solar energy into biomass, while algae can function slightly more efficiently, storing around 8% of solar energy. By contrast, thermally-driven industrial heterogeneous catalysis reactions (such as methanol synthesis or Fischer–Tropsch reactions) are extremely efficient at synthesizing carbon-containing products. However, these processes are extremely energy intensive, often operating at temperatures of 200-350 °C or more, and rely almost entirely on fossil-based energy inputs. This illustrates the tremendous potential to utilize heterogeneous catalysis with sunlight as the energy input instead of fossil-based thermal energy.

1.2.1 Hydrogen production and storage

Since the original 1972 paper by Fujishima and Honda, the majority of the photocatalysis field has focused on water splitting to produce hydrogen as a potential fuel source, however one of the major drawbacks to using hydrogen directly as a fuel is that it is difficult to transport and store. Reacting this photogenerated hydrogen with CO₂ to make carbon-based fuels could be an attractive alternative. In fact, this is what happens in natural photosynthesis. As elegantly explained by Nocera and co-workers, water splitting via photosynthesis accounts for the vast majority of solar energy storage in plants. The reversible potential for the water splitting reaction
is 1.23 V (Equation 1), while the reversible potential for carbohydrate production from CO\textsubscript{2} and water, which accounts for the water splitting reaction, is 1.24 V (Equation 2).\textsuperscript{28}

\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \quad (1)
\]

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \frac{1}{6}\text{C}_6\text{H}_{12}\text{O}_6 + \text{O}_2 \quad (2)
\]

Thus, in photosynthesis, CO\textsubscript{2} reduction to make carbohydrates does not significantly enhance the amount of energy stored and instead functions as a way for the plants to store the hydrogen and energy generated from water splitting.\textsuperscript{28}

A further benefit to carbon-based solar fuels is that they can function as drop-in replacements for conventional fossil-based fuels. This is especially important in the transportation sector where integration of solar fuel-based alternative fuels would require very minor modifications to the existing infrastructure.\textsuperscript{5,7,32} Methanol in particular, due to its high octane number, would be an excellent replacement for conventional gasoline and could be easily used in modern internal combustion engines with little to no modification.\textsuperscript{5} Dimethyl ether (DME), which can be produced via the dehydration of methanol, is an excellent diesel fuel substitute and can also replace liquefied natural gas (LNG) in most applications.\textsuperscript{5} Additionally, fossil-based carbon is not only used to create fuels but is also important source of raw materials for making plastics and other chemical products.\textsuperscript{4,18} This is another area where the combination of photochemically derived H\textsubscript{2} with CO\textsubscript{2} could make a significant contribution to lowering our dependence on fossil-based carbon reserves.

### 1.2.2 Carbon dioxide reduction

As described above, while much of the global research effort with respect to the artificial leaf has focused on H\textsubscript{2}O splitting, resulting in vast improvements in the feasibility of using H\textsubscript{2} as a renewable energy source,\textsuperscript{28,33,34} the photocatalytic reduction of CO\textsubscript{2} remains a significant challenge.\textsuperscript{5,35} The field of heterogeneous photocatalysis for CO\textsubscript{2} reduction can generally be divided into two areas: aqueous-phase and gas-phase systems. Aqueous-phase systems allow the direct reaction of CO\textsubscript{2} and water to produce hydrocarbons. This can be achieved photochemically, often by irradiating an aqueous suspension of nanoparticles, or photoelectrochemically by irradiating a photoactive electrode. In order to be able to reduce CO\textsubscript{2} and oxidize water, electrons and holes must be generated with sufficient reducing or oxidizing
power, respectively. Therefore the semiconductor’s conduction band must be higher in energy than the redox potential of the desired CO₂ reduction reaction. Conversely, in order to oxidize water to O₂ the valence band must be below the H₂O/O₂ redox potential. Inoue et al. showed in 1979 that this could be achieved using wide band gap semiconductors such as TiO₂, ZnO, WO₃ etc., however, this resulted in low activities as only a small fraction of the solar spectrum was being utilized. In order to enhance the light absorption, newer architectures have been designed in which these wide band gap semiconductor nanoparticles are sensitized with dyes or smaller band gap semiconductor materials which can absorb light and transfer photoexcited electrons or holes to the semiconductor. Another effective approach to enhancing the absorption of these photocatalytic systems is the so-called “Z-scheme” in which two different smaller band gap semiconductor photocatalysts are both suspended in solution with a reversible redox mediator. This two-step photoexcitation allows the use of smaller band gap semiconductors which can absorb more of the solar spectrum while still maintaining the necessary reduction/oxidation abilities for CO₂ reduction and water oxidation, respectively.

Photoelectrochemical reduction of CO₂ has some distinct benefits over the pure photochemical approach. In particular, by applying an external bias, electrical energy (ideally generated from a renewable source) can assist with an otherwise energetically difficult reaction, thereby enhancing reaction rates. In this way, light energy is used to subsidize the electrical energy input, minimizing the applied potential required to maintain the reaction. One of the major drawbacks to this approach is that the active materials are now immobilized on an electrode surface, which limits its contact with the solution and can lead to mass transfer issues. However, patterned electrodes, such as vertically aligned nanowires or 3D macroporous structures have shown to be particularly effective due to the enhancement in active surface area. The surfaces of these electrodes must also be carefully controlled. Detweiler et al. showed using anodized indium metal electrodes that the stability and reactivity was dramatically increased with the presence of a thin oxide layer. They attribute this increase to enhanced CO₂ adsorption by the oxide-coated electrode.

While there are many benefits to aqueous-phase approaches, gas-phase photocatalysis has been identified as the most practical and economically feasible. It is not limited by the solubility of CO₂ in the reaction medium and it can easily be integrated with existing infrastructure within the petrochemical industry. Gas-phase photocatalysts typically consist of single-component
semiconductor nanomaterials or heterostructures consisting of a semiconductor and a sensitizer or co-catalyst. In photocatalytic systems based on a single-component, oxygen deficient metal oxides have shown particular promise. These oxygen vacancies can function as active catalytic sites and enhance both the absorption of visible light and the photocatalytic activity.\textsuperscript{46,47} Some notable examples of this are black titania, \( \text{TiO}_2\times \text{H}_x \),\textsuperscript{48,11} and \( \text{W}_{18}\text{O}_{49} \) ultrathin nanowires\textsuperscript{49} which exhibit a substantial increase in light absorption and photoactivity relative to their stoichiometric counterparts. Intentionally adding impurity ions though doping has also been shown to increase the photoactivity of many semiconductors by narrowing the band gap and thus enhancing visible light absorption.\textsuperscript{50} For example, \( \text{TiO}_2 \) has been doped with both cations (e.g. Cu, Ag, Ce) and anions (e.g. N, I) all of which have shown an increase in activity.\textsuperscript{51–53} Enhancing the surface area and porosity have also been demonstrated to increase the reaction rates in many systems,\textsuperscript{54–56} although typically this is achieved through templating which can introduce carbon impurities that can complicate analysis of the product gases.\textsuperscript{57} As in aqueous-phase catalysis, decorating semiconductors with metal nanoparticle co-catalysts (e.g. Pt, Pd, and Cu) has proven to be an effective strategy to enhance the reactivity of these systems.\textsuperscript{10,50,57} This enhancement is typically attributed to improved separation of photogenerated electron–hole pairs, reducing recombination and allowing these charge carriers to perform useful chemistry.\textsuperscript{50}

Recently, an interesting hybrid system was reported by Centi and co-workers who have developed a novel gas-phase photoelectrochemical cell in which two electrodes are separated by a proton conduction membrane.\textsuperscript{58} One electrode, an array of \( \text{TiO}_2 \) nanotubes supported by a Ti film, serves to split water, releasing \( \text{O}_2 \) gas and transferring protons through the membrane. The \( \text{CO}_2 \) reduction electrode consists of a carbon cloth (to provide electrical contact) coated with either Fe- or Pt-decorated carbon nanotubes. Although the efficiencies are still quite low, this novel hybrid architecture illustrates the promise and creativity inherent in this field as we strive to generate carbon-based fuels from \( \text{CO}_2 \) using sunlight.

While this brief summary is by no means a comprehensive discussion of all of the interesting work going on in this rapidly growing area of research, hopefully it has served to orient the reader and will help to put the subsequent chapters into context.
1.2.3 The importance of $^{13}$C isotope tracing experiments

When studying photocatalytic reactions involving carbon dioxide reduction, particularly if the rates of product formation are low, it is imperative to confirm the origins of the observed carbon-containing products. As we will discuss in Chapter 3, this is particularly important when the photocatalytic materials were prepared from carbon-containing precursors. The residual carbon often left on the photocatalyst’s surface can undergo a variety of reactions to produce carbon-containing products leading to falsely elevated reaction rates.\textsuperscript{57,59,60} For example, Yang et al. have demonstrated using in-situ DRIFT spectroscopy on Cu/TiO$_2$-based photocatalyst that surface carbon can undergo several photochemical reactions to produce CO that has nothing to do with the inherent photocatalytic activity of the material.\textsuperscript{59} By using $^{13}$C-labelled CO$_2$ as a reactant, they were able to separate the signals associated with photochemical reactions involving residual surface carbon contamination from the real products generated by the materials’ intrinsic photocatalytic activity. Therefore, any study which does not perform this type of isotope tracing analysis to confirm the observed reaction rates should be treated with some degree of skepticism.

1.2.4 Properties of an ideal photocatalyst

Thus far in this chapter, I have discussed many examples of photocatalytic systems and various strategies for enhancing their reactivity. It is therefore useful, in the final paragraph of this section, to summarize what the properties of an ideal photocatalyst might be. As with all good catalysts, an ideal photocatalyst should exhibit high activity and selectivity for the desired product. It needs to be stable under the conditions of the reaction; and if we are to use it on a large scale, it must be cheap and made of earth-abundant, readily available elements. As a photocatalyst, it must also make good use of the solar spectrum, absorbing and storing as much solar energy as possible into the chemical bonds of the product molecule. There are many materials which satisfy several of these requirements; however there are few (if any) that can satisfy all of them. This is the great challenge associated with trying to create an efficient heterogeneous photocatalytic system that can function on a large enough scale to be able to address the environmental challenges discussed in the beginning of this chapter.
1.3 Indium Oxide

Indium oxide is a material with several unique optical and electronic properties. It has been studied for a wide variety of applications, such as gas sensing,\textsuperscript{61–65} catalysis,\textsuperscript{66–69} and photoelectrochemical water splitting.\textsuperscript{67} It is perhaps most well known for its use as a transparent conductive oxide (TCO).\textsuperscript{70} In its tin-doped form, indium tin oxide (ITO), it is one of the most widely used TCOs due to its high transparency and electrical conductivity, the origins of which will be discussed in further detail below. As a TCO, it is primarily used as a conductive coating in flat-panel LCD displays, organic light-emitting diodes (OLEDs), solar cells, functional glass, and energy efficient windows.\textsuperscript{70–72} Indium oxide nanostructures have also been extensively studied as conductivity-based gas sensors, exhibiting particular selectivity for ethanol\textsuperscript{61} and H$_2$S\textsuperscript{73} sensing.

1.3.1 Fundamental properties of indium oxide

1.3.1.1 Crystal structure

Indium oxide exists in two primary crystalline polymorphs, cubic and rhombohedral. The most stable phase of indium oxide is the body-centered cubic Bixbyite (MnFeO$_3$) crystal structure, which belongs to the $Ia\overline{3}$ space group. In this structure each indium atom is 6-fold coordinated by oxygen atoms in a distorted octahedral configuration. Half of these [InO$_6$] octahedra are vertex-sharing, while the other half are edge-sharing. The oxygen atoms within this structure are all 4-fold coordinated by indium in a distorted tetrahedral configuration.\textsuperscript{74} The unit cell of Bixbyite indium oxide contains 80 atoms, however this complex crystal structure can be more easily understood as a CaF$_2$-type lattice with 25\% of the tetrahedral anion sites vacant (Figure 1).\textsuperscript{75} This additional space in the bixbyite structure may result in more dynamic flexibility, especially at the nanoparticle surface, allowing for more

![Figure 1. The CaF$_2$ crystal structure with 25\% of the anion sites removed (illustrated by white circles). This structure is analogous to the cubic Bixbyite structure of In$_2$O$_3$.](image-url)
atomic mobility in the lattice; indeed \( \text{In}_2\text{O}_3 \) is a known solid ionic and protonic conductor.\(^{76,77}\)

The rhombohedral corundum-type indium oxide, which belongs to the \( \text{Rc}\bar{3} \) space group, is a metastable phase at ambient temperature and pressure.\(^{78,79}\) In this structure, the indium atoms are also 6-fold coordinated in a distorted octahedral geometry. These octahedra are face-sharing in the direction parallel to the c-axis and edge-sharing in the direction perpendicular to the c-axis. Recent synthetic advances have enabled its preparation,\(^{79-81}\) however the vast majority of work on indium oxide, including the work presented within this thesis, is focused on the cubic polymorph which is stable under ambient conditions. Recent theoretical and experimental studies comparing both rhombohedral and cubic indium oxide indicate that both materials have similar optical and electronic properties,\(^{78,82}\) however more work is needed to more fully understand the differences between these two materials.

1.3.1.2 Optical band gap

The nature of band gap in indium oxide has been the subject of considerable debate within the literature, with some groups reporting direct band gaps as high as 3.75 eV,\(^{83-85}\) and others reporting indirect band gaps of 2.6 eV.\(^{83,85}\) However, thanks to several in-depth, fundamental studies, it is now generally accepted that indium oxide has what is known as a direct “forbidden” band gap with a value of around 2.9 eV (illustrated schematically in Figure 2).\(^{75,86}\) When indium oxide absorbs light, electrons are still excited across the band gap in a direct vertical transition, with no change in momentum (i.e. no phonon is needed to assist the transition as is required for indirect band gap materials). However, due the character of the atomic orbitals that make up the states at the top of the valence band and the bottom of the conduction band, direct transition between these states is forbidden by dipole selection rules. Walsh et al. showed using theoretical calculations, supported by

![Figure 2. Schematic illustration of indium oxide’s direct “forbidden” electronic band structure. The black upwards arrow indicates an optically allowed vertical transition, while the red arrow indicates that this optical transition is forbidden by dipole selection rules.](image-url)
experimental data, that the states in the first 0.8 eV below the valence band maximum (VBM), consisting primarily of In 4d orbitals, have the same (even) parity as the states at the bottom of the conduction band, which are primarily composed of a In 5s and O 2s orbitals.\textsuperscript{86} Dipole selection rules dictate that the probability of light absorption causing the direct transition between two states goes to zero unless the states have opposing signs; therefore, direct transitions between the valence band and conduction band only become allowed for states more than 0.8 eV below the VBM, which have become sufficiently p-like in character and are of odd parity.\textsuperscript{86} They were also able to directly measure both the conduction band and valence band using both conventional X-ray photoemission spectra (XPS) as well as hard X-ray photoemission (HXPS). Their data indicates that the band gap associated with undoped indium oxide is around 2.9 eV. This matches very well with a study performed by Janowitz et al. who used angle-resolved photoemission spectroscopy (ARPES) to directly probe both the conduction band and valence band states.\textsuperscript{75} They detected two primary transitions in their measurements, a weak feature at 2.63 eV and a much stronger feature at 3.71 eV. They also attribute this weak feature to optically forbidden states and the much stronger transition to the optically allowed states below the VBM.

It should be noted that while these types of transitions are optically forbidden, they still can happen if there are defects which break the local symmetry. This could explain the recently reported red-shift in the band gap of N-doped In\textsubscript{2}O\textsubscript{3}\textsuperscript{87} e.g. the introduction of the N 2p levels above the VBM break the local symmetry, and produce a parity allowed transition which originates from the top of the valence band edge.\textsuperscript{86,87} This has profound implications for other types of defects and impurity ions present within an indium oxide material, which can dramatically impact the optical and electronic properties. Further, this type of “forbidden” transition has been shown in other materials to provide 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.\textsuperscript{88}

### 1.3.1.3 Origins of high conductivity in indium oxide

As discussed above, indium oxide is most well-known for its application as a transparent conductive oxide (TCO) due to its high transparency and electrical conductivity. Tin-doped indium oxide (ITO) thin films can exhibit conductivities as high as $10^5$ S/cm.\textsuperscript{77} Traditionally,
this high conductivity has been attributed to a bulk point defect model, involving intrinsic lattice defects such as oxygen vacancies,\textsuperscript{89–92} unintentional impurities like hydrogen,\textsuperscript{93,94} or extrinsic dopants such as tin in ITO.\textsuperscript{77,95–97} Even in the absence of intentional extrinsic dopants (e.g. tin), In$_2$O$_3$ still exhibits considerable n-type conductivity, in polycrystalline thin films reaching values as high as 1000 S·cm\textsuperscript{-1}.\textsuperscript{98} In this bulk defect model oxygen vacancies created within the lattice function as the primary electron donors. When an oxygen vacancy is created in the lattice, it can exist in either a neutral or doubly ionized state. The ionization of this vacancy from the neutral to the doubly ionized form donates electrons into the conduction band, resulting in the observed conductivity.\textsuperscript{77}

Recently, several groups have challenged this bulk defect model.\textsuperscript{98,99,77} Lany and coworkers demonstrated using both experimental and theoretical techniques that the high conductivities in nominally un-doped indium oxide thin films can be entirely explained by surface donor states.\textsuperscript{98} Using DFT calculations, they predict a large ionization potential for bulk oxygen vacancies (0.7 eV below the conduction band minimum) which implies that such deep donor levels would not contribute significantly to the conductivity at room temperature. Using temperature dependent conductivity measurements in controlled partial pressures of O$_2$, they were able to demonstrate that this theoretical model consistently explains the experimental conductivity and non-stoichiometry of pure bulk In$_2$O$_3$ samples. In contrast, they also performed the same measurements on thin films of In$_2$O$_3$, which exhibited conductivities that were 4 orders of magnitude higher than the bulk defect model could explain. Again using DFT, they modeled the formation of surface oxygen vacancies on the indium (111) surface and found that these defects create a doubly occupied state just below the conduction band minimum (CBM). Because this predicted energy is so close in energy with the CBM, these electrons can easily be thermally excited into the surface or bulk conduction band at room temperature, resulting in conductivity. Their calculation also show that the formation energies required for surface oxygen vacancies are 1.4 eV lower than for bulk vacancies indicating that there is likely to be a much higher population of these types of defects in experimental samples. In particular, under reducing conditions (e.g. low partial pressures of O$_2$ gas) the surface oxygen vacancy formation energies become negative, indicating that under such reduction conditions a large population of oxygen vacancies is likely. They also perform thickness dependent Hall measurements and find that surface conductivity dominates the total film conductivity up to a film thickness of 150 nm. They
further demonstrate that the conductivity of a polycrystalline film is an order of magnitude higher than an epitaxially grown film of the same thickness. This correlates well with theoretical calculations which indicate that the near-CBM electronic states created by these surface vacancies exhibit a considerable dispersion perpendicular to the film’s surface creating a 2D conductive layer. Using angle-resolved photoemission spectroscopy, Zhang et al. found similar results indicating the presence of a 2-dimensional electron gas at the surface of indium oxide. They also attribute the source of these surface delocalized electrons to doubly ionized surface oxygen vacancies. Their results demonstrate that the density of electrons at the surface is sufficiently high to induce significant change in the band structure, resulting in a reduced band gap at the surface relative to the bulk, which matches well with the theoretical predictions proposed by Lany et al. Both studies suggest that the surface band gap is reduced by approximately 0.8 eV. While there is still more work to be done to fully understand the origins of the conductivity in indium oxide and other TCOs, a coherent picture is beginning to emerge. The most likely cause of conductivity in indium oxide is due to surface oxygen vacancies which create shallow donor levels just below the conduction band. These levels are nearly degenerate with the CBM and can easily be thermally excited at room temperature to produce conduction electrons. Both theoretical and experimental evidence also suggests that these shallow states create a delocalized electron gas at the surface of indium oxide, explaining the much higher conductivities observed in thin films. These studies have also indicated that the band gap is lower at the surface relative to the bulk band gap, which may further facilitate the localization of electrons at the indium oxide surface. Bulk oxygen vacancy defects are still expected to contribute to the conductivity of indium oxide, however due to the high ionization energy (0.7 eV) it is unlikely that they play as significant a role as surface oxygen vacancies.

1.3.2 Synthesis of indium oxide

1.3.2.1 Thermal decomposition

There are several ways to make indium oxide nanomaterials. The simplest and most scalable is the thermal decomposition of indium hydroxide, which is the technique I employed to prepare the indium oxide nanomaterials discussed in subsequent chapters. This generalized three-step
process is illustrated in detail in Figure 3. To prepare the indium hydroxide precursor, a base is added to a solution containing an indium (III) salt, typically indium chloride. This causes the hydrolysis and condensation of \( \text{In}^{3+} \) species to produce an amorphous \( \text{InO}_{n-x} \text{H}_{n-2x} \) gel network. The second ripening step is optional, however Chen et al. have shown that doing so can allow rough control over the final particle size of the indium oxide nanoparticles, with longer ripening times resulting in smaller nanoparticles.\(^{65}\) They attribute this to the “pre-disintegration” of the amorphous gel network via the production of isolated, weakly crystalline domains, which form upon gentle heating. At longer heating times, more weakly crystalline domains are created which

![Figure 3](image)

**Figure 3.** An illustration of the formation and thermal decomposition of indium hydroxide to produce indium oxide nanoparticles.

function as nuclei for the generation of indium oxide nanoparticles. The greater the number of nuclei, the smaller the resulting particle size, which has been well-documented in many other systems.\(^{88}\) The maximum ripening time Chen and co-workers used was 2 hrs, so it is possible that there is a limit to this mechanism. Eventually these isolated \( \text{In(OH)}_3 \) nuclei will start to link together, decreasing the number of nuclei and resulting in larger nanoparticles.

The third and final step to this process is calcination of the dried indium hydroxide precursor. This initiates a solid state thermal decomposition reaction in which water is lost from the material via Equation 3:

\[
2 \text{In(OH)}_3 \rightarrow \text{In}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (3)
\]

As indium hydroxide is converted to cubic bixbyite indium oxide, at least two In-O bonds must be broken and half of the vertex sharing \([\text{InO}_6]\) octahedra in \( \text{In(OH)}_3 \) must rearrange to form at
least two new In-O bonds in edge sharing octahedra. This atomic rearrangement and associated loss of water from the lattice requires significant thermal energy to occur. It has been demonstrated using thermogravimetric and kinetic analysis that this transition cannot occur below 210 °C.\textsuperscript{100} As the temperature is increased, there is more thermal energy available to allow atomic rearrangement that minimizes the surface energy.\textsuperscript{18} This allows significant control over the defects present in the final material. Indium oxide prepared at temperatures close to this transition temperature would not have sufficient thermal energy to enable the passivation of many of the defects formed. As a result, this indium oxide material would contain a higher proportion of defects such as residual surface hydroxide groups and coordinatively unsaturated indium sites (oxygen vacancies), which could play a significant role in determining the optoelectronic properties of the resulting material. By carefully choosing the reaction the reaction temperature, our group and others have demonstrated that this can significantly impact the performance of indium oxide in a variety of applications.\textsuperscript{57,68}

1.3.2.2 Hydrothermal and solvothermal synthesis

Another very common way to prepare indium oxide nanomaterials is via the use of pressurized autoclaves. This can be divided into two categories: two-step hydrothermal processes and one-step solvothermal synthesis. In the two-step hydrothermal process, an In\textsuperscript{3+} salt is combined with a suitable base, such as NH\textsubscript{4}OH or urea under aqueous conditions and then heated to temperatures ranging from 140 - 210 °C. This process is analogous to the hydrolysis and condensation reaction described in the previous section. Structural control is achieved through the use of surfactants, which complex with the In\textsuperscript{3+} species and control their interaction with the newly forming nanostructures.\textsuperscript{101,102} The resulting In(OH)\textsubscript{3} nanoparticles are then dried and calcined in air as described above to convert them into In\textsubscript{2}O\textsubscript{3}. A wide variety of nanostructures have been prepared using this technique including nanocubes,\textsuperscript{103} nanosheets,\textsuperscript{104} and nanorods.\textsuperscript{102}

One-pot solvothermal syntheses have also been employed to prepare In\textsubscript{2}O\textsubscript{3} nanostructures directly from In\textsuperscript{3+} salts. Typically, these reactions are carried out at temperatures ranging from 150 – 200 °C in non-aqueous media. Indeed the presence of water has been shown to have a strong effect on the resulting product. Yan et al. demonstrated that indium oxide could only be directly formed under anhydrous conditions. If the concentration of water was between 1.5 - 9%
pure InOOH was formed, while concentrations of water above 33% resulted in the formation of pure In(OH)$_3$.\textsuperscript{105}

### 1.3.2.3 Colloidal synthesis

For the preparation of relatively monodisperse samples of In$_2$O$_3$ nanoparticles, the best technique is via standard colloidal synthesis techniques. A common way to achieve this is via hydrolysis and condensation of hydrated In$^{3+}$ precursors (e.g. InCl$_3$·4H$_2$O) in high-boiling, multi-dentate alcohols (polyols).\textsuperscript{70,96} These polyols act as both solvents and ligands, stabilizing the particle surfaces during nucleation and crystallization, thereby preventing particle growth and aggregation. As described in the previous section, minimizing the amount of water in the reaction solution is critical. A small amount of water is needed to facilitate the hydrolysis and condensation of the In$^{3+}$ precursors, however the amount provided by the hydrated salts, generally proves to be sufficient. Indeed most reactions of this type are performed under N$_2$ atmospheres.\textsuperscript{106}

Corundum-type In$_2$O$_3$ can also be prepared via colloidal synthesis. Several studies have shown while the decompositions of In(OH)$_3$ leads to cubic In$_2$O$_3$, thermal decomposition of InOOH, produces corundum-type In$_2$O$_3$.\textsuperscript{79,80,102} This is likely due to the symmetry of the crystal structures, In(OH)$_3$ and Bixbyite In$_2$O$_3$ are both cubic, however InOOH has an orthorhombic structure which may facilitate easier transformation to the hexagonal corundum-type In$_2$O$_3$.\textsuperscript{80,102} Lee et al. have demonstrated that monodisperse corundum-type In$_2$O$_3$ can be formed in a two step procedure.\textsuperscript{79} In the first step, colloidal InOOH is formed by heating In(O-i-Pr)$_3$ in oleylamine to 90 °C with trioctylamine as a surfactant. They then transferred this solution to a Schlenk line and rapidly heated the solution to 350 °C under flowing N$_2$, resulting in pure, monodisperse corundum-type In$_2$O$_3$.

While these types of syntheses are very valuable to produce well-defined nanostructures of In$_2$O$_3$, this is not a suitable route to prepare heterogeneous photocatalytic materials. Not only do the ligands used in the synthesis block the surface from interacting with the reactant gases, the residual carbon from the ligands could result in high background levels of carbon containing products that complicate analysis of the catalysis results.\textsuperscript{59}
1.3.3 Why indium oxide is a good candidate as a CO$_2$ reduction photocatalyst

There are many reasons why indium oxide is a compelling material to study as a CO$_2$ reduction photocatalyst, which we hope to demonstrate in detail in the subsequent chapters. In particular, the surface properties of In$_2$O$_3$ are particularly promising. As discussed in Section 1.3.1.3, In$_2$O$_3$ exhibits very high n-type conductivity which has been attributed to surface oxygen vacancies that create shallow donor levels just below the conduction band. Not only do these shallow states create a surface rich in electrons, which could further facilitate electron transfer to adsorbed molecules such as CO$_2$, but these oxygen vacancies could also help by acting as active site that facilitate CO$_2$ reduction reactions. Further, as discussed in Section 1.3.1.2, since In$_2$O$_3$ 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 dipole selection rules.$^{75,86}$ This could provide a built in mechanism for prolonging the lifetime of photo-excited electron-hole pairs, enhancing their chances of participating in CO$_2$ reduction reactions. Finally, while it is unclear how relevant aqueous-based redox potentials are to surface-mediated gas-phase reactions, the fact that indium oxide has a relatively high (CB) position with respect to the redox potentials for several CO$_2$ reduction reactions may provide photo-excited electrons with sufficient reducing power to drive artificial photosynthetic production of hydrocarbons and carbon monoxide.$^{16,87}$

1.3.4 Green chemistry considerations

I wanted to close this introductory chapter by offering my perspective on how this work fits into the broader context of Green Chemistry. Green Chemistry is not its own sub-discipline, but rather applies to all of chemistry, seeking to maximize efficiency and minimize adverse impacts and hazards associated with chemical reactions. In their 1998 book entitled “Green Chemistry Theory and Practice,” Paul Anastas and John Warner outlined 12 principles that provide chemists with a framework to assess reactions and make improvements, considering efficiency, safety, human health and the environment.$^{107}$ Catalysis is one of the cornerstones of these principles, facilitating more efficient use of resources, reducing the energy required for a reaction, enhancing reaction rates, and minimizing wastes produced.

Indium oxide, like all materials, has both positive and negative aspects in terms of Green Chemistry. For example, indium oxide has relatively low toxicity$^{108}$ and the solid state method
by which it is typically prepared generates very little waste.\textsuperscript{68} However, indium oxide is not a renewable material and indeed, because of its widespread use, it is projected to face shortages in the coming years.\textsuperscript{109} Therefore it is unlikely that indium oxide will be the photocatalyst of choice for large scale CO\textsubscript{2} reduction. Instead, it is our hope that by understanding how and why indium oxide works as a photocatalyst for CO\textsubscript{2} reduction, we can create a set of design parameters that help to enable the scientific community create better, more efficient photocatalytic materials, made of earth abundant elements, which can make large-scale solar fuel production a reality.

1.4 References


Chapter 2
Discovery and Evaluation of Nanocrystalline In$_2$O$_{3-x}$(OH)$_y$ as a Single Component Photocatalyst for Gas-Phase CO$_2$ Reduction Using Both UV and Visible Light

2.1 Statement of Contributions
Thomas Wood performed the catalysis experiments. Dr. Kristine Liao performed the XPS measurements and assisted with the data processing and analysis. Dr. Paul O’Brien assisted in performing and interpreting the UV-Visible reflectance spectroscopy experiments and calculations. The gas adsorption experiments were performed by Laura Reyes. I carried out all other synthesis, characterization, and experiments presented in this chapter. Thomas Wood and I drafted the manuscript for publication, which was edited by Professors Charles Mims and Geoffrey Ozin. Portions of this work have appeared in print$^1$ and are the subject of a United States patent application.$^2$

2.2 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 simulated solar irradiation. 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 0.25 μmol g$_{cat}^{-1}$ hr$^{-1}$ in a batch reactor under 2.2 suns of simulated solar irradiation at 150 °C. This rate is further improved by using a capillary flow reactor, reaching rates as high as 15 μmol g$_{cat}^{-1}$ hr$^{-1}$ under similar conditions. $^{13}$CO$_2$ isotope labelling 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
CO₂ reduction photocatalysts to be incorporated into current advanced systems for solar fuels generation.

2.3 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” - a material that converts light energy in the form of solar photons into chemical energy - using CO₂ as a feedstock to generate useful chemical species. Enabling this technology will allow the greenhouse gas, CO₂, emitted from energy production and manufacturing exhaust streams to be converted into valuable products (such as solar fuels or chemical feedstocks), thereby creating huge economic and environmental benefits by simultaneously addressing energy security and climate change issues.³-⁶ While the global research effort with respect to the artificial leaf has focused on H₂O splitting, the photocatalytic reduction of CO₂ remains a significant challenge⁷ and thus is the focus of our work.

A key component of this “artificial leaf” 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 CO₂ to fuels. As a result, semiconductor nanomaterials, which have the surface, optical, and electronic properties that can enable photocatalytic reduction of gas-phase CO₂ to generate solar fuels, are increasingly being studied for this purpose.⁷-¹⁴ 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.¹⁵

A class of materials capable of photocatalytically reducing CO₂ are oxygen deficient metal oxides. Oxygen vacancies can function as active catalytic sites and enhance both the absorption of visible light and the photocatalytic activity of the material.¹⁶,¹⁷ The most notable example of this is black titania, TiO₂ₓHₓ, which exhibits a substantial increase in light absorption and photoactivity for water splitting after hydrogen treatment.¹⁸,¹⁹ Another effective approach to increasing the photocatalytic activity of metal oxide nanomaterials is to improve the CO₂ capture capacity of the nanoparticle surface. Several groups have demonstrated that surface hydroxides can enhance the affinity of CO₂ for a photocatalytic surface, which can have a significant effect on the photocatalytic activity and CO₂ reduction rates.¹⁸-²⁰ 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.$^{15,17,19,21-23}$

Indium oxide is a material with surface, optical and electronic properties that make it a compelling choice as a CO$_2$ reduction photocatalyst. For example, its conduction band (CB) and valence band (VB) positions on an energy band diagram straddle the H$_2$O oxidation and CO$_2$ reduction half reaction energies required to drive artificial photosynthetic production of hydrocarbons and carbon monoxide.$^6,24$ Furthermore, since In$_2$O$_3$ 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.$^{25}$ This “forbidden” transition has been shown in other materials to provide 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.$^{26}$ In addition to these beneficial optical and electronic properties, the surface properties of In$_2$O$_3$ have garnered interest in the field of thermally driven heterogeneous catalysis. Sun et al. have demonstrated the high activity of In$_2$O$_3$ towards the reverse water gas shift (RWGS) reaction at high temperatures, specifically citing CO$_2$ capture as a key factor in enhancing the activity.$^{27}$ Ye et al. have suggested from computational modeling that surface oxygen vacancies could act as active sites to promote thermally driven methanol synthesis.$^{28}$

In this paper, hydroxylated indium oxide nanoparticles (In$_2$O$_{3-x}$(OH)$_y$), populated with surface hydroxides and oxygen vacancies, are investigated as a gas-phase CO$_2$ reduction photocatalyst. We use a temperature-programmed thermal dehydration reaction to make In$_2$O$_{3-x}$(OH)$_y$ nanoparticles from In(OH)$_3$. 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.$^{29}$ 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$_2$O$_3$ films for photoelectrochemical water splitting$^{30}$ as well as the photocatalytic degradation of dyes,$^{31}$ we produced, characterized and evaluated the photocatalytic performance of In$_2$O$_{3-x}$(OH)$_y$ nanoparticles prepared via thermal dehydration reactions at 250 °C, 350 °C and 450 °C, in addition to crystalline In(OH)$_3$ nanoparticles prepared from the same precursor.
Although minimal amounts of organics are present in our synthesis, we still took precaution by using $^{13}$C-labelled CO$_2$ ($^{13}$CO$_2$) as a reactant while testing the photocatalytic performance of these nanoparticles for CO$_2$ photocatalytic activity. Light-driven CO$_2$ 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{32} 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 increased recognition of the importance of these tests.\textsuperscript{33}

Herein we report gas-phase photocatalytic conversion of $^{13}$CO$_2$ in the presence of H$_2$ to generate $^{13}$CO at a rate as high as 0.25 $\mu$mol g$_{\text{cat}}^{-1}$ hr$^{-1}$ in a batch reactor at 150 °C under simulated solar illumination intensities of 2200 W m$^{-2}$ on hydroxylated indium oxide nanoparticle films. We then perform the isotope tracing experiments with coupled gas chromatography-mass spectroscopy (GC-MS) analysis to confirm - with complete certainty - that the observed gaseous products originate from $^{13}$CO$_2$ feedstock rather than adventitious carbon sources.\textsuperscript{34} Furthermore, under only visible light irradiation ($\lambda > 420$ nm) we find that our indium oxide nanoparticles photocatalytic reduce $^{13}$CO$_2$ at a rate of 70 nmol g$_{\text{cat}}^{-1}$ hr$^{-1}$ at the same light intensity. Finally, by using a capillary flow reactor under similar conditions but with flowing CO$_2$ and H$_2$, the observed CO production rate can be further increased to 15 $\mu$mol g$_{\text{cat}}^{-1}$ hour$^{-1}$. Our results show that by combining the favourable optical and electronic properties inherent to indium oxide with a judiciously tailored surface, In$_2$O$_{3-x}$(OH)$_y$ nanoparticles can function as an active photocatalyst for gas-phase CO$_2$ reduction. This study provides valuable insight about key parameters for the composition selection, materials design and performance optimization of photocatalysts suited for large-scale solar fuels production.

2.4 Experimental

2.4.1 Synthesis of In$_2$O$_{3-x}$(OH)$_y$ nanoparticles

An In(OH)$_3$ precursor was synthesized and subsequently dehydrated into In$_2$O$_3$ nanoparticles following a modified version of a previously published procedure.\textsuperscript{35} All chemicals were used as received without any further purification. In a typical synthesis, indium(III) chloride (3.6 g, 16.2 mmol, Sigma Aldrich, 98%) was dissolved in a 3:1 solution (72 mL) 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 aqueous ammonium hydroxide (18 mL, Caledon, 28-30% adjusted to 25 wt% with deionized water) and of anhydrous ethanol (54 mL). 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 either 185 °C, 250 °C, 350 °C, or 450 °C.

Sample films were prepared for photocatalytic testing by drop casting 20 mg of each sample powder - suspended via sonication in deionized, nanopure water (3 ml) - onto 1”x1” binder free borosilicate glass microfiber filters (Whatman, GF/F, 0.7 µm). This sample loading was selected to optimize CO production rates, as illustrated in Figure 8.

2.4.2 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 150 mm.

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.

X-ray photoelectron spectroscopy (XPS) was performed using a Perkin Elmer Phi 5500 ESCA spectrometer in an ultrahigh vacuum chamber with base pressure of $1 \times 10^{-9}$ 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.$^{36,37}$

### 2.4.3 Gas-phase photocatalytic measurements

Gas-phase photocatalytic rate measurements were conducted in a custom fabricated 1.5 mL stainless steel batch reactor with a fused silica view port sealed with Viton O-rings. A schematic diagram of this system is shown in Figure 1a. 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 6 mL/min and a stoichiometry of 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, with a thermocouple placed in contact with the sample. 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 (the spectral output is shown in Figure 1b) for a period of 16 hours. Product gases 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 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 60 m 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 300 W Xe Lamp (the spectral output is shown in Figure 1b) fitted with a combination of AM1.5, 420 nm high-pass and 615 nm highpass filters. Since each filter reduced the total irradiation intensity, the beam was focused using collimating lenses to maintain an irradiation intensity of 100 mW/cm$^2$. The spectral output was measured with a StellarNet Inc spectrophotometer. Irradiation intensity was measured by a Newport 91150V calibrated reference cell and meter.

Additional photocatalytic rate measurements were carried out in a borosilicate tube (3 mm outer diameter and 2.5 mm inner diameter) reactor packed with 24 mg (3 cm bed length) of In$_2$O$_3$-$x$(OH)$_y$ nanoparticle powder. Quartz wool was used to support either end. The reactor was
held in a custom designed stand. 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). A schematic illustration of this system is shown in Figure 2.38 The reactor was purged with H₂ (99.9995%) and CO₂ (99.999%) at a flow rate of 10 mL/min 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.

2.4.4 CO₂ capture capacity

The CO₂ 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 N₂ flow at a rate of 100 mL/min with a temperature ramp of 10 °C/min up to 150 °C; the temperature was held at 150°C for 3 hours. To measure the amount of CO₂ adsorption, the gas was then switched to 100 % dry CO₂ at a flow rate of 100 mL/min; the temperature was then maintained at 150 °C for 10 hours. The weight gain observed during this adsorption step was used to calculate the CO₂ capture capacity of the sample. Desorption of CO₂ was performed by switching the gas flow back to N₂ flow for 5 hours while keeping the temperature constant at 150 °C.
2.5 Results and Discussion

2.5.1 Characterization of hydroxylated $\text{In}_2\text{O}_{3-x}(\text{OH})_x$ via temperature-controlled decomposition of $\text{In(OH)}_3$

Hydroxylated indium oxide nanoparticles were produced via a thermal dehydration of $\text{In(OH)}_3$. As the transition from $\text{In(OH)}_3$ to $\text{In}_2\text{O}_{3-x}(\text{OH})_x$ does not occur until approximately 210 °C, only samples heated above this temperature undergo dehydration to form indium oxide.$^{39,40}$ The transmission electron microscopy (TEM) images in Figure 3 illustrate the change in nanostructure morphology with increasing calcination temperature. The $\text{In(OH)}_3$ sample calcined at 185 °C (Figure 3a) 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 3b and 3f). The overall clusters are similar in size to the $\text{In(OH)}_3$ sheets, indicating that the observed porosity is likely a result of water molecules being released from the lattice as the $\text{In(OH)}_3$ decomposes. As the calcination temperature increases further to 350 °C (Figure 3c and 3g) and 450 °C (Figure 3d and 3h), 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 4a confirm that each sample consists of a single pure crystalline phase. The sample treated at 185 °C crystallizes to form pure cubic $\text{In(OH)}_3$, 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 4b. As expected, the absorption edge of $\text{In}_2\text{O}_{3-x}(\text{OH})_x$ is significantly red-shifted in comparison to $\text{In(OH)}_3$. These diffuse reflectance spectra were fitted with a modified Kubelka-Munk function$^{41}$ (Figure 5) to determine the optical band gap of each sample, as indicated in Figure 4c. By correlating these values 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 2c), which corresponds well to what has been reported in the literature.$^{25,42}$ The position of the Fermi energy ($E_F$) just below the conduction band indicates that the as-prepared $\text{In}_2\text{O}_{3-x}(\text{OH})_x$ samples are n-type semiconductors$^{25,43}$ and the overall band
alignment suggests that all samples may have sufficient reducing power to photocatalytically drive gas-phase CO$_2$ reduction reactions.$^{15}$
Figure 4. (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 ($E_F$) were measured by XPS and the band gap was calculated by fitting the reflectance spectra using K-M theory (see Figure 5 for more details on the fitting).

Figure 5. Estimation of the electronic band gap of the $\text{In}_2\text{O}_3-(\text{OH})_y$ and In(OH)$_3$ 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)$_3$, (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)$_3$ film and 3/2 for the $\text{In}_2\text{O}_3-(\text{OH})_y$ films. The linear portion of the plot was extrapolated and its intercept with the abscissa provided the band-gap estimate.
2.5.2 Demonstration of photocatalytic activity using $^{13}$CO$_2$ labelling

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.$^{32}$ After 16 hours of reaction at 150 °C under both light (800 W m$^{-2}$ 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$_{cat}^{-1}$ 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 product ion-fragmentation pattern obtained using GC-MS (Figure 6) 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 0.25 μmol g$_{cat}^{-1}$ hour$^{-1}$ in batch reactors. Figure 7a 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

![Figure 6. GC-MS fragmentation of CH$_4$ produced from $^{13}$CO$_2$ isotope tracing measurements of I-250 plotted in contrast to a $^{12}$CH$_4$ 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.](image-url)
Figure 7. Photocatalytic performance of $\text{In}_2\text{O}_3$-$\text{x(OH)}_y$ and $\text{In(OH)}_3$ samples. (a) Mass spectrometry fragmentation pattern of CO generated with and without irradiation. The 28 AMU mass fragment peak corresponds to $^{12}\text{CO}$ and the 29 AMU mass fragment peak corresponds to $^{13}\text{CO}$. (b) Time dependent product gas formation with and without irradiation for I-250 at a reaction temperature of 150 °C.

AMU peak in the dark and the significant increase in its intensity under irradiation demonstrates that the conversion of $^{13}\text{CO}_2$ to $^{13}\text{CO}$ is light driven. This finding is further confirmed by a comparison of time dependent product formation. Figure 7b 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.

2.5.3 Optimization of photocatalyst loading

Sample loading can have a significant effect on the reported photocatalytic rates. For example, if the sample loading is too high, there will be an uneven distribution of light absorption throughout the film: the top of the film will absorb the majority of the incident light, effectively shielding the bottom portion of the film and lowering the overall per mass photocatalytic activity. Additionally, if the sample is too tightly packed, reactant gas molecules will be unable to access active surface sites, which will also suppress photocatalytic activity. We therefore examined the photocatalytic activity of I-250 films as a function of sample loading. All films were identical in geometric surface area (1 in$^2$) and were prepared side by side from the same sample batch to ensure consistency. As illustrated in Figure 8, the CO production increases with increasing
Sample loading up to 20 mg. Sample loading above 20 mg/in² did not result in higher CO production, indicating that the sample has likely become too thick and the bottom portion of the film is not participating in the reaction. Based on this data, a sample loading of 20 mg/in² was selected for all photocatalytic measurements reported herein as it maximizes light absorption per sample mass. Figure 9 shows SEM micrographs of a typical 20 mg In₂O₃ sample on the filter. Figure 9a shows a cross-section of the film, indicating its thickness is approximately 50 µm. The magnified image shown in Figure 9b indicates that the as-prepared sample maintains its high porosity, which as mentioned above is an important factor for surface-mediated gas-phase reactions.

2.5.4 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. 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 a set of In₂O₃ₓ(OH)ᵧ sample films, each loaded with 20 mg of sample and calcined at different temperatures (I-250, I-350 and I-450) as well as a 20 mg In(OH)₃ control sample film. The CO production rates for these samples under 800 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 10. In general, indium oxide samples calcined at lower temperatures produced CO at higher rates for the range of reaction temperatures studied. The photocatalytic CO₂ reduction rate at 150 °C for 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 control produced almost no CO at any temperature. Both I-250 and I-350
demonstrate an increase in photocatalytic CO production with increasing reaction temperature, reaching a maximum at 150 °C and decreasing in activity at 170 °C. Sample I-450, on the other hand, shows an increase in reaction activity at 170 °C relative to 150 °C, in contrast to I-250 and I-350. Due to limitations on the maximum operating temperature of the photoreactors, the reaction was not investigated at temperatures higher than 170 °C. The effect of irradiation on CO production rates for each sample at different reaction temperatures is shown in Figure 11. As expected, all samples produced very little CO under dark conditions, demonstrating that the observed gas phase CO$_2$ reduction is a light-driven process.

2.5.5 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, a 20 mg I-250 film 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 12 shows a linear increase in CO production rate with increasing light intensity, which further confirms that the CO$_2$ 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
Figure 10. Reaction temperature dependence of CO production rates for \( \text{In(OH)}_3 \), I-250, I-350 and I-450 measured under 1 sun irradiation.

Figure 11. CO production dependence on the presence of light and reaction temperature for samples (a) I-250, (b) I-350, and (c) I-450.

investigated (Figure 13). A single 20 mg 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 W m\(^{-2}\), 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\textsubscript{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\textsubscript{cat}^{-1}·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\textsubscript{cat}^{-1}·hour^{-1}. These results demonstrate that not only is the I\textsubscript{250} capable of converting gaseous CO\textsubscript{2} to CO using only visible light, which correlates well with the diffuse reflectance measurements (Figure 13b), but also that In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} is stable under these reaction conditions and can produce rates consistent with the initially measured values even after being irradiated continuously for 4 days.

2.5.6 Photocatalytic CO\textsubscript{2} reduction rates using a flow reactor

In an attempt to simulate more industrially relevant conditions, preliminary photocatalytic rate measurements were carried out in a tubular fixed bed flow reactor irradiated with a Newport 300W Xe lamp. This investigation of the In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} nanoparticles revealed that under similar conditions (2200 mW cm\textsuperscript{-2}, 150 °C and 3 atm), under flowing CO\textsubscript{2} and H\textsubscript{2}, CO is photocatalytically produced at a rate of 15 μmol·g\textsubscript{cat}^{-1}·hour^{-1} with 24 mg (3 cm bed length) of the I-250 nanoparticle powder sample. These rates are higher than previously reported CO production rates for other single component metal oxides; for instance 1.61 μmol·g\textsubscript{cat}^{-1}·hour^{-1} for MgO,\textsuperscript{44} and 0.56 μmol·g\textsubscript{cat}^{-1}·hour^{-1} for ZrO\textsubscript{2}.\textsuperscript{45} The reasons for this increased activity will be discussed in greater detail in Chapter 4. In this chapter, in order to ensure consistency when comparing different samples, the photocatalytic rate data presented here are limited to those from

![Graph showing CO production rate vs. irradiation intensity](image)
identical batch photoreactors. This mitigates effects caused by variations in particle size between I-250, I-350, and I-450 and allows us to more accurately make comparisons between these samples. Differences in particle size of powders packed in a catalyst bed can result in substantial variations in pressure gradients, making comparisons between samples more difficult.

### 2.5.7 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 14a shows that the In3d$_{5/2}$ 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 14b shows a sharp contrast between In(OH)$_3$ and In$_2$O$_{3-x}$(OH)$_y$ samples. There is a ~2.5 eV shift to lower binding energy of the main O1s peak, from 532.7 eV for In(OH)$_3$ to 530.2 eV for I-450. Additionally, a shoulder peak appears in the O1s core level peak of the In$_2$O$_{3-x}$(OH)$_y$ samples, indicating that there is more than one chemical state of oxygen present in the structure. Indeed, the O1s peak for the In$_2$O$_{3-x}$(OH)$_y$ 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.
Figure 14. Comparison of XPS spectra for $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ and $\text{In(OH)}_3$ samples. XPS spectra of the (a) In3d$_{5/2}$ and (b) O1s peaks. (c-e) De-convolution of the high-resolution O1s spectra for the I-250, I-350 and I-450 samples. The main peak at 530.3 eV is attributed to indium oxide. The two additional shoulder peaks at 531.7 eV and 532.5 eV are attributed to oxygen vacancies in the structure and surface OH groups, respectively.

and 532.5 eV (Figure 14c-e). The peak at 531.7 eV is commonly attributed to the presence of oxygen vacancies in the structure$^{46,47}$ and is consistent with the observed n-type position of the Fermi-levels relative to the conduction bands (Figure 4c), which is typically a result of non-stoichiometry.$^{48}$ This vacancy 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 centre 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$^{42}$ and agrees well with the O1s spectra for the pure $\text{In(OH)}_3$ peak. From these plots in Figure 14c-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 \textit{in-situ} to determine how the surface may change during reaction.

The hydroxide content of the samples was investigated further by both Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric measurements. The intensity of the OH stretches in the FT-IR spectra (Figure 15) 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 \textit{in-situ} inside a thermogravimetric analyzer. The weight loss observed was attributed to hydroxide condensation to form bridging oxides. Figure 16 shows the weight loss of each sample after calcination under air flow for 3 hours. 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 this data and the Brunauer-Emmett-Teller (BET) surface area described below, we estimate that the surface hydroxide coverage is on the order of 6 µmol m$^{-2}$.

![Figure 15. FT-IR-ATR spectra of In(OH)$_3$, I-250, I-350 and I-450 films used in photocatalytic reactions.](image-url)
for I-250 and 3 μmol m\(^{-2}\) for I-350. It is important to note that the exact stoichiometry of the amorphous indium hydroxide precursor is unknown and therefore these values are only rough estimations. However, this data clearly indicates that there is a significant population of retained surface hydroxides present in the I-250 and I-350 samples. 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.

2.5.8 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 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 temperatures. Figure 17 shows the
surface-area-normalized CO₂ capture capacities for each sample plotted together with their corresponding CO production rates. There is a notable strong correlation between CO₂ reduction rates and the normalized CO₂ capture capacity.

2.5.9 Designing a surface for CO₂ photocatalytic activity

The affinity of a photocatalyst’s surface for CO₂ has been identified in this study, as well as in others, as a critical factor influencing photocatalytic activity. As Figure 17 demonstrates, the CO₂ capture capacity of the In₃O₃₋ₓ(OH)ₓ nanoparticles corresponds very well with photo-reactivity, indicating that CO₂ adsorption plays an important role in the light-driven reaction. Intuitively, CO₂ molecules must be able to approach and interact with the surface for a sufficient amount of time in order for electron transfer to occur. Surface hydroxides have a known affinity for the Lewis-acidic CO₂. This could explain the strong positive correlation between CO₂ 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 has a significantly lower CO₂ capture capacity. This indicates that surface hydroxides alone are not sufficient to facilitate CO₂ capture and photocatalytic reduction of CO₂.

![Figure 17. Comparison of CO₂ reduction rate and CO₂ capture capacity of In₃O₃₋ₓ(OH)ₓ. The white bars correspond to the surface area-corrected CO production rates at 150 °C and the blue diamonds correspond to the surface area-corrected CO₂ capture capacity of each sample at 150 °C.](image-url)
In addition to hydroxides, the surface of the $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ nanoparticles is also populated with oxygen vacancies. The presence of these oxygen vacancies in the $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ samples is supported by the de-convolution of the XPS O1s core level peaks (Figure 14c-e). 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 $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ 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 $\text{In}_2\text{O}_3$. The cubic $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ 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 $\text{In}_2\text{O}_3$ 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 $\text{In(OH)}_3$ 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 $\text{In(OH)}_3$ and I-250.

Surface oxygen vacancies may also form due to interactions between surface oxygen sites and H$_2$ or CO under elevated reaction temperatures. $\text{In}_2\text{O}_3$ has been investigated experimentally$^{52,53}$ and theoretically$^{28,54}$ 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). Bielz et al. have demonstrated that oxygen vacancies are generated on the surface of $\text{In}_2\text{O}_3$ in H$_2$ environments at temperatures greater than 125 °C, as shown in Equation 1:

$$\text{H}_2 + [\text{O}]_{\text{lattice}} \rightarrow \text{H}_2\text{O} + [\ ]_{\text{lattice}} \quad (1)$$

H$_2$ reduction of the surface under these reaction conditions may suggest the temperature dependence of the CO production rates for the $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ is due to the availability of surface oxygen vacancies (Figure 3c). As shown, 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. While the
photocatalytic production increases from 110°C to 150°C, the activity decreases at 170°C. The decrease in CO production at 170°C may be due to oxidation of CO by lattice oxygen on the In$_2$O$_{3-x}$(OH)$_y$ surface as shown in Equation 2.52

$$\text{CO} + [\text{O}]_{\text{lattice}} \rightarrow \text{CO}_2 + [\ ]_{\text{lattice}} \quad (2)$$

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.55 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 takes place between CO$_2$ and the surface oxygen vacancies, as outlined in Equation 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 3.

$$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad (3)$$

While we have observed water as a product, an exact reaction stoichiometry is 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.

### 2.6 Conclusion

A functional single component CO$_2$ reduction photocatalyst must have surface, optical, and electronic properties working in concert for photocatalytic reduction of CO$_2$ to occur in the gas phase. In this study the In$_2$O$_{3-x}$(OH)$_y$ nanoparticles demonstrate activity for the photocatalytic reduction of CO$_2$ in the presence of H$_2$ at temperatures as low as 130 °C using both ultraviolet and visible light. Our work strongly suggests that the observed activity of In$_2$O$_{3-x}$(OH)$_y$ samples is associated with surface populations of oxygen vacancies and hydroxides, which may act in concert as active sites for CO$_2$ adsorption and charge transfer under simulated solar irradiation.
We have produced a series of nanostructured In$_2$O$_{3-x}$(OH)$_y$ materials via a temperature controlled thermal dehydration of In(OH)$_3$. Using $^{13}$CO$_2$ as a tracer molecule, strong light and temperature-dependent photocatalytic reduction of gaseous $^{13}$CO$_2$ to $^{13}$CO is confirmed in the presence of H$_2$. The surface hydroxide and oxygen vacancy content strongly correlates with both an increase in $^{13}$CO$_2$ capture capacity and an increase in photocatalytic activity for $^{13}$CO production. By combining the favourable surface, electronic and optical properties of nanostructured In$_2$O$_{3-x}$(OH)$_y$ with the bixylite crystal structure and its enhanced CO$_2$ 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 CO$_2$ reduction photocatalysts for solar fuels production.

2.7 References


Chapter 3
Precursor Dependence of the Photocatalytic Activity of Indium Oxide Nanoparticles

3.1 Statement of Contributions

Dr. Le He performed the catalysis experiments. Dr. Kristine Liao performed the XPS measurements and assisted with the data processing and analysis. Jia Jia measured the TEM images. Laura Reyes performed the surface area measurements. I carried out all other synthesis, characterization, and experiments presented in this chapter. Portions of this chapter are currently being prepared for publication.

3.2 Abstract

Defected indium oxide nanoparticles, $\text{In}_2\text{O}_{3-x}(\text{OH})_y$, have been shown to function as active photocatalysts for $\text{CO}_2$ reduction under simulated solar irradiation. Herein we demonstrate that the choice of starting material has a strong effect on the photocatalytic activity of indium oxide nanoparticles. We examine four indium oxide materials prepared via the thermal decomposition of various In (III) salts and correlate their stability and photocatalytic activity to the number and type of defect present in the material. Further, we use $^{13}\text{CO}_2$ isotope-tracing experiments to clearly identify the origins of the observed carbon-containing products. Significantly, we find that the oxidizing nature of the precursor anion has a substantial impact on the defect formation within the sample. This study demonstrates the importance of surface defects in designing an active heterogeneous photocatalyst and provides valuable insight into key parameters for the precursor selection, design, and performance optimization of materials for gas-phase $\text{CO}_2$ reduction.

3.3 Introduction

The role of bulk and surface defects in determining the photocatalytic activity of metal oxide semiconductor photocatalysts has been an area of intense research.$^{1-4}$ In metal oxides, perhaps the most ubiquitous and well-studied type of defect is the oxygen vacancy.$^{5-7}$ These oxygen vacancies have been shown to have a significant impact on the optical and electronic
properties. Typically acting as donor states, they are generally cited as the primary reason for the n-type conductivity associated with most metal oxides. Oxygen vacancies can also act as important active sites in heterogeneous catalysis reactions, facilitating reactant adsorption and conversion. For example, in TiO$_2$, it has been suggested that surface oxygen vacancies act as charge traps, facilitating electron transfer to adsorbed species, while bulk oxygen vacancies simply act as recombination centers, lowering the excited state charge carrier lifetimes and adversely affecting the photocatalytic activity. Surface hydroxide groups have also been shown to play a key role in photocatalysis reactions. In many materials, they have commonly been associated with facilitating the adsorption of gaseous reactant species. Indeed, surface hydroxides have a known affinity for the Lewis-acidic CO$_2$, typically forming surface adsorbed carbonate or bicarbonate species. Several groups have reported positive correlations with hydroxide content, CO$_2$ capture capacity, and enhanced photocatalytic activity.

In the previous chapter, we demonstrated that defected indium oxide nanoparticles, In$_2$O$_{3-x}$(OH)$_y$, could function as active photocatalysts for CO$_2$ reduction to CO via the reverse water gas shift reaction (RWGS). We correlated both the photocatalytic activity and CO$_2$ capture capacity to the oxygen vacancy and surface hydroxide content of the In$_2$O$_{3-x}$(OH)$_y$ samples, suggesting both play a key role in the reaction mechanism. These samples were produced via thermal dehydration of indium hydroxide. During this reaction, adjacent hydroxide groups condense to form a bridging oxide and release water. We demonstrated that the calcination temperature during the synthesis of these nanoparticles had a strong effect on the amount of hydroxide groups retained within the sample: lower temperatures resulted in less condensation and formation of bridging oxide bonds, resulting in the retention of more hydroxides. We observed a strong positive correlation between CO$_2$ capture capacity and hydroxide content. However, an In(OH)$_3$ control sample, which had the highest hydroxide content, also has a significantly lower CO$_2$ capture capacity, even when corrected for surface area. This indicated that surface hydroxides alone are not sufficient to facilitate CO$_2$ capture and subsequent photocatalytic reduction of CO$_2$. However, due to the temperature-dependence of the synthesis, which affects the retention of both hydroxides and oxygen vacancies, it is difficult to separate and evaluate the effects these defects have on the reactivity of the different samples.

In order to gain better insight into the reaction mechanism and understand the role hydroxides and oxygen vacancies play in the formation of an active indium oxide-based photocatalyst, we
sought to make indium oxide from other non-hydroxide containing precursors. We examine the photocatalytic activity of four different indium oxide samples prepared via the thermal decomposition of various indium (III) salts. Our results demonstrate that the choice of starting material has a significant effect on the number and type of defects present in the material. In particular, we find that the oxidizing nature of the precursor anion has a substantial impact on the defect formation within the sample, which strongly correlates with the stability and photocatalytic activity. This work further illustrates the importance of surface defects in designing an active material capable of functioning as a heterogeneous photocatalyst for gas-phase CO$_2$ reduction.

3.4 Experimental

3.4.1 Synthesis of indium oxide nanoparticles

All chemicals were used as received without any further purification. Each of the indium oxide samples were made by calcining 0.8 g of the respective precursor - either indium (III) nitrate hydrate (Sigma Aldrich, 99.9%), indium (III) acetate (anhydrous, Acros Organics, 99.99%), or indium (III) chloride (anhydrous, Alfa Aesar, 99.99%) - at 250 °C for 3 hrs. The resulting powders were finely ground with a mortar and pestle. The calcined indium nitrate and calcined indium chloride samples were used without further purification. However, the calcined indium acetate sample contained an obvious brownish residue, so it was subjected to an additional purification step in which it was washed three times with deionized nanopure and separated via centrifugation. 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 powder was again finely ground with a mortar and pestle. As a control, a sample of indium oxide made from an indium hydroxide precursor was prepared as described in section 2.4.1 and calcined at 250 °C for 3 hrs.

High surface area indium oxide made from the indium (III) nitrate precursor was prepared via a SiO$_2$-templating method, illustrated in Figure 5. Indium (III) nitrate hydrate (3 g, Sigma Aldrich, 99.9%) was dissolved in 30 g of Ludox HS-40 colloidal silica nanoparticles (Aldrich, 40 wt% in water) and sonicated for 30 min to ensure homogeneity. The solution was dried overnight at 80 °C and the resulting solid was directly calcined at 250 °C for 3 hrs. After calcination the solid changed from white to pale yellow indicating the formation of indium oxide. This In$_2$O$_3$/SiO$_2$...
mixture was then ground with an agate mortar and pestle and the SiO$_2$ was removed by base etching. Specifically, the In$_2$O$_3$/SiO$_2$ powder sample was dispersed in 2M NaOH (10x excess by mass) and sonicated overnight (approximately 20 hrs). The suspension was then heated to 80 °C with a high stirring rate and heated for an additional 24 hrs. The resulting sample was separated via centrifugation and purified by washing five times with deionized nanopure water, sonicating between washings to ensure adequate removal of any trapped impurities. The final precipitate was dried overnight at 70 °C in a vacuum oven and finely ground with a mortar and pestle. Several control samples were also prepared. The indium nitrate was replaced with the indium hydroxide precursor (0.6 g, preparation described in detail in section 2.4.1), combined with 10 g of Ludox HS-40, sonicated, dried, calcined, etched, and purified in exactly the same way as described above. Additionally, two indium oxide samples (0.5 g, prepared without SiO$_2$ from standard indium nitrate and indium hydroxide precursors as described in the previous paragraph) were placed in 50 ml of 2M NaOH, exposed to the same basic etching conditions and purified in the same way as described above.

Sample films were prepared for photocatalytic testing by drop casting 20 mg of each sample powder - suspended via sonication in deionized, nanopure water (3 ml) - onto 1”x1” binder free borosilicate glass microfiber filters (Whatman, GF/F, 0.7 µm).

### 3.4.2 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 characterized by transmission electron microscopy using a Hitachi H-7000 TEM at 100 kV. The diffuse reflectance of the samples was measured using a Perkin Elmer Lambda 1050 UV/VIS/NIR spectrometer equipped with an integrating sphere with a diameter of 150 mm.

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. All data analyses were carried out using the Multipak fitting program and the binding energies were
3.4.3 Gas-phase photocatalytic measurements

Gas-phase photocatalytic rate measurements were conducted in a custom fabricated 1.5 mL stainless steel batch reactor with a fused silica view port sealed with Viton O-rings as described in section 2.4.3. Briefly, the reactors were evacuated using an Alcatel dry pump prior to being purged with H₂ gas (99.9995%) at a flow rate of 6 mL/min for 1 hour. The outlet valve was sealed and the reactors were injected with 1 atm of ¹³CO₂ (99.9 atomic % Sigma Aldrich). The inlet valve was then sealed and the reactors were heated to 150°C. The reactor temperatures were controlled by an OMEGA CN616 6-Zone temperature controller, with a thermocouple placed in contact with the sample. 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 (the spectral output is shown in Figure 1b in Chapter 2) for a period of 16 hours. Product gases 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 13a and 6’ Haysep D column. Isotope product gases were measured using an Agilent 7890A gas chromatographic mass spectrometer (GC-MS) with a 60 m GS-Carbonplot column fed to the mass spectrometer.
this sample has formed a mixture of crystalline indium oxy-chloride phases and no indium oxide phases are present. Figure 2 shows transmission electron microscope (TEM) images of the three samples that formed indium oxide phases. From the images it is clear that the sample morphology differs significantly between the samples. The hydroxide-based indium oxide sample (Figure 2a) is comprised of agglomerated nanoparticles with diameters less than ca. 10 nm. On the other hand, the nitrate-based indium oxide sample (Figure 2b) exhibits larger, more-faceted polydisperse nanoparticles in the range of 10-50 nm. The acetate-based indium oxide sample (Figure 2c) exhibits two distinct morphology types: very small nanoparticles (less than ca. 5 nm) and significantly larger rod-like structures.

Figure 3 shows the photocatalytic activity of the three indium oxide samples under 800 W m$^{-2}$ (0.8 suns) illumination at 150 °C under 2 atm of $^{13}$C-labelled $^{13}$CO$_2$ and H$_2$ in a 1:1 ratio (stoichiometric for the reverse water gas-shift reaction). As described in the previous chapter, $^{13}$C-labelling is essential to prove the source of the carbon containing products originates from

**Figure 1.** Powder X-ray diffraction patterns for samples made from different indium (III) precursors.

**Figure 2.** Transmission electron microscope (TEM) images of the three samples that formed indium oxide phases. (a) Indium oxide made from indium (III) hydroxide, (b) indium oxide made from indium (III) nitrate, and (c) indium oxide made from indium (III) acetate.
the reactant CO\textsubscript{2} and not from carbon contamination on the catalyst’s surface or in the reactor. Of the three samples tested, indium oxide made from both the hydroxide-based and acetate-based precursors showed activity for \textsuperscript{13}CO\textsubscript{2} reduction, while the nitrate-based indium oxide sample showed no evidence of CO or CH\textsubscript{4} production above the baseline level over the course of the 3 measurements. The hydroxide-based indium oxide sample produces pure \textsuperscript{13}C-labelled CO at a rate of 1.38 \textmu mol\cdot g\textsubscript{cat}\textsuperscript{-1}\cdot hr\textsuperscript{-1} with no evidence of any CH\textsubscript{4} production. This indicates, as reported in the previous chapter, that \textsuperscript{13}CO is the sole product of CO\textsubscript{2} reduction, originating from the reactant \textsuperscript{13}CO\textsubscript{2} gas and not from adventitious carbon contamination. The acetate-based indium oxide sample produced significant amounts of both CH\textsubscript{4} and CO. The CH\textsubscript{4}, produced at an average of 0.37 \textmu mol\cdot g\textsubscript{cat}\textsuperscript{-1}\cdot hr\textsuperscript{-1}, consists entirely of \textsuperscript{12}CH\textsubscript{4} and decreases in concentration over the course of the 3 measurements, indicating that all CH\textsubscript{4} can be attributed to carbon contamination. This is likely a result of residual acetate decomposition products that were not removed during calcination or the additional purification step. Indeed as the UV-visible reflectance spectra in Figure 4a illustrate, the acetate-based sample displays a considerable absorbance tail throughout the visible portion of the spectrum compared to the nitrate- and hydroxide-based samples. Its light brown color, when compared to the pale yellow color of the other two indium oxide samples, suggests that despite this extra purification step, a significant quantity of carbonaceous material remains. The acetate-based indium oxide sample also produced CO at an average rate of

![Figure 3. Photocatalytic performance of the three indium oxide samples made from different precursors under 800 W m\textsuperscript{-2} (0.8 suns) illumination at 150 °C. All values for carbon monoxide or methane production were confirmed using isotope tracing. Only \textsuperscript{13}C labelled products originate from \textsuperscript{13}CO\textsubscript{2} reduction. \textsuperscript{12}C labelled products are a result of carbon contamination in the sample or in the reactor.](image)
0.63 μmol·g_{cat}^{-1}·hr^{-1}. However, isotope tracing experiments revealed that 15% of that signal comes from $^{12}$CO, indicating that while some of the CO produced is a result of direct $^{13}$CO$_2$ reduction, a significant portion of the CO signal arises from carbon contamination. The interpretation of this CO production data is further complicated by the fact surface reactions between CO$_2$ and adventitious carbon can also produce $^{13}$C-labelled products. Yang et al. have demonstrated using in-situ DRIFT spectroscopy that the reverse Boudard reaction (Equation 1) can be a significant source of $^{13}$CO.

$$^{13}\text{CO}_2 + ^{12}\text{C}_{\text{surf}} \rightarrow ^{13}\text{CO} + ^{12}\text{CO}$$

In this reaction, gaseous CO$_2$ reacts with surface carbon to produce two CO molecules, one originating from $^{13}$CO$_2$ and the other resulting from the oxidation of the surface carbon species. Although this still results in $^{13}$CO production, it is not indicative of any intrinsic catalytic property of the material. For example, if all of the $^{12}$CO was produced via Equation 1, only 70% of the CO signal, 0.44 μmol·g_{cat}^{-1}·hr^{-1}, can be attributed to $^{13}$CO production by the acetate-based indium oxide sample. The high percentage of residual carbon content complicates drawing conclusions about the photocatalytic activity of this sample and illustrates the importance of controlling the carbon content of any material intended to be studied as a CO$_2$ reduction.

**Figure 4.** UV-visible reflectance spectra of indium oxide samples prepared from different precursors.
photocatalyst. For these reasons, as well as the substantially different morphology of the acetate-based sample, I will focus only on the comparison of the hydroxide-based and nitrate-based indium oxide samples in the rest of this chapter.

3.5.2 Investigating the effects of surface area on photocatalytic activity

Surface area is an important factor in heterogeneous photocatalysis so in order to understand the difference in activity between the nitrate-based and hydroxide-based indium oxide samples, we measured their BET surface areas and found that there was a stark difference: 3 m$^2$/g for nitrate-based sample and 125 m$^2$/g for the hydroxide-based sample. Because the photoreduction of CO$_2$ on indium oxide is a surface-mediated reaction, the significantly lower surface area of the nitrate-based sample could be the sole cause for the lack of activity reported in Figure 3. In order to be able to more directly compare the nitrate- and hydroxide-based samples, we sought to synthesize a higher surface area nitrate-based indium oxide sample. As we showed in the previous chapter, the calcination temperature has a significant impact on the catalytic activity, so we needed to maintain the calcination time and temperature while still being able to tune the surface area. Because indium oxide is generally considered to be very stable under basic conditions, we chose to use SiO$_2$ spheres as an inert template, which could then be etched away using a strong base. In this process, illustrated in Figure 5, the indium nitrate precursor is dissolved in an aqueous suspension of SiO$_2$ nanoparticles and allowed to dry slowly overnight, encapsulating the SiO$_2$ nanoparticles within the indium nitrate salt and forming a solid plug of material at the bottom of the reaction vessel. Once dry, the sample is then put directly into a pre-

![Figure 5. Schematic illustration of the SiO$_2$ templated synthesis of high surface area indium oxide from the indium (III) nitrate precursor.](image-url)
heated oven and calcined for 3 hours at 250 °C to convert the indium nitrate into indium oxide. To remove the SiO₂, the sample is mechanically ground into a fine powder and then dispersed in a strongly basic solution. In order to reduce particle aggregation and ensure as much of the SiO₂ is exposed to the basic solution as possible, this suspension was sonicated overnight prior to heating at 80 °C for 24 hours to complete the etching procedure. The resulting fine powder was washed extensively with deionized water to remove impurities.

Figure 6. (a) TEM micrograph of the high surface area (HSA) indium oxide sample prepared from indium nitrate via the SiO₂ templating method. (b) Powder X-ray diffraction patterns of indium oxide samples prepared from indium nitrate or indium hydroxide. (c) Comparison of surface area, crystallite size, and optical band gap of the different indium oxide samples. The crystallite size was calculated from the PXRD patterns using the Scherrer equation. The band gap was calculated by fitting the reflectance data using the Kubelka-Munk approximation and extrapolating the linear portion of the K-M absorbance onset. Full details of this fitting process are given in Figure 5 in Chapter 2. (d) UV-visible reflectance spectra of the indium oxide samples.
Figure 6a shows an TEM image of the high surface area (HSA) nitrate-based sample prepared using this method. The highly porous structure is evident from this image and BET gas adsorption measurements indicate that surface area of the nitrate sample was increased from 3 m²/g to 181 m²/g. The PXRD patterns in Figure 6b show the comparison of the HSA-nitrate-based sample with the original nitrate-based sample and the hydroxide-based sample. As the PXRD pattern indicates, the HSA-nitrate sample is comprised of pure crystalline indium oxide. No evidence of any crystalline side phases or residual amorphous SiO₂ is observed. The peaks of the HSA-nitrate sample show significant broadening relative to the nitrate- and hydroxide-based samples, indicating a decrease in particle size. The average crystallite sizes, calculated using the Scherrer equation, are shown in Figure 6c. The nitrate-based sample has the sharpest peaks and largest crystallite size, which correlates well with its low surface area. The hydroxide-based sample has an intermediate crystallite size and surface area, while the HSA-nitrate-based sample has the smallest average crystallite size and largest surface area, indicating that the SiO₂-templating method is effective at producing high surface area, crystalline indium oxide. Figure 6d shows UV-Vis reflectance spectra for all three samples. Both nitrate-based samples appear to be slightly blue-shifted relative to the hydroxide sample. However, by fitting the linear portion of the K-M absorbance, we are able to extract information about the band gap for the three samples which is quite similar (Figure 6c).

The photocatalytic activity of the hydroxide-based, nitrate-based, and HSA-nitrate-based indium oxide samples is shown in Figure 7. No evidence of any CO or CH₄ was detected for either nitrate-based sample, indicating that surface area alone is not responsible for the low activity of the nitrate-based samples.
Figure 8. XPS survey spectra of (a) \( \text{In}_2\text{O}_3 \) from hydroxide, (b) \( \text{In}_2\text{O}_3 \) from nitrate, and (c) high surface area \( \text{In}_2\text{O}_3 \) from nitrate.
3.5.3 Characterization of defect formation as a function of indium oxide precursor

In order to better understand why the nitrate-based samples are inactive, XPS measurements were performed to characterize the defects present in the indium oxide samples, as well as confirm the sample composition to determine if there are any impurities which might be adversely impacting the photocatalytic activity. Figure 8 shows the survey spectra for all three samples, which are remarkably similar. No nitrogen signal is observed in either of the nitrate-based samples (Figure 8b and c). The N 1s peak should appear at a binding energy between 397-408 eV, however there is no evidence of any signal in this region of the spectrum. This indicates that nitrogen is sufficiently removed upon calcination of the indium nitrate and should not affect the photocatalytic performance of the nitrate-based samples. The only obvious difference in these spectra is the appearance of Si 2s and 2p peaks at 157 ev and 105 eV, respectively in the HSA-nitrate-based sample (Figure 8c). This is likely due to residual SiO\textsubscript{2} nanoparticles that were completely encapsulated by indium oxide and therefore inaccessible to the NaOH etching solution. It is unlikely that residual SiO\textsubscript{2} nanoparticles had a negative impact on the photocatalytic activity of the HSA-nitrate-based samples. All of our photocatalytic tests reported herein were performed on glass microfiber filters, which are primarily silica-based and indeed silica is often used as an inert support for many heterogeneous catalysts. Based on these results, we do not expected that impurity atoms are responsible for the difference in reactivity between the hydroxide-based and nitrate-based indium oxide samples.

Another possible reason for the difference in activity between the samples could be related to the type and quantity of defects within the indium oxide itself. In the previous chapter I discussed the effect of calcination temperature on the photocatalytic activity of the indium oxide samples and the strong correlation of activity to both oxygen vacancies and surface hydroxides. As the calcination temperature was increased, the quantity of both hydroxide and oxygen vacancy defects decreased, as did the photocatalytic activity. In this chapter, all samples were calcined at the same temperature, 250 °C, however as the O1s core level peaks shown in Figure 9 indicate, there is substantial difference between the three indium oxide samples. The shoulder peak that appears at higher binding energies indicates that there is more than one chemical state of oxygen present in the structure. Indeed, the O1s peak can be de-convoluted into three distinct peaks: the main oxide peak at 529.9 eV and two additional peaks at 531.0 eV and 532.1 eV (Figure 9b-d).
The peak at 531.0 eV is commonly attributed to the presence of oxygen vacancies in the structure and the peak at 532.1 eV is generally attributed to surface OH groups.\textsuperscript{25} From these plots, one can obtain a qualitative understanding of the relative differences in defect type and quantity in the three indium oxide samples. As shown in Figure 9a, the regular nitrate-based and the hydroxide-based samples have shoulder peaks with similar intensities, however the primary difference between them is their shape. The nitrate-based sample has a higher signal at higher binding energies, indicating a greater contribution from hydroxides (Figure 9c), while the

\textbf{Figure 9.} Comparison of XPS spectra for indium oxide samples prepared from either indium hydroxide or indium nitrate. (a) Overlay of the O1s peaks for all samples. Qualitative de-convolution of the O1s peaks for indium oxide prepared from (b) indium hydroxide, (c) indium nitrate, and (d) high surface area indium nitrate. The main peak at 529.9 eV is attributed to indium oxide. The two additional shoulder peaks at 531.7 eV and 532.5 eV are attributed to oxygen vacancies in the structure and surface OH groups, respectively.
hydroxide-based sample has a higher intensity at intermediate binding energies, indicating a greater contribution from oxygen vacancies (Figure 9b). Indeed the hydroxide sample has the highest contribution from oxygen vacancies of all three samples that were measured. The HSA-nitrate-based sample has the highest shoulder peak overall, and has a substantial contribution in the hydroxide region (Figure 9d), which is not surprising given that this sample was prepared by etching in strong base for two days. These results indicate that this difference in hydroxide and oxygen vacancy content between the nitrate-based and hydroxide-based samples could be responsible for the observed difference in photocatalytic activity.

3.5.4 Investigating the effect of precursor choice on sample stability under basic conditions

Because the synthesis of the HSA-nitrate sample necessitated strongly basic etching conditions to remove the SiO$_2$ template, it is important to establish if this treatment could have adversely affected its reactivity. As a control, a sample of hydroxide-based indium oxide, which has been studied in detail in the previous chapter, was subjected to identical conditions with the intent to test its photocatalytic activity and compare it to the HSA-nitrate-based sample. However, as the powder X-ray diffraction pattern in Figure 10a indicates, the indium oxide sample, which originally was comprised of pure crystalline indium oxide prior to etching, was converted into pure crystalline In(OH)$_3$ following the etching procedure. This was quite a surprising result because the HSA-nitrate-based sample withstood this treatment very well and showed no evidence of In(OH)$_3$ formation. Figure 10d shows the PXRD patterns of the HSA-nitrate sample before and after base etching to remove its SiO$_2$ template. The diffraction pattern before etching shows a broad amorphous peak around 22 degrees 2 theta, originating from the amorphous SiO$_2$ nanoparticles, but the rest of the pattern is comprised of crystalline indium oxide. The diffraction pattern after etching shows pure crystalline indium oxide with no evidence of any other phases, crystalline or amorphous. This raises two questions: how does the presence of SiO$_2$ affect sample stability under etching conditions? And is there something chemically different about the nitrate-based indium oxide vs. the hydroxide-based indium oxide?

To answer these questions, I subjected two additional samples to the same basic etching conditions: a pure nitrate-based indium oxide sample (made without SiO$_2$) and a hydroxide-based sample that was combined with SiO$_2$, dried and calcined in exactly the same way as the HSA-nitrate-based sample. The result of etching the pure nitrate-based sample is shown in
Figure 10b. While the nitrate-based indium oxide started out as a highly crystalline indium oxide sample, after etching the diffraction pattern shows a mixture of crystalline indium oxide and crystalline In(OH)$_3$. This demonstrates that the pure nitrate-based sample is not as stable as the HSA-nitrate-based sample that was etched in the presence of SiO$_2$. The result of etching the second hydroxide-based control sample is shown in Figure 10c. The diffraction pattern before etching is completely amorphous, despite increasing the data collection time to enhance the signal to noise ratio. It is possible that the presence of the SiO$_2$ template inhibited the formation of the indium oxide, however the sample turned pale yellow after calcination, which is indicative of indium oxide formation. It is also possible that the indium oxide particles are so small, due to the presence of the SiO$_2$ template that they do not diffract well enough to be seen over the
Regardless of whether indium oxide was or was not formed, it is very interesting to note that, as shown in the diffraction pattern after etching, the sample does not form crystalline In(OH)$_3$ under the basic etching conditions. In fact, this weakly crystalline pattern is almost identical to the starting diffraction pattern of the original indium hydroxide precursor (Figure 11). From these data, we can conclude that SiO$_2$ is preferentially etched over indium-containing species and the presence of SiO$_2$ seems to inhibit the formation of crystalline In(OH)$_3$, likely by preferentially consuming hydroxide ions.

Additionally it is evident that nitrate-based samples are significantly more stable than hydroxide-based samples under these conditions. A possible explanation for this enhanced stability of nitrate-based samples under basic conditions could be explained by the differences in thermal decomposition reactions of the indium nitrate and indium hydroxide precursors. When indium hydroxide decomposes, it releases water via Equation 2:

$$2 \text{In(OH)}_3 \rightarrow \text{In}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (2)$$

However, when indium nitrate decomposes, it releases a significantly more oxidizing gas mixture, specifically NO$_2$ and O$_2$, as shown in Equation 3:

$$2 \text{In(NO}_3)_3 \rightarrow \text{In}_2\text{O}_3 + 6\text{NO}_2 + \frac{3}{2}\text{O}_2 \quad (3)$$

As the indium nitrate decomposes and begins forming indium oxide, the NO$_2$ that gets released can oxidize surface vacancies that are formed in the sample, as illustrated in Figure 12a. NO can easily be re-oxidized to NO$_2$ under our reaction conditions,$^{27}$ via Equation 4:
NO + \( \frac{1}{2} \) O\(_2\) \( \rightarrow \) 2 NO\(_2\) \hspace{1cm} (4)

and continue to oxidize the surface of the nitrate-based indium oxide sample. Without this coordinatively unsaturated indium site, it is now much more difficult for the surface to react with hydroxide ions during the etching procedure, as illustrated in Figure 12b. XPS data for both nitrate-based samples (Figure 9c and d) indicate a significant contribution to the O1s core level peak from oxygen vacancies, however if these vacancies are buried within the bulk of the sample, they would not be accessible to react with the evolving gases and therefore would be retained in the sample, even under these oxidizing conditions. It is unlikely that all vacancies would be consumed via this oxidation mechanism, which could explain why the nitrate-based sample (without SiO\(_2\)) was partially converted to In(OH)\(_3\) under the etching conditions.

The hydroxide-based sample on the other hand is not subjected to such oxidizing conditions during its formation and retains a significantly higher proportion of its oxygen vacancies. This makes these samples much more susceptible to attack by hydroxide ions during the etching procedure, as illustrated in Figure 13c. This could explain why neither one of the hydroxide-based indium oxide samples could withstand the etching conditions.

**Figure 12.** Schematic illustration of hydroxide attack on (a) a hydroxylated indium oxide surface and (b) a hydroxylated surface with oxygen vacancies.
3.5.5 Correlation of surface defects to photocatalytic activity

The oxidizing nature of the nitrate-based indium oxide formation environment may also help to explain the significant difference in reactivity between the nitrate-based and hydroxide-based samples. Much in the same way that a coordinatively unsaturated indium site appears necessary to facilitate the conversion of indium oxide into In(OH)_3 under basic conditions, this higher energy sites could also function as the active site for CO_2 reduction. As we demonstrated in the previous chapter, higher defect concentrations in hydroxide-based indium oxide corresponded to significantly higher photocatalytic activity. In this chapter we have shown, using XPS spectroscopy, that both the nitrate-based and hydroxide-based samples have a significant quantity of hydroxide groups. However as we discussed in the previous chapter, surface hydroxide groups alone are not enough to explain the photocatalytic activity and suggested that both surface oxygen vacancies and hydroxide groups are required in an active photocatalyst. The HSA-nitrate-based sample has a comparable surface area and an even higher concentration of surface hydroxide groups than the hydroxide-based sample, however it shows no evidence of photocatalytic activity for CO_2 reduction. Its stability under basic etching conditions indicates that the surface of this sample is very stable and likely lacks the coordinatively unsaturated indium sites (oxygen vacancies) needed to facilitate CO_2 reduction. The hydroxide based sample on the other hand, has both hydroxide groups as well as these coordinatively unsaturated indium surface sites, making it unstable under basic etching conditions and active as a photocatalyst for CO_2 reduction. This stark difference in photocatalytic activity provides further evidence to support the hypothesis that a combination of surface defects – both oxygen vacancies and hydroxides – are crucial to preparing an active surface capable of driving photocatalytic reduction.

3.6 Conclusions

In this study we have demonstrated that the choice of precursor has a strong effect on the photocatalytic activity of indium oxide nanoparticle samples. The oxidizing nature of the reaction atmosphere during the nanoparticle synthesis plays a significant role in the defect formation within the sample. Precursors, such as indium nitrate, that release oxidizing gases will produce indium oxide nanoparticles with a reduced number of surface oxygen vacancies, rendering this material inactive as a photocatalyst. On the other hand, precursors such as indium
hydroxide, which produce more mild gaseous byproducts, allow the retention of more of these surface oxygen vacancies and correlates to higher photocatalytic activities. We have further confirmed that while hydroxide groups may be important to the overall CO$_2$ reduction reaction, simply increasing the concentration of hydroxide groups alone will not make a more active catalyst. These results show that surface defect sites generated during indium oxide synthesis play an important role in determining the final photocatalytic activity. This study provides valuable insight into key parameters for the precursor selection, materials design, and performance optimization of heterogeneous gas-phase CO$_2$ reduction photocatalysts.

### 3.7 References


Chapter 4
Probing the Carrier Dynamics in Nanocrystalline In$_{2}$O$_{3-x}$(OH)$_{y}$ Films: The Role of Surface Defects and Implications for Photocatalysis

4.1 Statement of Contributions
Dr. Paul Szymanski performed the transient absorption experiments, spectral modeling, and assisted with the analysis. Dr. Le He performed the catalysis experiments. Dr. Kristine Liao collected the XPS measurements. Dr. Qiao Qiao measured the HR-STEM images. I carried out all other synthesis, characterization, experiments and analysis presented in this chapter. Portions of this work are currently being prepared for publication.

4.2 Abstract
The photocatalytic activity of indium oxide (In$_{2}$O$_{3-x}$(OH)$_{y}$) is strongly correlated to the number of oxygen vacancy and hydroxide defects present in the system. In order to better understand how defects affect photo-generated electrons and holes in these materials, we have studied the relaxation dynamics of three In$_{2}$O$_{3-x}$(OH)$_{y}$ samples with varying concentration of defects using two different excitation energies corresponding to above band gap (318 nm) and near band gap (405 nm) excitation. Our results demonstrate that defects play a significant role in the excited state charge relaxation pathways. Higher defect concentrations correspond to enhanced near-IR absorption on short time scales which is indicative of charge trapping by oxygen vacancies close in energy to the conduction band edge. At longer times ($\tau > 10$ ns) a significant enhancement in the signal around 450 nm is observed in the In$_{2}$O$_{3-x}$(OH)$_{y}$ sample with the greatest number of defects and is attributed to hole trapping in hydroxide groups with energy states near the valence band edge. The relaxation behavior of charge carriers excited with energy significantly above the band gap is distinct from charge carriers excited with energies near the band gap. Near band gap excitation preferentially populates surface traps states and leads to longer lifetimes. Above band gap excitation results in the production of more energetic charge carriers which are more mobile, leading to increased electron-hole recombination and shorter excited state lifetimes. In all cases, In$_{2}$O$_{3-x}$(OH)$_{y}$ samples with higher defect concentrations lead to longer excited state lifetimes,
which may be due to improved charge separation as a result of charge trapping, and correlates well with observed trends in photocatalytic activity. This enhanced understanding of the role defects play in determining optoelectronic properties and charge carrier dynamics in defected In$_2$O$_{3-x}$(OH)$_y$ can provide valuable insight towards the rational development of more efficient photocatalytic materials.

4.3 Introduction

In the previous two chapters, we have demonstrated that defected In$_2$O$_{3-x}$(OH)$_y$ nanoparticles function as an effective gas phase photocatalyst for the reduction of CO$_2$ to CO via the reverse water gas shift reaction (RWGS). This reactivity strongly correlates to the number and type of defect present in the system. In particular a combination of both oxygen vacancies (O$_v$) and hydroxides (OH) appear to be necessary to facilitate efficient CO$_2$ reduction at the surface of indium oxide.$^{1,2}$ To help us gain insight into how to design a more efficient photocatalyst, we sought to probe more deeply into the optoelectronic properties of this defected In$_2$O$_{3-x}$(OH)$_y$ to better understand how these defects affect photo-generated electrons and holes in these materials.

Transient absorption (TA) spectroscopy is a powerful technique that enables the detection of excited state charge carriers on the femtosecond ($10^{-15}$ s) to millisecond timescales and has been used extensively to understand the optoelectronic properties of semiconductor metal oxide materials.$^3$–$^{10}$ This detailed understanding of the processes which govern the relaxation dynamics of photoexcited electrons and holes has resulted in significant improvements in the performance of semiconductor nanomaterials and composites in a wide variety of applications, most notably in photovoltaics$^{11,12}$ and photocatalysis.$^{12}$ In both cases, the performance depends strongly on the excited state lifetime of the photoexcited charge carriers, with longer lifetimes affording more opportunity for the electrons or holes to perform their desired function. In photocatalysis, it is necessary for these photogenerated electrons and holes to migrate to the surface of the nanoparticle where they can participate in useful chemistry, reducing or oxidizing adsorbed species.$^8$,$^{12}$ By understanding the processes which lead to fast charge carrier recombination, researchers have been able to intentionally engineer materials to reduce the occurrence of undesired recombination pathways, enhancing overall reactivity.$^{12}$

In semiconductors, when a photon with sufficient energy is absorbed to create an electron/hole pair, these excited state charge carriers can follow many different pathways to relax back down
to the ground state. TA spectroscopy probes these relaxation processes by exciting the sample with a short, single-wavelength “pump” pulse to populate higher energy states, and then measures the changes in absorption using a broadband “probe” pulse at different time delays following the initial excitation. The path towards equilibrium of these excited state charge carriers is influenced by numerous factors, such as nature of the electronic band structure, surface and bulk defects, trap states, and interactions with other charge carriers, all of which will affect the relaxation dynamics apparent in the TA spectra.\textsuperscript{10,13,14} By modeling the TA decay as a function of both time and wavelength a more detailed understanding of the dominant charge carrier relaxation processes can be obtained.\textsuperscript{8,13,14}

Many studies have demonstrated that defects within a material can have a substantial impact on the relaxation dynamics.\textsuperscript{3,9,10,13–15} Generally, defects are associated with the creation of mid band gap states. These defect states can function as electron or hole traps that facilitate charge separation, prolonging excited state lifetimes. Conversely, they can also act as charge recombination centers that facilitate the rapid recombination of photoexcited electrons and holes, reducing excited state lifetimes. Their chemical nature and location within the band gap largely determines their role in the relaxation pathway.\textsuperscript{8–10,13,14} In metal oxides, both bulk and surface oxygen vacancies can act as traps for excited state electrons,\textsuperscript{8,16,17} while surface hydroxyl groups typically function as hole traps.\textsuperscript{8,9}

Another key factor in determining the relaxation pathway is the initial potential of the charge carriers, which is determined by the energy of the photons hitting the sample.\textsuperscript{8,14} Triggiani et al have demonstrated in colloidal anatase TiO\textsubscript{2} nanorods that excitation energies above the band gap produce charge carriers with sufficient energy to behave independently, exhibiting distinct relaxation dynamics for electrons and holes.\textsuperscript{8} Because of their excess energy, these charge carriers are more mobile and can undergo a variety of processes as they relax down to the ground state, such as trapping, de-trapping, and hopping between states. This enhanced mobility resulted in significantly reduced excited state lifetimes. On the other hand, when they used excitation energy resonant with the band gap of TiO\textsubscript{2} they found that the excited electrons and holes did not behave independently of one another and instead behaved as coulombically bound excitons. They attribute this to the direct formation of charge carriers trapped in surface defect states. Because of the lower initial excitation energy, the electrons and holes were trapped in localized
states, resulting in longer excited state lifetimes. In general, compared to free excitons, bound excitons give rise to lower carrier mobilities.\textsuperscript{18–20}

Although the optoelectronic properties of indium oxide have been widely studied in relation to its use as a transparent conductive oxide material,\textsuperscript{17,21,22} to our knowledge only one other group has looked at these processes in detail using TA spectroscopy.\textsuperscript{23,24} Tsokkou et al. examined the charge carrier relaxation dynamics of both In\textsubscript{2}O\textsubscript{3} nanoparticles\textsuperscript{23} and gold-decorated In\textsubscript{2}O\textsubscript{3} nanorods.\textsuperscript{24} In both samples they observed average excited state lifetimes from 110 ps to 1.5 ns depending on the pump fluence and indicated that both shallow and deep trap states played a significant role in the carrier dynamics. However, these In\textsubscript{2}O\textsubscript{3} samples were prepared at very high temperatures (1000 °C and 700 °C, respectively) and are essentially stoichiometric, containing a minimal numbers of defects. In order to understand how these processes work in photocatalytically relevant samples, a detailed understanding of the charge carrier relaxation dynamics in highly defected indium oxide In\textsubscript{2}O\textsubscript{3-x}(OH\textsubscript{y}) samples is necessary.

In this work, we have used transient absorption spectroscopy to study the relaxation dynamics of three photocatalytically active In\textsubscript{2}O\textsubscript{3-x}(OH\textsubscript{y}) samples prepared with varying concentrations of surface hydroxide and oxygen vacancy defects. We use two different excitation energies corresponding to above band gap (318 nm) and near band gap (405 nm) excitation to better understand how excited state charge carriers with different potential energies interact with the different defect states available within the samples. By studying these two photocatalytically relevant excitation regimes, we can gain a better understanding of how In\textsubscript{2}O\textsubscript{3-x}(OH\textsubscript{y}) might behave under broadband solar irradiation. Using multi-exponential functions to fit the data, we are able to extract information on various relaxation processes occurring within the sample at both short and long time scales. Finally, we discuss the role these defects states play in determining photoexcited charge carrier localization, excited state lifetimes, and ultimately correlation with the photocatalytic activity of the samples. Our results demonstrate that defects play a significant role in the excited state charge carrier relaxation pathways. This enhanced understanding of the interplay between the optoelectronic properties and photocatalytic activity of defected In\textsubscript{2}O\textsubscript{3-x}(OH\textsubscript{y}) can help to facilitate the rational design and synthesis of efficient photocatalytic materials.
4.4 Experimental

4.4.1 Synthesis of In$_2$O$_{3-x}$(OH)$_y$ nanoparticles

The synthesis of the In$_2$O$_{3-x}$(OH)$_y$ nanoparticles has been described in Section 2.4.1. Briefly, an amorphous indium hydroxide precursor was synthesized by dissolving indium(III) chloride (3.6 g, 16.2 mmol, Sigma Aldrich, 98%) in a 3:1 solution of anhydrous ethanol (54 ml, Commercial Alcohols) and deionized, nanopure water (18 ml, resistivity 18.2 MΩ cm). A separate solution of 3:1 mixture of ethanol (54 ml) and ammonium hydroxide (18 mL, Caledon, 28-30 % adjusted to 25 wt% with deionized water) was rapidly added, resulting in the immediate formation of a white precipitate. The resulting suspension was immediately immersed in a pre-heated oil bath at 80 °C and stirred at a high rate for 10 min. 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 250 °C. Sample films were prepared for photocatalytic testing by drop casting 20 mg of sample powder - suspended via sonication in deionized, nanopure water (3 ml) - onto 1”x1” binder free borosilicate glass microfiber filters (Whatman, GF/F, 0.7 µm).

4.4.2 Physical characterization

Powder X-ray diffraction (PXRD) was performed on a Bruker D2-Phaser X-ray diffractometer, using Cu Kα radiation at 30 kV. Sample morphology was determined using high angle annular dark field (HAADF) high resolution scanning transmission electron microscopy (HR-STEM). The images were taken with a Nion UltraSTEM200 at 200 kV. The low magnification HAADF-STEM images were taken with a JEOL ARM200CF at 200 kV. Both of these microscopes are aberration corrected. 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 150 mm.

4.4.3 Catalysis measurements

Gas-phase photocatalytic rate measurements were conducted in a custom fabricated 1.5 mL stainless steel batch reactor with a fused silica view port sealed with Viton O-rings as described in section 2.4.3. Briefly, the reactors were evacuated using an Alcatel dry pump prior to being
purged with H₂ gas (99.9995%) at a flow rate of 6 mL/min for 1 hour. The outlet valve was sealed and the reactors were injected with 1 atm of ¹³CO₂ (99.9 atomic % Sigma Aldrich). The inlet valve was then sealed and the reactors were heated to 150°C. The reactor temperatures were controlled by an OMEGA CN616 6-Zone temperature controller, with a thermocouple placed in contact with the sample. 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 (the spectral output is shown in Figure 1b in Chapter 2) for a period of 16 hours. Product gases 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 13a and 6’ Haysep D column. Isotope product gases were measured using an Agilent 7890A gas chromatographic mass spectrometer (GC-MS) with a 60 m GS-Carbonplot column fed to the mass spectrometer.

4.4.4 Transient absorption spectroscopy measurements

Measurements were carried out with a Helios UV-visible spectrometer (Ultrafast Systems), which is illustrated schematically in Figure 1. Two different pump wavelengths were used to compare above-optical-band-gap (318 nm) with near-band-gap (405 nm) excitation. Pump light at 318 nm was obtained from the fourth harmonic of the signal from a Coherent OPerA Solo optical parametric amplifier which was pumped by a Coherent Libra regeneratively-amplified Ti:sapphire laser (809 nm, 50 fs pulses, 1 kHz repetition rate). The fundamental laser output was passed through a β-BaB₂O₄ crystal, then spectrally filtered by a wavelength-selective mirror and glass long-pass filter, to produce pump light at the second harmonic wavelength of 405 nm. A series of movable mirror mounts was used to quickly select the desired pump beam. A broadband probe beam was produced by focusing a small fraction of the fundamental wavelength into a sapphire or CaF₂ crystal. Both pump and probe were focused and overlapped on the surface of the substrate. The transmitted probe light is used to determine the transient absorption by focusing it into a fiber-coupled Si array detector with a detection range of 300–907 nm. Scattered pump light is blocked by a long-pass filter or UV band-pass filter placed before the detector. A rotating mechanical chopper blocks every other pump pulse with the difference between two consecutive spectra — one with the pump beam, and one without — yielding the TA signal ΔA(t), where t is the time delay between pump and probe pulses.
Figure 1. Schematic illustration of the transient absorption setup. The diagram in the top left corner illustrates how the pump and probe beams overlap on the sample.

The spot size of the pump beam incident on the sample is used to determine the fluence, or energy per laser pulse divided by the irradiated area. For one-photon absorption, the number of absorbed photons is proportional to the incident fluence. The spatial profile of the laser beam spot on the sample surface is approximately a two-dimensional Gaussian. The radius of the beam is defined as the length over which the intensity falls from the maximum to $1/e^2$ times the maximum. This radius was measured by the knife-edge method, in which a beam block with a straight edge (in this case, a razor blade) is translated through the laser spot and the power is recorded as function of the beam block position. The razor blade was placed in the Helios sample holder and translated by a Newport NSA12 motorized actuator, with the power measured by a calibrated Si photodiode optical power sensor (Newport 818-UV).

Data was analyzed in MATLAB (Mathworks) software using the Nedler-Mead simplex algorithm for fitting. Each data set, collected with a single pump wavelength, incident pump fluence, and a series of probe wavelengths ($\lambda$), was fit to a sum of exponentials (described in more detail in Section 4.5.3). When fitting dynamics for $\lambda < 400$ nm, the negative ground-state bleach signals are treated as positive for easier comparison with data at other probe wavelengths.
For estimating uncertainties in the parameters, the bootstrap Monte Carlo method was used with 1000 simulated data sets for each experimental data set. For each parameter, the distribution of fit values was analyzed to find the width of the central 68% of the distribution to obtain the standard deviation. The standard deviations are quoted after the "±" in the tables of fit parameters.

4.5 Results and Discussion

4.5.1 Physical characterization of the In$_2$O$_{3-x}$(OH)$_y$ nanoparticles

In order to gain a better understanding of the role surface and bulk defects have in determining the optoelectronic properties of indium oxide nanoparticles, we have prepared indium oxide samples with different concentrations of oxygen vacancy and surface hydroxide groups. As previously shown in Chapter 2, this can be achieved by controlling the calcination temperature during the thermal dehydration reaction of indium hydroxide. The atomic rearrangement and associated loss of water from the lattice during the conversion of indium hydroxide to cubic bixbyite indium oxide requires significant thermal energy and will not occur below 210 °C. As the calcination temperature is increased, there is more thermal energy available to allow atomic rearrangement that minimizes the surface energy. This affords significant control over the defects present in the final material. Indium oxide samples prepared at temperatures close to this transition temperature would not have sufficient thermal energy to enable the passivation of many of the defects formed and, as a result, would contain a higher proportion of defects such as residual surface hydroxide groups and coordinatively unsaturated indium sites (oxygen vacancies) which could play a significant role in determining the optoelectronic properties responsible for driving the photocatalytic reduction of CO$_2$. To this end we have prepared indium oxide samples calcined at three different temperatures, 250 °C, 350 °C and 450 °C. For clarity these samples will be referred to as I-250, I-350, and I-450 respectively.

Figure 2 shows the high angle angular dark field (HAADF) transmission electron microscope (TEM) images of the three samples. The high resolution images on the right column indicate that all three In$_2$O$_{3-x}$(OH)$_y$ samples are highly crystalline. The lower resolution images in the left column show that, as expected, the sample morphology changes with increasing temperature. The I-250 sample exhibits the smallest particle size and highest porosity. I-350 has slightly larger particles size and exhibits more faceting than the I-250 sample. The morphology of the I-450
Figure 2. High angle annular dark field (HAADF) STEM images of the In$_2$O$_3$-(OH)$_y$ samples (a,b) I-250, (c,d) I-350, (e,f) I-450

sample is comprised of much larger particles and reduced porosity relative to the other two samples. This can be attributed to the minimization of surface energy at higher calcination
temperatures, resulting in increased particle size, passivation of defects and reduction in dangling surface bonds.

The powder X-ray diffraction (PXRD) patterns shown in Figure 3a further confirm the crystalline nature of the In$_2$O$_{3-x}$(OH)$_y$ samples. All three samples are composed of pure crystalline bixbyite indium oxide with no evidence of other side phases (crystalline or amorphous). The full width at half maximum (FWHM) of the PXRD peaks decreases with increasing calcination temperature, indicating an increase in crystallite size, correlating well with the HR-TEM data presented in Figure 2. Figure 3b shows the XPS O1s core level spectra for the three samples. The main portion of the peak is centered around 530 eV and is associated with...
indium oxide. The shoulder peak at higher binding energies is commonly attributed to a combination of defects with contribution from both oxygen vacancies, with a peak centered around 531 eV, and hydroxides with a peak centered around 532 eV. The light gray curves in Figure 3b represent a qualitative deconvolution, scaled by 60%, of the O1s spectrum of the I-250 sample and are intended for illustrative purposes only. This data provides further evidence that amount of defects present in the three sample decreases with increasing calcination temperature.

The optical properties of the three samples are shown in Figure 3c and d. The diffuse reflectance spectra in Figure 3c indicates that the steady-state absorption of the three samples is very similar. The inset shows that there is a very slight blue-shift in the absorption onset for samples calcined at lower temperatures. However like most metal oxides, the Bohr exciton radius of indium oxide is very small, around 2.4 nm, so it is unlikely that this slight shift is due to the effects of quantum confinement. Fitting the absorption onset using a modified Kubelka-Munk approximation (the details of which are described in Section 2.5.1) confirms that the band gaps of all samples are very similar (values shown in Figure 3d). The two peaks in the near-IR region of the reflectance spectra centered around 1450 nm and 1925 nm correspond to vibrational overtones and combination modes of hydroxyl groups and surface bound water. The highest contribution of these signals is seen for I-250, which is consistent with the higher concentration of residual hydroxyl groups remaining in the sample after calcination. The other key feature in the reflectance spectra is the gradual increase in absorbance (i.e. decrease in reflectance) in the near-IR region of the spectrum, which is indicative of conduction electrons within the material. This is consistent with XPS measurements that reveal a high, n-type position of the Fermi-levels relative to the conduction bands (Figure 3d), indicating that there are a significant number of donor defects present in the samples. While the Fermi level of I-450 appears to be slightly lower than the other two samples, which could indicate a decrease in donor states due to the higher calcination temperature, this difference is within the experimental error of the XPS measurements and may not be significant.

4.5.2 Photocatalytic activity correlates with defect concentration

Figure 4 demonstrates the photocatalytic activity of the In$_2$O$_{3-x}$(OH)$_y$ samples decreases with increasing calcination temperature. Even when corrected for differences in surface area (Figure 4b), this trend remains. As previously discussed in Chapter 2, we attribute this effect to a
Figure 4. (a) Photocatalytic activity of the In$_2$O$_{3-x}$(OH)$_y$ samples per mass of catalyst and (b) surface area normalized photocatalytic rate. All data was measured under 800 W m$^{-2}$ (0.8 suns) illumination at 150 °C and confirmed using $^{13}$C isotope tracing.

decrease in the number of possible active defect sites, specifically hydroxides and oxygen vacancies, within the material. In a separate study which combined theoretical simulations and kinetics experiments (described in detail in Chapter 5), our group confirmed that both hydroxides and oxygen vacancies are needed at the active site to facilitate the reduction of CO$_2$ to CO.$^2$

Significantly, we were able to demonstrate that there is a reduction in the activation energy for the light driven reaction relative to the dark reaction, indicating that light plays an important role in activating this defected In$_2$O$_{3-x}$(OH)$_y$ material to facilitate photocatalysis on its surface.

4.5.3 Excited state charge carrier dynamics in In$_2$O$_{3-x}$(OH)$_y$

In order to understand how photo-generated electrons and holes interact with these catalytically relevant defects, we studied the excited state carrier dynamics of In$_2$O$_{3-x}$(OH)$_y$ using transient absorption (TA) spectroscopy. In TA spectroscopy, an ultrafast, single-wavelength laser “pump” pulse is used to put the sample into an excited state. It is then followed by a second broadband laser “probe” pulse, which measures the excited state absorption spectra of the sample at different time delays after the initial excitation (illustrated schematically in Figure 1). Figure 5 shows the TA spectra of the three In$_2$O$_{3-x}$(OH)$_y$ samples at different time delays between pump
Figure 5. Transient absorption spectra at different time delays between pump and probe pulses of the In$_2$O$_{3-x}$(OH)$_y$ samples excited with above band gap (318 nm) light (a-c) and near band gap (405 nm) light (d-e). The gap centered at ~809 nm is due to the strong residual laser fundamental in the probe beam, which led to poor data within this region.

and probe pulses. Both above band gap (318 nm) and near band gap (405 nm) pump pulses were used to excite the samples. Above band gap excitation leads to distribution of absorption with similar intensity throughout the visible and near-IR regions of the spectra (Figure 5a-c). There does not appear to be any significant difference in the spectral shapes between the samples, indicating that the relaxation processes are similar for all three samples when excited with above band gap light energy. On the other hand, near band gap excitation (405 nm) results in substantial differences in the transient absorption spectra when comparing between samples (Figure 5d-f). The same broad, featureless absorption in the visible region is observed for all samples, however I-250 shows a significantly higher absorbance in the near-IR, which does not decay down to the baseline even at long delay times (>3 ns). The broad, featureless absorption in the visible region observed in all spectra is indicative of the formation of coulombically bound excitons.\textsuperscript{8,10,33} The presence of near-IR absorption is attributed to electrons located in shallow trap states created by oxygen vacancies lying below the conduction band edge.\textsuperscript{3,9,10} Under 405 nm excitation, this near-IR signal decreases with increasing sample calcination temperature.
which is consistent with the loss of oxygen vacancies due to surface defect passivation at higher temperatures.

This is illustrated more clearly in Figure 6, which shows the normalized transient absorption spectra after a 1 ps time delay between the pump and probe pulses for each sample excited with either 318 nm or 405 nm light. Because the excitation wavelength determines the initial potential energy of the excited state charge carriers it is possible to generate different distributions of populated states. Using near band gap excitation, trap states and shallow donor (acceptor) states near the conduction (valence) band edge can be directly excited. The lower potential energy of the photogenerated charge carriers means they are more likely to be trapped at these localized surface states, leading to longer lived excited states. Because the population of these oxygen vacancy donor states is highest in I-250 and decreases with increasing calcination temperature, this could explain the difference in near-IR signal. On the other hand, 318 nm excitation produces higher energy charge carriers which are more mobile and able to access many different relaxation pathways, resulting in shorter excited state lifetimes. The absence of a substantial near-IR signal likely indicates that this above band gap excitation does not relax via the same localized surface trap pathway as with the 405 nm excitation.

4.5.4 Modeling excited state charge carrier relaxation in In$_2$O$_{3-x}$(OH)$_y$

In order to better understand the complex processes apparent in the TA spectra, we used a multi-exponential decay to model the different charge carrier relaxation dynamics in the material. Each
data set, collected with a single pump wavelength, incident pump fluence, and a series of probe wavelengths ($\lambda$), was fit to a sum of exponentials:

$$\Delta A(\lambda, t) = c(\lambda) + f(\lambda, t) \ast \sum_{n} A_n(\lambda) \exp\left[-\frac{t - t_0(\lambda)}{\tau_n(\lambda)}\right]$$

(1)

where $A_n$ and $\tau_n$ are the amplitudes and time constants for the exponential decays, respectively, $c$ is a constant term, $f$ is the instrument-response function (a Gaussian of width 240 fs, empirically measured using blanks), and the $\ast$ operator represents convolution.\(^8\) The $t_0$ is the position of zero delay time between pump and probe, which is wavelength-dependent because of the chirp in the broadband probe beam. Empirically, $t_0$ was treated as a 3\(^{rd}\)-order polynomial function of $\lambda$ with parameters that were fit globally to all probe wavelengths. Because the highly defected, heterogeneous nature of the samples results in many decay processes occurring simultaneously within the material, we did not constrain the fitting to a specific number of decay processes, but rather let it vary as needed to obtain the best fit of the data, using up to a maximum of 4 exponential terms. Analyzing the exponential decay processes in this manner across the entire spectral region gives us a more comprehensive picture of the different relaxation pathways present within the In$_2$O$_3$-$x$(OH)$_y$ samples.

Figure 7 illustrates the different time constants extracted from fitting the exponential decay curves at various wavelengths and pump intensities for I-250. The plots are noticeably flat, indicating that the lifetimes of the various charge carriers do not change as a function of probe wavelength. This confirms that electrons and holes within the material do not relax independently of one another and instead behave as coulombically bound excitons, as discussed above.\(^8\) Averaged values of the fitting parameters for each of these plots are listed in Table 1. The time constants have been roughly grouped into 4 categories based on the types of processes they represent. The first, indicated by the green squares, corresponds to fast processes occurring within the first 20 ps, which can be attributed to several relaxation pathways. One such pathway is the redistribution of charge carriers among shallow states close in energy to the initial excited state, which typically occurs within the first few ps after photoexcitation,\(^8,14\) although this process is often much faster. For example, initial trapping of free carriers in anatase TiO$_2$ was reported to occur in less than ~200 fs.\(^8\)
Table 1: Average Fitting Parameters for the Transient Absorption Temporal Decay for I-250*

<table>
<thead>
<tr>
<th>Excitation wavelength</th>
<th>Pump Fluence</th>
<th>A1</th>
<th>τ1</th>
<th>A2</th>
<th>τ2</th>
<th>A3</th>
<th>τ3</th>
<th>A4</th>
<th>τ4</th>
</tr>
</thead>
<tbody>
<tr>
<td>318 nm</td>
<td>65 µW (UV)</td>
<td>0.17</td>
<td>8.5 ± 0.7</td>
<td>0.58</td>
<td>50 ± 4</td>
<td>0.35</td>
<td>230 ± 30</td>
<td>0.15</td>
<td>730 ± 40</td>
</tr>
<tr>
<td>318 nm</td>
<td>90 µW (Vis/NIR)</td>
<td>0.37</td>
<td>11.6 ± 0.7</td>
<td>0.47</td>
<td>39.5 ± 0.5</td>
<td>0.34</td>
<td>268 ± 5</td>
<td>0.07</td>
<td>660 ± 80</td>
</tr>
<tr>
<td>318 nm</td>
<td>175 µW</td>
<td>0.25</td>
<td>8.8 ± 0.2</td>
<td>0.47</td>
<td>38 ± 1</td>
<td>0.23</td>
<td>235 ± 7</td>
<td>0.11</td>
<td>840 ± 20</td>
</tr>
<tr>
<td>318 nm</td>
<td>300 µW</td>
<td>0.33</td>
<td>7.5 ± 0.1</td>
<td>0.47</td>
<td>34.2 ± 0.6</td>
<td>0.19</td>
<td>252 ± 6</td>
<td>0.06</td>
<td>780 ± 30</td>
</tr>
<tr>
<td>405 nm</td>
<td>200 µW</td>
<td>0.04</td>
<td>2.3 ± 0.1</td>
<td>0.44</td>
<td>58.3 ± 0.7</td>
<td>0.86</td>
<td>340 ± 20</td>
<td>0.50</td>
<td>1220 ± 20</td>
</tr>
<tr>
<td>405 nm</td>
<td>650 µW</td>
<td>0.23</td>
<td>11.3 ± 0.6</td>
<td>0.66</td>
<td>59 ± 1</td>
<td>0.51</td>
<td>319 ± 6</td>
<td>0.47</td>
<td>840 ± 30</td>
</tr>
<tr>
<td>405 nm</td>
<td>1320 µW</td>
<td>0.33</td>
<td>11.1 ± 0.2</td>
<td>0.40</td>
<td>45.2 ± 0.6</td>
<td>0.23</td>
<td>218 ± 3</td>
<td>0.10</td>
<td>900 ± 40</td>
</tr>
</tbody>
</table>

*The errors were calculated by propagating the error inherent in each calculation for a single probe wavelength. All errors for the amplitude are less than 0.01.
Decay processes occurring on these short time scales can also be attributed to second order relaxation dynamics, such as Auger recombination, which involves non-radiative energy transfer between multiple charge carriers. Tsokkou et al. have demonstrated that Auger recombination processes occur in In$_2$O$_3$ within the first ~10 ps and become a significant relaxation pathway at pump fluences above 3 µJ/cm$^2$. Auger recombination tends to dominate the short relaxation processes at higher pump intensities when more excited state charge carriers are present. Therefore, an estimation of the Auger constant can be obtained by examining the time constants at the highest pump fluences, where Auger recombination is expected to dominate. Using this method, we have found Auger constants between 5 – 11 ps (see Tables 1-3), depending on the sample and excitation wavelength, which is consistent with the data reported by Tsokkou et al.

As evident in Figure 7a and 7d, there is very little contribution to the relaxation dynamics from these fast processes at lower pump fluences, providing further evidence that this signal can be attributed primarily to Auger recombination.

The next grouping of time constants, represented by the blue squares, is associated with further relaxation into shallow surface defect states and deeper trap states at lower energies. These processes generally dominate the relaxation dynamics at time delays of ~20 - 100 ps. The final two groups of time constants, represented by red (100-500 ps) and black (>500 ps) squares, are related to the recombination and ultimate decay processes.
**Figure 9.** Time constants from the multi-exponential decay fitting of the transient absorption spectra as a function of wavelength for I-350 at different excitation wavelengths and intensities (a) 318 nm excitation, 90 µW (b) 318 nm excitation, 175 µW. (c) 318 nm excitation, 300 µW. (d) 405 nm excitation, 650 µW. (e) 405 nm excitation, 950 µW. (f) 405 nm excitation, 1300 µW. The time constants have been roughly grouped into four categories: \( \tau < 20 \) ps (green squares), 20 < \( \tau < 100 \) ps (blue squares), 100 < \( \tau < 500 \) ps (red squares), and \( \tau > 500 \) ps (black squares).

**Table 2:** Average Fitting Parameters for the Transient Absorption Temporal Decay for I-350*

<table>
<thead>
<tr>
<th>Excitation wavelength</th>
<th>Pump Fluence</th>
<th>( A_1 )</th>
<th>( \tau_1 ) (ps)</th>
<th>( A_2 )</th>
<th>( \tau_2 ) (ps)</th>
<th>( A_3 )</th>
<th>( \tau_3 ) (ps)</th>
<th>( A_4 )</th>
<th>( \tau_4 ) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>318 nm</td>
<td>90 µW</td>
<td>0.26</td>
<td>9.3 ± 0.1</td>
<td>0.58</td>
<td>35.9 ± 0.1</td>
<td>0.25</td>
<td>230 ± 2</td>
<td>0.17</td>
<td>730 ± 20</td>
</tr>
<tr>
<td>318 nm</td>
<td>175 µW</td>
<td>0.46</td>
<td>9.0 ± 0.1</td>
<td>0.39</td>
<td>49 ± 1</td>
<td>0.19</td>
<td>153 ± 6</td>
<td>0.18</td>
<td>500 ± 200</td>
</tr>
<tr>
<td>318 nm</td>
<td>300 µW</td>
<td>0.53</td>
<td>7.1 ± 0.1</td>
<td>0.38</td>
<td>39.8 ± 0.4</td>
<td>0.13</td>
<td>202 ± 7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>405 nm</td>
<td>650 µW</td>
<td>0.21</td>
<td>10 ± 1</td>
<td>0.50</td>
<td>46.2 ± 0.9</td>
<td>0.55</td>
<td>286 ± 6</td>
<td>0.37</td>
<td>770 ± 20</td>
</tr>
<tr>
<td>405 nm</td>
<td>950 µW</td>
<td>0.48</td>
<td>14 ± 1</td>
<td>0.52</td>
<td>43 ± 1</td>
<td>0.52</td>
<td>285 ± 9</td>
<td>0.50</td>
<td>690 ± 50</td>
</tr>
<tr>
<td>405 nm</td>
<td>1300 µW</td>
<td>0.48</td>
<td>8.1 ± 0.7</td>
<td>0.56</td>
<td>41.4 ± 0.9</td>
<td>0.47</td>
<td>260 ± 5</td>
<td>0.41</td>
<td>1180 ± 70</td>
</tr>
</tbody>
</table>

*The errors were calculated by propagating the error inherent in each calculation for a single probe wavelength. All errors for the amplitude are less than 0.03
relaxation back to the ground state of long-lived trapped charge carriers. The broad timescale over which this occurs (from ~100 ps to >10,000 ps) is indicative of the many different relaxation pathways and associated trap states that can occur.\textsuperscript{8,14,23} Figure 8a illustrates the distribution of time constants within this range for all samples. Unsurprisingly, there is a greater population of time constants corresponding to faster processes, which is likely due to the many relaxation pathways possible within such highly defected materials. Figure 8b shows the relative contribution from each of the three In$_2$O$_{3-x}$(OH)$_y$ samples. While the distributions for I-350 and I-450 are relatively similar, with much greater number of time constants corresponding to faster decay processes, I-250 has a substantially greater population of time constants corresponding to longer relaxation processes. This is apparent when comparing the distribution of time constants in Figure 7 to those for I-350 (Figure 9) and I-450 (Figure 10). On short time scales, the relaxation dynamics in I-350 and I-450 are relatively similar to I-250. The primary difference between the three In$_2$O$_{3-x}$(OH)$_y$ samples is on the longest time scale (>500 ps), indicated by the black squares. While there is a substantial contribution to this long lived signal in nearly all of the I-250 plots, almost no time constants greater than 500 ps are observed for I-450. I-350 falls in the middle of these to samples, exhibiting some longer lived components, particularly when excited with 405 nm, however their contribution is significantly lower than in I-250. This trend correlates with increasing number of intentional defects in the samples, indicating that these longer-lived excited states may be due to trapped excited state charge carriers localized in these extrinsic OH and [O]v defects.

4.5.5 Estimation of long-lived excited state component in In$_2$O$_{3-x}$(OH)$_y$

Long-lived excited states have been identified as an important attribute in an effective photocatalyst, with longer lifetimes typically associated with higher photocatalytic performance.\textsuperscript{8,9,11,34} While the measurement window in this study was restricted to 3 ns due to instrument limitations, it is possible to estimate long-lived components using the model described in the previous section. Specifically, the constant term $c$ is interpreted as the fraction of the signal that would be observed to be non-decaying over the maximum 3 ns time window of the instrument. This long-lived signal, if representing the absorption of excited carriers, would possess a lifetime of at least ~10 ns.\textsuperscript{8} Values of $c < 0$ can occur at wavelengths where the signal is weak and are interpreted as the absence of long-lived carriers combined with experimental noise and possibly other effects, such as transient heating. The long-lived component for each
Figure 10. Time constants from the multi-exponential decay fitting of the transient absorption spectra as a function of wavelength for I-450 at different excitation wavelengths and intensities (a) 318 nm excitation, 90 µW. (b) 318 nm excitation, 175 µW. (c) 318 nm excitation, 300 µW. (d) 405 nm excitation, 200 µW. (e) 405 nm excitation, 650 µW. (f) 405 nm excitation, 1300 µW. The time constants have been roughly grouped into four categories: $\tau < 20$ ps (green squares), $20 < \tau < 100$ ps (blue squares), $100 < \tau < 500$ ps (red squares), and $\tau > 500$ ps (black squares).

Table 3: Average Fitting Parameters for the Transient Absorption Temporal Decay for I-450*

<table>
<thead>
<tr>
<th>Excitation wavelength</th>
<th>Pump Fluence</th>
<th>$A_1$</th>
<th>$\tau_1$ (ps)</th>
<th>$A_2$</th>
<th>$\tau_2$ (ps)</th>
<th>$A_3$</th>
<th>$\tau_3$ (ps)</th>
<th>$A_4$</th>
<th>$\tau_4$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>318 nm</td>
<td>90 µW</td>
<td>0.27</td>
<td>10.2 ± 0.2</td>
<td>0.57</td>
<td>36.3 ± 0.4</td>
<td>0.26</td>
<td>190 ± 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>318 nm</td>
<td>175 µW</td>
<td>0.42</td>
<td>9.8 ± 0.1</td>
<td>0.46</td>
<td>49.7 ± 0.3</td>
<td>0.25</td>
<td>126 ± 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>318 nm</td>
<td>300 µW</td>
<td>0.45</td>
<td>5.2 ± 0.1</td>
<td>0.44</td>
<td>45.4 ± 0.6</td>
<td>0.14</td>
<td>210 ± 60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>405 nm</td>
<td>200 µW</td>
<td>0.08</td>
<td>9 ± 7</td>
<td>0.46</td>
<td>72 ± 5</td>
<td>0.56</td>
<td>240 ± 10</td>
<td>0.29</td>
<td>700 ± 200</td>
</tr>
<tr>
<td>405 nm</td>
<td>650 µW</td>
<td>0.07</td>
<td>4.0 ± 0.5</td>
<td>0.57</td>
<td>63.1 ± 0.9</td>
<td>0.40</td>
<td>276 ± 6</td>
<td>0.27</td>
<td>1020 ± 40</td>
</tr>
<tr>
<td>405 nm</td>
<td>1300 µW</td>
<td>0.12</td>
<td>9.4 ± 0.5</td>
<td>0.61</td>
<td>51.3 ± 0.4</td>
<td>0.32</td>
<td>269 ± 4</td>
<td>0.24</td>
<td>700 ± 20</td>
</tr>
</tbody>
</table>

* The errors were calculated by propagating the error inherent in each calculation for a single probe wavelength. All errors for the amplitude are less than 0.02
Figure 11. Fraction of long-lived signal (τ >~10 ns) at different pump fluences for I-250 excited with (a) 318 nm light, and (b) 405 nm light.

sample at under both 318 nm and 405 nm excitation are shown in Figures 11-13. While there is no significant wavelength dependant relaxation processes on short time scales, at longer time scales a clear wavelength dependence is observed. In Figure 11, a high fraction of long lived excited states, centered around 450 nm, is observed for I-250 under both 318 nm and 405 nm excitation. This signal decreases with increasing pump fluence, likely as a result of enhanced Auger recombination at higher light intensities, which facilitates faster relaxation. TA signals in this wavelength region of the spectrum are typically associated with trapped holes.8–10 In metal oxides, it has been demonstrated that surface hydroxyl groups are very efficient hole traps,9,10 and in some cases have been attributed to helping to enhance the overall excited state lifetime of charge carriers in the material. For example, Wang et al. reported an increase in charge carrier relaxation rates upon vacuum heat treatment, which removed surface hydroxyl groups on anatase TiO₂.9 The fact that we do not observe a peak associated with trapped electrons, which typically appears around 700 nm, suggests that the electrons were somehow removed.10 Because these measurements were performed in air, it is possible that electron scavenging by O₂ is responsible for this long lived charge-separated state.10,35

While there is a clear wavelength dependence of the long-lived component of the I-250 spectra, there is no such dependence observed for I-350 or I-450. This could be due to the reduced concentration of surface hydroxyl groups in these samples, which would reduce the amount of
available hole traps in the material. All three samples using a 405 nm excitation source produce a higher signal from the long-lived component than 318 nm excitation. One possible explanation of this, as discussed above could be the direct excitation of trap states, producing less mobile, more localized charge carriers. In I-250 it is significant that both 318 and 405 nm excitation produce a pronounced signal in the same region of the spectrum. This indicates that the generation of trapped holes in this long lived charge separated state is a property of the material,
likely resulting from high concentrations of surface hydroxyl groups, and not an effect of the excitation source.

4.5.6 Correlation of charge carrier relaxation dynamics to photocatalytic activity in \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \)

The excited state charge carrier relaxation dynamics have significant implications for photocatalysis, determining the population of electrons and holes available with sufficient energy to facilitate charge transfer to surface adsorbed reactant molecules, such as \( \text{H}_2 \) and \( \text{CO}_2 \). Figure 14 illustrates the numerous relaxation pathways these excited state charge carriers can take. After initial excitation, high energy electrons and holes will relax to the conduction and valence band edges, typically within the first few ps.\(^9,14,33\) Indium oxide has a somewhat unique direct forbidden band structure in which the states at the top of the valence band are of the same parity as the states at the bottom of the conduction band, so the direct vertical transition (i.e. without the assistance of a phonon) is forbidden by dipole selection rules.\(^21,22\) We do not observe any photoluminescence signals, therefore this type of radiative relaxation pathway is not thought to be significant in our samples. Instead, the primary relaxation pathways are likely non-radiative.

Once these excited charge carriers have reached the band edge, they can undergo various trapping and de-trapping processes as well as relaxation into deeper states within the band gap, which typically occurs within \(~100\) ps after the initial excitation.\(^14,33\) The length of time these charge carriers remain in these mid-gap states before ultimately recombining and relaxing back down to the ground state depends largely on the nature and type of the defect state itself.\(^14\) Several studies have demonstrated that, in metal oxides, oxygen vacancies and surface hydroxyl groups create mid gap states that act as electron and hole traps, respectively.\(^8,9,16,17\) Generally, oxygen vacancies create donor states just below the conduction band edge, while surface hydroxyl groups create acceptor states just above the valence band edge. For oxygen vacancies in particular, the energy difference from the conduction band edge depends on the location of the vacancy. Lany et al. have demonstrated that bulk oxygen vacancies create deep trap states that are located approximately 0.7 eV below the conduction band and generally are thought to behave as localized point defects. On the other hand, surface oxygen vacancies act as shallow donor states located just below the conduction band edge and create a more delocalized band-like group of states, which has been implicated as the primary cause of the observed n-type behavior of
nominally un-doped In\textsubscript{2}O\textsubscript{3}.\textsuperscript{17,36} As indicated in Figure 14, the relaxation processes involving such a large number of defect states is highly complex and it is therefore very difficult to draw conclusions about the specific relaxation pathways the charge carriers travel on their route towards the ground state in these materials.

However, several key trends have emerged in this study that can help to explain the observed trends in photocatalytic activity. Our results indicate that in In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y}, a higher concentration of defects corresponds to both longer lifetimes and higher photocatalytic rates. This suggests that these intentional defects not only facilitate the photocatalytic reduction of CO\textsubscript{2} by creating active surface sites, but that they also positively impact the optoelectronic properties, enhancing the population of available photogenerated charge carriers to facilitate light-driven catalytic reactions. On short time scales (< 3 ns), we have observed an increase TA signal in the near-IR region, indicative of transitions from photogenerated electrons populating oxygen vacancy sites near the conduction band edge.\textsuperscript{3,9,10} This signal intensity is highest for I-250, indicating a higher population of electrons in these states, which is likely due to the greater number of vacancy states available. On longer time scales (> 10 ns) we demonstrate a significant enhancement in the signal for I-250 around 450 nm, which is attributed to holes trapped in surface hydroxyl groups.\textsuperscript{9} The lack of long-lived signal corresponding to trapped
electrons, indicates the generation of a charge-separated state. We attribute this to electron scavenging by \( \text{O}_2 \).\textsuperscript{10,35} Similar results were reported by my colleague, Dr. Le He, who studied the transient absorption of defected \( \text{In}_2\text{O}_3\text{a}(\text{OH})_y \) nanocrystal nanorod superstructures at long time delays (ns - \( \mu \)s time scale). Using \( \text{Ag}^+ \) as an electron scavenger, he observed the same signal, centered at 450 nm, associated with trapped holes.

The localization of electrons in oxygen vacancies and holes in surface hydroxyl groups has significant implications for the surface-mediated, light-driven RWGS reaction mechanism. This trapping of photo-excited electrons and holes at these surface sites is proposed to increase their basicity and acidity, respectively. As will be discussed in detail in Chapter 5, this could explain the lower observed activation energy for the light-driven reaction at the surface of defected \( \text{In}_2\text{O}_3\text{a}(\text{OH})_y \) relative to the dark, thermally-driven reaction. While the interaction of light with defected \( \text{In}_2\text{O}_3\text{a}(\text{OH})_y \) materials is very complex, a clearer picture is beginning to emerge regarding the role defect states play in determining both the excited state lifetimes of photogenerated charge carriers as well as their localization in catalytically relevant defects, which ultimately determines the photocatalytic activity of the material.

### 4.6 Conclusions and future work

In this study, three photocatalytically active \( \text{In}_2\text{O}_3\text{a}(\text{OH})_y \) samples were prepared with varying concentration of defects. Femtosecond TA measurements demonstrate that these defects play a significant role in the excited state charge relaxation pathways which strongly correlates to photocatalytic activity. Higher defect concentrations result in longer excited state lifetimes which is attributed to electron and hole trapping in oxygen vacancies and surface hydroxyl groups, respectively, which have been shown to play a central role in the photocatalytic reaction mechanism. Ongoing studies examining the relaxation dynamics under \( \text{H}_2 \) and \( \text{CO}_2 \) atmospheres to more closely mimic reaction conditions will provide further insight into the reaction mechanism, in particular the role of excited state electron transfer to surface adsorbed reactant species. Additionally, we are currently using computational modeling to better understand how the introduction of these intentional defects changes the density of states and charge localization in \( \text{In}_2\text{O}_3\text{a}(\text{OH})_y \) materials. A deeper understanding of how intentional defects such as oxygen vacancy and surface hydroxyl groups impact the optoelectronic properties of photocatalytically
active materials like indium oxide, can provide valuable insight into how to rationally tune these defects to optimize the photocatalytic performance.

4.7 References


Chapter 5
Mechanistic and Kinetic Insights into the Photocatalytic Reduction of CO$_2$ on Nanocrystalline In$_{2}$O$_{3-x}$(OH)$_{y}$

5.1 Statement of Contributions

This chapter represents a summary of our collective understanding of the kinetic and mechanistic aspects of how In$_{2}$O$_{3-x}$(OH)$_{y}$ functions as an active photocatalyst. The data presented herein is based on In$_{2}$O$_{3-x}$(OH)$_{y}$ materials that I synthesized, with the exception of the indium oxide nanorods briefly discussed in the final section, which were synthesized and characterized by Dr. Le He. Thomas Wood and Dr. Le He performed the catalytic experiments. Dr. Kulbir Kaur Ghuman performed the theoretical calculations. Dr. Kulbir Kaur Ghuman, Thomas Wood, and Dr. Le He drafted the original manuscripts, which were edited by myself and Professors Charles Mims, Chandra Veer Singh and Geoffrey Ozin. A portion of this work has appeared in print, and another portion has been submitted for publication.

5.2 Abstract

There are many parameters than can affect the photocatalytic performance of a material, however in order to rationally design and optimize these parameters a detailed understanding is required. This chapter contains a summary of a proposed reaction mechanism, derived from both computational and experimental data, for the reduction of CO$_2$ to CO on the surface of In$_{2}$O$_{3-x}$(OH)$_{y}$ nanoparticles. In this mechanism a surface active site composed of a Lewis acidic, coordinatively unsaturated indium atom adjacent to a Lewis basic hydroxide, assists the adsorption and heterolytic dissociation of H$_2$ that enables the adsorption and reaction of CO$_2$ to form CO and H$_2$O as products. This mechanism, which has its analogue in molecular frustrated Lewis pair (FLP) chemistry and catalysis of CO$_2$ and H$_2$, is supported by preliminary kinetic investigations. The effects of inter-particle charge transfer on photocatalytic activity in In$_{2}$O$_{3-x}$(OH)$_{y}$ nanocrystal nanorod superstructures is also briefly discussed. In theses samples, increased nanorod length leads to longer photogenerated electron and hole lifetimes. This enhancement has been attributed to the surface trapping of photogenerated electrons and holes and can enhance the overall photocatalytic reaction rate. The results of both studies emphasize
the importance of tailoring the surface and morphology of nanostructures to facilitate gas-phase and photocatalytic carbon dioxide reduction reactions at technologically significant rates.

5.3 Introduction

Gaining a deeper understanding the photocatalytic mechanism is critical to optimizing the performance of In$_2$O$_3$-based photocatalysts and can also help facilitate the development of other more efficient CO$_2$ reduction photocatalysts. In Chapter 2, we established that In$_2$O$_{3-x}$(OH)$_y$ nanoparticles, prepared with varying surface hydroxide and oxygen vacancy content, are capable of reducing CO$_2$ to CO. The samples with the highest hydroxide and oxygen vacancy content also had the highest photocatalytic activity. Additionally, the surface hydroxide and oxygen vacancy concentrations correlated well with the CO$_2$ adsorption capacity, suggesting both surface species play a key role in the reaction mechanism. Using In(OH)$_3$ as a control sample, we were able to demonstrate that hydroxides alone are not responsible for CO$_2$ capture capacity. While this sample had the highest hydroxide concentration, the stoichiometric In(OH)$_3$ with its perovskite structure does not have a significant concentration of surface oxygen vacancies. This suggested that a combination of both oxygen vacancies and hydroxides were required to facilitate CO$_2$ capture and reduction.

In Chapter 3, we further confirmed that hydroxides alone are not able to account for the observed differences in reactivity and stability of indium oxide samples produced from different precursors. In particular, an In$_2$O$_3$ sample produced from indium nitrate had the highest hydroxide concentration; however it exhibited no activity for CO$_2$ reduction. Based on this samples’ stability under strongly basic etching conditions, we hypothesized that the strongly oxidizing conditions resulting from the thermal decomposition of indium nitrate resulted in a sample that lacks the coordinatively unsaturated indium sites (oxygen vacancies) needed to facilitate CO$_2$ reduction.

In this chapter I will briefly review two studies performed in our group which help to further our understanding of the mechanism of CO$_2$ reduction to CO on the surface of In$_2$O$_{3-x}$(OH)$_y$ nanoparticles. In the first study, using a combination of density functional theory (DFT) calculations and experimental measurements, my colleagues Dr. Kulbir Kaur Ghuman and Thomas Wood were able to elegantly establish a possible mechanism for the photocatalytic reduction of CO$_2$ on the surface of In$_2$O$_3$. The entire catalytic cycle is illustrated in Fig. 1. In this
mechanism, an $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ surface containing both hydroxides and oxygen vacancies reacts first with $\text{H}_2$ to create an activated site. Then $\text{CO}_2$ is adsorbed on this site and is subsequently reduced to $\text{CO}$. The active site is regenerated following desorption of $\text{CO}$ and $\text{H}_2\text{O}$. As the results show, the active site requires both hydroxides and oxygen vacancies to facilitate $\text{CO}_2$ reduction and only occurs in the presence of $\text{H}_2$, which correlates well with experimental results.

The second study, lead by my colleague, Dr. Le He, focuses on understanding the differences in photocatalytic activity of indium oxide mesocrystals comprised of interconnected nanoparticles in an overall nanorod shape. These nanocrystal-nanorods are also produced via the thermal decomposition of $\text{In}(\text{OH})_3$ at 250 °C and are therefore quite comparable to my $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ nanoparticle samples. In his study, he examined the photocatalytic activity of the samples as a function of nanorod length. His results demonstrate that increased nanorod length leads to longer photogenerated electron and hole lifetimes, which corresponds to higher photocatalytic activities. He also proposed a mechanism by which the surface trapping of photogenerated electrons and holes can enhance the overall photocatalytic reaction rate. Both of these studies represent a significant enhancement in our understanding of how defected indium oxide materials function as a photocatalyst and will certainly help guide the way towards designing even more efficient photocatalysts for solar fuel generation.

5.4 Mechanistic Understanding of $\text{CO}_2$ Reduction on the Surface of Nanocrystalline $\text{In}_2\text{O}_{3-x}(\text{OH})_y$

5.4.1 Interaction of $\text{CO}_2$ with indium oxide surfaces

As described in previous chapters there are two primary types of defects, oxygen vacancies and hydroxides, which we believe to be important for the photocatalytic reduction of $\text{CO}_2$ on the surface of indium oxide. In order to better understand how these defects may affect the interaction of the $\text{In}_2\text{O}_3$ and $\text{CO}_2$, we used density functional theory to examine indium oxide (111) surfaces. The (111) surface in particular was chosen because it has been shown to be the most abundant crystal face from a thermodynamic equilibrium perspective, however a survey of crystal faces using transmission electron microscopy (TEM) did not reveal any preferred faces in the experimental samples. Thus, although the (111) surface was found to be present, the
experimental samples also contain many other crystal faces. Three types of indium oxide (111) surfaces were created: pristine In$_2$O$_3$, In$_2$O$_3$ containing oxygen vacancies (In$_2$O$_{3-x}$), and In$_2$O$_3$ containing both oxygen vacancies and hydroxides (In$_2$O$_{3-x}$(OH)$_y$). The pristine In$_2$O$_3$ surface showed almost no interaction with CO$_2$, further confirming our hypothesis that defects are a requirement in an active photocatalyst. The vacancy-only surface, In$_2$O$_{3-x}$, showed moderate interactions with CO$_2$, primarily due to the relatively higher energy surface electrons created by the vacancy defect. As anticipated based on previous experimental results, the In$_2$O$_{3-x}$(OH)$_y$ surface containing both hydroxides and oxygen vacancies showed the strongest interaction with CO$_2$. In this case, the excess electron density provided by the oxygen vacancy donates charge to the oxygen of the incoming CO$_2$ molecule, while the oxygen of the adjacent surface hydroxide group accepts electron density from the C atom of CO$_2$. The energetically favored interaction of CO$_2$ with In$_2$O$_{3-x}$(OH)$_y$ can be described as a bi-dentate surface bicarbonate. These results provide further evidence for our hypothesis that both types of defects are required for CO$_2$ capture, however it is important to note that CO$_2$ did not dissociate to form CO on any of these surfaces, indicating that the reactant gas H$_2$ plays a key role in the mechanism.

5.4.2 H$_2$ dissociation on the surface of In$_2$O$_3$

In order to more closely model experimental conditions, a fourth surface was created by allowing the In$_2$O$_{3-x}$(OH)$_y$ surface, containing both oxygen vacancies and hydroxides, to interact with H$_2$ (stages II and III in Figure 1). It was found that H$_2$ is adsorbed molecularly at this site and
undergoes heterolytic splitting during the absorption process. Figure 2 illustrates this process in more detail. When the H₂ molecule binds to the surface, the Lewis basic oxygen of the surface hydroxide group interacts with one of the H atoms, while Lewis acidic indium accepts the electron density from the H₂ molecule, forming a protonic HO-H species and a hydridic In-H species. This process is analogous to H₂ splitting observed in a class of molecular catalysts known as Frustrated Lewis Pairs (FLPs). FLPs are obtained when a 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. This unquenched nature of such Lewis pairs results in the observation of unique chemical reactivity. In our material, the In₂O₃-x(OH)y also has what can be described as Lewis acid–base proximal sites. The oxygen of the surface hydroxide group acts as a Lewis base and the coordinatively unsaturated indium adjacent to the oxygen vacancy acts as Lewis acid. It is therefore possible that the formation of Lewis acid–base pairs accounts for the heterolytic dissociation of H₂ on the In₂O₃-x(OH)y surface.

5.4.3 CO₂ reduction on an activated In₂O₃-x(OH)y surface

When CO₂ is placed near the surface of the hydrogenated In₂O₃-x(OH)y, the oxygen atom of the CO₂ inserts into the In-H bond (as illustrated in Figure 3). Both carbon and oxygen atoms of CO₂ interact with the surface (In, O and H) atoms to generate a formate-like complex. This initial configuration is highly unstable because of the repulsion between the surface proton and hydride with the electrophilic carbon and nucleophilic oxygen of CO₂, respectively. This adsorbed CO₂ eventually dissociates into CO and H₂O exothermically. The CO is then spontaneously released from the surface. The final step involves the proton exchange from the surface OH group to the newly-formed In-OH site forming an adsorbed water molecule. The catalytic cycle is completed by desorption of this water molecule, regenerating the active FLP site. Activation energy barrier calculations indicate that the dissociation steps for both H₂ and CO₂ are endothermic with activation barriers of 0.66 eV and 1.03 eV respectively. This high activation barrier for CO₂ dissociation indicates that this is the most difficult, and thus rate determining step of the reaction.
Figure 2. Detailed mechanism reduction of CO$_2$ to CO on the surface of hydrogen-activated In$_2$O$_{3-x}$(OH)$_y$. Adapted from Ref. 1 with permission from the PCCP Owner Societies.

5.4.4 Experimental insights into the reaction mechanism

The In$_2$O$_{3-x}$(OH)$_y$ photocatalyst was also investigated experimentally to gain further insight into the reaction mechanism. Using the same capillary flow reactor described in Chapter 2, we measured the photocatalytic activity of In$_2$O$_{3-x}$(OH)$_y$ as a function of temperature and light. As illustrated in Figure 4a, we observed a 4-fold increase in reaction rate under light vs. dark conditions. The maximum operating temperature, 190 °C, was chosen to ensure sample stability. It has been demonstrated by Bielz and coworkers that In$_2$O$_3$ can be reduced to In$^0$ in H$_2$ environments at temperatures above 200 °C. The CO$_2$ reduction rate at 190 °C under 1000 W·m$^{-2}$ (1 sun) of illumination was 153 µmol g$_{cat}$·hr$^{-1}$. In the dark, while measurable CO production was not observed until 165 °C, it increases to 35.7 µmol g$_{cat}$·hr$^{-1}$ at 190 °C. By assuming that the apparent reaction rate constant, k, is proportional to the CO production rate, we prepared a pseudo-Arrhenius plot (Figure 4b) to estimate the apparent activation energy of both the dark and light reactions. The apparent activation energy of the light-driven RWGS reaction was estimated to be 86 kJ·mol$^{-1}$ while for the dark reaction it was estimated to be 107 kJ·mol$^{-1}$. Previous studies reported activation energies of 40 kJ·mol$^{-1}$ or less for photocatalytic reactions,
where the primary reaction barrier was due to 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.\(^6\) This is consistent with the theoretical results presented in the previous sections, which suggest that the dissociation of CO\(_2\) is rate determining. It is therefore possible that photogenerated electrons and holes may assist in this step, resulting in a lower activation energy barrier.

![Figure 3](image)

**Figure 3.** (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. Reproduced from Ref. 1 with permission from the PCCP Owner Societies.

### 5.4.5 Summary of FLP photocatalysis on the surface of \text{In}_2\text{O}_{3-x}(\text{OH})_y

The combination of experimental and theoretical studies discussed herein demonstrates that CO\(_2\) can be reduced at the surface of \text{In}_2\text{O}_{3-x}(\text{OH})_y only in the presence of heterolytically dissociated H\(_2\). The oxygen vacancies in this defected indium oxide create an electron-rich surface, leading to the formation of coordinatively unsaturated indium surface sites (Lewis acid). When formed adjacent to surface indium hydroxide (Lewis base) sites, this combination of Lewis acid-base pair is thought to behave similarly to molecular FLPs. No dissociation of CO\(_2\) was observed in the absence of a H\(_2\) activated site, even if O vacancies and OH groups were present and CO\(_2\) was in vicinity of these defects. Energy barrier calculations indicate that the rate determining step is CO\(_2\) dissociation, correlating well with experimentally derived activation energies. Further work
is needed to understand why the apparent activation energy for light driven RWGS reaction is approximately 20 kJ·mol⁻¹ less than the dark reaction. Currently, excited state DFT calculations are ongoing which should help to answer this question.

5.5 Effect of Inter-Particle Charge Transfer on Photocatalytic Activity in In₂O₃₋ₓ(OH)ₙ Nanocrystal Nanorods

5.5.1 Correlation of photocatalytic activity to excited state lifetimes

In order to gain a better understanding of In₂O₃₋ₓ(OH)ₙ-based photocatalysts, my colleague, Dr. Le He sought to more precisely control their size, shape, and morphology to systematically vary key parameters that affect the material’s activity. The samples describe in this section are mesocrystals composed of interconnected In₂O₃₋ₓ(OH)ₙ nanoparticles in an overall nanorod shape. They are prepared via a thermal decomposition of In(OH)₃ nanorods in a process that is very similar to the one I have used in the previous chapters. By changing the growth time of the precursor In(OH)₃ nanorods, the length of the final In₂O₃₋ₓ(OH)ₙ nanocrystal-nanorods can be tuned. The photocatalytic activity of five In₂O₃₋ₓ(OH)ₙ nanocrystal-nanorod samples of varying lengths is shown in Figure 5a, increasing from samples S1 (shortest) to S5 (longest). As illustrated by this data, the photocatalytic activity correlates well with sample length: longer nanorods lead to higher activity. Figure 5b shows the XPS O1s core level peaks for all five samples. The shoulder peak, which as described in previous chapters corresponds to oxygen vacancies and hydroxides, decreases with increasing nanorod length. This is opposite to the trend that I observed in my In₂O₃₋ₓ(OH)ₙ samples under simulated sunlight irradiation. (b) O1s core level XPS spectra, Reproduced with permission from Dr. Le He.
nanoparticle samples, where more active samples have a higher shoulder peak. One possible explanation for this discrepancy could be related to better intra-particle connectivity in the longer nanocrystal-nanorods. In order to obtain longer rods, the In(OH)$_3$ precursors were heated for longer times, which likely resulted in a greater degree of crystallinity in the longer nanorod precursors. When these In(OH)$_3$ nanorod precursors are then calcined to prepare In$_2$O$_3$ - x(OH)$_y$, this increased crystallinity could lead to better intra-particle contact between the individual nanoparticles, facilitating better charge separation between samples.

In order to confirm if this charge separation hypothesis is correct, transient absorption spectroscopy measurements were carried out on three of the five nanocrystal-nanorod samples, S1, S3, and S5. Figure 6a and b show the normalized transient absorption signal decay at longer time scales (ns-µs regime), which generally correspond to long-lived charge separated states. As is evident in the data presented in Figure 8a, the transient signal at 750 nm – commonly attributed to trapped electrons$^8,9$ - decays much more quickly for S1 than it does for S5, providing strong evidence that long lived charge carriers do exist in these samples. Indeed, the average exciton lifetime increases with increasing length: 1.78 µs for S1, 2.50 µs for S3 and 4.81 µs for S5, respectively. The presence of such long electron lifetimes in the In$_2$O$_{3-x}$(OH)$_y$ nanorod samples suggests the occurrence of an internanocrystal charge transfer process through charge hopping, similar to that observed for mesocrystalline TiO$_2$ superstructures.$^{10,11}$ It is interesting to note that the transient signal decay at 500nm – commonly attributed to trapped holes$^8,9$ - shows no dependence on nanocrystal-nanorod length (Figure 6b). This difference between electron and hole carrier dynamics indicates

![Figure 5](image)

**Figure 5.** Normalized transient absorption traces observed for S1, S3 and S5 at (a) 750 nm and (b) 500 nm. Reproduced with permission from Dr. Le He.
that they are not coulombically bound and therefore behave independently of one another. This data suggests that the electrons are more mobile within the samples and are strongly influenced by nanocrystal-nanorod length, while the holes are trapped in more localized states and are therefore length-independent. This illustrates that inter-particle charge transfer is another important parameter to consider in the design of an effective CO$_2$ reduction photocatalyst.

5.5.2 Photo-enhanced frustrated Lewis pairs

Based on the transient absorption spectroscopy data presented in this chapter and the previous chapter, we have shown that oxygen vacancy sites function as electron traps and surface OH groups function as hole traps. This key insight helps to frame our understanding of the surface FLP mechanism. While the RWGS reaction is thermodynamically uphill ($\Delta G^0 = 29.6$ kJ/mol), as shown in Figure 7, the trapping of photo-excited electrons and holes at FLP surface sites is proposed to increase their basicity and acidity, respectively, and therefore make the hydrogenated In$_2$O$_{3-x}$(OH)$_y$ surface more reactive to CO$_2$ relative to the ground state in the dark, which has the effect of lowering the activation energy for the rate determining step of the RWGS reaction as discussed in Section 5.4.4. Such a difference between Frustrated Lewis Pairs in the
excited compared to the ground state could account for the significantly higher CO$_2$ conversion rate observed for both nanocrystalline In$_2$O$_{3-x}$(OH)$_y$ and In$_2$O$_{3-x}$(OH)$_y$ nanocrystal-nanorod samples in the light compared to the dark. Future work is still needed to understand in detail how the electronic structures and optical properties of the In$_2$O$_{3-x}$(OH)$_y$ samples affects their photocatalytic performance. This improved understanding of the photocatalytic process will help to shed light on the design of photocatalysts with optimized structural, optical, electronic and surface properties to enable more efficient solar fuel production.

5.6 Conclusions

In this chapter I have summarized several key findings from two studies recently completed by our group. We have theoretically and experimentally identified a photocatalytic mechanism for the reduction of CO$_2$ to CO on the surface of In$_2$O$_{3-x}$(OH)$_y$ that requires an active site containing a combination of Lewis basic surface hydroxide groups with adjacent Lewis acidic oxygen vacancies. This surface frustrated Lewis acid-base pair provides an active site capable of heterolytically dissociating H$_2$. Without this H$_2$ activation step, CO$_2$ will not react with the surface. Indeed our calculations indicate that this hydrogenated In$_2$O$_{3-x}$(OH)$_y$ surface is the only surface capable of dissociating CO$_2$ to CO. This mechanism correlates well with data presented in previous chapters that suggested that both surface hydroxides and oxygen vacancies were required in an active photocatalyst.

We have also experimentally demonstrated that the activation energy for the RWGS reaction is 21 kJ mol$^{-1}$ lower in the presence of light. This activation energy of around 80 kJ mol$^{-1}$ which indicates that a chemical reaction step may be the rate determining step.$^5$ This is consistent with the theoretical results which suggest that the dissociation of CO$_2$ is rate determining. It is therefore possible that photogenerated electrons and holes may assist in this step, by migrating to electron and hole traps localized in oxygen vacancies and surface hydroxides, respectively. This could have the effect of making the Lewis basic OH groups more basic and the Lewis acidic groups more acidic, resulting in a lower activation energy barrier for the overall RWGS reaction.

Finally we have demonstrated that while surface defects, such as hydroxides and oxygen vacancies, are very important factors in creating an active photocatalyst, there are many other parameters which can influence the reactivity of a material. By creating an interconnected nanoparticle network in the In$_2$O$_{3-x}$(OH)$_y$ nanocrystal-nanorods, better inter-particle charge
transfer was achieved, resulting in longer electron-hole lifetimes and higher photocatalytic activity, despite slightly lower concentrations of defects in those samples. The results of these studies emphasize the importance of understanding how the surface, defects and morphology of nanostructures function in concert to facilitate gas-phase photochemical carbon dioxide reduction reactions.

5.7 References


Chapter 6
Indium Oxide Coated Silicon Nanowire Arrays: A Hybrid
Photothermal and Photochemical Approach to Solar Fuels
Production

6.1 Statement of Contributions

Dr. Paul O’Brien performed the catalysis experiments. Abdinoor Jelle fabricated the SiNW substrates. I carried out all other synthesis, characterization, and experiments presented in this chapter. Portions of this chapter are currently being prepared for publication.

6.2 Abstract

The field of photcatalysis seeks to harness and convert solar energy into chemical energy to drive useful molecular transformations. Of particular interest is the capture and conversion of greenhouse gas CO$_2$ into carbon-based fuels and chemical feedstocks, with the ultimate goal of providing a more sustainable alternative to traditional fossil-fuels. Defected indium oxide nanoparticles denoted In$_{2}$O$_{3-x}$(OH)$_{y}$ have been shown to function as active photocatalysts for CO$_2$ reduction to CO under simulated solar irradiation. However, the relatively wide band gap (2.9 eV) of indium oxide, which results in utilization of only ~9% of the solar irradiance, and the elevated temperatures (150-190°C) required to facilitate product desorption lower the overall energy efficiency of the process. Herein we report the fabrication of a hybrid material consisting of a vertically aligned silicon nanowire (SiNW) array evenly coated by In$_{2}$O$_{3-x}$(OH)$_{y}$ nanoparticles, which utilizes the vast majority of the solar spectrum and can produce CO at a rate of 22.0 µmol·g$_{cat}$⁻¹·hr⁻¹ without the need for external heating. Further, improved light harvesting efficiency of the In$_{2}$O$_{3-x}$(OH)$_{y}$/SiNW films due to reduction of reflective losses and light trapping within the SiNW array resulted in ~6-fold increase in photocatalytic conversion rates over identical In$_{2}$O$_{3-x}$(OH)$_{y}$ films prepared on roughened glass substrates. This study demonstrates an effective strategy to improve the light harvesting ability, efficiency, and activity of photocatalytic nanomaterials for gas-phase photocatalysis through the use of nanostructured photothermal catalyst support materials.
6.3 Introduction

The emerging field of Solar Fuels seeks to efficiently store radiant solar energy in the form of chemical bonds, which can then be used as fuels or as chemical feedstocks. In order for this challenging goal to become a reality, materials are needed which can efficiently absorb light, using this energy to catalyze useful chemical transformations. For any photo-driven process, utilizing light from the entire solar spectrum is important to achieve optimal efficiency. In the previous chapters, we have demonstrated that defected In$_2$O$_{3-x}$(OH)$_y$ can function as an efficient gas-phase photocatalyst to reduce CO$_2$ to CO via the reverse water gas shift (RWGS) reaction using both UV and visible light. However, indium oxide has a relatively wide band gap (2.9 eV), enabling it to absorb only the blue and UV portions of the solar spectrum. The rest of the light energy hitting the sample is either transmitted or reflected, resulting in a significant loss of efficiency. Further, as was demonstrated in Chapters 2 and 5, optimal temperatures for this reaction are in the range of 150 – 190 °C, which is necessary to facilitate desorption of H$_2$O to regenerate the catalytic site. However, this need for external heating decreases the overall energy efficiency of process.

Recently, our group demonstrated that vertically aligned silicon nanowires (SiNWs) could be used as a photoactive support for Ru-nanoparticle-based thermal catalysts to produce CH$_4$ from CO$_2$ via the Sabatier reaction. Due to its small band gap (1.1 eV) silicon is able to harvest 85% of the light in the solar spectrum. This can be further enhanced by nanostructuring, which has been shown to substantially reduce reflective losses. When these vertically aligned SiNWs absorb light, the majority of the light energy is converted into heat via the thermalization and non-radiative recombination of photo-excited electron and hole pairs. By using concentrated light (~15-20 suns) temperatures of 150 °C can easily be reached without the need for external heating. Such concentrated solar energy can be generated by simple, inexpensive parabolic trough solar concentrators. Using these photoactive SiNW supports, O’Brien et al were able to demonstrate efficient conversion of CO$_2$ to CH$_4$ with rates on the order of 1 mmol·g$_{cat}$⁻¹·hr⁻¹ without the use of external heating. Further, these results suggest that in addition to supporting the reaction photothermally by providing heat energy, a very small fraction of photons absorbed by the SiNWs (approximately 10 out of every billion) were able to generate electron-hole pairs that could directly activate the Sabatier reaction photochemically by facilitating the formation of active hydrogen atoms that participate in the overall photomethanation reaction.
Based on these promising results, we sought to combine these two systems to determine if SiNW supports could enhance the reaction rates of our $\text{In}_2\text{O}_3-x(\text{OH})_y$ nanoparticle photocatalysts, improve the utilization of the solar spectrum, and remove the need for external heating. To this end, we have prepared vertically aligned SiNWs evenly coated by $\text{In}_2\text{O}_3-x(\text{OH})_y$ nanoparticles, which can reduce CO$_2$ to CO at a rate of 22 µmol·g$_{\text{cat}}$·hr$^{-1}$ using no external heating. This stands in stark contrast to both $\text{In}_2\text{O}_3-x(\text{OH})_y$ coated glass substrates and $\text{In}_2\text{O}_3-x(\text{OH})_y$ nanoparticles deposited on SiNW supports in a bi-layer configuration, which exhibit 1-2 orders of magnitude lower reaction rates under the same conditions. Using high-pass cut-off filters we further demonstrate that while some photogenerated electron transfer from the SiNW support to the $\text{In}_2\text{O}_3-x(\text{OH})_y$ nanoparticle catalysts is possible, it is not enough to explain the dramatic enhancement in activity. Instead we propose that the higher CO production rates of the evenly coated $\text{In}_2\text{O}_3-x(\text{OH})_y$/SiNW hybrid structures is a result of improved light harvesting efficiency, which is supported by reflectance measurements. These results demonstrate that evenly coated $\text{In}_2\text{O}_3-x(\text{OH})_y$/SiNW hybrid structures can make much better use of the solar spectrum, simultaneously increasing reaction rates and removing the need for external heating, thereby improving the overall energy efficiency of the process.

6.4 Experimental

6.4.1 Sample preparation

Silicon nanowires substrates were fabricated using a metal-assisted chemical etching (MaCE) technique as previously reported. Briefly, p-type silicon wafers (University wafers, 1-100 Ω/cm) were cut into 1 inch squares and then cleaned with ethanol, acetone and de-ionized water. The wafers were further cleaned by soaking in piranha solution ($\text{H}_2\text{SO}_4$:$\text{H}_2\text{O}_2$ = 3:1 by volume) for 3 hrs and then rinsed with de-ionized water. To grow the silicon nanowires, the cleaned wafers were immersed in 23 ml of an etching solution consisting of 5 M HF (48%HF, Sigma Aldrich) 0.02 M AgNO$_3$ (VWR redi-pak) and allowed to etch for 1 h at room temperature. After the etching process, silver dendrites covering the silicon nanowires were washed off with deionized water. To ensure all the silver nanoparticles and dendrites were removed the etched wafers were placed in concentrated nitric acid (18 M HNO$_3$) for 30 min. The wafers were then washed and dried before being cut into 1 cm$^2$ pieces.
In(OH)$_3$ nanoparticles were synthesized by dissolving 0.3 g of InCl$_3$ (anhydrous, Alfa Aesar, 99.99%) in 10 ml of deionized nanopure water and adding 11 ml of an NH$_4$OH solution (1 ml, Caledon, 28-30 %, diluted with 10 ml of deionized nanopure water) drop-wise at a rate of 20 ml/hr using a syringe pump (KD Scientific). To ensure adequate mixing, the solution of InCl$_3$ was vigorously stirred and the drops of NH$_4$OH solution were added directly into the vortex. After addition of the base, the solution turned opalescent-white, indicating the formation of In(OH)$_3$ nanoparticles. The nanoparticles were separated via centrifugation and washed 3 times with deionized nanopure water, sonicating in between washings to ensure adequate removal of any trapped impurities. The particles were then redispersed in 5 ml of deionized nanopure water and sonicated overnight (approximately 20 hrs) to break up any agglomerated particles. The resulting solution was opalescent and the nanoparticles were colloidally stable for over a month.

Indium oxide nanoparticle coatings were prepared by diluting the In(OH)$_3$ nanoparticle solution 3 times with deionized nanopure water and drop-coating 150 µl onto the SiNW substrate and drying in a oven at 100 °C for approximately 15 min. The films were then calcined for 3 hrs at 250 °C in a pre-heated furnace to convert the In(OH)$_3$ to In$_2$O$_{3-x}$(OH)$_x$ and obtain sample loadings of ~1.5 mg for each sample. As a control, In$_2$O$_3$ films on frosted glass substrates (Erie Scientific) were also prepared by the same method. Frosted glass substrates which were chosen instead of planar glass to improve the mechanical stability of the film as well as more closely mimic the non-planar nature of the SiNW substrate.

6.4.2 Physical characterization

Powder X-ray diffraction (PXRD) was performed on a Bruker D2-Phaser X-ray diffractometer, using Cu Kα radiation at 30 kV. Sample morphology was characterized by scanning electron microscopy using a QUANTA FEG 250 ESEM. High angle annular dark field (HAADF) high resolution scanning transmission electron microscope (HR-STEM) images were taken with a Nion UltraSTEM200 at 200 kV. The low magnification HAADF-STEM images were taken with a JEOL ARM200CF at 200 kV. Both of these microscopes are aberration corrected. The diffuse reflectance of the samples was measured using a Perkin Elmer Lambda 1050 UV/VIS/NIR spectrometer equipped with an integrating sphere with a diameter of 150 mm.
6.4.3 Catalysis measurements

Gas-phase photocatalytic rate measurements were conducted in a custom-built 12 mL stainless steel batch reactor with a fused silica view port sealed with Viton O-rings. The pressure inside the reactor was monitored using an Omega PX309 pressure transducer. For light tests, the reactors were illuminated by a 300 W Xe Lamp (Newport) and focused onto the sample. The light intensity was determined using a Spectra-Physics power meter (model 407A). For heated tests the reactor temperatures were controlled by an Omega temperature controller combined with a thermocouple placed in direct contact with the back side of the SiNW support. Product gases were analyzed with a flame ionization detector (FID) 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 reactor was purged with H$_2$ for 10 min prior to being infiltrated with CO$_2$ and H$_2$ to a pressure of 2 atm at a ratio of 1:1 (stoichiometric for the reverse water gas shift reaction). Isotope product gases were separated using a 60 m GS-Carbonplot column and measured using an Agilent 7890A gas chromatographic mass spectrometer (GC-MS).

6.5 Results and Discussion

In order to establish if using SiNW supports could positively impact the light harvesting efficiency and reaction rates of our In$_2$O$_{3-x}$(OH)$_y$ nanoparticle photocatalysts, as a proof of concept, we drop-cast an aqueous suspension of our most active In$_2$O$_{3-x}$(OH)$_y$ nanoparticle photocatalyst material (denoted I-250 in previous chapters) onto the SiNW support. As illustrated in Figure 1a, the interconnected nature of the pre-formed In$_2$O$_{3-x}$(OH)$_y$ nanoparticles prevented efficient penetration into the SiNW network and resulted in a bi-layer structure. In order to evaluate its photocatalytic activity, this In$_2$O$_{3-x}$(OH)$_y$/SiNW bi-layer film was placed in a custom-designed stainless steel reactor, which was charged with a 1:1 mixture of H$_2$ and $^{13}$CO$_2$ (stoichiometric for the reverse water gas shift reaction) at a pressure of 2 atm and allowed to react for 3 hrs under dark or light conditions. Despite the lack of significant, direct contact between In$_2$O$_{3-x}$(OH)$_y$ nanoparticles and the SiNW supports, we were able to achieve CO production rates of $\sim$0.2 µmol·g$_{cat}$·hr$^{-1}$ with this I-250/SiNW bi-layer structure under $\sim$15 suns of illumination.$^7$ This rate is nearly identical to the CO production rate for original I-250 nanoparticles films under $\sim$ 2 suns of illumination.$^5$ Additionally, as expected, in the absence of
light, almost no CO was produced. These results confirmed that the photocatalytic RWGS reaction on In$_{2O_{3-x}}$(OH)$_y$ nanoparticles could be driven entirely with light energy. However, as illustrated in Figure 1a, the distribution of the In$_{2O_{3-x}}$(OH)$_y$ nanoparticles on the SiNW created by simply drop-casting preformed In$_{2O_{3-x}}$(OH)$_y$ nanoparticles is not optimal; apart from the interface between the two layers, each component is almost entirely isolated from the other. In order to determine if there could be any synergistic effects by more intimately combining the two materials, as suggested by the results of O’Brien et al, we sought to improve the contact between the SiNWs and the In$_{2O_{3-x}}$(OH)$_y$ nanoparticles by first coating the SiNW substrate with an indium hydroxide precursor and then calcining the entire ensemble to produce evenly coated In$_{2O_{3-x}}$(OH)$_y$/SiNW hybrid materials.

6.5.1 Synthesis of indium hydroxide precursor nanoparticles

As demonstrated in Chapter 3, the choice of precursor has a very strong effect on the reactivity of the final In$_{2O_{3-x}}$(OH)$_y$ photocatalyst, controlling the number and type of defects present. Indium hydroxide-based precursors produce the most active In$_{2O_{3-x}}$(OH)$_y$ photocatalysts, which has been attributed to the maximization of surface hydroxide and oxygen vacancies that create active sites for the surface-mediated reduction of CO$_2$ to CO. However, indium hydroxide is very insoluble in water and readily forms an interconnected gel-like precipitate upon the addition of base. In order to efficiently infiltrate and evenly coat the SiNW structure, small, isolated, colloidally stable indium hydroxide nanoparticles are necessary. The rapid reaction of In$^{3+}$ salts...
with hydroxide ions presents a synthetic challenge that is typically overcome with the use of ligands such as sodium citrate or EDTA, which have been demonstrated to enable significant control of the morphology of the resulting In(OH)$_3$ nanostructures.$^{10,11}$ However, because the ultimate application is gas-phase heterogeneous catalysis, which is a surface-mediated process, ligands can adversely impact the reactivity of the sample by blocking active surface sites. Further, carbon contamination resulting from residual carbon-containing species can complicate the analysis of photocatalytic activity. One ligand-free method that has been employed in the literature is the slow addition of base to prevent pH gradients and allow more homogeneous, controllable reactions. For example, the gradual decomposition of urea at elevated temperature has been employed by my colleague Dr. Le He (as described in the previous chapter) and others, to produce size- and shape-controlled In(OH)$_3$ nanostructures.$^{11-13}$

In order to be able to more directly compare these new materials with the indium oxide photocatalysts produced in previous chapters, we sought to alter as few reaction parameters as possible. To this end, we developed a modified version of the original indium hydroxide precursor synthesis which employs the same starting materials: InCl$_3$ as the In$^{3+}$ source and ammonium hydroxide (NH$_4$OH) as the base, but employs a similar strategy of controlled, gradual addition of the basic component. In this modified procedure, a syringe pump is used to very slowly add dilute NH$_4$OH to a vigorously stirred dilute aqueous solution of InCl$_3$. This results in the production of a translucent suspension of indium hydroxide nanoparticles, which can be separated from solution via

**Figure 2.** Comparison of the powder X-ray diffraction patterns of as-prepared indium hydroxide nanoparticle precursor and the standard indium hydroxide precursors used in previous chapters. The vertical black lines correspond to a standard cubic In(OH)$_3$ diffraction pattern. The asterisks correspond to unidentified peaks that may be attributed to weakly crystalline InOOH phases.$^{14}$
centrifugation and washed with water to remove any residual chloride or ammonium impurities. This washing step, while necessary to ensure the purity of the resulting indium hydroxide precursor, results in some aggregation of the as-formed indium hydroxide nanoparticles. To overcome this, we found that rigorously sonicking the particle suspension overnight (approximately 20 hours) was sufficient to break up any agglomerated particles. The resulting solution was opalescent and the nanoparticles were colloidally stable for over a month. The powder X-ray diffraction (PXRD) pattern in Figure 2 demonstrates that the indium hydroxide nanoparticle precursor is very similar to the original gel-like indium hydroxide precursor used in the previous chapters. Both samples appear to be weakly crystalline, showing evidence of both In(OH)$_3$ and InOOH crystalline phases. Because the starting materials are the same and the reaction conditions are comparable, the similarity of the resulting indium hydroxide precursors is unsurprising and suggests that indium oxide nanomaterials prepared from such precursors will also likely be very similar.

Figure 3. Cross-sectional scanning electron microscope (SEM) images of In$_2$O$_{3-x}$(OH)$_y$/SiNW sample (a and c) and In$_2$O$_{3-x}$(OH)$_y$ on glass (b and d).
6.5.2 Fabrication and characterization of evenly-coated In$_2$O$_3$/SiNW hybrid samples

Evenly-coated In$_2$O$_{3-x}$(OH)$_y$/SiNW samples were prepared by drop-casting the colloidally stable indium hydroxide nanoparticle suspension onto freshly prepared SiNW arrays. The resulting films were dried and then calcined at 250 °C for 3 hr in a process analogous to the original In$_2$O$_{3-x}$(OH)$_y$ synthesis described in previous chapters. As a control, the same quantity of indium hydroxide nanoparticle suspension was drop cast onto a roughened glass substrate. As shown in the scanning electron microscope (SEM) images in Figure 3, using the indium hydroxide nanoparticle suspension results in an even coating of both the SiNW and glass substrates. From the higher magnification images of the In$_2$O$_{3-x}$(OH)$_y$/SiNW and In$_2$O$_{3-x}$(OH)$_y$/glass samples in Figure 3c and 3d, respectively, it is clear that the In$_2$O$_{3-x}$(OH)$_y$ nanoparticle sizes are quite small, in most cases much less than 100 nm. The energy dispersive X-ray (EDX) mapping data in Figure 4 confirms that the observed particles coating the SiNW and glass substrates are In- and O-containing. In particular, on the SiNW substrate, it is important to note that the distribution of In and O is very even throughout the nanowires structure, indicating that the nanoparticles are able to penetrate all the way to the base of the nanowires, even with the simple drop-casting.
One possible reason for this is the SiNW are highly hydrophilic and, upon addition, the indium hydroxide nanoparticle aqueous suspension is visibly drawn into the inter-nanowire spaces by capillary forces.

The PXRD patterns shown in Figure 5 confirm that after calcination the indium hydroxide nanoparticles deposited on both the SiNWs and on glass produce pure crystalline cubic, bixbyte indium oxide. The two diffraction patterns are almost identical with the only difference being the two very sharp peaks at 33° and 62° 2 theta (marked with an asterix) in the $\text{In}_2\text{O}_{3-x}(\text{OH})_y$/SiNW pattern. These reflections originate from the [100] face of the Si wafer which was etched to make the SiNW substrate. The fact that only those two peaks appear, and not the rest of the peaks in the Si diffraction pattern, indicates that the preferred orientation is maintained and the SiNWs remain single-crystalline.

### 6.5.3 Photocatalytic activity of the $\text{In}_2\text{O}_{3-x}(\text{OH})_y$/SiNW hybrid structure

In order to evaluate their photocatalytic activity, these evenly-coated $\text{In}_2\text{O}_{3-x}(\text{OH})_y$/SiNW and $\text{In}_2\text{O}_{3-x}(\text{OH})_y$/glass films were placed inside of a custom-designed stainless steel reactor, which was charged with a 1:1 mixture of H$_2$ and $^{13}$CO$_2$ (stoichiometric for the reverse water gas shift reaction) at a total pressure of 2 atm. For experiments requiring light, the sample was illuminated with a 300 W Xe lamp, focused to an intensity of ~20 suns. Figure 6a and b show the GC-MS spectra corresponding to the 29 amu mass fragment for both the $\text{In}_2\text{O}_{3-x}(\text{OH})_y$/SiNW and $\text{In}_2\text{O}_{3-x}(\text{OH})_y$/glass samples, respectively. As was discussed in previous chapters, the 29 amu mass
Figure 6. (a) GC-MS spectra at 29 amu of In$_2$O$_3$-x(OH)$_y$ on SiNW in both dark and light. (b) GC-MS spectra at 29 amu of In$_2$O$_3$-x(OH)$_y$ on glass in dark and light, as well as light with external heating to bring the temperature up to 150 °C. (c) $^{13}$CO production rates of In$_2$O$_3$-x(OH)$_y$ on SiNW in light and In$_2$O$_3$-x(OH)$_y$ on glass in light with external heating.

Fragment is significant because it corresponds to $^{13}$C-labelled CO. Such isotope-tracing experiments are crucial to distinguishing between carbon-containing products produced by the direct reduction of $^{13}$CO$_2$ and carbon-containing products resulting from reactions with adventitious carbon contamination, which is comprised of the more naturally abundant $^{12}$C isotope. Figure 6a shows the $^{13}$CO production of the In$_2$O$_3$-x(OH)$_y$/SiNW film both in the dark and under ~20 suns of illumination. It is clear that no $^{13}$CO is produced under dark conditions, however under light conditions, a substantial $^{13}$CO peak is observed. Under such strong light intensity, the SiNW substrate easily reached a temperature of 150 °C, which as demonstrated in previous chapters is required to facilitate catalytic turnover of the active site by releasing the water byproduct of the RWGS reaction. As expected based on the results of the preliminary tests using the In$_2$O$_3$-x(OH)$_y$/SiNW bi-layer structure, these results demonstrate that the SiNW substrate is capable of facilitating the photocatalytic reduction of CO$_2$ to CO via the reverse water gas shift reaction without the use of an external heat source.

On the other hand, as shown in Figure 6b, the In$_2$O$_3$-x(OH)$_y$/glass control sample shows no evidence of $^{13}$CO production in both the dark and under ~20 suns of illumination. Using only concentrated light, the substrate and sample were able to reach a maximum of 110 °C, which is not sufficient to facilitate the RWGS reaction on the In$_2$O$_3$-x(OH)$_y$ surface. In order to provide a more fair comparison between the two films, a third test was run for the In$_2$O$_3$-x(OH)$_y$/glass sample in which external heating was applied to the reactor to bring the temperature up to 150 °C. Under illumination with the addition of this external heat, a clear $^{13}$CO peak is observed.
Figure 6c shows the $^{13}$CO production rates calculated for both the In$_{2}$O$_{3-x}$(OH)$_{y}$/SiNW and In$_{2}$O$_{3-x}$(OH)$_{y}$/glass samples. It is clear that the In$_{2}$O$_{3-x}$(OH)$_{y}$/SiNW sample produces substantially more $^{13}$CO than the In$_{2}$O$_{3-x}$(OH)$_{y}$/glass sample. Indeed, the In$_{2}$O$_{3-x}$(OH)$_{y}$/SiNW sample produces $^{13}$CO at a rate of 22.0 µmol·g$_{cat}$·hr$^{-1}$, while the In$_{2}$O$_{3-x}$(OH)$_{y}$/glass sample produces $^{13}$CO at a rate of 3.8 µmol·g$_{cat}$·hr$^{-1}$. This represents nearly a 6-fold increase in reaction rate for the In$_{2}$O$_{3-x}$(OH)$_{y}$/SiNW sample under identical temperature and light conditions.

6.5.4 Investigation of the substrate’s role in enhancing the CO$_2$ reduction rates

In order to gain a better understanding of the underlying cause of this enhancement, we sought to probe more deeply into the role of the substrate in the CO$_2$ reduction reaction. In the study performed by O’Brien et al., they demonstrated that photogenerated electron transfer from SiNW to Ru was responsible for a portion of the CH$_4$ produced via the photomethanation reaction on Ru/SiNW hybrid structures. The work function of Ru lies at a lower energy than the conduction band minimum (CBM) of Si, which likely provided the necessary driving force to facilitate photogenerated electron transfer. Figure 7a shows a band offset diagram for Si and In$_{2}$O$_{3-x}$(OH)$_{y}$. As illustrated, the CBM of Si lies above the CBM of In$_{2}$O$_{3-x}$(OH)$_{y}$, indicating that photogenerated electron transfer from Si to the CB of In$_{2}$O$_{3-x}$(OH)$_{y}$ may be possible. In order to test this hypothesis, we examined the $^{13}$CO production rates of the In$_{2}$O$_{3-x}$(OH)$_{y}$/SiNW film both with and without a 495 nm high-pass cut off filter. Because the absorption onset of In$_{2}$O$_{3-x}$(OH)$_{y}$ is around 425 nm (2.9 eV), by blocking all photons with energy greater that 495 nm, we can

![Diagram](image.png)

**Figure 7.** (a) Band diagram indicating the respective energy level offsets for the conduction band (CB) and valence band (VB) of Si and In$_{2}$O$_{3-x}$(OH)$_{y}$. (b) GC-MS spectra at 29 amu and (c) $^{13}$CO production rates of In$_{2}$O$_{3-x}$(OH)$_{y}$ on SiNW in light both with and without a 495 nm high-pass cut-off filter.
selectively excite the SiNWs. By using a filter, a portion of the solar spectrum is removed, so in order to ensure a fair comparison between the two tests, we increased the intensity of the lamp to ensure the temperature of the SiNW support reached 150°C, in order to keep the temperature the same for tests with and without a filter. As shown in Figures 7b and 7c, the reaction rate for $\lambda > 495$ nm is substantially lower than the rates for the sample without a filter. However, a small $^{13}$CO peak is observed, even with the 495 nm cut-off filter, corresponding to a $^{13}$CO production rate of 0.8 $\mu$mol·g$^{-1}$·hr$^{-1}$. This indicates that while photogenerated electron transfer from Si to In$_2$O$_{3-x}$(OH)$_y$ may occur to a small extent, it is not likely the dominant cause for the significant enhancement in the rates for In$_2$O$_{3-x}$(OH)$_y$/SiNW over In$_2$O$_{3-x}$(OH)$_y$/glass.

Another possible explanation for the observed enhancement in $^{13}$CO production rates for the In$_2$O$_{3-x}$(OH)$_y$/SiNW sample is the dramatically different optical properties of the two substrates. Figure 8a shows the reflectance spectra, collected using an integrating sphere, for both the In$_2$O$_{3-x}$(OH)$_y$/SiNW and In$_2$O$_{3-x}$(OH)$_y$/glass samples as well as the reflectance spectra for a bare SiNW film. The reflectance spectrum of the In$_2$O$_{3-x}$(OH)$_y$/SiNW sample overlaps almost perfectly with the reflectance spectrum of the bare SiNW film, averaging a 3.4% reflectance over the entire UV to near-IR spectral range. By contrast, the In$_2$O$_{3-x}$(OH)$_y$/glass sample shows substantially higher reflectance across the entire spectral range, with an average reflectance of 12.5%. However, it should be noted that while the In$_2$O$_{3-x}$(OH)$_y$/SiNW sample is opaque, the In$_2$O$_{3-x}$(OH)$_y$/glass sample is translucent, as shown in the photograph in Figure 8b. In the case of the In$_2$O$_{3-x}$(OH)$_y$/SiNW sample where transmittance is negligible, low reflectance implies enhanced light trapping and absorption in the SiNW support. On the other hand, for the In$_2$O$_{3-x}$(OH)$_y$/glass sample where transmittance is not negligible, while the reflectance averages around 12.5%, the amount of light actually absorbed by the sample is significantly lower. In order to estimate the light absorption by the In$_2$O$_{3-x}$(OH)$_y$/glass film, we measured a second reflectance spectrum in which the transmission is blocked by covering the back of sample film with an opaque Spectralon film, which was used as the 100% reflectance standard for all 4 measurements. As expected, the In$_2$O$_{3-x}$(OH)$_y$/glass film absorbs very little light throughout the visible and near-IR region of the spectrum and only begins to absorb strongly at wavelengths $>500$ nm, which corresponds to the onset of absorption of In$_2$O$_{3-x}$(OH)$_y$. The effect of this difference in optical properties between the In$_2$O$_{3-x}$(OH)$_y$/SiNW and In$_2$O$_{3-x}$(OH)$_y$/glass can be clearly seen in Figures 8c and 8d, respectively. These photographs depict the two samples in the
Figure 8. (a) UV-Vis-NIR reflectance spectra of In$_2$O$_{3-x}$(OH)$_y$ on SiNW and glass. Due to the transparency of the In$_2$O$_{3-x}$(OH)$_y$/glass film, a second reflectance spectrum is also shown in which the transmission is blocked by covering the back of the sample film with a 100% reflectance standard. For comparison, the reflectance spectrum of bare SiNWs is also shown. (b) Photographs of the In$_2$O$_{3-x}$(OH)$_y$ films on SiNW (left) and glass (right). (c and d) Photographs of the sample films inside the reactor under the same light intensity: (c) In$_2$O$_{3-x}$(OH)$_y$ on SiNW (d) In$_2$O$_{3-x}$(OH)$_y$ on glass.

reactor under identical illumination conditions (~20 suns). The In$_2$O$_{3-x}$(OH)$_y$/SiNW film exhibits some reflection, however the dark color of the substrate is still visible despite the intense illumination. By contrast, the reflection from the In$_2$O$_{3-x}$(OH)$_y$/glass film is so bright that it is saturating the camera’s detector, indicating that a substantial portion of the incident light is reflected away from the sample and is not utilized to drive the photocatalytic reduction of CO$_2$.

Light harvesting ability is an important property for any photo-driven process and clearly, as these results demonstrate, this type of reflective loss can greatly impact the photocatalytic performance. The main cause of reflection at the interface of a material is due to refractive index mismatch, which in this case would be between the reactant gases and the surface of the
In$_2$O$_{3-x}$(OH)$_y$/SiNW sample films. Porous materials with sub-wavelength features, such as the SiNWs used in this study, can form refractive index gradients where the effective refractive index depends on the volume fraction of the gas and solid phases.\textsuperscript{8,15} Such gradients reduce the refractive index mismatch, significantly lowering the amount of light reflected, which appears to be the case in our SiNW films. Moreover, the surface roughness of the SiNW substrate induces scattering, which can increase the path-length of light, resulting in greater light absorption. This is further enhanced by the high aspect ratio of the vertically aligned nanowires, which provides more opportunities to trap the incident light by internal reflection.\textsuperscript{8,15} In the case of the evenly-coated In$_2$O$_{3-x}$(OH)$_y$/SiNW films, this effect is significant because it can enhance the ability of weakly absorbing tail states near the band edge of In$_2$O$_{3-x}$(OH)$_y$ to absorb light and participate in the photocatalytic reaction. Conversely, these anti-reflection and light-trapping effects are absent in the In$_2$O$_{3-x}$(OH)$_y$/glass films, which is why the amount of reflected and transmitted light is so high, and the photocatalytic rates are comparatively low.

Light-trapping within the SiNW film could also explain the significant difference between the I-250/SiNW bi-layer structure and the evenly-coated In$_2$O$_{3-x}$(OH)$_y$/SiNW film. In the bi-layer structure the In$_2$O$_{3-x}$(OH)$_y$ is located on top of the SiNW film and is not present inside the pores created by the SiNW, so the light-trapping ability of the film cannot enhance the absorption of the In$_2$O$_{3-x}$(OH)$_y$ nanoparticles. Therefore the only role the SiNW substrate plays in that case is to provide a source of heat, via its photothermal properties. This then can explain why there does not appear to be any enhancement in photocatalytic rates over the original I-250 sample deposited on glass microfiber filter substrate and heated externally (described in detail in previous chapters).

6.5.5 Designing a substrate for improved photocatalytic performance

As demonstrated in the previous sections, the substrate can play an active role in enhancing the photocatalytic performance of an already active nanomaterial. In photocatalysis, utilizing light from the entire solar spectrum is important to achieve optimal efficiency. Vertically aligned SiNW substrates are an attractive option that can harvest light energy from the UV to near-IR. As demonstrated herein, light with energy above the band gap of In$_2$O$_3$ is utilized to drive the photochemical reduction of CO$_2$ to CO, while light with energy below the band gap of In$_2$O$_{3-x}$(OH)$_y$ is absorbed by the SiNW and converted into heat energy to facilitate water
desorption and catalytic turnover of the active site on \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \). Unlike the Ru/SiNW study, transfer of photogenerated electrons from the SiNWs to \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \) does not appear to play a significant role in enhancing the photocatalytic rates. Instead, the enhancement can be attributed to the superior optical properties of the SiNW substrate, which resulted in more interaction with the incident light, and consequently a higher photocatalytic activity than the \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \)/glass sample, despite the two films being coated with identical amounts of the same \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \) material. The longer path length travelled by incident photons within the SiNW array facilitates light absorption by more weakly absorbing tail states, which enhances the overall amount of light captured and converted into chemical energy to facilitate the reduction of \( \text{CO}_2 \) to \( \text{CO} \).

In addition to the optical properties of the SiNW substrates, the distribution of the \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \) nanoparticles on the SiNW films may also play a role in the improved photocatalytic rates. For example, in the evenly-coated \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \)/SiNW film, because of the improved contact between the \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \) nanoparticles and the SiNWs, localized heating resulting from the photothermal effects within the Si may also help to enhance the rates. Further, as the SEM images in Figure 2 illustrates, depositing \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \) nanoparticles on the SiNW substrates increases the accessible surface area which can improve the gas-nanoparticle contact, reducing mass-transfer limitations resulting from restricted reactant or product gas diffusion.

The strategies described herein are not limited to \( \text{CO}_2 \) reduction applications and could foreseeably be applied to enhance the photocatalytic activity of many different materials for a variety of reactions. Further, as demonstrated herein, it is not necessary for photogenerated electron transfer to occur in order to observe a substantial increase in reaction rates. This type of hybrid support structure, which combines both photothermal effects and improved light harvesting ability, would be suitable for any gas-phase reaction that requires both light energy and heat energy.

### 6.6 Conclusions

In this study, we have examined the impact of using vertically aligned SiNWs as an active support for \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \)-based gas-phase photocatalysts. These hybrid nanostructured materials utilize the solar spectrum more efficiently than \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \) alone. Solar photons with energy greater than the band gap of \( \text{In}_2\text{O}_{3-x}(\text{OH})_y \) (>2.9 eV) contribute to the photocatalytic reduction of \( \text{CO}_2 \), while sub-band gap photons (<2.9 eV) are absorbed or trapped by the SiNW arrays,
generating heat to drive the reaction using only light energy. Further, our results demonstrate that by evenly coating In$_2$O$_{3-x}$(OH)$_y$ nanoparticles onto these SiNW arrays, the photocatalytic reduction rates of CO$_2$ can be significantly enhanced. We have achieved a nearly 6-fold enhancement over identical In$_2$O$_{3-x}$(OH)$_y$ films on roughened glass substrates, which we attribute to improved light harvesting efficiency and light trapping due to internal reflections within the SiNW array. The longer path length travelled within the SiNW array facilitates light absorption by more weakly absorbing tail states in In$_2$O$_{3-x}$(OH)$_y$, effectively increasing the visible light absorption of the In$_2$O$_{3-x}$(OH)$_y$ photocatalyst. Finally, the even distribution of the In$_2$O$_{3-x}$(OH)$_y$ nanoparticles on the SiNW array may also allow for localized heating effects that can further enhance the photocatalytic reaction rates. The utilization of nanostructured photothermal support materials to provide a direct source of heating and enhance the light absorbing properties of active photocatalytic materials represents an effective strategy for improving the photocatalytic conversion rates for gas-phase reactions that requires both light and heat energy.

6.7 References


Chapter 7
Conclusions and Future Work

7.1 Conclusions

In the work presented within this thesis, we have demonstrated that highly defected indium oxide (In$_2$O$_{3-x}$(OH)$_y$) nanoparticles can function as effective gas-phase photocatalysts for CO$_2$ reduction to CO via the reverse water gas shift (RWGS) reaction. Significantly we have found that the number and type of defects have a strong effect on the photocatalytic activity of these nanomaterials. Specifically, both oxygen vacancies and surface hydroxide groups appear to be necessary to facilitate the reaction. The concentration of these defects can be controlled through many reaction parameters. For example, lower calcination temperatures result in a higher concentration of both hydroxides and oxygen vacancies, resulting in more active photocatalytic materials. Further, the choice of precursor plays a significant role in the formation and retention of these defects. Oxidizing anions, such as nitrate, inhibit the formation of oxygen vacancies, producing an inactive indium oxide material, while hydroxide-based precursors allow the creation and retention of both oxygen vacancies and hydroxides within the sample, resulting in the highest activities for all the precursors studied herein.

In order to understand why both hydroxides and oxygen vacancies appear to be necessary in an active indium oxide based photocatalyst, we probed more deeply into the optoelectronic properties of a series of indium oxide samples containing varying concentrations of both types of defects. Using transient absorption spectroscopy we demonstrated that these defects play a significant role in the excited state charge relaxation pathways which strongly correlates to photocatalytic activity. Higher defect concentrations result in longer excited state lifetimes which is attributed to electron and hole trapping in oxygen vacancies and surface hydroxide groups, respectively. This supports the proposed reaction mechanism, developed using both DFT calculations and kinetic analysis, which shows electron and hole localization in these defects may play a central role in the photocatalytic reaction mechanism. In this reaction mechanism, a surface active site composed of a Lewis acidic, coordinatively unsaturated indium atom (created by the presence of an oxygen vacancy) adjacent to a Lewis basic hydroxide, assists the
adsorption and heterolytic dissociation of H₂, which enables the adsorption and reaction of CO₂ to form CO and H₂O as products. Further, without this H₂ activation step, CO₂ will not react with the surface. This mechanism has its analogue in molecular frustrated Lewis pair (FLP) chemistry and catalysis of CO₂ and H₂ and, to our knowledge, represents one of the first descriptions of such an FLP active site in a heterogeneous photocatalytic material.

Finally, preliminary investigation into creating indium oxide/silicon nanowire (In₂O₃₋ₓ(OH)ᵧ/SiNW) hybrid structures indicates that reaction rates for In₂O₃₋ₓ(OH)ᵧ-based photocatalysts can be substantially improved by combining it with a substrate that can enhance the efficiency of solar light harvesting and utilization. These vertically aligned SiNW substrates not only improve reflective losses and facilitate light trapping in the region of the solar spectrum corresponding to light absorption by In₂O₃₋ₓ(OH)ᵧ, increasing reaction rates, but also act as a photothermal support, converting the light energy not absorbed by In₂O₃₋ₓ(OH)ᵧ into localized heat energy that removes the need for external heating, thereby improving the overall energy efficiency of the process.

7.2 Future Work

Despite these advances, there is still much work to be done in order to make large scale solar fuel production possible. While we have substantially increased our understanding of how and why such defected indium oxide nanomaterials can harness light energy to facilitate gas-phase CO₂ reduction via the RWGS reaction, there are still many aspects of this process that remain unknown. If we hope to apply what we have learned from this material to rationally design new and more efficient photocatalysts, we will need to obtain a better fundamental understanding of the excited state CO₂ reduction mechanism. As discussed in the previous chapters, preliminary results suggest that photogenerated charge carrier localization in hydroxides and oxygen vacancies is responsible for enhancing reaction rates under illumination; however, more work is needed to pin down exactly how CO₂ interacts with the photo-activated, hydrogenated surface. This can be achieved by examining the charge carrier dynamics using transient absorption spectroscopy under H₂ and CO₂ atmospheres to more closely mimic reaction conditions. We anticipate that these studies will provide further insight into the reaction mechanism, in particular the role of excited state electron transfer to surface adsorbed reactant species. Additionally, we
are currently using computational techniques to develop an excited state reaction mechanism that can help to explain how H₂ and CO₂ react with these light activated surfaces.

There is also more work to be done to understand how the surface properties of In₂O₃₋ₓ(HOH)ᵧ affect reactant adsorption and product desorption. Both \textit{in situ} infrared (IR) and \textit{in situ} thermogravimetric analysis (TGA) measurements under reaction conditions could help to explain exactly how these molecules interact with the In₂O₃₋ₓ(HOH)ᵧ surface in the dark vs. in the light. Further, \textit{in situ} IR spectroscopy in the presence of probe molecules such as CO and NH₃ could help to provide a more direct measure of the Lewis acidic and basic sites, respectively, existing within our In₂O₃₋ₓ(HOH)ᵧ materials.¹⁻³ Such in-depth understanding of the interplay between the photocatalytic activity, surface chemistry and the materials properties, particularly in the presence of light, will help enable us to determine which components can be improved upon to enhance the reaction rates.

On the more applied side, while indium oxide is a very interesting material to study from a scientific standpoint, there are several key issues that preclude its use on an industrial scale. First, indium oxide is a relatively expensive material, and is not very earth-abundant. Therefore, in order to realize large scale solar fuel production, it is crucial to develop other photocatalytic materials that are based on more earth-abundant, less expensive elements. Further, the reaction rates reported herein are not sufficiently high enough, and would need to be increased by several orders of magnitude to be competitive with current thermally activated heterogeneous catalysts. However, it is our hope that by applying the concepts described within this work, the rational design of the next generation of more active, earth abundant photocatalysts can be achieved.

Some specific areas of interest are the synthesis of other oxygen deficient hydroxylated metal oxide nanomaterials prepared via similar thermal dehydration reactions that convert metal hydroxides to metal oxides. By carefully controlling the transition temperature, it may be possible to preserve sufficient residual OH content within the material and generate surface oxygen vacancies and coordinately unsaturated metal sites which are analogous to the active site in In₂O₃₋ₓ(HOH)ᵧ. Of particular interest, building on the surface frustrated Lewis pairs (FLP) mechanism described herein, are metals which can enhance the Lewis acidity or basicity of surface active sites. Likely, a mixture of different metals will be needed to achieve higher reactivity, so a good starting point could be preparing (M,In)₂O₃₋ₓ(HOH)ᵧ mixed metal oxides to
determine how varying the elemental compositions affects the photocatalytic activity relative to pure $\text{In}_2\text{O}_3\cdot x(\text{OH})_y$. Controlling the distribution of metal sites within these new materials will be synthetically challenging and will likely require some trial an error, however computational simulations may help to more rationally guide materials selection and reduce the number of elements to explore. Another possible way to tune the FLP surface site could be by replacing the surface hydroxide groups with more basic amine groups, which may provide a simple way to enhance the reactivity of $\text{In}_2\text{O}_3\cdot x(\text{OH})_y$ and other catalytic materials. Clearly, much more work is needed both computationally and experimentally to determine which modifications will produce more active photocatalytic materials, however, this surface FLP mechanism provides an interesting framework to use to tune the materials properties and thus the photocatalytic activity.

Another area of materials design that is important to consider for photocatalytic applications is improving the visible light adsorption. While we have demonstrated that choosing an appropriate substrate can help to improve light harvesting efficiency even in relatively wide band gap materials such as indium oxide, in order to further enhance the light harvesting efficiency, the next generation of defected metal oxide-based photocatalysts should be designed to have smaller band gaps, and thus directly absorb a higher proportion the incident solar irradiation. Elements of choice in this regard include Mn, Fe, Co and Ni due to the high visible absorption of metal oxides prepared from these elements.

Finally, an interesting property of indium oxide that has yet to be explored in the context of photocatalysis is the effect of the high surface conductivity resulting from shallow donor states created by surface oxygen vacancies that form a surface rich in electrons, which could further facilitate electron transfer to adsorbed molecules such as CO$_2$. It would be interesting to investigate other conductive metal oxides such as SnO$_2$, Ga$_2$O$_3$, and ZnO, to determine if surface conductivity is also an important design parameter to consider.

While, there is still much to be done before large scale solar fuel production becomes a commercially viable technology, it is our hope that the work described herein will provide some help and guidance in elemental composition selection and materials design for the next generation of gas-phase CO$_2$ reduction photocatalysts.
7.3 References

