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Photocatalytic Carbon Dioxide Conversion to Fuel for Earth and Mars

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Photocatalytic Carbon Dioxide Conversion to Fuel for Earth and Mars

by

Anne J. Meier

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
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DEDICATION

In memory of my mother, who wanted to be an engineer, but was told she could not. Her memory is a force of nature that inspires me to never give up. To Eric, who encouraged me through all stages of this journey. And to all of those who have come before me, and to those who will come after me, with goals to work hard and achieve good things for our ‘spaceship Earth’.

Per aspera ad astra.
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ABSTRACT

As far as we know, we only have one planet to live on, with a delicate atmospheric system providing us safety and life. Global CO₂ emissions continue to plague the environment of Earth, primarily due to the processing of fossil fuels, deforestation, and industrialization. There are several avenues of pursuing CO₂ reutilization, each having their own benefits and limitations. Direct and indirect thermochemical approaches of CO₂ conversion boast of efficient CO₂ conversion rates but have limitations associated with the use of renewable hydrogen and high temperatures of operation. The work in this dissertation investigates low temperature photocatalytic CO₂ conversion, a simple principle, which provides opportunity for fuel production while harvesting solar energy. Large scale implementation of this process has been plagued by limitations such as fast electron/hole recombination rates, poor quantum efficiency, product selectivity, catalyst stability, and the band gap energy (Eg) being too large to harvest solar light. Our long term goals and applications look to utilize sustainable fuel generation in-situ on Mars for human exploration. We must use available Mars resources to generate fuel to save launch and resource costs from Earth, utilizing the Sun, Mars atmospheric CO₂ (95%), and H₂O that can be harvested from subsurface ice. Visible light activated catalysts are needed for applications of CO₂ conversion on Earth and Mars due to the intensity and abundance of visible light available in the solar spectrums.

The dissertation presents the development of photocatalysts for CO₂ reduction in the presence of H₂O under visible light irradiation. Detailed chemical analysis and characterization were performed on the photocatalysts for improved understanding of material design, including
optical and elemental properties, charge transport, stability, catalytic function and scalability. Induced defects and impurities were implemented to understand $E_g$ tunability. Introducing defects through impurities reduced the electron confinement effects in some cases, increasing the photocatalytic activity.

Three material regimes were synthesized, tuned, and tested for catalytic function. The first was a series of $(\text{ZnO})_{1-x}(\text{AlN})_x$, materials that had not been synthesized previously, nor ever demonstrated in CO$_2$ and H$_2$O under solar irradiation. The Zn:Al materials were derived from layered double hydroxides. The second material set was $(\text{ZnO})_{1-x}(\text{GaN})_x$, also derived from layered double hydroxides. To the best of our knowledge, these Zn:Ga materials were demonstrated for the first time in CO$_2$ reduction to CO under visible light without the use of any noble metal co-catalysts or dopants. The third set of materials were MoS$_2$ nanoflowers synthesized via chemical vapor deposition that, to our pleasant surprise, produced thinly stacked sheets in the form of nanoflowers that contained large edge-site exposure, which was vastly different from the morphology of commercially purchased MoS$_2$.

The preliminary results from this work have demonstrated that tunable band gap energy is achievable. The $(\text{ZnO})_{1-x}(\text{AlN})_x$ $E_g$ ranged from 2.84 to 3.25 eV. The Zn:Al solid solution materials were tuned by increasing nitridation time, and varying the cationic ratio. Increasing the cationic ratio in this study more than tripled CO production under solar light irradiation compared to lower cationic ratios. The $(\text{ZnO})_{1-x}(\text{GaN})_x$, materials had a $E_g$ range from 2.33 eV to 2.59 eV. The $E_g$ was also easily tunable from varying nitriding time and cationic ratio. The highest CO production rate was the Zn:Ga cationic ratio of 3:1 at 20 min of nitriding time at 100 °C, which produced 1.06 $\mu$mol·g$^{-1}$·h$^{-1}$. This production was higher than both of our controlled TiO$_2$ experiments, and other reported pure TiO$_2$ solar photoreaction experiments. The results indicate a delicate balance of
nitridation and Zn:M$^{3+}$ ratio should be selected, along with precursor material cation ratios in order to obtain the desired final product and crystal structure. The controlled introduction of imperfections or crystal defects through MoS$_2$ synthesis variations also revealed the tuning ability of flake edge morphology, nanoflower diameter, stacked-sheet thickness, optical Eg and catalytic activity. The nanoflower Eg ranged from 1.38 to 1.83 eV, and the production rates of CO nearly doubled when post treating the nanoflowers in a reduction step.

These developments support tunable gas phase photocatalytic activity and can be enhanced further for further photocatalytic reactions, optoelectronics and field emitter applications. The photoreactor studies indicated that careful tuning of the parent material is imperative to understand before adding a co-catalyst or doping process, as the edge site morphology, crystal phase stability, and strain-induced defects impact the photocatalytic performance.
CHAPTER 1: INTRODUCTION AND BACKGROUND

1.1 Photocatalytic CO₂ Conversion with H₂O

CO₂ emissions are a continuous problem on Earth primarily due to the processing of fossil fuels. Consumption of coal, oil, and natural gas contributes to an annual release of over 30 billion tons of CO₂ into the environment, and is the main suspect to the dramatic climate change on Earth [1,2]. Renewable fuel resources and alternative-energy research have expanded with attempts to alter and reverse this problem, with many photocatalytic reactions looking to convert the CO₂ into CO or C-H containing fuels such as methanol and methane [3]. The concept of light irradiation (Figure 1) onto a photocatalyst material, along with the photogenerated charge carrier formation of holes (h⁺) at the valence band (vb), and electrons (e⁻) in the conduction band (cb) was first reported over 43 years ago by Honda and Fujishima using TiO₂ (tiania) and is now one of the most studied photocatalysts [4].

This technology was predicted to solve the world’s energy problems through photochemical conversion via a renewable source. Photocatalyst studies have investigated preparation techniques, reactants, light sources and desired product formation for CO₂ conversion [5,6]. A main photocatalytic application in these studies is for H₂O splitting, CO₂ conversion and pollution reduction, which have many avenues of complexity and difficulty, and has still not been scaled up for an economically or industrially sustainable solution [7,8]. CO₂ activation is one of the biggest challenges in chemistry, due to molecule stability [9]. The typical stages involved in a photocatalytic process include (1) electron-hole pair (e⁻/h⁺) generation from the excitation of the catalyst via a light (photon) source, (2) charge separation and movement to the catalyst surface,
and (3) redox reactions on the catalyst surface. A photocatalyst that can absorb visible light and have a high enough cb position is challenging because an overpotential is needed as the driving force for charge carrier transport and further desired reactions [3]. Photocatalytic conversion of CO$_2$ to CH$_4$ at high selectivity is also a complicated process requiring 8 e$^-$/h$^+$. The hydrogen evolution reaction (HER) can be the proton source of the photocatalytic CO$_2$ reduction reaction, needing a band gap energy (Eg) range of 1.23 to 2.4 eV [10–14]. The HER and CO$_2$ reduction reaction are dependent on many activities synchronizing correctly, including the formation of the OH radical, crystal phase of the catalyst and delay of the recombinations of the photogenerated e$^-$/h$^+$ pairs [15,16]. The charge separation is one of the most important factors that determine how efficiently a photocatalytic system will operate. The sooner e$^-$ and h$^+$ arrive at their “destination” after being generated by photons, the less likely they will recombine.

Photocatalyst studies have investigated preparation techniques, reactants, light sources and desired product formation, including CO$_2$ conversion [5,6]. Doped, composite, and co-catalyst semiconductor TiO$_2$ based systems have typically used noble metals to extend the responsiveness of photocatalysts into the visible range for CO$_2$ photoreduction [17–20]. It is being realized that for CO$_2$ reduction, doping may slow down charge recombination, but these supplemental materials are costly and not as abundant for scale up. Photocatalysis performance of the materials developed in this work are compared to TiO$_2$ and note that the brookite phase is reported in literature as one of the highest producers of CO and CH$_4$ in CO$_2$ reduction studies [21]. A summary of various TiO$_2$ and ZnO photocatalytic systems are provided in Table C-1 of the Appendix. Experiments are difficult to compare if the light intensity and spectrum are different or not reported in detail. Studies have started to turn to semiconductor heterostructures, which have enhanced light absorption and charge separation, aiding in e$^-$ and h$^+$ movement [3]. Other mechanisms, such as increasing the
surface area of the catalyst (i.e. nanoparticles) to enable more active surface sites, have shown to delay recombination through lattice defects [15,22,23]. This is what has led to the investigation of layered double hydroxide (LDH) materials followed by nitridation, as well as two-dimensional (2D) heterostructures for transition metal dichalcogenide (TMD) materials. These materials are growing in the applications of sensors, fuel cells, and batteries, as well as visible light photocatalysis [6,24,25]. The material structures were also expected to have good photo stability and photocatalytic efficiency, so they were used an ideal baseline and comparative measure before doping or adding co-catalyst material [26,27]. Understanding the materials first is the ideal research plan for a natural progression into more complex studies and understandings.

1.2 Solar Utilization and CO$_2$ Abundance on Earth and Mars

As researchers look to find a solution to the energy problem on Earth, the space program is also advancing their technologies to explore neighboring planets, specifically Mars [28]. To succeed on a long-duration Mars mission, utilization of surrounding resources will be required for fuel production, life support for humans, and energy production, since the up-mass of all required consumables from Earth would be extremely expensive [29]. Pertinent Mars resources available for harvest include the sun, atmospheric CO$_2$, the regolith (Martian soil) and subsurface ice. Success and data validation of photovoltaic solar cells from Mars exploration rovers give confidence for future solar-powered technologies and applications on the Mars surface [30].

On Earth, approximately 4-8% of the solar spectrum lies within the UV energy region and 40-46% lies in the visible energy region at the surface. Varying differences arise from scattering and absorption, latitude, zenith angle, cloud-cover and thickness of the ozone layer on Earth. The solar spectrum on Mars is similar to Earth, but at shorter wavelengths (UV) the solar spectrum is depleted due to suspended dust particles in the atmosphere and surface temperature swings. The
available UV and visible light, is displayed in Figure 1C. The accepted solar constant for Earth is 520.3 W-m$^2$ and on Mars is 223.7 W-m$^2$. The light output measured in this work was closer to the Earth solar constant, which was an acceptable starting point. If a catalyst could perform reasonably near the accepted Earth solar constant, further considerations would be made for Mars applications. Solar concentrators on the surface of Mars could be used to increase the intensity of the solar constant as well.

Sparse previous research exists for CO$_2$ conversion utilizing the Mars atmosphere for fuel production. Chemical reactions between CO$_2$ and H$_2$O under UV irradiation with hematite (a well-known Mars surface abundant iron mineral) have been investigated under laboratory conditions for Mars applications. The experiment was carried out under terrestrial atmospheric pressure and earth ambient temperature. The studies reported the conversion of CO$_2$ to CH$_4$ as well as the formation of several oxygenates [31–33]. Since the atmospheric pressure of Mars is significantly less than that of Earth, photochemical processes would happen on the surface of Mars or near the surface.

On Mars, CO$_2$ conversion in the presence of H$_2$O vapor would be ideal over liquid reactions, as liquid H$_2$O is heavy to launch and carry in transit to Mars. H$_2$O could be extracted from Mars soil and used to support the necessary requirements for a vapor reaction, but it would not be ideal to expect enough H$_2$O for an aqueous reaction, especially when H$_2$O extracted would be desired for O$_2$ production. Another drawback of aqueous suspensions for Mars applications is the low solubility of CO$_2$ in H$_2$O and the reactant ratios are more challenging to tune. Liquid also flows differently in reduced gravity and could add additional design complexity, and so we focus on the gas phase reactions in this study.
1.3 Goals and Objectives

Finding a technology that uses solar irradiation to convert CO$_2$ into fuels or other commodities in a gas phase reaction, is a favorable avenue of development, as it would reduce launch mass from Earth, and spin off into technologies on Earth for greenhouse gas reduction. Since visible light is more abundant on Mars and Earth surface than UV, materials irradiated by solar light, especially those active in visible light, are investigated to observe reaction effects for CO$_2$ conversion in the presence of H$_2$O. The long term goal is to determine efficacy of high performance visible light catalysts, and the ability to tune the visible light properties through synthesis variations and induced defects states. The overall objective of this work was to provide preliminary development of tunable photocatalysts and demonstrate the performance in the presence of H$_2$O and CO$_2$ under visible light for Earth and Mars CO$_2$ conversion to fuel applications. The execution of specific goals that has led to accomplishment of the overall objective included:

1. Synthesis and characterization of solid solution based visible light photocatalysts derived from layered double hydroxide (LDH) precursors: with and without defects and impurities.

2. Synthesis and characterization of 2-dimensionally (2D) grown visible light photocatalysts derived from multi layered and stacked sheets of transition metal dichalcogenides (TMDs), with and without defects and impurities.

3. Demonstrate CO$_2$ conversion in a photoreactor under solar irradiation in the presence of H$_2$O to show reduction of CO$_2$ and the effects of tuning on catalyst performance.
Figure 1. (A) Illustration of the Earth and Mars photocatalysis concept for CO2 conversion to fuels. (B) Process of photocatalytic charge transfer on photocatalyst materials. (C) The available UV and visible light, mean solar irradiance, and accepted solar constant on Earth and Mars[34–36].
CHAPTER 2: MATERIALS AND METHODS

2.1 2D Transition Metal Dichalcogenide Derived Visible Light Photocatalysts

2D TMDs were investigated for their high conversion potential of CO₂ under visible light [37]. Transition metals have d-electrons that fill up different levels, resulting in varying electronic properties, and have potential enhancement of the photocatalytic performance resulting from higher surface availability and increased charge transfer rate. Initial theory on high performance of 2D TMD materials emerged from computational density functional theory (DFT) [38–40], which reported TMD MoS₂ could be used as a successful replacement for noble metals in terms of the HER free-energy diagrams [41]. 2D MoS₂ is built in stacked layers of Mo in hexagonal arrays that are sandwiched between S layers. The crossover from an indirect to direct gap material was accounted for on the thickness-dependent properties of MoS₂. Hence, 2D MoS₂ has potential applications for a variety of fields including catalysis, batteries, photovoltaics, and optoelectronics.

Insight from DFT calculations claim that only the S-Mo-S atomic edge-sites are active for hydrogen adsorption and Mo is responsible for adsorption of H₂. This behavior is similar to that of Pt coated catalyst surfaces, a common dopant in TiO₂ studies. It is important to have as many edge sites exposed as possible for exploitation of the edge sites that possess metallic electronic states during photocatalytic reactions. Therefore, MoS₂ defect sites will have significant interaction with CO₂ or H₂ molecules, and are ideal for gas phase reactions as Mo-S bonds have strong covalent bonding, and interactions between the S layers exist van der Waals interactions, which make the stacked layers of MoS₂ easily separable, but also ideal for gas phase reactions [41–43].
MoS\textsubscript{2} growth using chemical vapor deposition (CVD) synthesis has been one of the most successful synthesis techniques for layer formation, preservation and monolayer sheets thickness control [38,44–51]. Different morphologies of MoS\textsubscript{2} such as flowers, nanoflakes, and nanosheets, have been reported using various precursors (i.e. MoO\textsubscript{3}, MoS\textsubscript{4}, MoCl\textsubscript{5}, and sulfur (S) powders) with vapor deposition onto substrates. Other synthesis techniques have included low pressure CVD (LPCVD) and wet chemical synthesis for low-quality MoS\textsubscript{2} flakes with abundant active sites [52,53].

Intrinsic structural defects are inevitable during CVD and 2D material growth, which can be controlled and systematically exploited for materials evaluation and photocatalytic activity design [54,55]. This aspect of intrinsic structural defects, such as S vacancies on edge sites, were investigated in this research to tune the MoS\textsubscript{2} intrinsic structural defects and surface impurities to play a role in the transport properties at the atomic layers [56–58].

2.1.1 Synthesis of Transition Metal Dichalcogenides

The CVD process in this work utilized a single zone tube furnace (SZF) and a three zone tube furnace (TZF) to produce bulk powder MoS\textsubscript{2} nanoflowers and stacked sheets of MoS\textsubscript{2} flakes grown on Si substrates. Commercially purchased MoS\textsubscript{2} powder was used for baseline characterization comparison. The precursor materials were MoCl\textsubscript{5} and S powder, prepared in an Ar-purged glove box and mixed together in a porcelain combustion boat, and then placed into a fused quartz tube purged with Ar gas. The CVD synthesis equipment is shown in Figure B-1 in the Appendix.

The precursors were set in the respective tube furnace and underwent thermal vapor deposition processing. Si substrates were placed at strategic distances downstream of the precursor boats (see Figure C-1 and C-2 in the Appendix for exact distances), and Ar was flowed at
atmospheric pressure during the operation. During CVD, S vaporized first (melting temperature 115 °C), followed by MoCl\textsubscript{5} (melting temperature 194 °C). The specific temperature settings and variables of the TZF CVD syntheses are displayed in Table C-2 in the Appendix. The SZF samples were performed prior to the TZF samples, and it was later found that holding for 10 or 15 min at 700 °C did not change the product formation as observed by SEM and XRD. To reduce synthesis time, the samples were only held for 10 min after this realization. A shorter time of 5 min was not investigated. The powder formation in the precursor combustion dish was possible because of the large starting mass of the precursor material, which was ~3 g of combined MoCl\textsubscript{5} and S. Additional synthesis details are discussed in Chapter 5.

2.2 Layered Double Hydroxide Derived Visible Light Photocatalysts

The solid solutions of ionic pairs ZnO and GaN, have gained attention for photocatalysis and visible light driven reactions for H\textsubscript{2}O splitting and CO\textsubscript{2} conversion for over 10 years [26]. GaN is known to form a solid solution with ZnO with the same Wurtzite crystal structure, and here we demonstrate the same for AlN. Zn rich solid solutions synthesized from LDH precursors have been shown to absorb light in the visible region well above 500 nm, and will shift to longer wavelength with increasing Zn content [6]. To our knowledge, this is the first time the Zn-Al-CO\textsubscript{3} LDH has been nitrided and closely compared to the same treatment of the Zn-Ga-CO\textsubscript{3} LDH with nitridation, for an in depth study of cationic ratios for tuning in order to observe trends and behaviors of M\textsuperscript{3+} replacement for catalytic function.

Recent work with LDHs also report tunable properties, and are often comprised of abundant materials, decreasing the cost of synthesis. Defects induced by thermal treatment on ZnO materials have been investigated, and considered the increasing specific surface area effect on the
increase in density of surface states from dangling orbitals, and lattice defects. LDH structures have alternating positive and negative layers with an overall Wurtzite structure and take the form $[(M^{2+})_{1-x}(M^{3+})_x(OH)_2]^{x+}(A^{n-})_{x/n}*yH_2O$. $M^{2+}$ and $M^{3+}$ represent the divalent and trivalent cations, and the $A^{n-}$ represents the interlayer anion [59–62]. Implementing an LDH as a precursor is an attractive alternative to traditional materials, as gaseous species can easily diffuse through the interlayer regions and react with the anionic species with minimal additional energy. After a nitridation process on the solid solution LDH, a brucite-like layer results, and a general microscopic hexagonal shape of the catalyst is expected for both pre and post nitridation. It was reported that a Zn-O-Ga-Al-type solid solution reduced $CO_2$ to $CH_4$ at the rate of 9.2 $\mu$mol g$^{-1}$hr$^{-1}$ under visible light illumination [25]. A (GaN)$_{1-x}$(ZnO)$_x$ solid solution catalyst developed from LDH precursors, and porous ZnGaNO also demonstrated potential for HER under visible light irradiation [24].

Since these materials were expected to have good photo stability and photocatalytic efficiency, they were used an ideal baseline and comparative measure before being doped or adding any co-catalyst materials [26,27]. Solid solution based LDH photocatalysts have applications in the field of sensors, fuel cells, and batteries [6,24,25]. These materials have also been shown to support photodegradation of organic pollutants, and have higher photocatalytic activity when decorated with a co-catalyst[63].

### 2.2.1 Synthesis of Layered Double Hydroxides

The synthesis of the solid solutions were prepared using a previously reported co-precipitation method that incorporated a Zn-Ga-CO$_3$ LDH precursor followed by nitridation to obtain the final solid solution (ZnO)$_{1-x}$(GaN)$_x$ [64]. The illustration of the synthesis process is displayed in Figure 2. Here we also introduce the Zn-Al-CO$_3$ LDH to form the final solid solution
(ZnO)\(_{1-x} \) (AlN)\(_x\). The LDH and nitridation processes were supported by literature to yield strong formations of the cationic members and prevent later Zn loss during nitridation [65,66].

For production of the Zn-Al-CO\(_3\), the correct amounts of Zn(NO\(_3\))\(_2\)\(\cdot\)6H\(_2\)O (Sigma-Aldrich) and Al(NO\(_3\))\(_3\)\(\cdot\)9H\(_2\)O (Sigma-Aldrich) for the desired Zn:Al atomic ratio were mixed in deionized (DI) H\(_2\)O and dissolved completely. Separately, Na\(_2\)CO\(_3\) (Fisher) was dissolved in DI H\(_2\)O. The nitrate solution was then slowly added dropwise to 74.5 mL of a 1 M Na\(_2\)CO\(_3\) solution. The solution containing the nitrates was added dropwise, slowly into the carbonate solution, forming the LDH as a precipitate. The initial and final precipitation stage before aging and drying is displayed in Figure C-3 in the Appendix. The pH was checked to be at 8. The precipitate was aged for 22 hours at 80 °C. After aging, the precipitate was rinsed with DI H\(_2\)O (500 mL) via vacuum filtration. The precursor was then dried at 100 °C in a vacuum oven for 1 hour. The dried LDH was ground with a mortar and pestle for approximately 10 min to result in a fine powder. This process was similarly repeated for the Zn:Ga materials.

A desired trait for using the LDH was because the M\(^{2+}\):M\(^{3+}\) ratio can be tailored according to need. The cations were located in the center of an oxygen octahedral, which form a positively charged layer that was balanced by an interlayer containing organic or inorganic anionic species (CO\(_3\))\(^2-\) was the interlamellar anion). The LDH atomic ratio of Zn:Ga or Zn:Al was synthesized for 1:1, 2:1, and 3:1 in the precipitate formulation. These ratios allowed for an observation with increasing Zn content during analysis.

Nitridation of the LDH solids took place with the powders placed in a combustion dish and placed in a tube furnace (Lindberg/Blue) under a constant anhydrous NH\(_3\) gas flow rate of 300 ml/min with a heat rate of 5 °C/min from ambient to 800 °C. The nitridation reactor is shown in Figure B-2 in the Appendix. The thermal boundary of 800 °C was selected because this
temperature provided good crystallinity formation and prevented Zn from completely volatilizing. The 2:1 cationic ratio of Zn:M$^{3+}$ at 20 min of nitridation was the central variable for comparison, since these factors were a good basis for synthesis supported by literature [63,64,67]. The final samples of (ZnO)$_{1-x}$(AlN)$_x$ and (ZnO)$_{1-x}$(GaN)$_x$ nitrided powders were labelled as “M$^{2+}$:M$^{3+}$ (Y:1), ZZ min or Zn:Al (X:1), YY min”, where M$^{3+}$ and M$^{2+}$ represents Zn:Al or Zn:Ga, Y represents the cationic molar ratio of 1, 2, or 3, and ZZ represents 10, 20 or 30 min of nitridation time. Nitridation time in previous research has been upwards of 10 hours[68] and 20 hours[69]. We chose to investigate the shorter nitridation efforts that yielded good crystalline products for reasonable scale up considerations.

The NH$_3$ is an extremely hazardous substance that is caustic and explosive. Care should be taken for proper safety precautions and handling of NH$_3$. The materials were made repeatedly by at least 4 different lab members following the same procedure. LDH and post nitrided solid solution samples were spot checked by testing the samples against XRD, Scanning electron microscopy (SEM) and energy-dispersive X ray spectroscopy (EDS) data to confirm elemental composition and morphology of samples. Additional synthesis and characterization details are discussed in Chapter 3 and 4.

2.3 Characterization Techniques for Photocatalysis

Characterization methods used to study the catalytic materials and will be briefly described in this section. Unless otherwise noted, the instruments and methods listed here were identical to all three regimes of materials that are discussed in the later chapters. Additional information can be found in each of the subsequent chapters.
2.3.1 Microscopy

SEM and transmission electron microscopy (TEM) were utilized to aid in size determination, morphology, abundance, and elemental analysis. A Zeiss EVO 50 with Oxford INCA EDS was utilized, as well as a JEOL JSM 7500F Field Emission (FESEM). The FESEM provided higher resolution than the Zeiss SEM, based on the instrument settings. Some of the FESEM samples were prepared by ultra-sonication in ethanol for 30 min, followed by air drying on the SEM stub. The samples were analyzed on both carbon tape and a C/Cu grid and so the lacy carbon can be seen in the background of some of the images.

Atomic resolution and additional imaging were obtained with a TALOS F2000S TEM and high-resolution TEM (HRTEM). Samples were prepared for TEM analysis by ultra-sonication of the bulk powder in an ethanol cleaner bath for approximately 5 min. The dispersed samples were then mounted on a 3 mm carbon-Cu grid. Lattice spacing was resolved, and diffraction areas were determined for selected samples. This technique was used for crystal determination, lattice spacing, and in some cases, crystal disruptions or defects.

2.3.2 Elemental Analysis

The oxygen and nitrogen content of the solid solutions were measured using a LECO TC 600 elemental analyzer according to the “Oxygen and Nitrogen in Nitride Material” method provided by LECO. For LECO analysis, the powder materials were placed in a tin capsule and inserted into a Ni basket, which was transferred to the loading head for analysis. Standards (ZnO, GaN, and AlN) were purchased from Sigma-Aldrich for calibrating the LECO Elemental Analyzer to validate collected sample data. Data was averaged from 5 samples of each synthesized material and standard. EDS from the Zeiss instrument was also used for elemental analysis to determine atomic composition and quantify impurity in the bulk powders.
2.3.3 X-Ray Powder Diffraction

X-ray powder diffraction (XRD) patterns were obtained using a PANalytical Empyrean machine with Cu Kα radiation (λ = 0.15406 nm) at a scan rate (2θ) of 0.02 degrees per second. The XRD accelerating voltage and applied current were 40 kV and 40 mA, respectively. The lattice parameters and unit cell volume were calculated using Equation 1 and 2 for hexagonal structures where hkl are the Miller indices, d is the spacing between the hkl plane, a and c are the lattice constants, and V is the volume of the unit cell.

\[
\frac{1}{d_{hkl}} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{t^2}{c^2} \quad \text{Equation 1}
\]

\[
V = \frac{\sqrt{3}a^2c}{2} \quad \text{Equation 2}
\]

The XRD reference patterns were obtained from the ICDD, which was provided by the HighScore XRD Software library.

In-situ XRD experiments were performed with a PANalytical X’Pert Pro with an XRK-900 accessory at 1000 mbar (~1 atm) and 10 °C/min ramp from 25 to 200 °C in CO₂ and air. This technique was used to determine structural stability at elevated temperatures in both ambient and reactant conditions.

2.3.4 Bang Gap Energy Determination

Optical absorption properties were analyzed using a Jasco V-760 UV-visible (UV/Vis) spectrophotometer equipped with an ISN-723 Integrating Sphere to obtain diffuse reflectance spectroscopy (DRS). The UV/Vis was operated at ambient conditions with wavelength widths from 300 nm to 800 nm, a 2.0 nm bandwidth, and scan speed of 1000 nm/min at a continuous scan
mode. Eg estimation was obtained from the Jasco VWBG-773 Eg Program Software. The program calculated the Eg from the reflection spectra, converting it to the Kubelka-Munk function, F(R), which is proportional to the absorption coefficient, $\alpha$. The absorption coefficient of the Tauc equation (Equation 3) was substituted with F(R), and the expression became Equation 4, where $h$ is Planck’s constant, $\nu$ is frequency of vibration, and $n$ is the nature of the sample transition [70].

$$
(h\nu\alpha)^{1/n} = A(h\nu - E_g)
$$  
Equation 3

$$
(h\nu F(R))^{1/n}
$$  
Equation 4

Equation 4 was plotted against $h\nu$ (eV) and the first derivative of the curve was taken. The tangent line at the first point of inflection was the Eg (eV). Single-layer TMDs are a direct allowed transition, whereas bulk powders are classified as indirect allowed transitions. In this work, because the TMDs were multistacked, bulk powders, $n = 2$. For LDH materials followed by nitriding, $n = 1/2$.

2.3.5 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectrometry (XPS) measurements were prepared in air and conducted with a Thermo Scientific K-Alpha instrument using Al K\(\alpha\) radiation. The depth profiling used a 300 eV etch energy, 5 second etch cycle, at ~0.35 nm of etching per second.

2.3.6 Raman Spectroscopy

Raman spectroscopy measurements were performed on two different instruments. This technique was used to give insights on impurities or defects laden in the materials. The TMD measurements were collected with a LabRAM HR Evolution under ambient conditions at room temperature. The excitation source was an Ar-ion laser with a wavelength of 532 nm, and the
power was 2 mW. The ZnO based nitrided solid solution Raman spectroscopy data was collected with a Thermo Scientific DXR2 Raman Microscope at 10X, with a high resolution DXR 532 nm laser. The laser power was 6 mW and the aperture was a 50 μm pinhole with a 900 line/cm grating and 2.1 μm spot size. The resolution was 5.5-8.3 cm⁻¹.

2.3.7 Surface Area Characterization

Surface area of the materials in this work was analyzed using a Quantachrome Autosorb IQ automated gas sorption analyzer. Outgassing of the powders before each measurement was done at 200 °C for a time suitable for the material. Adsorption-desorption isotherms were generated via nitrogen physisorption while the samples were submerged in a liquid nitrogen bath at 77.35 K (−195.8 °C). The Brunauer-Emmett-Teller (BET) isotherm allowed for the determination of each surface area. Each physisorption was performed three times.

2.3.8 Thermal Gravimetric Analysis

Thermogravimetric analysis (TGA) of TMD powders was carried out on a TA Instruments TGA Q5000 SA. The TGA heating rate was 25 °C/min to 90 °C and then held for 5 min; the gas flow was air with a flow rate of 25 sccm. TGA was only performed on TMD samples and not LDH or nitrided solid solutions.

2.4 CO₂ Photoreduction Reactor

Some detailed description of the photoreactor experimental procedure and solar simulator hardware is discussed in this section. Additional details can be found in each of the subsequent chapters. There are important considerations for the design of an efficient photoreactor. These considerations include: 1) use of a photocatalyst with high selectivity, 2) provide a large light illumination area with equal distributions of wavelength on the catalyst surface to reduce the loss of photons, and 3) improve the charge carrier recombination and expose as much surface area of
photocatalyst as possible by utilizing efficient catalyst immobilization techniques. Common techniques to immobilize catalysts in a reactor include coating a catalyst or utilizing a fixed bed reactor. Coated catalysts often involve surface coated substrates such as glass, optical fiber, coated reactors, and monolith coated reactors[37].

2.4.1 Photoreactor Experimental Procedure

The photoreactor window was carefully positioned at a specific height from the catalyst support area that allowed the fullest illumination of light on the catalyst surface (due to the relationship of the angles of incidence and refraction through the quartz window onto the 1 inch diameter catalyst holding area). The catalyst was immobilized on two layers of support. Approximately 50 mg of catalyst powder was loaded on a top layer of quartz felt that rested on top of a 25 mm diameter ¼” fritted glass filter (Adams & Chittenden Scientific Glass P0 standard porosity, 35% pore volume size from 160-250 microns). The quartz felt held the catalyst in place while the fritted glass allowed for secondary containment and encouraged mixing and dispersion during gas recirculation. The silicon O-ring located between the quartz window and reactor cell body enabled a gas-tight system. The photoreactor cell is displayed in Figure B-3 in the Appendix. The photoreactor, fluid lines, and solar simulator lamp housing and associated filters were located inside of a UV-resistant polycarbonate box covered with blackout fabric (ThorLabs) during experiments to prevent any outside light from entering the system. The reactor temperature was controlled with external heat tape and monitored continuously (Extech SDL200 4-channel thermometer). The schematic of the photoreactor system is displayed in Figure 3.

The reactant gases were supplied via gas cylinders (k-bottle type) as dry CO₂ (99.8% purity) and dry Ar (99.997% purity). The feed gas was sent into the photoreactor system lines with controlled mass flow. Once the desired pressure was reached, the gases were then shut off and the
system locked. The gas was re-circulated via a peristaltic pump which flowed through a flow meter (FM), analog pressure gauge (P) and thermocouple tees (T). The flow rate was verified by a calibrated in-line gas flowmeter (Sierra Instruments Inc.) and a rotameter.

Before a photoreactor experiment, the fluid lines, reactor cell, window, and glass frit were cleaned. The materials were rinsed in an Alconox and DI H₂O solution, rinsed with DI H₂O, and then dried in an oven at 100 °C for approximately 2 hr. The O-ring, although resistant to UV degradation, was replaced with a new one after each experiment.

The system was first evacuated and held under vacuum as a leak check. Then the empty system was purged with Ar for 30 min, followed by evacuation and pressurization of Ar to 10 PSI for a leak check. The system was circulated for 5 min with Ar, evacuated and circulated with Ar at 10 PSI again for approximately 5 cycles until a final purge cycle was performed. The top of the reactor lid was removed during Ar purge, and the clean glass frit was placed on top of the reactor cell counter bore, followed by quartz felt and the catalyst powder. The catalyst powder was spread evenly over the quartz felt and charged with 100 μL of de-ionized H₂O (18.62 MΩ-cm) on the catalyst surface with a syringe. The reactor lid was sealed, followed by evacuation and then re-pressurization to 10 PSI with Ar, and held for 30 min. The system was circulated for 30 min and a mass spectrometer (MS) purity check was run to determine no air was in the system or other products. The system was then evacuated and filled with CO₂ to 10 PSI. A MS purity check was run to determine no Ar was in the system. The CO₂ was circulated in the dark for 30 min to allow adsorption and desorption of gases to reach equilibrium, and then three background samples were collected on the chromatograph (GC) and MS system. After this background collection, three control gas analysis samples were collected in the dark. The light was illuminated on
the sample for the desired illumination time (30 min). At the end of each test, 5 GC/MS gas samples were collected for analysis. The light and heat were turned off, and the system was purged with dry Ar.

2.4.2 Solar Simulation

The solar simulator system (Figure B-4 and B-5 in the Appendix) was equipped with a 1600 W Xe arc lamp (set to 1400W), lamp housing (Newport 66870 housing with 3177 heat sink and 69922 power supply), aluminum liquid filter (Newport 6123NS, 2 inch), a quick change filter holder (Newport 71260) and a fiber bundle focusing assembly (Newport 77776). The H₂O filter limited the lamp output range to approximately 280-950 nm. The H₂O filter was fitted with an external chiller loop kept at 16 °C when in operation. A Newport AM0 filter was used in the quick change filter. An L-shape curve 304 stainless steel tube (galvanized 0.5-inch OD, 0.049-inch wall thickness, 2-inch-long on each side) was used to pass light from the solar simulator to the photoreactor quartz surface.

Miniature spectrometers (Ocean Optics USB4000-VIS-NIR and USB4000 UV-VIS) were used to determine the general irradiance profile that was being output by the solar simulator, after it passed through a stainless steel tube, through the quartz window and onto the catalyst surface. A LI-COR LI-200R Pyranometer (400-1100 nm range) with a LI-250A light meter was used to measure the global solar radiation output of the solar simulator system in W·m⁻². The meters aided in determining the approximate solar irradiance from Earth and Mars. The light output measured directly onto the region of catalyst after equipment pass through was measured at 589 W/m² for the 400-700 nm range (Figure C-4 in the Appendix) for all experiments. The same photoreactor and light sources were used in all photoreactor studies.
2.4.3 Gas Analysis

Evolved gases were separated and analyzed with an IonCam 2020 GC/MS system, equipped with a thermal conductivity detector (TCD) (SRA Instruments with 99.9999% He carrier gas and PlotQ GC column). This system was used to first separate selected constituents based on molecular weight using GC, and then feeding into the MS for quantification, which uses electrons to bombard the gas and break the molecule down into fragments that can be analyzed to determine the molecular weight of the original gas molecule. The system was calibrated for low concentrations of CO, H$_2$, CH$_4$, and O$_2$. The same gas analysis instrument was used in all photoreactor studies.

Figure 2. Illustration of LDH precursor synthesis to produce Zn-Al-CO$_3$ or Zn-Ga-CO$_3$ solid solution followed by the nitridation process to yield (ZnO)$_{1-x}$(AlN)$_x$ or (ZnO)$_{1-x}$(GaN)$_x$. 

1. Make dissolved solution (A) for desired Zn:M ratio.
2. Add solution (A) in a dropwise form to solution (B) to form LDH precipitate, (C).
3. Collect precipitate and age solution for 22 hours at 80°C.
4. Rinse and vacuum dry LDH powder, and grind with mortar and pestle.
5. Nitridation for 10, 20 and 30 min. at 800°C.
Figure 3. Schematic of system used for photocatalytic reduction of CO$_2$ in the presence of H$_2$O. V = Valve, FC = Flow Controller, CV = Check valve, FM = Flow meter, P = Analog pressure gauge, T = Thermocouple, RM = Rotameter, P = Peristaltic pump, GC/MS = Gas chromatograph / Mass spectrometer.
3.1 Introduction

Sustainable energy generation has been an issue of prime focus over the last few decades. With increasing population and the advent of more and more automation, we have witnessed a sharp rise in demand for energy supply. Remarkably similar trends of increasing concentration of atmospheric CO\textsubscript{2} and the rise of global temperature of Earth have been observed since the industrial revolution [1,2]. The critical concern over the alarming consequences of global warming and climate change associated with this fast-paced development of human civilization has led to a focus on development of energy resources that are sustainable in the long run with no adverse effect on world. This century has seen a tremendous interest in the scientific community towards CO\textsubscript{2} mitigation and alternative ways of energy generation. Though sincere efforts are being spent on CO\textsubscript{2} capture and sequestration, another promising route being projected for the future is CO\textsubscript{2} capture and reutilization. This route serves a dual purpose of CO\textsubscript{2} reduction as well as generating energy-dense hydrocarbon fuels paving the way for a closed loop carbon-neutral cycle.

Along with the progress in sustainable energy generation over earth, this generation has witnessed significant leap in the space program. In the current situation, these long-duration space missions are required to carry fuel supply from Earth accounting for a major fraction of the space mission expenditure. This also creates a huge burden on the sustainable fuel-starved Earth. To succeed on a long-duration space missions like Mars, utilization of surrounding on-site resources
will be required for fuel production, life support for humans, and energy production, since the up-
mass of all required consumables from Earth would be extremely expensive [28]. It currently costs
$10,000 to launch 1 pound of payload out of Earth’s gravitational pull into low earth orbit[71], and
would cost more in deep space transit or on to Mars. We look to develop technologies in-situ on
Mars with materials already present in the extra-terrestrial environment. Some resources that are
present on Mars and available for harvesting include the sun, atmospheric CO₂, and elements found
in the regolith (Martian soil) and H₂O from subsurface ice. Success and data validation of
photovoltaic solar cells from Mars exploration rovers give confidence for future solar-powered
technologies and applications on the Mars surface [30]. Visible light is more abundant than UV on
the Martian surface, which is depleted due to suspended dust particles in the atmosphere and
surface temperature swings. The Mars atmosphere is comprised of approximately 95% CO₂,
along with 2.7% N₂, 1.6% Ar, and trace constituents as O₂, CO, and H₂O vapor thus garnering
interest in the research community towards on-site hydrocarbon fuel generation schemes from CO₂
[72]. It is also known that the Mars regolith contains elements such as Fe, Al, Mg, O, Si, Ca, S, Cl
and Ti[73]. Solar photocatalytic process using these Mars-abundant elements presents a perfect
sustainable model for on-site fuel generation that not only reduces the fuel transportation costs and
fuel demand on Earth but also paves the way for long-duration Mars missions.

Photocatalysis has been studied for several decades and has demonstrated promising
results. Though it has been touted as one of the simplest and go-to solutions for organic dye-
degradation and H₂O splitting, CO₂ reduction still requires more attention and research.
Photocatalysis presents several advantages in terms of low temperatures of operation and simple
reaction systems. However, one of the best photocatalytic materials till date, TiO₂, still demands
the use UV light, limiting its application in large scale solar-photocatalytic processes [4].
Moreover, problems associated with fast exciton recombination rates and material stability have resulted in poor photocatalytic reaction rates [7,8]. In this scenario, it is a dire necessity to spend active effort on tuning material properties so as to witness enhanced photocatalytic reaction under visible light. This interest has led to modifying TiO$_2$ either through novel heterostructures or with different dopants and further investigating other metal oxides and hydroxides for their photocatalytic activity [74,75]. LDHs have garnered some interest in recent times due to their promising activity[64]. They present a nice platform for varying cations and thereby tuning the material properties. Zn based LDH has demonstrated improved catalytic performance for H$_2$O splitting. However, these LDHs exhibit large Eg and hence are only suited for UV-based applications. Nitriding these LDH materials paves the way for oxynitride synthesis with reduced Eg. ZnO:GaN has been used for photocatalytic reduction of CO$_2$ but with the use of expensive noble metals. Apart from tuning material property via composition variation, several other ways to modify photocatalytic performance are to induce vacancy defects and lattice strain.

We are focused to develop materials that can exhibit solar photocatalytic CO$_2$ reduction on Mars using on-site resources. This limits us to the use of materials that are Mars abundant and moreover tune that material property to better the reaction performance. With inspiration from the performance of ZnO:GaN, we investigated the material properties of ZnO:AlN heterostructures and demonstrated its photocatalytic activity [59–62]. A thorough study has been conducted on these materials to determine the band states tunability as a function of composition, vacancy and lattice strain [6,24,25]. These parameters are intrinsically related to any material’s activity. Variation of composition is the key to modulate the electronic states of the material, often resulting in under-coordinated atoms or dangling bonds that act as e$^-$/h$^+$ traps. Affecting the exciton recombination rates in this fashion is key towards enhancing the photocatalytic activity. Lattice
strain induced in the materials, particularly the ones grown on substrates, has a governing role towards changing the material Eg. These are even more relevant in heterostructures, where there is intrinsic lattice strain along with that induced from substrate lattice mismatch[3]. Finally, vacancy defects are closely related to any catalytic activity, more so with photocatalysis. Oxygen vacancy has been described as the primary route for e⁻/h⁺ trapping and modifying electronic states. These vacancies create local electronic hot-spots thereby behaving as potential active sites for CO₂ adsorption. Combining all these different control parameters for electronic property tuning is an ideal way of achieving better photocatalytic materials. These ZnO:AlN based heterostructures can potentially behave as infinite series of potential wells thereby reducing recombination and also enhancing faster charge transport for photocatalytic reactions. We hereby demonstrate for the first time CO₂ photocatalytic reduction by these ZnO:AlN material solely under visible light. Further progress in terms of smart fabrication of these materials, with better control of composition, strain and defects can lead to unprecedented CO₂ conversion performance.

3.2 Methods Used

The synthesis of the solid solutions were prepared using a previously reported coprecipitation method that incorporated a Zn-Al-CO₃ LDH precursor followed by nitridation to obtain the final solid solution (ZnO)₁₋ₓ(AlN)ₓ [64]. The LDHs were prepared by heterogeneously mixing the precursor materials at the atomic scale to form a precipitate that contained the carbonate interlayer anions. A desired trait for using the LDH was because the M²⁺:M³⁺ ratio can be tailored according to need. The cations were located in the center of an oxygen octahedral, which form a positively charged layer that was balanced by an interlayer containing organic or inorganic anionic species (CO₃)²⁻ was the interlamellar anion Nitridation was discussed in Chapter 2. The synthesis technique consistently produced up to 4.5 g of fine powders per batch. The powders that were
nitrided 10, 20, and 30 min with varying $M^{2+}:M^{3+}$ ratios are displayed in Figure C-5 in the Appendix. As the Zn content and nitriding time was increased, the materials changed from grey to white for samples with Al.

3.2.1 Materials and Characterization

The oxygen and nitrogen content of solid solutions were measured using a LECO, XRD and In-situ XRD experiments were measured, and SEM, FESEM, and TEM were collected as described in Chapter 2. UV/Vis with DRS, XPS and Raman spectroscopy data was also collected as previously described in Chapter 2. The XPS C 1s binding energy reported at 285.3 eV.

3.2.1.1 Photoreactor System

The photocatalytic reactions took place in the systems for measurements and gas analysis as previously described in Chapter 2. The light output was measured directly onto the region of catalyst after equipment pass through, and measured at 589 W/m$^2$ for the 400-700 nm range.

3.3 Results and Discussion

3.3.1 Morphology, Elemental and Structural Analysis

ZnO:AlN solid solutions were synthesized with a co-precipitation technique followed by nitridation as previously described in Chapter 2 [64]. The cation ratios of Zn$^{2+}$:Al$^{3+}$ in the LDH precursor were varied as 1:1, 2:1, and 3:1. The role of nitriding towards synthesis of these solid solutions was also explored. The resulting materials had excellent distribution of Zn, O and Al confirmed by elemental mapping (Figure 4 A-D). The LDH powders (Figure 4, E) and nitrided powders (Figure 4, F-G) appeared homogeneous in hexagonal plate morphology for the 2:1 samples both before and after nitridation. TEM images (Figure 4, H-K) revealed clusters of particles with the preferred hexagonal orientation of (001). Further elemental analysis divulged the changes in the cation and anion concentration as the Zn volatilized out of the system during longer
nitriding times, with the lower Zn:Al ratios losing more mass with increased nitriding times than the 3:1 ratio (Figure 5A-B). Material loss was minimum at 10 min for all samples and maintained close to the original LDH ratio. Regarding mass loss and cell volume, the 3:1 ratio demonstrated the highest mass and structural stability. Increase in N content was observed for all samples, as expected from the NH₃ intrusion during nitridation. The loss of oxygen in the 1:1 structure at 30 min was attributed to structural collapse of ZnO and the crystalline phase, as observed by XRD and elemental analysis.

The XRD patterns (Figure 6) confirmed the formation of Zn-Al-CO₃ LDH structures for all the three compositions prior to nitriding. The 3:1 Zn:Al LDH powder displayed amorphous traits with the presence of impurities (i.e. ZnO and ZnAl₂O₄ spinel phases). The ionic radii of Zn²⁺ (0.074 nm) is smaller than Al³⁺ (0.51 nm)[76] which may have caused structural weakening in the 3:1 LDH which was already tightly packed. The nitrided XRD scans revealed a crystallized ZnO Wurtzite structure for the 3:1 and 2:1 ratio, where the oxygen atoms are arranged in a closely packed hexagon and the Zn atoms occupy the tetrahedral sites. At a constant cation ratio, the nitridation time increased particle size of the (ZnO)₁₋ₓ(AlN)ₓ solid solution, which also corresponded to the cell volume results. Surface area increased as nitridation time increased (Figure 7), which was due to the LDH structure becoming weak with increased Zn loading, causing low-density product yield to form during the atmospheric pressure nitridation process [59,77].

The 10-minute nitrided samples of all Zn/M³⁺ ratios were analyzed via in-situ XRD. No XRD change was present in any sample from 25 °C to 200 °C in both air and CO₂ at 1000 mbar, except for the 1:1 Zn:Al structure that was nitrided for 10 min (Figure 10). The peaks that disappeared with increasing temperature were those associated with Al(OH)₃ reflections. Al(OH)₃
is known to decompose at elevated temperatures much higher than 500 °C, but the hydroxide is likely forming an intermediate product with the C and O from the atmospheric CO₂ and air.

The presence of Al(OH)₃ (gibbsite) peaks were present at 18° and 20° 20 angles for all nitrided 1:1 ratios and 30 min 2:1 ratio, which were also observed in SEM images as occasional orthorhombic crystal protrusions from the bulk material[78]. The SEM images also revealed some cubic structures impurities. Figure C-6 in the Appendix contains more FESEM images that were used for characterization purposes. It was evident that the tightly packed LDH structures under stress and strain applied distortions to the hydroxide layers and disrupted crystal formation during nitridation, as mass was volatilized out of the powder[79]. Reconstruction of the crystal lattice occurred, enabling these hydroxide formations. Upon heating of Al(OH)₃, the structure is known to thermally decomposes to Al₂O₃, which also has a hexagonal structure with Al atoms octahedrally aligned [78]. The lattice cell parameters for a and c also declined for the 1:1 and 2:1 ratios at 30 min, while remaining fairly stable for the 3:1 ratio at 30 min of nitridation.

3.3.2 Optical and Surface Analysis

Independently, ZnO and AlN are wide-band-gap semiconductor materials that have reported Eg of 3.37 eV [59] and 6.2-6.28 eV [80,81], respectively. These materials exhibit a Wurtzite crystal structure with similar lattice constants. Not all of the material properties from the precursor are inherited to the solid solution, as a reduction in the bandgap exists in the final solid solutions. Zn:Al LDHs have Eg reported at 3.22-3.3 eV[60,61,79] and ZnAl₂O₃ has a Eg of 3.8 eV[82]. Calculated Eg values from this work are shown in Figure 8, ranging from 2.84-3.25 eV. The lowest Eg reported by the highest Zn:Al ratio of 3:1 at 30 min of nitriding time. The Kubelka-Munk function did not have inflection points to properly calculate Eg values for the 2:1 and 1:1 Zn:Al samples at 30 min of nitriding. For a constant cationic ratio, increasing nitridation time
decreased the \( E_g \). The \( E_g \) values here were not as low as the range observed for the HER and CO\(_2\) processes, which predicts low photocatalytic activity in the presence of visible light irradiation.

The XPS scans of the Zn 2p, O1s, and Al 2p values for the nitrided samples are displayed in Figure 9. There was no loss feature between the Zn 2p\(_{3/2}\) and Zn2p\(_{1/2}\) spin-orbits, which confirmed the presence of ZnO. A slight right shift exists for the 1:1 samples and the 2:1 30 min samples, indicated a higher presence of Zn-N bonds, which was expected as Zn-O is volatalized out of the powder. The shift to lower binding energy for O 1s by the 1:1 (10 min), 3:1 (20 min.), and 3:1 (30 min.) samples, also revealed lower energy with higher Al presence. Figure C-7 in the Appendix displayed additional elemental confirmation of oxygen content of the powders and was in agreement with the LECO elemental analysis results.

Raman spectroscopy was examined for the 2:1 and 3:1 Zn:Al nitrided samples (Figure 11). The phonon frequencies expected for unstrained pure AlN at 300K for \( E_{2(\text{low})}, E_{2(\text{high})}, A_{1(\text{TO})}, E_{1(\text{TO})}, A_{1(\text{LO})} \) were \( E_{1(\text{LO})} \) are 248, 657, 610, 670, 890, 912 cm\(^{-1}\), respectively\[83\]. Stress and crystalline quality are typically observed from the \( E_2 \) phonon frequency, which was apparent at 248 cm\(^{-1}\), where the vibration was prominent with higher crystal stability of the 3:1 cationic ratios. Here the ZnO \( A_{1(\text{LO})} \) mode was not definitive, and adjacent to the intense AlN \( A_{1(\text{TO})} \) mode. The Raman rules guide us to the conclusion that for AlN, when \( A_{1(\text{LO})} \) and \( E_2 \) are present, the powders are all highly c-axis oriented \[84\]. The vibrations seen at 568 cm\(^{-1}\) correlated with the phonons of bulk ZnO \[85\], and overcame some AlN effects at the 3:1 ratio where more ZnO was present in the bulk phase, than at the lower 2:1 cationic ratio. At lower nitridation times and lower cationic ratio, the 568 cm\(^{-1}\) disappeared. The shifts and asymmetry of the Raman spectra indicate that the crystal heterostructures were prominent with stress and strain defects. At low wavenumbers, the disappearance of the Raman vibrations correlated with oxygen vacancies, which may have been
present for the 2:1 ratios at 10 and 20 min. The 574 cm\(^{-1}\) range also corresponded to the ZnO\(_1\)(LO) phonon peak and was associated with the A\(_1\)(TO) phonon, of Wurtzite AlN. The broad shifts between these two ranges were due to the shared phase with the ZnO and AlN, but also optical phonon confinement defect or impurity in the nanocrystal.

**3.3.3 Photoreactor Studies**

The results of the photocatalytic tests at 25 °C and 100 °C for 1:1 and 3:1 Zn:Al ratios at 20 min of nitriding time are displayed in Figure 12, along with our controlled TiO\(_2\) experiments. Negligible product formation occurred for CH\(_4\) and H\(_2\) (less <0.05 µmol formation). H\(_2\) and O\(_2\) were not detected well in this study because of the low sensitivity of the TCD detector with He carrier gas and ultra-low concentrations. The highest CO production rate of our new materials was demonstrated by the 3:1, 100 °C at 0.3 µmol·g\(^{-1}\)·h\(^{-1}\). The Eg was wider, but oxygen vacancy formation observed in elemental analysis along with higher ZnO content support the increase in catalytic activity, which had charge instability on the surfaces[86]. The photocatalytic conversion of CO\(_2\) into CO in the presence of H\(_2\)O is a 2 H\(^+\)/2e\(^-\) process (Figure 13). ZnO materials typically result in CO as the dominant product [87]. Since CO is an important building block for the production of hydrocarbon fuels, and serves as an important intermediate step for industry, this product is favorable[88]. At low cationic ratios, an increase in recombination, caused low transfer efficiency of photo-generated e\(^-\)/h\(^+\) [63,89]. The higher Zn content may have promoted the formation of hetero-junction structures to generate a more efficient photocatalyst and will be studied in future investigations.

Since the HER and CO\(_2\) conversion to fuel are competing reactions in liquid systems, and more so if a co-catalyst is involved since e\(^-\) could become trapped in the co-catalyst (unavailable for CO\(_2\) reduction), a preferred gas phase reaction for Mars is ideal. A decline in CO evolution
with decreasing Zn:M$^{3+}$ ratio for 20 min of nitriding time was observed. Applying heat to the reaction resulted in higher activity of CO formation, due to higher mobility of H$_2$O vapor in the gas phase, increasing molecular and e$^-$ promotion onto active surface sites.

Detailed structural investigation of these materials is often difficult due to the nitridation process, which causes structural disordering such as stacking faults, short range bond ordering, and crystallite-size effects [69]. This demonstration through experimentation have validated that a delicate balance of nitridation and Zn:M$^{3+}$ ratio should be selected, along with precursor material cation ratios in order to obtain the desired final product and crystal structure. The subtle synthesis changes highly influence tuning properties by introducing small crystal grains, impurities, and changes to the Wurtzite structure, including poor crystallinity[67]. It was demonstrated that it was relevant to disrupt a tightly packed crystal structure only slightly, and not create a completely amorphous structure that had higher Eg and minimal crystallinity. A deeper understanding of these varied parameters demonstrated in this work could support the ability to increase the quantum efficiency and conversion yields trough additional experimentation.

TiO$_2$ had higher CO production in this work, due to the poor light response of AlN and the higher and misaligned band gap energy state of the bands. Remember, Al was implemented due to its availability on Mars as a proof of concept here, and may not be the most ideal candidate for future applications for visible light photoreduction. However, higher intensity UV light applications should be considered in future work. Co-catalysts have been demonstrated in modified TiO$_2$ structures that have co-catalyst additions such at Pt, and Cu [9]. Co-catalysts can provide active sites while also reducing the activation energy barrier. The type of co-catalyst material is also quite important for the CO$_2$ reduction selectivity pathway. For example, Pt, Ni, and Pd have a tendency to form hydrocarbons. A transition metal with reliable stability, such as Fe could also
be used to aid in the splitting of H$_2$O [90]. It is studies such as this that start at the baseline of material development (without co-catalysts or dopants at first) that can contribute to escalation in future catalyst design and continue to make contributions to Mars solar CO$_2$ photocatalytic conversion work.

3.4 Conclusion

The Zn:Al solid solution materials can be tuned by increasing nitridation time, and varying the cationic ratio. The Eg was easily tunable with values ranging from 2.84 to 3.25 eV. Al was demonstrated here in this composition for the first time, and considered due to its availability on Mars. Future experiments with these materials that consider co-catalyst or dopants to level the band alignments will be considered for improved catalytic activity. The results indicated a delicate balance of nitridation and Zn:M$^{3+}$ ratio should be selected, along with precursor material cation ratios in order to obtain the desired final product and crystal structure. The subtle synthesis changes highly influenced tuning properties by introducing small crystal grains, impurities, and changes to the Wurtzite structure. Increasing the cationic ratio in this study more than tripled CO production under solar light irradiation. Photocatalysis must not only consider Earth based applications, but also to help us pioneer and explore Mars so we can harvest fuel from a sustainable resource. This is just the beginning of an exciting application of photocatalysis as humans look to have boots on the ground on Mars in the 2030s, or sooner.
Figure 4. FESEM and EDS data. (A) Electron image of Zn:Al 2:1 at 10 min of nitriding, with the corresponding EDS mapping of O (B), Al (C), and Zn (D); (E) FESEM image of the LDH Zn-Al-Co$_3$ for a Zn:Al ratio of 2:1., and nitrided for 20 min in (F); (G) 3:1 ratio at 20 min of nitriding; (H) Selected area diffraction pattern of the particles; (I-K) TEM cluster of Zn:Al 2:1 nitrided for 20 min particles on a holy C-Cu grid.
Figure 5. ZnO:AlN material characterization results: Composition ratios of cations and anions respectively at different nitriding times.

Figure 6. The X-ray diffraction patterns of the LDH precursors (A) and their corresponding nitrided samples (B-C).
Figure 7. (A) Cell volume calculations of the hexagonal powders; (B) Lattice parameter calculations a, c; (C) BET surface area calculations.

Figure 8. Calculated Eg (eV) for the nitried Zn:Al powders.

Figure 9. XPS scans for the nitried Zn:Al powders.
Figure 10. In situ XRD results of (ZnO)_{1-x}(AlN)_x, Zn:Al = 1:1 in CO\textsubscript{2} (left) and air (right).
Figure 11. Raman spectroscopy of the 2:1 and 3:1 Zn:Al LDH powders that have been nitrided for 10, 20 and 30 min.
Figure 12. Photocatalytic CO Evolution of Zn:Al materials that had LDH ratios of 3:1, 2:1, and 1:1, followed by 20 min of nitriding time. Reaction conditions: Photocatalyst CO$_2$ at 10 psig, 100 μL of H$_2$O, AM0 solar simulator light source, irradiation time: 30 min.

Figure 13. Possible reaction pathways of CO$_2$ and H$_2$O during visible light irradiation reactions.
4.1 Introduction

Energy and environmental scenario continues to be a point of concern and active research topic throughout the world. With more and more advancement in human civilization, the energy need has seen a steep rise with close correlation to the increase in the global atmospheric CO$_2$ concentrations. Now, at a critical time where climate change and sustainable energy generation is of prime focus, huge efforts have been spent towards efficient repurposing of waste CO$_2$ to hydrocarbon fuels. There are several avenues of pursuing this goal of CO$_2$ reutilization with each having their own benefits and limitations. There are strong proponents of direct or indirect thermochemical approaches of CO$_2$ conversion. Though these processes boast of efficient CO$_2$ conversion rates, the major limitations associated with these methodologies are the use of renewable hydrogen and high temperatures of operation. Though significant improvements are being achieved to reduce the operation costs via novel material design, the use of renewable hydrogen is still costly in current standards. Electrochemical CO$_2$ conversion routes are still marred by stability issues and electrode passivation and degradation. Thus, decades-old photocatalytic route still bears the hope of efficient CO$_2$ conversion using the abundant solar energy at temperatures as low as room temperatures.

The search for earth-abundant visible light catalysts has led to the research on other metal oxides, metal oxide heterostructures and even layered double hydroxides. Interest over LDH has
increased due its potential to accommodate varying cations enabling better material property tuning. The choice of cations in the LDH can be customized based on the reaction requirements. It has been reported that Zn:Al LDH could convert CO₂ to CO with 94% selectivity under the presence of UV-light, while the presence Cu ions enhanced methanol selectivity over the same LDH. LDH based materials present an ideal platform to tune material properties simply by modulating the different cations present. However, since LDH present a higher Eg, unsuitable for visible light photocatalysis, nitriding these LDH allows to create novel oxynitrides that have Eg suitable for solar photocatalytic reactions.

Among the metal oxynitrides, ZnO based materials are quite popular. ZnO:GaN has specifically been known to demonstrate H₂O splitting under visible light. Even ZnO:GaN nanorods demonstrated CO₂ photoreduction under visible light but with the presence of 0.5 wt% Pt loadings as co-catalyst. Further improvements of the photocatalytic activity of these materials are primarily dependent on better charge transfer, reducing the photogenerated e⁻/h⁺ pair recombination rates and exposition of crystal facets that encourage/facilitate CO₂ reduction.

Tuning of these properties can be achieved through intelligent material design and fabrication with varying metal composition, inducing strain and vacancy defects and with better facet/interface control for heterojunctions. Implementing an LDH as a precursor is an attractive alternative to traditional materials, as gaseous species can easily diffuse through the interlayer regions and react with the anionic species with minimal additional energy. Modifying the coordination state of the metal ions can potentially lead to better active sites. Often these are associated with localized e⁻/h⁺ traps that helps the reduction of recombination rates. Lattice strain is another key feature in crystals, predominant in 2D layered materials grown on substrates. With the rise in interest in the materials community to synthesize 2D heterostructures in order to expose
crystal facets for enhanced reactivity, investigating the effect of induced lattice strain towards tuning the electronic density of states of the active metals is crucial. Introducing point defects like vacancy and interstitials is another major way to modulate the electronic state of the material. Along with exhibiting direct effect on the Eg of the materials, vacancies are prone to change the \( e^- \) densities localized over the active metal sites. Generation of anion vacancies creates under-coordinated metal sites that demonstrate superior reactivity. Finally smart heterojunction designs are the pathway to lower recombination rates. Heterojunctions across the c-axis are known to behave as potential wells thus restricting the easy flow of \( e^- \) and \( h^+ \). Moreover the interface atoms present different electronic states from that of the bulk with possibilities of being better adsorption and reaction sites.

We present a detailed study of the effect of composition, strain and vacancy defects on ZnO:GaN based materials, which also presents conditions for Eg tuning. The diverse behavior of the bulk and interface atoms motivates controlled fabrication of such heterojunctions for unprecedented photocatalytic reactions. We have synthesized several ZnO:GaN solid solutions via co-precipitation technique. The cation ratios of \( \text{Zn}^{\text{+2}}:\text{Ga}^{\text{+3}} \) in the LDH precursor were varied as 1:1, 2:1, and 3:1. The role of nitriding towards synthesis of these solid solutions was explored by varying nitridation time from 10, 20, and 30 min. To the best of our knowledge, these materials demonstrated for the first time \( \text{CO}_2 \) reduction to \( \text{CO} \) under visible light without the use of any noble metal co-catalysts. Further improvements in terms of better defect and facet control will lead to much better \( \text{CO}_2 \) conversion performance. Apart from photocatalytic reactions, these materials are well suited for different applications like diodes, sensors etc. Innovation in terms of controlling exciton recombination rates and customized facet exposure will have positive impacts on these fields as well.
4.2 Methods Used

4.2.1 Materials and Characterization

The synthesis of the solid solutions were prepared using a previously reported co-precipitation method that incorporated a Zn-Ga-CO₃ LDH precursor followed by nitridation to obtain the final solid solution (ZnO)₁₋ₓ(GaN)ₓ[64] which was previously described in Chapter 2 and similarly in Chapter 3. The resulting golden/yellow powders after nitridation can be found in Figure C-8 in the Appendix.

As described in Chapter 2, the methods described for collection and characterization using LECO, XRD, In-situ XRD, SEM, FESEM, TEM, UV/Vis with DRS, XPS and Raman spectroscopy were applied. Raman spectroscopy was collected using the Thermo Scientific DXR2 instrument. The XPS C 1s binding energy was reported at 285.3 eV.

4.2.2 Photoreactor System

The photocatalytic reactions took place in the systems for measurements and gas analysis as previously described in Chapter 2. The light output was measured directly onto the region of catalyst after equipment pass through, and measured at 589 W/m² for the 400-700 nm range.

4.3 Results and Discussion

4.3.1 Morphology, Elemental, and Structural Analysis

Figure 14(A-B) revealed the elemental changes in the cation and anion concentration along with nitridation durations. As reported in literature, Zn was found to leave the system with longer nitriding time, due to its volatility. This makes the weight percent of Ga more prevalent in the nitrided samples, and decreased the Zn:Ga ratio. The increase in N content was expected with nitriding time, while the loss of oxygen was attributed to the volatilization of ZnO, or generation of oxygen vacancies. Material loss is minimum at 10 min of nitriding time. The 3:1 cation ratio
demonstrated the most stability after nitridation, maintaining its original LDH ratio compared with the 2:1 and 1:1 powders.

The XRD patterns (Figure 15A) display the Zn-Ga-CO$_3$ LDH formation for all the three compositions. The sharp and narrow peaks of the LDH revealed good crystalline powders with characteristic reflections of basal peaks at (003) and (006) at low 2θ angles, and non-basal peaks at (110) and (113) at high 2θ angles. Post-nitriding XRD revealed the formation of (ZnO)$_{1-x}$(GaN)$_x$ phases. From Figure 15B, the 32°, 34°, 36°, and 47° 2θ angles corresponded to hexagonal reflections of ZnO and GaN. The 32° 2θ angle corresponded to the Wurtzite (100) plane. Poor crystallinity and mixed phases were observed in the 1:1 ratio, with the high temperature of 800 °C facilitating volatilization of the powder. This elemental loss of Zn disrupted the crystal formation during nitridation, and further formation of the ZnO phase was stifled due to impurities or crystal grains in these structures, as observed by wider peak formations.

The increased nitridation increased the cell volume because the NH$_3$ interrupted the interlayer anions of the LDH precursor containing (CO$_3$)$_2^-$. As CO$_2$ and H$_2$O were driven off, the nitrogen migrated to interlayer regions, increasing the surface area. Nitrogen and oxygen were replaced in the interlayer of the structure and recombined to form a hexagonal single-phase crystal. The cell volume and lattice parameter data was calculated for hexagonal structures (Figure 14 C and D).

The 1:1 ratio had an overall decrease in c, and an increase in the Eg. The 2:1 ratio also had a decrease in c, and therefore relaxed tensile strain, which supported an overall increase in the Eg. The 3:1 ratio had a slight increase in c, corresponding to a decrease in Eg. We take note that a was fairly stable for the 3:1 ratio, which corresponds to the steady looking cell volume, but is overtaken
by the tensile strain to promote decreasing $E_g$. The Wurtzite crystal structure phases of $a$ and $c$ for GaN are ~3.2 Å and ~5.2 Å respectively and ~3.3 Å and ~5.2 Å, respectively for ZnO [91].

The LDH powders and nitrided powders appeared homogeneous in hexagonal plate morphology for the 2:1 samples and was validated by SEM and EDS data (Figure 16). The 2:1 and 3:1 ratios maintained hexagonal plates at varying nitriding times. Impurities in the bulk powders increased with decreasing Zn content, and the Zn:Ga 1:1 SEM images displayed porous hexagonal plates that deteriorated in structure as nitridation time increased. Additional FESEM images can be found in Figure C-9 in the Appendix. Flakes and rod-like structures observed on the surface of LDH structures in the 1:1 cation ratio were identified with ZnO and ZnGa$_2$O$_4$ spinel phases [79]. Incomplete LDH formation with impurities in the microstructure enabled different phases to nucleate during nitridation. The ZnGa$_2$O$_4$ phase was observed to coexist with the Wurtzite structure under similar synthesis conditions, which was in agreement with XRD results in this work [68]. At the 2θ angle of 57°, the (110) reflection widens for 1:1 ratio as well, which is between the range of Wurtzite GaN and ZnO. This represented a mixture of the separated phases.

4.3.2 Optical and Surface Analysis

Raman spectroscopy was collected for the 2:1 and 3:1 Zn:Ga nitrided samples (Figure 17). The A and B peaks were associated with GaN $A_1$ (LO) and GaN $E_2$ (high) phonon, respectively. For B, the unresolved peaks appeared to be within the range of 500 to 700 cm$^{-1}$ [92]. Once resolved with a Gaussian/Lorentzian peak fitting method with a linear baseline, the B peaks range from 575-583 cm$^{-1}$. The 574 cm$^{-1}$ range also corresponds to the ZnO $1$(LO) phonon peak and was associated with the $A1$(LO) phonon, on the c-axis of Wurtzite ZnO. When perpendicular, the $E1$ (LO) phonon was observed at 583 cm$^{-1}$ [93]. This implied that the shift and broad range was due to the shared phase with the GaN, but also optical phonon confinement, defect or impurity in the
nanocrystal. The shift in the GaN E2(high) and ZnO A1(LO) revealed that stress and strain are present in the heterostructures.

The XPS scans (Figure 18) reveal a no loss feature between the Zn 2p\textsubscript{3/2} and Zn2p\textsubscript{1/2} spin-orbits, which confirmed the presence of ZnO. A slight right shift exists for the 1:1 samples for Zn 2p\textsubscript{3/2} which indicated prevalent formation of Zn-N bonds. Oxygen had a subtle shift in the right for the 1:1 (10 min), 3:1 (20 min.), and 3:1 (30 min.) samples. GaN binding energy is found at 19.0, while a higher energy shift is towards the Ga-O bond.

Not all of the material properties from the precursor were inherited to the solid solution, as a reduction in the bandgap existed in the final solid solutions. The visible Eg varied with nitridation duration and cationic ratio as shown in Figure 19A. Despite the mass loss, and loss of Zn content from the nitriding process, it was shown that the Eg is fairly stable within the nitrided materials and can be tuned based from the behavior of the LDH precursor ratio, as well as the nitriding time. As N was introduced into a structure, the vb of an oxynitride had a hybridization of N 2p and O 2p orbitals, and the N 2p contribution became larger than that of O 2p which resulted in a lower Eg [86]. This effect of the N\textsubscript{2} increase was seen with a decline in the Eg of the 2:1 and 3:1 materials for 20 and 30 min of nitriding time.

4.3.3 Photoreactor Studies

The results of the photocatalytic tests at 25 °C and 100 °C for the different Zn:Ga ratios at 20 min of nitriding time are displayed in Figure 19B. The highest CO production rate was the 3:1 ratio of Zn:Ga with 20 min of nitriding time at 100 °C, which produced 1.06 µmol-g\textsuperscript{-1}-h\textsuperscript{-1}, which was 2.5 more times than our control TiO\textsubscript{2} at 100 °C, 1.2 times more than our 25 °C TiO\textsubscript{2} control, and 7.3 times as more production to other reported TiO\textsubscript{2} solar simulator experiments[94]. This was also higher product formation than with ZnO/GaN nanoparticles and nanotubes[95], but less
production when compared with modified TiO₂ structures that have co-catalyst additions such as Pt and Cu [9].

Activity of the higher Zn:Ga ratio was also aided by the additional presence of GaN, which had charge instability on the surfaces [86]. The Eg values were close to the range for the HER and CO₂ processes, which require the minimum energy per photon in the range of ~1.23 and 1.33 eV.

At low cationic ratios, an increase in recombination, caused low transfer efficiency of photo-generated e⁻/h⁺ [63,89]. It is likely that the e⁻ and h⁺ generated from the light irradiation (Table 1, Equation 3) only reached the point of CO formation due to the easier mechanism of 2 e⁻ /h⁺ availability. Some defects of surface states will not always contribute to surface oxidation, which can enhance material stability and delay or diminish corrosion [86]. The materials with better crystal structure (higher cationic ratios) and prone to more defects and impurities, aided the gas diffusion, allowing rapid advancement along grain boundaries and over free surfaces than through the interiors of the crystal. The bonding between the host sheets and the interlayer ions of solid solutions was also considered to be weak and were partially driven off during nitriding. This was an appealing trait for the gaseous interactions in the interlayer regions through diffusion, which occurred with the anionic species at minimal energy [64]. When the crystalline structure declined, and Eg increased, the impurities acted as e⁻ wells that stifled photoreaction.

We reiterate through this work through experimentation and theory, that a delicate balance of nitridation and Zn:M³⁺ ratio should be selected, along with precursor material cation ratios in order to obtain the desired final product and crystal structure. The subtle synthesis changes can highly influence tuning properties by introducing small crystal grains, impurities, and changes to the Wurtzite structure, including poor crystallinity [67]. Since no co-catalyst was present on these materials, this work creates a good baseline for future co-catalysts additions, which can provide
active sites while also reducing the activation energy barrier. The presence of dislocations and structural defects can also cause surface states to act as recombination regions. Fewer lattice distortions in the tightly packed Zn:M$^{3+}$ as observed in XRD may have supported a decrease in recombination at high cationic ratios.

4.4 Conclusion

We conclude in this work that the Zn:Ga solid solution materials can be tuned by increasing nitridation time, and varying the cationic ratio. The Zn:Ga materials had a Eg range from 2.33 eV to 2.59 eV. The Eg was easily tunable from varying nitriding time and cationic ratio. The highest CO production rate was Zn:Ga (3:1) at 20 min of nitriding time at 100 °C, which produced 1.06 µmol-g$^{-1}$-h$^{-1}$, higher than both of our controlled TiO$_2$ experiments, and other reported pure TiO$_2$ solar photoreaction experiments.
Figure 14. ZnO:GaN material characterization results: (A), (B) Composition ratios of cations and anions respectively at different nitriding times; (C) Cell volumes for hexagonal Zn:M3+ materials that had LDH ratios of 1:1, 2:1, and 3:1, followed by 10, 20 and 30 min of nitriding time; (D) Lattice parameter calculations of a, and c for the hexagonal nitrided structures.
Figure 15. The X-ray diffraction patterns of the LDH precursors (A) and their corresponding nitrided samples (B,C).
Figure 16. FESEM and EDS data. (A) Electron image for the corresponding EDS mapping for elements to the right: Zn, O, Ga, and N. (B) LDH 3:1 Zn:Ga ratio (45,000X). (C) SEM image for Zn:Ga ratio of 2, 10 min. nitridation time at (18,000X). (D) SEM image for Zn:Ga ratio of 3 at 10 min. nitridation (18,000X).

Figure 17. Left: Raman spectroscopy spectrum of the Zn:Ga 2 and 3 ratios at varying nitridation times. Top right: An example of the Gaussian/Lorentzian peak fitting method for resolving the peak ranges for A, B, C and D. Bottom right: Raman peak location values for the Zn:Ga materials (cm\(^{-1}\)).
Figure 18. XPS scans of the Zn:Ga nitrided powders for Zn 2p, O 1s, and Ga 3d.

Figure 19. Photocatalytic CO Evolution of Zn:Ga materials that had LDH ratios of 3:1, 2:1, and 1:1, followed by 20 min of nitriding time. TiO$_2$ P25 control experiments are also displayed. Reaction conditions: Photocatalyst CO$_2$ at 10 psig, 100 μL of H$_2$O, AM0 solar simulator light source, irradiation time: 30 min. at 25 °C and 100 °C.

Table 1. Mechanistic pathways of CO$_2$ photodegradation reaction in the presence of H$_2$O.

<table>
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<th>Reaction Pathway</th>
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<tr>
<td>1</td>
<td>CO$_2$ + 2H$^+$ + 2e$^-$ $\rightarrow$ CO + H$_2$O</td>
</tr>
<tr>
<td>2</td>
<td>CO$_2$ + 8H$^+$ + 8e$^-$ $\rightarrow$ CH$_4$ + 2H$_2$O</td>
</tr>
<tr>
<td>2a</td>
<td>CO$_2$ + e$^-$ $\rightarrow$ CO$_2^-$ $\rightarrow$ CO $\rightarrow$ C + H $\rightarrow$ CH $\rightarrow$ CH$_2$ $\rightarrow$ CH$_3$ $\rightarrow$ CH$_4$</td>
</tr>
<tr>
<td>3</td>
<td>(ZnO)$<em>{1-x}$(GaN)$<em>x$ $\xrightarrow{hv}$ e$</em>{cb}^-$ (ZnO)$</em>{1-x}$(GaN)$<em>x$ + h$</em>{vb}^+$ (ZnO)$_{1-x}$(GaN)$_x$</td>
</tr>
<tr>
<td>4</td>
<td>2H$_2$O + 4H$^+$ $\rightarrow$ 4H$^+$ + O$_2$</td>
</tr>
<tr>
<td>4a</td>
<td>2H$^+$ + 2e$^-$ $\rightarrow$ H$_2$ (low pH)</td>
</tr>
<tr>
<td>4b</td>
<td>2H$_2$O + 2e$^-$ $\rightarrow$ H$_2$ + 2OH$^-$ (high pH)</td>
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5.1 Introduction

Environmental CO$_2$ reduction research via sustainable technology development still requires much attention to assist in reversing our global climate change conundrum. Despite efforts over the last several decades, photocatalysis for H$_2$O splitting and CO$_2$ reduction to synthetic fuels has not reached practical applicability in industry [7,96]. A fundamental cause leads back to the need for improved understanding of the photocatalyst material design, including optical and elemental properties, charge transport, stability, catalytic function and scalability.

In this work, the fundamental goal was to synthesize highly active photocatalysts for CO$_2$ reduction in the presence of H$_2$O under visible light irradiation. The CVD synthesis parameters for 2D MoS$_2$ TMDs were manipulated to study the properties of controlled tuning for edge-rich nanoflower morphology, optical response of the Eg and crystal phase stability. Materials with stacked sheets, and uniform layers with thin open edges, such as nanoflowers, are ideal for enhanced photoreaction experiments, since heterostructures have better light absorption and charge separation properties, aiding in the e$^-$/h$^+$ transport [3,49]. More moieties containing unsaturated and dangling bonds exist at the stacked sheet edges, as opposed to the planar surface and internal bulk locations, making the nanoflowers ideal for catalytic reactions [38–41]. The materials synthesized here show promise as an effective substitute for noble metals to support photocatalytic activity through p-n junction repair and enhancement of the photo-generated e$^-$/h$^+$
alignment to accelerate the charge carriers [39,40,49]. Chalcogenides are inexpensive photosensitizers with ideal band positions and straightforward nanoparticle synthesis.[97] MoS$_2$ is also ideal for stability against corrosion during photoreactions when in solution, due to its antibonding state and interaction between Mo and S orbitals at the top of its vb [98]. Our CVD synthesis was reliable and built off observations from previous works that aim to control TMD monolayer thicknesses[38,44–51], vertical layers[99,100], flowers[101] and nanosheets[102–104].

Intrinsic structural defects such as atomic point vacancies and crystallinity distortion are inevitable during CVD synthesis and 2D growth and were exploited through our controlled variations to report sheet thickness, crystal phase stability, and Eg tuning properties. The Eg of these materials was desired for visible light activation in support of the HER (1.2 to 2.4 eV)[37,105–108] to provide a proton source during CO$_2$ reduction. Single-layer MoS$_2$[53] (1.0 to 1.96 eV[41,43,49]) and bilayer/bulk values (1.3 to 1.6 eV)[109,110] were ideal for further investigation. It is known that MoS$_2$ has poor conductivity, and nanoflower with multiple edge sites can help overcome this issue by increasing conductive sites while still remaining nanosized [111]. Catalytic doping utilizes expensive precious metals (not ideal for scale up) and may slow down charge recombination. MoS$_2$ only, is being considered here before any type of doped, composite or co-catalyst effect is introduced into the pure materials, as synthesis effects alone can have a great influence on tunable light adsorption behaviors. Increasing the surface area of the catalyst by enabling more active surface sites, have shown to delay recombination through lattice defects [15,22,23].

This work contributes to thoughtful material design for future catalytic applications in the field of photocatalysis and field emitter applications[54,56–58]. Longer-term visionary goals
include developing technologies that can be used in space applications. Technologies such as photocatalysis can be developed to produce fuel in-situ on a Mars surface with available resources such as the Sun (specifically visible light)[30], atmospheric CO₂[72] (95% abundant) and the subsurface ice.

5.2 Experimental Section

5.2.1 Materials and Methods

The CVD process in this work was very straightforward and utilized a SZF and a three zone tube furnace (TZF) to produce the bulk powder MoS₂ nanoflowers and stacked sheets of MoS₂ flakes grown on downstream Si substrates. Commercially purchased MoS₂ powder (Sigma-Aldrich 99% pure molybdenum (IV) sulfide, <2 µm particle size, 5.06 g/mL density, CAS Number 1317335) was used for baseline characterization comparison. The CVD synthesis schematic is displayed in Figure 20. The precursor materials MoCl₅ (Strem Chemical, Inc., anhydrous, 99.6% by weight, CAS # 10241-05-1) and S powder (ACROS Organics, 99.999% trace metal basis) were prepared in an Ar-purged glove box and mixed together in a porcelain combustion boat (CoorsTek) without further purification. Caution should be taken when working with MoCl₅ as it is highly corrosive and toxic, and must be handled under an inert gas. S should be handled in a dry, well ventilated place, as it is combustible in air.

The initial precursor masses were measured for an ideal 2:1 atomic ratio of S:Mo. The precursors were mixed together with a plastic spatula in a CoorsTek porcelain combustion boat, placed into a 1-inch-outer-diameter fused quartz tube purged with Ar (99.997%). The precursors were set in the 24-inch-long SZF (Lindberg/Blue M) or 40-inch-long TZF (Thermo Scientific Lindberg/Blue) quartz tube inlet, with a second boat used as an offset cover, allowing gas flow through the precursor filled boats (Figure 21). Si substrates (undoped (100) crystal wafers) were
placed at strategic distances downstream of the precursor boats, and Ar was flowed (5 sccm) at atmospheric pressure during the operation. The CVD system was kept gastight with Swagelok Ultra-Torr fittings containing silicone O-rings on the quartz tube. The effluent gas was sent through a NaOH liquid diffuser system to capture Cl released during the reaction, and the residual gas was vented into the laboratory hood. The powder formation in the precursor combustion dish was possible because of the large starting mass of the precursor material, which was ~3 g of combined MoCl₅ and S.

The SZF samples were ramped at 5, 10 and 20 °C/min, until 700 °C was reached and held for 10 min (noted as SZF-5, SZF-10, and SZF-20, respectively). The TZF samples were ramped at 2, 5, and 10 °C/min (noted as TZF-2, TZF-5, and TZF-10, respectively), until 700 °C was reached, and also held for 10 min. All samples naturally cooled to ambient. Three batches of TZF-5 nanoflowers were post-treated in 5 sccm of 1% H₂/Ar at 5°C/min to 480 °C in a tube furnace at ambient pressure for 10, 20, and 30 min (noted as TZF-5-10H₂, TZF-5-20H₂, TZF-5-30H₂, respectively). The 480 °C temperature was determined by TGA and intended to create S vacancies through S atomic bonding to the H₂ and carried away as H₂S.

Imaging and elemental analysis were obtained using SEM with EDS, and FESEM (JEOL JSM 7500F). The fine scale morphology and the crystal structure of the CVD MoS₂ were determined using a high-resolution TEM. XPS, XRD, In-Situ XRD and UV/Vis DR measurements were collected with methods previously described in Chapter 2. The selected nanoflower powders measured for surface analysis and were characteristic of slit-shaped pores and nonporous materials. Raman spectroscopy measurements were collected with LabRAM HR Evolution under ambient conditions at room temperature. Raman was utilized to try and observe thickness-dependent properties of MoS₂.
5.2.2 Photoreactor System

The photocatalytic reactions took place in the systems for measurements and gas analysis as previously described in Chapter 2. The light output was measured directly onto the region of catalyst after equipment pass through, and measured at 589 W/m² for the 400-700 nm range.

5.3 Results and Discussion

5.3.1 Influence on Morphology

SEM and EDS results revealed uniform nanoflowers composed of stacked sheets with high edge site exposure (Figure 22.). The nanoflower diameter increased with increasing ramp rate, where SZF-5 nanoflowers were ~10-20 μm, with a stacked sheet thickness of ~26 nm, and SZF-10 and SZF-20 were ~20-40 μm each, with a stacked sheet thickness of ~57 nm. Higher ramp rates (>5 °C/min) yielded some undeveloped flake formations in the bulk and amorphous particles on the nanoflower surface that gave the impression of surface contamination. Ultra-sonication for 10 min in deionized H₂O, followed by drying, did not eliminate contamination off of the nanoflower surface, and the nanoflower remained intact. The surface contamination was more prevalent in the TZF than the SZF powders. The SZF-20 powders produced the smallest yield of overall nanoflower formations, accompanied by amorphous bulk solids. Sigma-Aldrich powder contained unorganized amorphous solids and no organized stacked sheets or nanoflower products.

The EDS mapping confirmed an even distribution of S and Mo in the bulk powder (Figure 23 A-C), while elemental analysis confirmed Mo:S atomic ratio reduction as ramp rate increased (Figure 23, bottom). Trace Cl was identified with EDS at inconsistent locations throughout the bulk powders of the TZF and high ramp rates of SZF synthesized powders. Higher ramp rates enabled rapid layer formation and precursor material (MoCl₅) to linger, reducing the overall MoS₂ purity. Thicker stacked sheet assemblies at high ramp rates were in the diffusion controlled region,
which facilitated homogeneous nucleation, causing crystal structure deformations. Slower ramp rates (<5 °C/min) encourage heterogeneous nucleation and thinner sheets via controlled epitaxy and thermal stability[112]. A thermodynamic evaluation of Mo-S-Cl-H-Ar system revealed that a high Ar dilution supports good reduction of MoCl₅ in the presence of S. Literature also supports 700 °C as a good processing temperature for vapor deposition, with the ability to produce pure MoS₂[113]. The downstream carrier gas aided in a high yield deposit of stacked MoS₂ flakes on Si substrates (Figure 22.). Consistent flake thicknesses of ~100 nm sheet stack thickness was achieved for MoS₂ growth on the substrates, but were only confirmed and not further investigated in this paper.

TEM images (Figure 23E-G and Figure C-19 and C-11 in the Appendix), displayed the morphology of a single sheet layer confirming the hexagonal MoS₂ structure with lattice parameters a = 3.2 Å and c = 12.3 Å for SZF-5 material. The HRTEM showed atoms clearly resolved in (110), (010), and (100) planes, and the d-spacing of 0.27 nm. The H₂ treatment did not change the overall diameter or nature of the nanoflower shape, but rather the intrinsic structural defects and sheet thickness. Atomic point vacancies of the TZF-5 powders that were post-treated in 1% H₂/Ar at 480°C were unresolved with our available TEM.

The TGA results had two major degradation stages. The first loss was 10% weight at approximately 380 °C. The second 80% weight loss at 550 °C. The first loss accounted for moisture uptake by the material while stored in air, and any organic impurities, while the second accounted for loss of S content. This thermal data was used to determine the post synthesis calcination temperature to induce S point vacancies. The post processing temperature of 1% H₂/balance Ar was recommended to occur before 550 °C, and in this work, 480 °C was selected for 5 °C/min CVD samples. The TGA plot of selected data is found in Figure C-12 in the Appendix.
TEM was in agreement with XRD results. The 2H-MoS\(_2\) phase was dominant in the CVD nanoflowers and Sigma-Aldrich MoS\(_2\) powder. The 2H phase is the most stable with two layers per unit cell stack repeat, and has the strongest mechanical and semiconducting properties[42,43]. The diffraction lines positioned at 14.3°, 32.7°, 33.6°, 58.4°, and 60.5° were assigned to planes (002), (100), (101), (110), and (112) respectively of the 2H-MoS\(_2\) phase. Sharp peaks at slower ramp rates (<5°C/min) demonstrated higher crystallinity. The strong (002) peak correlated to the stacked structures oriented along the c-axis. As ramp rates increased, impurities were introduced and disrupted the crystal formation, as seen in broader peak formation. The asymmetry along the (100) peak was due to disordered laminar structures which was more prevalent in higher ramp rates. Peaks positioned at 14.5° (003) and 38.3° and 41° (104) were assigned to the unstable 3R-MoS\(_2\) phase, which has 3 layers per unit stack repeat, in the rhombohedral symmetry with trigonal prismatic coordination[41]. The 3R phase was not present in the Sigma-Aldrich powder, but present in all CVD powders. In the 1%H\(_2\)/Ar samples, 2H was dominant with a 3R presence, and the line positioned at 26.3° was assigned to (111), the most dominant plane of H\(_2\)S.

The reported 2H-MoS\(_2\) phase lattice values are \(a = 3.15\) Å, \(c = 12.3\) Å and a cell volume of 105.7 Å\(^3\), while 3R-MoS\(_2\) has \(a = 3.16\) Å and \(c = 18.33\) Å and a cell volume of 158.51 Å\(^3\). The TZF-2 XRD lattice parameter calculation results (Figure 22.) unveiled smaller lattice parameters than the reference 2H values. Smaller crystal formation was due to the thermodynamic control in the tube furnace during the slower ramp rate of 2 °C/min, with stability and finer nucleation during vapor deposition. The increased ramp rates of 5 and 10 °C/min had larger lattice parameter and cell volumes, aiding in structural strain as it stretches towards the unstable 3R phase. The H\(_2\) treated samples had fluxuations in a and c as stress and strain was introduced during treatment, but
maintained stable cell volume. These stress and strain observations in the crystal structure are important to note for the observed catalytic results discussed later in this paper.

5.3.2 Surface and Optical Properties

The XPS measurements (Figure 24, bottom) confirm the MoS$_2$ purity by the Mo 3d$_{3/2}$, Mo 3d$_{5/2}$, and overlap of S 2S peak regions at ~232.5, 229.5, and 226.5 eV, respectively. The Mo 3d$_{5/2}$ peak position at 229.6 eV is the ideal MoS$_2$ location, and a shift to higher binding energy indicated the presence of MoCl$_x$, which are not very strong on the surface here, while lower binding energy shifts indicated the presence of impurities towards lower Mo-oxide states towards elemental Mo, accounting for the reduced powders treated in H$_2$. Clear splitting of the spin orbit doublet in the S 2p region was present at slower ramp rates and became an overlapping spin-orbit doublet at higher ramp rates and 1%H$_2$/Ar samples. This S shift at lower binding energy attributed to impurities effecting the S loss at the 10 and 20 °C/min ramp rates and the longer H$_2$ treatments. The XPS depth profiling (Figure C-13 in the Appendix) performed on the Si substrate verified under-layer purity of the MoS$_2$ formation, showing promise for pure product formation on substrates.

The surface area was reported at an average of 20.7 m$^2$/g, and average distance between the stacked nanoflower sheets is 10 nm. Surface area acquired via BET has been reported in literature at a higher value of 35 m$^2$/g for nanoflowers synthesized with the assistance of polystyrene microspheres[102].

The calculated Eg values are shown in Figure 25A and ranged from 1.38 to 1.82 eV (+/-0.04 eV). The Eg was independently controllable as a function of ramp rate and of post-treatment in 1% H$_2$/Ar. Since the cb position of bulk MoS$_2$ is slightly more positive than that for HER, a negative bias or quantum confinement effect, such as those found through impurities or increased edge site exposure, can help overcome the negative bias and confinement effects[114]. Higher
ramp rate increased the nanosheet thickness and nanoflower diameter, and decreased the Eg, which may seem counterintuitive to the quantum confinement effects for nanoparticles, but the contamination or impurities from unresolved nanosheet formation or precursor material may have contributed to this Eg shift, which resulted with absorption to longer wavelengths. In this case, instead of decreasing the number of layers to transform the MoS$_2$ from an indirect to direct-band-gap semiconductors, we are increasing the amount of active edge sites with disruption of the sulfurization process to interfere with stacking geometry and create more multifunctional edge-site through impurities of MoCl$_x$ and H$_2$ in the structure to contribute to the lower Eg values. Lattice structure can also influence light absorption[5], without changing the optical Eg, not actually aiding in the parent photocatalytic Eg reduction, but only surface effects, which we see in the 3R and lattice parameter defects.

Raman spectroscopy measurements (Figure 26) were performed with a LabRAM HR Evolution under ambient conditions at room temperature. The excitation source was an Ar-ion laser with a wavelength of 532 nm, and the power was 2 mW. Raman was utilized to try and observe thickness-dependent properties of MoS$_2$. Since nanoflower materials are more than five stacked layers, comparison of literature data with the current Raman collected data of MoS$_2$ was not expected. The Raman shift was almost nonexistent for the COTS powder and for the CVD substrate growth material as displayed by the low intensity of the 383 cm$^{-1}$ region. The E$_1^{2g}$ (Mo-S) mode and A$_{1g}$ (Mo-S) mode do not shift considerably, and, therefore, changes in layer thickness cannot be revealed. The difference between the two modes is ~25 cm$^{-1}$, which is larger than the reported one to five layers.
5.3.3 Photoreactor Studies

The CO evolutions from photoreactor experiments are displayed in Figure 27. All samples were run at 10 PSI and a temperature of 25 °C and 100 °C. Negligible CO production (<0.01 μmol-g_{cat}^{-1}hr^{-1}) was observed in most samples at 25 °C, and was not plotted in Figure 6B. The H₂ and CH₄ production rates were also negligible (<0.01 μmol-g_{cat}^{-1}hr^{-1}) and not reported. Low concentration H₂ and O₂ were difficult to quantify in this study with the low sensitivity of the TCD detector and He carrier gas. Photocatalytic systems are often run at ambient temperature since the e⁻/h⁻ are activated by photons. Here, the increased temperature enabled mobility of the H₂O vapor in the gas phase, along with a higher rate of adsorption and desorption on the surface sites. The amplified frequency of collision increased the reaction productivity, enabling higher product evolution than those at room temperature.

A volcano-type plot is generated in Figure 27B demonstrating that the tunable SZF and TZF impurities and defects were both a benefit and consequence for catalytic activity. The slowest ramp rate, 2 °C/min, had one of the lowest CO productions rates. TZF-2 was tuned as a stable composition with the thinnest edge-site stacks and higher Eg than TZF-5 and TZF-10 samples. The opposite scenario of too much surface contamination and lower nanoflower abundance (less edge sites), at the highest ramp rate (20 °C/min), also increased Eg, along with increasing the crystal structure deformity. This scenario hindered light adsorption, encouraging recombination and lowering photocatalytic activity. The ‘sweet spot’ of higher catalytic activity was found in those with plentiful thick edge-site abundance and defect laden crystal structures at 5 and 10 °C/min. The ample edge-sites with dangling bonds, and slight crystal impurities assisted in lowering the Eg to achieve materials that reduced recombination and enhanced faster charge transport for photocatalytic reactions. The declined activity at high and low ramp rates was
ascribed to the interlayer interactions. If nanoflowers were not abundant for gas phase reactions at
the edge sites, the g widened. Slowing the ramp rate provided thinner layers and less impurity but
also having a large Eg with band misalignment and not enough charge transport support from
thicker edge sites and impurities to increase the catalytic activity. These upper and lower thresholds
were overcome by quantum confinement effects. Thicker edge sites or strain defects were therefore
imperative for increased photocatalytic activity. SZF-5 has smaller nanoflower diameters which
also enabled higher surface area and edge site exposure than the larger TZF-5, SZF-10 and TZF-10 samples.

The samples treated in H₂ (Figure 5C) had increased photoactivity with increased H₂
exposure. 30 min of treatment nearly doubled the production rate to that without post treatment.
The H₂ post treatment boosted the overall CO production, but did not increase any additional H₂
and CH₄ production. The HER and CO₂ reduction reaction is dependent on many activities
synchronizing correctly, including the formation of the OH radical, crystal phase of the catalyst,
and delay of the recombination of the photogenerated e⁻/h⁺ pair[15,16]. CO₂ photocatalytic
conversion to CH₄ at high selectivity requires 8 e⁻/h⁺ whereas CO is achievable in the presence of
H₂O at a 2 e⁻/h⁺ process. In this reaction, H₂O was the limiting reagent and so higher hydrocarbon
formation was challenging. Since CO is an important building block for the production of
hydrocarbon fuels, and serves as an important intermediate step for industry, this product was
desirable[88]. More e⁻/h⁺ formations would be needed in the reactants to selectively form higher
hydrocarbons from these materials and plan to be studied in future work.

Figure 6C included control TiO₂ P25 reactions performed in identical reaction conditions
at 25 and 100°C, with recorded CO evolutions at 0.82 and 0.42 μmol/gₐ₅-tₐ₅-hr, respectively. The H₂
and CH₄ production rates were negligible (<0.01 μmol/gₐ₅-tₐ₅-hr. Other work with TiO₂ in CO₂/H₂O
photoreactions does not typically report H₂ as a product, but rather CO, CH₄ or CH₃OH, and generally when doped with a co-catalyst, such as Cu, Pt, or other precious metal. TiO₂ supported on glass wool, as in this work, only reported CO and CH₄ production in a H₂O/CO₂ photoreaction[23]. It is a well-known fact that H₂O/CO₂ feed molar ratio has a great effect on production rates[115]. Here, we see the decline in production at 100 °C. This decline in TiO₂ aligns with literature that reports the optimum range of photocatalysis activity to be between 293 to 353 K due to the rate limiting step of exothermic adsorption of reactants as the boiling temperature of water is approached [116,117]. In general, it is seen that a temperature threshold of catalysts can be met, and the desorption of products plays an important role in the reaction rate at higher temperatures, while hybrid catalysts have demonstrated higher photocatalytic activity at higher temperature[118].

It is apparent that many vectors contribute to production rates, and here we demonstrate these tuning behaviors for MoS₂, without aide of a co-catalyst or dopant and see it does effect production rates. The introduction of imperfections or atomic vacancies has revealed the tuning of flake edge morphology, Eg and catalytic performance on high edge site nanoflowers. The synthesis parameters are achievable, controllable, and need to be a focus for photocatalyst design, and should not be taken blithely.

5.4 Conclusion

We demonstrated that photocatalytic production was increased with thicker sheet stacks, correlating to DFT literature supporting the rich edge-site exposure enabled more photocatalytic activity due to superior moieties containing unsaturated and dangling bonds than to planar sheet surfaces. The loss of elemental S and increased surface impurities reached a production threshold that is tantamount with declined photocatalytic activity.
The CVD synthesis of freestanding, durable MoS$_2$ nanoflower powders and orderly flake deposits on downstream Si were demonstrated to have abundant edge sites with tunability that can be applied to gas phase photocatalytic reactions. The synthesis parameters were modified to achieve controllable stacked sheet thickness, and nanoflower diameter. The powders also exhibited structural stability in CO$_2$ and air. The Eg was independently tuned through synthesis control and post-treatment gas processing in a reducing environment, with values ranging from 1.38 to 1.83 eV. The simple and reliable CVD synthesis for the controlled nanoflower formations demonstrated repeatability and tunability, to aid in enhanced understanding of synthetic parameters for the control of defect-laden, well-defined edge-site rich and elegant 2D TMD nanoflower structures. These developments support tunable gas phase photocatalytic applications, optoelectronics, field emitters, and so on. We also note from this work that the field of photocatalysis must not only consider Earth based applications, but also extra-terrestrial applications, as humans are driving forward on to Mars, where we will be required to harvest fuel from a sustainable resources from our Sun.

Figure 20. (Left) Single-layer MoS$_2$ hexagonal structure. (Right) Schematic of the CVD synthesis technique.
Figure 21. The CVD synthesis concept with combustion boat placements for the SZF (top) and TZF (bottom).

<table>
<thead>
<tr>
<th>Magnification</th>
<th>Sigma Aldrich</th>
<th>SZF-5</th>
<th>SZF-10</th>
<th>SZF-20</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,500x</td>
<td></td>
<td>B</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>10,000x</td>
<td></td>
<td>F</td>
<td>H</td>
<td></td>
</tr>
</tbody>
</table>

Figure 22. SEM micrographs showing the MoS$_2$ particle morphology at 2,500X and 10,000X for SZF and TZF nanoflowers. Also displayed is the SZF substrate growth and the TZF average cell volume and lattice parameter calculations.
Figure 22. (Continued)

<table>
<thead>
<tr>
<th>Magnification</th>
<th>TZF-2</th>
<th>TZF-5</th>
<th>TZF-10</th>
<th>TZF-5-10H₂</th>
<th>TZF-5-20H₂</th>
<th>TZF-5-30H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,500x</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
<tr>
<td>10,000x</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
<td><img src="image9" alt="Image" /></td>
<td><img src="image10" alt="Image" /></td>
<td><img src="image11" alt="Image" /></td>
<td><img src="image12" alt="Image" /></td>
</tr>
</tbody>
</table>

Cell Volume, Å³

- a
  - 3.13
  - 3.16
  - 3.76
  - 3.15
  - 3.19
  - 3.14

- c
  - 12.30
  - 12.40
  - 12.76
  - 12.25
  - 12.44
  - 12.32

Figure 23. (A-C) MoS₂ EDS elemental mapping; (D) Hexagonal phase lattice parameters a and c.; (E-G) HRTEM Hexagonal phase determination for SZF-5; (H) EDS elemental analysis of bulk powders in TZF.
Figure 24. Top: XRD patterns of all MoS$_2$ samples. Bottom Left: Mo 3d XPS scan; Bottom Right: S 2p XPS scan
Figure 25. Band Gap Energy Values, eV.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band Gap (eV)</th>
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<tbody>
<tr>
<td>Single Zone Tube Furnace</td>
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</tr>
<tr>
<td>SZF-20</td>
<td>1.49</td>
</tr>
<tr>
<td>SZF-10</td>
<td>1.50</td>
</tr>
<tr>
<td>SZF-5</td>
<td>1.67</td>
</tr>
<tr>
<td>Three Zone Tube Furnace</td>
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<tr>
<td>TZF-5-30H₂</td>
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<tr>
<td>TZF-5-20H₂</td>
<td>1.40</td>
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<tr>
<td>TZF-5-10H₂</td>
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<tr>
<td>Control</td>
<td></td>
</tr>
<tr>
<td>MoS₂ Sigma Aldrich</td>
<td>1.82</td>
</tr>
</tbody>
</table>

Figure 26. Raman spectroscopy. $E_{2g}^{1}(\text{Mo-S})$ modes and $A_{1g}(\text{Mo-S})$ modes of MoS₂ selected samples.

5.3.3 Photoreactor Studies
Figure 27. (A) Band Gap Energy Values, eV. (B) Photocatalytic CO Evolution with MoS$_2$ Powders at 100 °C reactor temperature conditions. (C) Photocatalytic CO Evolution with SZF-5 MoS$_2$ Powders post treated in 1% H$_2$ for 0, 10, 20 and 30 min compared with TiO$_2$ P25 at 25 °C and 100 °C reaction temperatures.
CHAPTER 6: CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

As presented in chapter 1, the specific goals of this work included:

1. Synthesis and characterization of solid solution based visible light photocatalysts derived from LDH precursors: with and without defects and impurities.
2. Synthesis and characterization of 2D grown visible light photocatalysts derived from multi layered and stacked sheets of TMDs, with and without defects and impurities.
3. Demonstrate CO₂ conversion in a photoreactor under solar irradiation in the presence of H₂O to show reduction of CO₂ and the effects of tuning on catalyst performance.

Relative to the first goal, Chapter 3 and 4 presented Zn:Al and Zn:Ga solid solution materials derived from LDHs that were tunable by increasing nitridation time and varying the cationic ratio. \((\text{ZnO})_{1-x}(\text{AlN})_x\) was demonstrated for the first time in this work and \((\text{ZnO})_{1-x}(\text{GaN})_x\) was demonstrated in CO₂ and H₂O photocatalyst reactions without any co-catalyst or dopant materials. The results indicate a delicate balance of nitridation and Zn:M³⁺ ratio should be selected, in order to tune and obtain the desired final product, crystal structure and catalytic activity. The subtle synthesis changes can highly influence tuning properties by introducing small crystal grains, impurities, and changes to the Wurtzite structure, including poor crystallinity.

The CVD synthesis of freestanding, durable MoS₂ nanoflower powders and orderly flake deposits on downstream Si were demonstrated to have abundant edge sites with tunability that can be applied to gas phase photocatalytic reactions. The synthesis parameters were modified to achieve controllable stacked sheet thickness, and nanoflower diameter. The powders also exhibited
structural stability in CO₂ and air. The Eg was independently tuned through synthesis control and post-treatment gas processing in a reducing environment, with values ranging from 1.38 to 1.83 eV.

Finally, the photoreactor studies demonstrated photocatalytic function of the tuning parameters which had an effect on catalytic activity. The highest CO production rate was Zn:Ga (3:1) at 20 min of nitriding time at 100 °C, which produced 1.06 µmol-g⁻¹-h⁻¹, higher than both of our controlled TiO₂ experiments, and other reported pure TiO₂ solar photoreaction experiments. We also demonstrated (ZnO)₁₋ₓ(AlN)ₓ in a photoreactor study for the first time, which had low production rates, but increasing the cationic ratio in this study more than tripled CO production under solar light irradiation when compared to the lowest cationic ratio. For the MoS₂ nanoflowers, the ‘sweet spot’ of higher catalytic activity was found in those with plentiful thick edge-site abundance and defect laden crystal structures at 5 and 10 °C/min. The ample edge-sites with dangling bonds, and slight crystal impurities assisted in lowering the Eg to achieve materials that reduced recombination and enhanced faster charge transport for photocatalytic reactions. The samples treated in H₂ had increased photoactivity with increased H₂ exposure. 30 min of treatment nearly doubled the production rate to that without post treatment. The H₂ post treatment boosted the overall CO production, but did not increase any additional H₂ and CH₄ production.

These preliminary photoreactor studies indicated that careful tuning of the parent material is imperative to understand before adding a co-catalyst or doping process, as the edge site morphology, crystal phase stability, and strain-induced defects impact the photocatalytic performance.
6.2 Future Work

Future work is recommended to focus on the design of these photocatalysts for further in-depth understanding to perform in long duration photoreactor studies, and with varying light probing experiments to see if higher UV-light will improve the photocatalytic performance. Band edge determination in the tuned catalysts would be beneficial to determine cb and vb placements and see the internal band effects and relationships due to tuning. The use of electrochemical impedance spectroscopy would be ideal to obtain the Mott Schottky plots, of which the flat band potential and band edge determination would be calculated. Finally, bringing the insights of the ‘pure’ tuned materials into effect with a composite, doped, or co-catalyst environment would likely enhance the photocatalytic activity and be ideal for natural progression of the photocatalytic performance enhancement. Now that the understanding of the parent materials are prescribed, linking enhanced synthesis with other materials to aid in the reduction of charge recombination. There are so many variables in photocatalysis to investigate, which makes the field an important area of study, so that advancements can be made for technology advancements that are applied into practice.
REFERENCES


Appendix A Instrumentation

Figure A-1. CVD synthesis equipment images. (A) Ar purge box to prepare CVD precursor materials; (B) SZF; (C) TZF.

Figure A-2. Tube furnace reactor used for nitridation.

Figure A-3. Left: Exploded view of a cross section of photoreactor cell. Right: Top view of the reactor cell with glass removed, exposing fritted glass insert.
Figure A-4. Solar simulator set up inside polycarbonate black box (left) and reactor cell output (right).

Figure A-5. Solar simulator and reactor cell inside black box, with GC/MS (right) and chiller, fluid flow equipment.
### Table B-1. Summary of various TiO$_2$ and ZnO photocatalytic systems.

<table>
<thead>
<tr>
<th>Material</th>
<th>Light Source</th>
<th>Major Product</th>
<th>Formation Rate$^a$</th>
<th>Reaction Conditions</th>
<th>Selectivity for CO$_2$ reduction [%]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$–P25</td>
<td>60 W daylight bulb ($\lambda$ = 400-850 nm)</td>
<td>CH$_4$</td>
<td>0.5</td>
<td>CO$_2$ (99.99%) in the presence of water, ambient temperature</td>
<td>NA</td>
<td>[119]</td>
</tr>
<tr>
<td>TiO$_2$–P25</td>
<td>100 W Hg vapor lamp ($\lambda$ = 365 nm) $\sim$ 110 W/m$^2$</td>
<td>CH$_4$</td>
<td>$\sim$ 1.97</td>
<td>CO$_2$ (0.04-0.15 mmol) and H$_2$O (0.04-0.25 mmol)</td>
<td>NA</td>
<td>[115]</td>
</tr>
<tr>
<td>TiO$_2$ (anatase)</td>
<td>75 W high-pressure Hg lamp with water and color filters (UV, $\lambda$ &gt; 280 nm)</td>
<td>CH$_4$</td>
<td>0.173</td>
<td>CO$_2$ in presence of H$_2$O vapor, atmospheric pressure</td>
<td>NA</td>
<td>[120]</td>
</tr>
<tr>
<td>Pt-TiO$_2$</td>
<td>350 W Xe lamp with 420 nm cut-off filter. 34.8-38.2 mW/cm$^2$</td>
<td>CH$_4$</td>
<td>2.85</td>
<td>CO$_2$ with H$_2$O over 0.020 g catalyst, 0.2 Mpa, 4 mL H$_2$O, 4 hours</td>
<td>39</td>
<td>[121]</td>
</tr>
<tr>
<td>TiO$_2$ (anatase)</td>
<td>100 W Xe Lamp UV-VIS 320-780 (580 mW/cm$^2$) and 320-400 nm (60 mW/cm$^2$)</td>
<td>CO</td>
<td>1.7</td>
<td>CO$_2$ and H$_2$O vapor</td>
<td>41</td>
<td>[9]</td>
</tr>
<tr>
<td>Ag-TiO$_2$</td>
<td>1000 W Xe lamp AM 1.5 solar simulator (1,000 mW/cm$^2$)</td>
<td>CH$_4$</td>
<td>0.192</td>
<td>CO$_2$ and H$_2$O vapor</td>
<td>80</td>
<td>[94]</td>
</tr>
<tr>
<td>Cu/TiO$_2$</td>
<td>200 W Xe lamp $\lambda$ = 320-780 nm</td>
<td>CO</td>
<td>2.5</td>
<td>CO$_2$ with H$_2$O over 0.020 g catalyst, 0.2 Mpa, 4 mL H$_2$O, 5 hours</td>
<td>47</td>
<td>[122]</td>
</tr>
<tr>
<td>Pt-Cu/TiO$_2$</td>
<td>100 W Xe Lamp UV-VIS 320-780 (580 mW/cm$^2$) and 320-400 nm (60 mW/cm$^2$)</td>
<td>H$_2$</td>
<td>51</td>
<td>CO$_2$ and H$_2$O vapor</td>
<td>97</td>
<td>[123]</td>
</tr>
<tr>
<td>Cu/Pt/TiO$_2$</td>
<td>300 W Xe lamp</td>
<td>CH$_4$</td>
<td>0.83</td>
<td>CO$_2$ and H$_2$O vapor</td>
<td>85</td>
<td>[124]</td>
</tr>
<tr>
<td>Ordered mesoporous TiO$_2$</td>
<td>300 W Xe lamp</td>
<td>CO</td>
<td>33</td>
<td>CO$_2$ and H$_2$O vapor</td>
<td>94</td>
<td>[124]</td>
</tr>
<tr>
<td>0.5% Cu/TiO$_2$-SiO$_2$ catalyst</td>
<td>200 W Xe-lamp $\lambda$ = 250-400nm 2.4 mW/cm$^2$</td>
<td>CO</td>
<td>60</td>
<td>CO$_2$ and H$_2$O vapor (through bubbler) CO$_2$:H$_2$O volume ratio is 6:1. 60C</td>
<td>QY: 0.85%</td>
<td>[123]</td>
</tr>
<tr>
<td>Amorphous boron</td>
<td>300 W Xe lamp</td>
<td>CO</td>
<td>1.0</td>
<td>CO$_2$ and H$_2$O 3mL distilled water, 80kPa of pure CO$_2$ gas.</td>
<td>QY: 0.56%</td>
<td>[124]</td>
</tr>
<tr>
<td>ZnO/GaN nanotubes</td>
<td>300 W Xe arc lamp with filter ($\lambda$ &gt; 420 nm)</td>
<td>CH$_4$</td>
<td>0.072</td>
<td>4 mL DI water injected into high purity CO$_2$ gas.</td>
<td>NA</td>
<td>[95]</td>
</tr>
<tr>
<td>300 W Xe arc lamp (UV-VIS)</td>
<td>300 W Xe arc lamp with filter ($\lambda$ &gt; 420 nm)</td>
<td>CH$_4$</td>
<td>0.033</td>
<td>4 mL DI water injected into high purity CO$_2$ gas.</td>
<td>NA</td>
<td>[95]</td>
</tr>
</tbody>
</table>

$^a$Units in µmol g$^{-1}$ h$^{-1}$ unless otherwise noted.
Figure B-1. Single-zone tube furnace (SZF) CVD setup with placement of combustion dishes, precursor, and substrates.

Figure B-2. TZF CVD placement of combustion dish with precursor and substrates.

Table B-2. TZF ramp rate conditions.

<table>
<thead>
<tr>
<th>Reference Name</th>
<th>TZF Ramp Rate (°C/min)</th>
<th>Temperature Setting Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>TZF-2</td>
<td>2</td>
<td>Zone 1 &amp; 2 ramped to 700°C in 342 min, held 20 min. Zone 3 ramped to 300°C in 142 min, held 10 min, then ramped to 700°C in 200 min, held 10 min.</td>
</tr>
<tr>
<td>TZF-10</td>
<td>10</td>
<td>Zone 1 &amp; 2 ramped to 700°C in 68 min, held 20 min. Zone 3 ramped to 300°C in 28 min and held for 10 min, then ramped to 700°C in 40 min, held for 10 min.</td>
</tr>
<tr>
<td>TZF-5</td>
<td>5</td>
<td>Zone 1 &amp; 2 ramped to 700°C in 137 min, and held for 20 min. Zone 3 ramped to 300°C in 57 min and held for 10 min, then ramped to 700°C in 80 min and held for 10 min. Three samples were treated in 1%H₂/99%Ar at 5°C/min and held to 480°C for 10, 20 and 30 min.</td>
</tr>
<tr>
<td>TZF-5-10H₂</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>TZF-5-20H₂</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>TZF-5-30H₂</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>
Figure B-3. LDH Synthesis. Left: Initial Precipitation Stage; Right: Final precipitation stage (bubbling).

Figure B-4. Relative irradiance of solar simulator spectrum output in experimental configuration with AM0 filter.
Figure B-5. Zn:Al nitrided powders at varying nitridation durations and cationic LDH ratios.

Figure B-6. FESEM images for (ZnO)\textsubscript{1-x}(AlN)\textsubscript{x}, Zn:Al = 1:1 with nitriding times at 10 min (A1, A2), 20 min (B1, B2), and 30 min (C1, C2). Zn:Al = 2:1 with nitriding times at 10 min (D1, D2), 20 min (E1, E2), and 30 min (F1, F2). Zn:Al = 3:1 with nitriding times at 10 min (G1, G2), 20 min (H1, H2), and 30 min (I1, I2). (J-L): TEM images for Zn:Al = 3:1 with 10 min nitridation.
Figure B-7. Elemental analysis of oxygen content for nitried LDH materials.

Figure B-8. Zn:Ga nitried powders at varying nitridation durations and cationic LDH ratios.
Figure B-9. FESEM images for (ZnO)$_{1-x}$(GaN)$_x$. Zn:Ga =1:1 with nitriding times at 10 min (A1, A2), 20 min (B1, B2), and 30 min (C1, C2); Zn:Ga = 2:1 at 18,000X with nitriding times at 10 min (D), 20 min (E), 30 min (F). Zn:Ga = 2:1 at 18,000X with nitriding times at 10 min (G), 20 min (H), 30 min (I).

Figure B-10. TEM images of MoS$_2$ flakes.
Figure B-11. TEM images of TZF MoS$_2$ flakes.

Figure B-12. TGA plot of selected MoS$_2$ powders.
Figure B-13. XPS depth profile of MoS$_2$ substrate film. Top: Mo 3d depth profile. Bottom: S 2p depth profile.