**Final Outcomes Report**

**ERA Project ID: F0160014**

# Field-Deployment of a Carbon Dioxide Transformation System Powered by Sunlight

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# 1. Executive Summary

The ERA-supported project, “Field-Deployment of a Carbon Dioxide Transformation System Powered by Sunlight” was successfully completed. In this project we built a field-deployable demonstration unit, which was tested in Alberta and produced solar fuels under ambient sunlight conditions with performance comparable to the lab demonstrations. The technology is based on sunlight as the primary energy input - in a process which resembles, to a large degree, solar panels. The major findings are: 1) We have scaled the technology from a centimeter laboratory demonstration to a meter outdoor field deployment, while maintaining the high efficiency. 2) The growth of nanowires on Si substrate has been demonstrated with high yield. 3) High Faradaic efficiency (selectivity) for $CH_4$ generation and for syngas generation from $CO_2$ reduction has been proved using rationally designed co-catalysts. 3) The effect of water and $CO_2$ purity levels, and solar flux on the efficiency, stability, and product selectivity has been tested. The knowledge gained in the demonstration system bridges the gap between the laboratory demonstration and a large scale solar fuel production plant, as the fundamental building blocks in large-scale solar refinery plant are solar wafers with sizes similar to the demonstration unit. The successful completion of the project paves the way for the installation of a large-scale $CO_2$ conversion plant in Alberta in the near future and its full-scale commercial deployment.

# 2. Project Description

## 2.1 INTRODUCTION AND BACKGROUND

Carbon dioxide ($CO_2$) is the major greenhouse gas that causes irreversible climatic change around the world. Geographical formations, such as declining oil fields, unmineable coal seams, and deep oceans have been proposed and utilized to sequestrate $CO_2$. However, the long-term effectiveness and safety of these approaches, as well as any associated environmental impact, including ocean acidification has remained unclear. Alternatively, $CO_2$ can be chemically transformed into hydrocarbons, which store solar energy in the form of chemical bonds. More importantly, such value-added products have wide marketability and can significantly reduce, or even offset the cost associated with $CO_2$ capture.

Due to the high stability of $CO_2$ molecule, conventional approaches generally involve the use of very high temperature, high pressure, and/or extremely reactive reagents.[3] As a consequence, this process is neither economically feasible nor environmentally friendly. Artificial photosynthesis, by mimicking the natural photosynthesis process, converts $CO_2$ and water into commercially valuable chemical products, such as $H_2$, $CH_4$ and $CH_3OH$. In the artificial photosynthesis process, solar energy is absorbed by the semiconductor, which results in the generation of electron/hole pairs. The energetic photogenerated electrons can reduce $CO_2$ to higher energy compounds and photogenerated holes will oxidize water into $O_2$. In the process, the intermittent solar energy is directly converted into storable chemical fuels and, at the same time, greenhouse gas emission is mitigated from the atmosphere.

Semiconductor materials play a key role in the artificial photosynthesis process. Recently, we develop a new $CO_2$ transformation system using metal-nitride and Si, which are the two most produced semiconductor materials in industry. The rapid development of these industries has led to drastically reduced cost for the mass production of these materials. Therefore our technology is entirely scalable and cost effective. The technology has been protected by a strong IP portfolio to support the goal of commercialization. This project aims to build a field-deployable demonstration unit, which bridges the gap between the laboratory discovery and a large scale solar fuel production plant.

Although the next stages of scale up are not part of this project, it is expected that the development of our technology will follow the trend of solar cells and can be readily scaled up in the near future. The technology will take advantage of existing energy infrastructures, while also creating local jobs and raising the productivity of marginal land. The technology will make a significant impact on reducing greenhouse gas emissions in Alberta and around the world, which will ultimately lead to a carbon-neutral sustainable society and position Alberta and Canada as a world-leader in the utilization of $CO_2$.

## 2.2 TECHNOLOGY DESCRIPTION

In the artificial photosynthesis process, illustrated in Figure 1, solar energy is captured by the semiconductor, which leads to the generation of electron/hole pairs. The energetic photogenerated electrons can reduce $CO_2$ to higher energy carbon-based compounds such as CO and $CH_4$, if the conduction band minimum is more negative than the reduction potential of $CO_2$. Photogenerated

holes will involve in the oxidization of water into $O_2$. In the form of artificial photosynthesis, both photocatalytic and photoelectrochemical routes have been widely studied. Semiconductor material, as an artificial leaf, plays a key in the solar fuels production process. To date, a number of materials, mainly metal oxides, have been developed for the artificial photosynthesis process, however, the efficiency is generally very low.

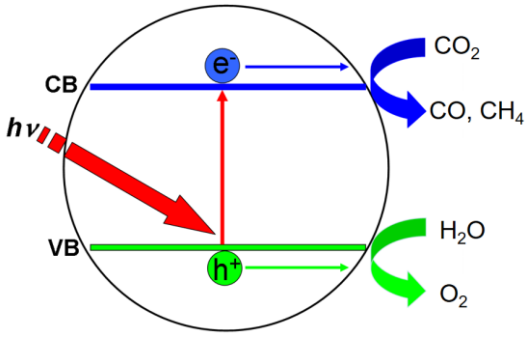


**Figure 1.** Schematic illustration of the mechanism for the photo-reduction of $CO_2$.

Recently, III-nitride materials have drawn considerate attention due to their unique electrical, optical and structural properties. III-nitrides have large light absorption coefficients and excellent charge carrier transport properties. Moreover, the energy bandgap of InGaN can be tuned from 0.65 eV (InN) to 3.4 eV (GaN) by varying the alloy compositions, which cover nearly the entire solar spectrum while still straddle the redox potentials of water splitting and $CO_2$ reduction. For example, InGaN is the only known III-V semiconductor material whose conduction and valence band edges straddle water redox potentials under deep visible and even possibly near-infrared light irradiation. The structural, electronic, and optical properties of the III-nitride photocatalyst can be precisely engineered using the following strategies for maximum photocatalytic performance.

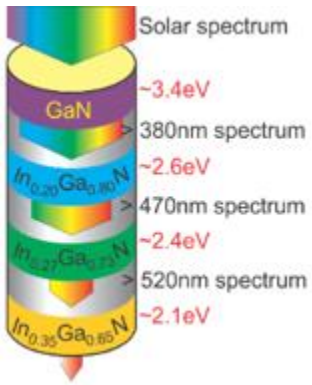


**Figure 2.** Schematic illustration of multi-band InGaN to split solar spectrum.

**Multi-band nanowire structures to harvest sunlight.** To date, the lack of abundant visible-light (~ 43% in solar spectrum) photocatalytic material has been identified as the primary barrier for the market penetration of the emerging artificial photosynthesis technology. In this context, we have developed a fundamentally different approach, with the use of multi-band InGaN nanowire arrays, for achieving high-efficiency solar fuel generation under UV, blue and green-light irradiation, illustrated in Figure 2.

**Tuning the surface band bending for efficient charge transfer.** We have identified that one of the major obstacles for achieving high efficiency and stable solar fuels generation over the emerging nanostructured photocatalyst is directly related to the uncontrolled surface charge properties. By tuning the Fermi level on the nonpolar surfaces of GaN nanowire arrays through controlled dopant incorporation, we have demonstrated that the surface charge properties, including the surface band bending can be precisely controlled. By precisely engineering the surface charge properties, we demonstrated that the efficiency of overall water splitting was enhanced by nearly two orders of magnitude.

The field deployable demonstration system consists of photocatalyst wafer, reaction chamber, solar concentrator, and pipes. The photocatalyst wafers consisted of metal nitride nanowires on silicon substrate. The wafers were fixed in the inner side of the chamber to catalyze the reaction, and the chambers were placed in a manner similar to the solar panels to capture sunlight. The chambers were tilted toward the Earth's equator and were oriented at an angle from the horizontal equal to the local latitude for optimal solar photon collection. A solar concentrator of lens was placed above the reaction chamber to tune the solar flux by varying the distance from the concentrator to the reaction chamber. During the reaction, the generated reduction products and oxidation product were collected from the chamber. The reduction product distribution can be tuned by simply varying the catalyst composition.

## 2.3 PROJECT GOALS

The objective of this project was to build a field-deployable demo unit and evaluate its performance for solar fuel generation under real sunlight condition. The solar refinery reactor is powered by solar energy and contains a solar utility for harvesting sunlight and a catalytic converter to generate solar fuels. The success metrics include: 1) demonstration of a functional solar fuel generation system, and 2) demonstration of stable and efficient operation under natural sunlight. The effects of $CO_2$ purity level for the generation of solar fuels are evaluated, and the system performance and stability are investigated, which pave the way for the installation of a large scale $CO_2$ conversion plant in Alberta in the near future.

## 2.4 WORK SCOPE OVERVIEW

An overview of the scope of this project are described below.

**Task 1 To develop metal-nitride nanowire photo-catalysts using the high throughput, low cost industrial standard epitaxial growth process.** In this task, the growth conditions, such as the growth temperature and partial pressures of the reactant gases, were investigated and optimized to improve the nanowire yield on Si substrate. The morphology, optical property and composition of the nanowires were studied by various characterization tools such as scanning electron microscopy (SEM).

**Milestone 1.1: To establish the basic experimental conditions for improving the yield of nanowires on Si substrate.**

The nanowire growth conditions such as growth temperature and growth time were thoroughly studied to improve the yield of nanowires on Si substrate.

**Milestone 1.2: To demonstrate the growth of nanowires on Si substrate with over 90% yield.**

The nitrogen flow rate, gallium and indium fluxes in the process of epitaxial growth were finely tuned to further improve the yield of nanowires on Si substrate.

**Milestone 1.3: To demonstrate the growth of nanowires on Si substrate with over 95% yield.**

The doping level of magnesium or germanium in the nanowire, and thermal pretreatment prior to nanowire growth (oxide desorption of silicon oxide on the surface of Si substrate) were fully optimized to achieve further improved yield.

**Task 2 To increase the efficiency from 10% to >15-30%.** The properties of metal-nitride nanowires and the co-catalysts were finely tuned to boost the efficiency. In addition, the solar flux was optimized to establish the lowest cost solar energy concentration ratio for balance of system implementation considerations.

**Milestone 2: To demonstrate the integration of nanowire photo-catalysts on Si with an efficiency in the range of 15-30%.**

**Task 3 To evaluate the effect of water and $CO_2$ purity levels on the efficiency, stability, and product selectivity.** Our solar refinery reactor had been demonstrated with high efficiency and stability using high purity $CO_2$ sources. However, the performance of our reactor under the condition of using industrial $CO_2$ sources (e.g., flue gases) was still unknown before the project start. In this task, various working conditions such as $CO_2$ concentration, pressure, temperature, and purity level were investigated to evaluate the potential commercialization deployment.

**Milestone 3: To identify the feedstock requirements, including $CO_2$ and water purity levels.**

**Task 4 (April 2018 to March 2019) To build a field-deployable demonstration unit and evaluate its performance, stability, and product selectivity.** We built a field-deployable solar fuel production system with a relatively large size. The system consisted of nanowire photo-catalyst wafer, reaction chambers, filters, and pipes. The system performance and stability were thoroughly evaluated for an extended period under ambient conditions.

**Milestone 4: To perform detailed testing on the system efficiency and stability.**

# 3. Outcomes and Learnings

In this two-year project, we have built a field-deployable demonstration unit, that can generate solar fuels using natural sunlight as the primary energy input. The growth conditions of metal nitride nanowires on Si substrate have been optimized. The energy conversion efficiency of photocatalyst, and the selectivity of $CO_2$ conversion towards $CH_4$ and syngas generation has been improved. We have successfully met, or exceeded the project milestones. In what follows, the literature background, technology development, and some results of experiments and project outcomes are presented, followed by important lessons learned.

## 3.1 LITERATURE REVIEW

$CO_2$ is the primary greenhouse gas responsible for the global warming and abnormal changes in the global climate. On the other hand, $CO_2$ can be considered as an ideal one-carbon (C1) building block for fuel or chemical synthesis due to its abundance, availability, nontoxicity and recyclability. The conventional approaches of $CO_2$ conversion into hydrocarbons generally involves the use of severe reaction conditions (high temperature, high pressure) and/or extremely reactive reagents to activate $CO_2$, limiting the application of such methods. In this regard, solar photocatalysis/photoelectrocatalysis, which mimics natural photosynthesis, provides a mild and promising route to generate hydrocarbons from $CO_2$ reduction at room temperature and ambient pressure. However, $CO_2$ is an extremely stable molecule and its reduction is thermodynamically and kinetically difficult. In addition, the competing $H_2$ evolution reaction and a broad distribution of products (e.g., CO, $CH_4$, $CH_3OH$, HCOOH, HCHO, higher hydrocarbons and higher alcohols) of $CO_2$ reduction usually lead to very poor selectivity of the system. Therefore, the design and fabrication of high-efficiency materials system with high conversion efficiency and selectivity for $CO_2$ reduction remain a grand challenge.

Over the past four decades, various types of semiconducting materials have been studied, mostly metal-oxide based photocatalysts/photoelectrodes owing to their high photostability in aqueous solution. However, most of the metal-oxides work only under UV light due to their large bandgap. On the other hand, research on metal-nitride (i.e., group III-nitride, GaN, InGaN) photocatalysts and photoelectrodes for artificial photosynthesis has drawn attention since mid-90's. In early-90's, in an effort to enhance the performance of blue light emitting diodes (LEDs), the epitaxial growth techniques of high crystalline quality III-nitrides were substantially improved. Detailed photoelectrochemical characterization revealed that the bandgap of GaN straddles the redox potential of water with sufficient overpotentials, thus that photolysis of water is possible on GaN without external bias. Compared to the conventional oxide-based photoelectrodes, III-nitride semiconductors offer distinct advantages including tunable energy bandgap across nearly the entire solar spectrum, conduction and valence band edges that can straddle $CO_2$ reduction and $H_2O$ oxidation potentials under deep visible and near-infrared light irradiation, and high efficiency charge carrier separation and extraction. Moreover, the one-dimensional nanowire structure can be exploited to achieve higher surface areas, to enhance charge transport properties and to decouple the directions of light absorption and charge-carrier collection. More importantly, such III-nitride nanowire arrays also exhibit a high level of stability in aqueous solution.

Usually, the semiconductor has to combine with a co-catalyst that is capable of activating inert $CO_2$ molecules. $CO_2$ adsorption and activation on catalyst surface is the initial step for the whole $CO_2$ reduction process, which usually determines the efficiency of the $CO_2$ photoconversion and the distribution of final products. Cocatalysts can effectively improve the surface reaction kinetics through lowering the activation energy or overpotential for $CO_2$ reduction. In addition, cocatalysts can promote the charge carrier separation and migration at the semiconductor/cocatalyst interface. Metallic cocatalysts, particularly those capable of suppressing $H_2$ evolution reaction, have been shown to be effective for selective $CO_2$ reduction. The electrochemical reduction of $CO_2$ on metal electrodes has been extensively studied by Hori and coworkers. It was found that electrocatalytic metals could be generally classified into four groups depending on the product selectivity. The first group, including Pt, Rh, Ni, is characterized by $H_2$ as the dominate product due to the low $H_2$ evolution potential. The second group consists of Au, Ag and Zn, which produce CO as the main

product owing to a medium $H_2$ evolution potential and weak CO adsorption strength. The third group, including Sn, Pb, Bi, exhibit the major production of formate. Metallic Cu is the only member of the fourth group, which can convert $CO_2$ into hydrocarbons such as $CH_4$ and $CH_3OH$. The key innovation of our technology is the invention of extremely efficient and stable metal-nitride nanowire photocatalysts and their integration with specific cocatalysts towards desirable $CO_2$ reduction products.

Our technology is one of many efforts to pursue what is now known as artificial photosynthesis. Using industrial by-products (carbon dioxide and non-potable water) and solar energy to produce usable fuel would be a fundamental, game changing achievement. Not surprisingly, governments, research labs and entrepreneurs around the world are pursuing this challenge.

## 3.2 TECHNOLOGY DEVELOPMENT AND MAJOR RESULTS OF EXPERIMENTS

### 3.2.1 Nanowire Yield Optimization on Silicon Wafer

The optimization of nanowire yield on Si wafer was achieved by tuning the nanowire growth/synthesis conditions including growth duration, growth temperature, nitrogen flow rate, gallium flux, doping with Mg or Ge/Si in the nanowires, and thermal pretreatment prior to nanowire growth. Through detailed studies, we have significantly improved the yield of nanowires to be close to 100%.

### 3.2.2 Selective Carbon Dioxide Conversion

The Faradaic efficiency (selectivity) of $CO_2$ conversion to methane and syngas has been improved to 51% and ~80-100% respectively, by optimizing the photocatalyst growth/synthesis and co-catalyst deposition.

#### 3.2.2.1 $CO_2$ Conversion to Methane

High selectivity towards desirable product is very important because it means fewer waste products and less separation cost to remove the by-products. This is particularly challenging for $CO_2$ reduction into $CH_4$ because of the chemical inertness of $CO_2$, the severe competition of hydrogen evolution, and the myriad reaction pathways, as solar-driven conversion of $CO_2$ into methane involves eight electrons transfer. Previously, the best reported selectivity for $CH_4$ generation in photoelectrochemical cell was below 20%. Recently, we developed a high Faradaic efficiency of 51% for $CH_4$ generation from photoelectrochemical $CO_2$ reduction using rationally designed bimetallic co-catalysts integrated with GaN nanowires/$n^+$-p Si platform.

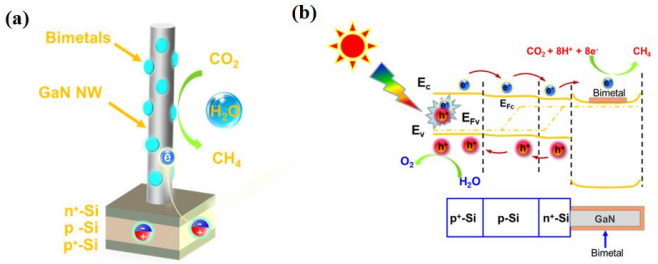

**Figure 3.** (a) Schematic illustration and (b) energy diagram of bimetallic co-catalysts supported on GaN nanowires/Si for photoelectrochemical $CO_2$ reduction towards $CH_4$.

The scheme and the corresponding energy diagram of the device are illustrated in Figure 3. Under simulated sunlight illumination, $n^+$-p silicon junction functions as the light absorber to generate electron-hole pairs. GaN nanowire offers an ideal charge carrier channel for extracting electrons from silicon substrate to the surface of the bimetallic co-catalysts. The bimetallic co-catalysts then drive the conversion of carbon dioxide to methane. The device was synthesized via nanostructure-engineering combination of epitaxial growth of GaN nanowires and electrodeposition of the bimetallic co-catalysts. The structure of the device was characterized by a variety of technologies. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image in Figure 4a demonstrates that GaN nanowire is coated with a thin bimetallic layer (light-yellow framework in Figure 4a), presenting an interesting core-shell nanostructure. The elemental distribution mapping images (Figures 4b-e) suggest that the bimetallic co-catalysts are uniformly dispersed on GaN nanowires and exhibit an interesting alloyed geometry. SEM image in Figure 4f further illustrates that GaN nanowires vertically aligned on silicon substrate possess a length of about 300 nm and the diameter approximately 30-40 nm. It can be used as an ideal platform for harvesting sunlight and extracting photo-excited electrons. Furthermore, GaN nanowire arrays are favourable for exposing the bimetallic co-catalysts with high-density nanostructured grain boundaries and reduced amount, thus enhancing the $CO_2$ reduction reaction. As a result, shown in Figures 4g and 4h, a record-high Faradaic efficiency of 51% as well as an impressive turnover frequency number of 2176 $h^{-1}$ were achieved under simulated sunlight illumination, which, to our knowledge, is among the best performance demonstrated for photoelectrochemical $CO_2$-towards-$CH_4$ conversion.

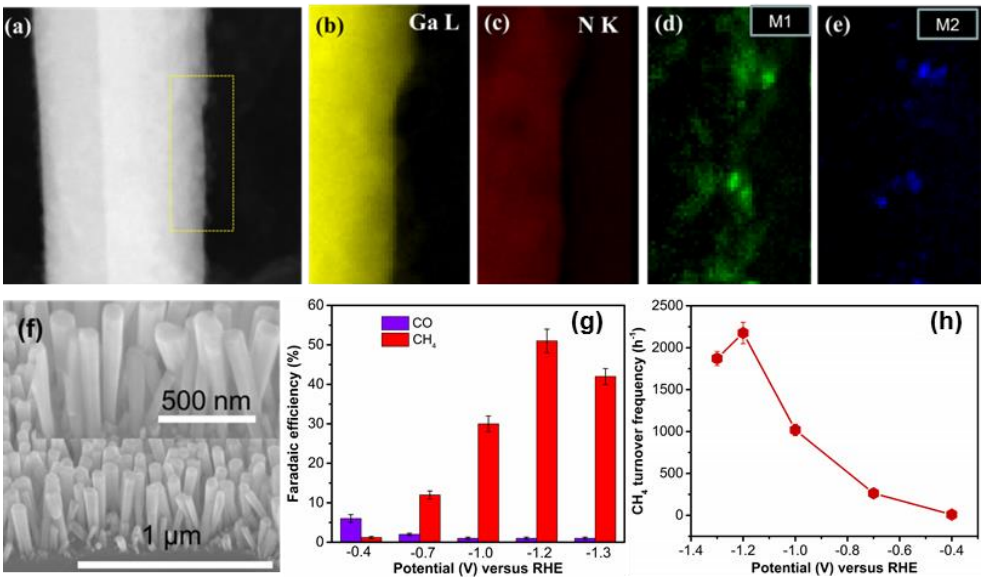


**Figure 4.** Structure of photoelectrode and photoelectrochemical performance for $CO_2$ conversion to methane. (a) HAADF-STEM image of GaN nanowire modified with bimetallic co-catalysts. The elemental distribution mapping of (b) Ga, (c) N, (d) M1 and (e) M2. (f) SEM images of GaN nanowire modified with bimetallic co-catalysts. Dependence of (g) Faradaic efficiency, and (h) turnover frequency number of methane on applied potentials.

### 3.2.3.2 $CO_2$ Conversion to Syngas

Syngas (synthesis gas, CO+$H_2$ mixtures) is a key chemical feedstock to produce various kinds of liquid fuels, such as methanol and hydrocarbons including synthetic jet, kerosene and diesel fuels, via established industrial process (e.g. Fischer–Tropsch reaction). Currently, syngas is commonly produced from coal gasification and natural gas reforming, which requires very high temperature and high pressure. Recently, we have developed renewable syngas production from $CO_2$ conversion in an aqueous photoelectrochemical cell using solar energy. We have demonstrated high Faradaic efficiency, in the range of 80-100%, for syngas generation using Pt-$TiO_2$/GaN/$n^+$-p Si photoelectrode, with no appreciable amount of other $CO_2$ reduction products detected.

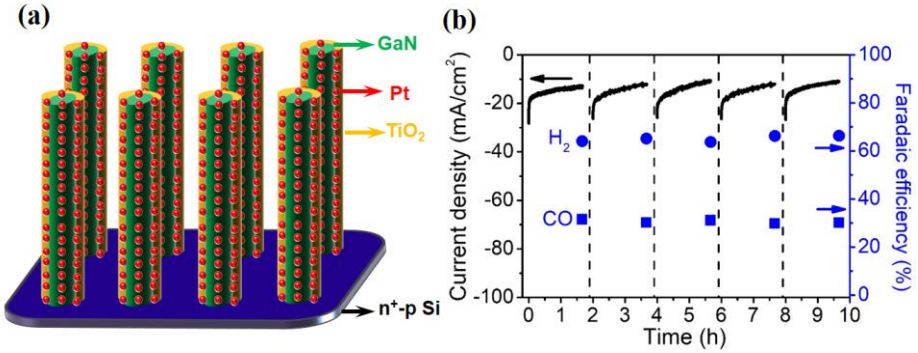


**Figure 5.** (a) Schematic illustration and (b) performance of Pt-$TiO_2$/GaN/$n^+$-p Si photoelectrode.

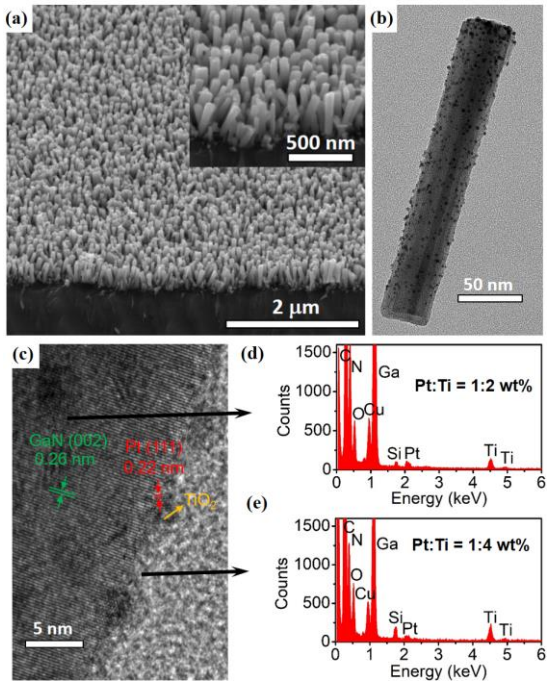


**Figure 6.** Characterization of Pt-$TiO_2$/GaN/$n^+$-p Si sample. (a) 45°-tilted SEM image shows GaN nanowire growth vertically on the Si substrate, (b) TEM image illustrates Pt nanoparticles distributed uniformly on the GaN nanowire surface, (c) HRTEM image, and EDX analysis of the

center (d) and edge region (e) indicates the coating of GaN nanowire and Pt nanoparticles with ultrathin $TiO_2$ layer. The Cu peaks in EDX arise from the TEM sample grid.

The schematic structure of Pt-$TiO_2$/GaN/$n^+$-p Si photoelectrode is illustrated in Figure 5a. The sample was prepared in two major steps. First, GaN nanowire arrays were grown directly on p-n Si wafer. Second, Pt nanoparticles and $TiO_2$ ultrathin layer were deposited on GaN nanowires surface in sequential order using photodeposition and atomic-layer deposition process, respectively. The intimate Pt/$TiO_2$ interface provides multiple active sites for $CO_2$ conversion into syngas. As shown in Figure 5b, a total Faradaic efficiency of nearly 100% was obtained for the co-generation of CO and $H_2$, with no detectable amount of other $CO_2$ reduction products. In addition, the photoelectrode showed high stability in terms of photocurrent density and product selectivity during the five runs of 10 h operation. The CO/$H_2$ ratio in the syngas product was kept around 1:2 during the five cycles of operation, which is a desirable syngas composition for synthetizing downstream products including methanol and liquid hydrocarbons.

The morphology and chemical component of the Pt-$TiO_2$/GaN/$n^+$-p Si photoelectrode were investigatied using SEM, transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) analysis. The cross-sectional SEM image (Figure 6a) shows that the GaN nanowires are aligned vertically to the Si substrate with an average diameter of ~50 nm and height of 250 nm. TEM image in Figure 6b reveals that Pt nanoparticles of 2-3 nm size are uniformly deposited on the GaN nanowires surface. High-resolution TEM (HRTEM) image (Figure 6c), along with EDX analysis in the centre and edge regions of nanowire (Figures 6d and 6e, respectively), indicates the coating of GaN nanowire with ultrathin $TiO_2$ layer of ~1 nm thickness. It is worth mentioning that the optimized thickness of ~1 nm $TiO_2$ can produce maximum catalytic activity and selectivity towards syngas. Very thin $TiO_2$ deposition yields fewer active sites, while increasing the $TiO_2$ thickness over 1 nm results in limited charge carrier transport.

### 3.2.4 Effect of Feedstock and Solar-Flux on Performance

We have demonstrated the presence of a small level of $O_2$, $NO_x$ and $SO_x$ impurities in $CO_2$ does not produce any appreciable influences on the performance of $CO_2$ conversion. In addition, it was found that the efficiency of solar fuels generation remained nearly the same using seawater as the water source for our system. The solar flux dependant photocatalytic activity has also been investigated, revealing the optimum sunlight concentration of ~30 suns for the maximum solar energy conversion efficiency.

### 3.2.5 System Demonstration and Evaluation

We have built field-deployable demonstration systems and evaluated their performance under real sunlight condition. The knowledge gained in the demonstration systems bridges the gap between the laboratory discovery and a large-scale solar fuel production plant that can be potentially deployed in the near future.

#### 3.2.5.1 First System Demonstration and Evaluation

The first field deployable demonstration unit was tested in Southern Alberta Institute of Technology (SAIT) last year, as shown in Figure 7. The demonstration unit has a size of 1.5 m ×

1.5 m × 1.5 m. The system contains a solar utility for harvesting sunlight and a catalytic converter to produce solar fuels. The sunlight harvesting system is a solar concentrator of lens with the solar flux can be tuned by varying the distance from the concentrator to the solar fuel production reactor. The reactor system was tilted at a certain degree to allow the efficient collection of sunlight. It is noted that our wafer-level photocatalyst is much easier to be handled and recycled compared with the conventional powder suspension system. The results of the first demonstration system prove that the laboratory discoveries can be readily extended to a relatively large scale prototype of solar fuel generation system operating under natural sunlight, which provided the distinct opportunity for us to further optimize the chamber design to achieve better performance as shown in the Section below.

**Figure 7.** Field deployable demonstration unit tested for outdoor solar fuels production in Alberta.

### 3.2.5.2 Improved Chamber Design and Performance Evaluation

Based on the results of first demonstration system, we improved the chamber design to allow rapid release of fuel products without forced convection. Stable and efficient operation of the system under real sunlight condition has been proved with similar performance to the laboratory discovery. The demonstration of an integrated solar-powered fuel generation reactor on a system level paves the way for the installation of a large-scale $CO_2$ conversion plant in the near future in Alberta. The technology is based on the metal-nitride nanowire arrays and their direct integration with low cost, large area Si wafers, which leverages well established semiconductor manufacturing processes and can be easily scaled. The technology is an excellent fit for Alberta to utilize the best solar resource in the country and can take full advantages of its existing energy storage and transport infrastructures while minimizing, or eliminating their negative environmental impacts.

The major technical challenge that need to be resolved before commercialization is to demonstrate our nanowire photocatalysts can be produced at a low cost on a large scale, while maintaining the extremely efficiency and stability as shown in our lab discoveries. The remaining technical steps include reducing the manufacturing cost associated with materials synthesis by using the high-

throughput and low-cost industrial standard epitaxial approach and improving the nanowire yield and solar energy conversion efficiency. With those technical challenges addressed, we believe our solar refinery technology is much more attractive and competitive compared to the existing technology in the market (i.e., carbon dioxide capture and storage), as in our technology the carbon dioxide waste gas is not stored but converted into valuable chemical fuels (e.g. methane and methanol) using the abundant solar energy.

### 3.3 PROJECT OUTCOMES

The major project outcomes are listed below.

**Major outcome 1:** We have demonstrated the growth of nanowires on Si substrate with high yield, which was achieved by the optimization of nanowire growth conditions including duration time, growth temperature, nitrogen flow rate, gallium flux, doping with Mg or Ge, and oxide desorption of silicon oxide.

**Major outcome 2:** We have demonstrated energy conversion efficiency of photocatalyst over 16% in half cell reaction, by optimizing the photocatalyst growth/synthesis and co-catalyst deposition.

**Major outcome 3:** We have demonstrated the efficient conversion of $CO_2$ and water into methane and syngas under sunlight illumination. We have shown that the Faradaic efficiency (selectivity) of 51% for $CO_2$ reduction to methane and Faradaic efficiency of ~80-100% for $CO_2$ reduction to syngas.

**Major outcome 4:** We have investigated the effect of $CO_2$ purity level and solar flux on the system performance and stability. The existence of a small level of $O_2$, $NO_x$ and $SO_x$ in $CO_2$ does not produce any significant effect on the performance of $CO_2$ conversion. Seawater can also be used as the water source for the feedstock.

**Major outcome 5:** We have built a field deployable, fully functional demonstration unit and evaluated its performance. Stable and efficient operation of the system under real sunlight condition has been demonstrated with similar performance to the laboratory discovery. The knowledge gained in the demonstration system bridges the gap between the laboratory demonstration and a large-scale solar fuel production plant.

### 3.4 IMPORTANT LESSONS LEARNED

While significant progress has been made in the project, we have also learned some very valuable lessons, described below.

**Lesson 1: Identified the important role of metal/oxide interface in $CO_2$ activation and conversion**. From our studies, we have learned that the metal/oxide interface provides multifunctional catalytic sites with complementary chemical properties for $CO_2$ activation and conversion, which is difficult to be achieved by a pure metal catalyst with a simple monofunctional site. By integrating different compositions of metal/oxide cocatalyst with GaN nanowire arrays on

planar $n^+$-p silicon wafer, highly efficient and selective $CO_2$ reduction to syngas and methane has been demonstrated. We have learned that the synergistic interactions at the metal/oxide interface provide unique reaction channels that structurally and electronically facilitate high-performance $CO_2$ conversion.

**Lesson 2: Built a field deployable demonstration system in the early stage of the project**. When scaling the technology from laboratory discovery to a relatively large scale prototype of solar fuel generation system, some unexpected results appeared. A thick reactor chamber is detrimental to the mass transfer of gas products from the photocatalyst surface and thus decreases the efficiency. Later, we improved the chamber design with a much thinner body, which allows rapid release of fuel products without forced convection. Stable and efficient operation of the system has been demonstrated with similar performance to the laboratory discovery.

**Lesson 3: To engage industrial cooperators during the technology development process.** People from the industry sector such as the oil and mining industry in Alberta showed great interest in the development and commercialization of our transformative technology. They provided us new dimensions and ideas from a business and market perspective, which shed light on how to move the technology from the lab to the market on a system level.

# 4. Greenhouse Gas and Non-GHG Impacts

**GHG Impact.** The immediate greenhouse gas emissions reductions resulted from the completed project (i.e., the building of prototype demo unit) are small. However, the expected greenhouse gas emissions reductions in the future may follow the trend of solar cells and can be readily scaled up with the mature of technology and drastic cost reduction during the scale-up process. The growth of solar cell market has been close to exponential in the past few decades, which evolved from a niche market of small-scale applications to an important electricity source. In 2018, the solar cell farm has a total capacity of 512 GW, which is expected to increase to 4,600 GW by 2050. Following a similar projection, it is expected there is a surge growth of our solar-powered $CO_2$ conversion technology in the future after its commercial implementation. The estimated annual GHG emission reductions by the years 2025 and 2030 are ~0.7 Mt and ~70 Mt, considering installing a 1 GW and 100 GW solar refinery plant, respectively. By 2040, it is expected to establish $CO_2$ conversion plant with a capacity of 500 GW, which could annually reduce $CO_2$ more than 350 Mt. This is higher than the total annual carbon emissions in Alberta (263 Mt in 2016). This would ultimately lead to carbon-neutral chemical fuel-based economies in Canada, which will take full advantages of its existing energy storage and transport infrastructures while minimizing, or eliminating their negative environmental impacts.

**Environment Impact.** The proposed technology would have a positive overall impact to the environment in addition to reducing $CO_2$ emissions. By producing useful products from $CO_2$, this should help promote more rapid deployment of $CO_2$ capture systems that also provide the benefit of filtering out other air pollutants. In the future, because the technology uses solar energy and can produce fuels including hydrogen and methanol. Hydrogen can be added to enrich natural gas in pipelines, or when hydrogen storage and distribution technologies are developed this green hydrogen can displace other fossil fuels. Methanol can be used directly as fuels. Additionally, the technology has demonstrated the potential using non-potable waste water reducing and perhaps eliminating the requirement for an additional water supply while providing possible oil & gas waste water remediation through dehydration of polluted water. The installation of the technology will approximate a solar farm installation and consequently require land usage. However, these installations do not require significant changes to the land other than a relatively level and stable surface. It may be possible to deploy these solar farms on top of oil sands tailings and over old open pit operations as a useful land remediation strategy.

**Employment Prospects.** With the successful commercial implementation of this technology, it is anticipated that both highly skilled manufacturing and installation jobs will be created. In addition, engineering positions to design the specific installations will be required. Given the potential for this breakthrough technology to fundamentally change the management of $CO_2$ produced by industrial activity, there is strong likelihood for the establishment of a significant pool of technical expertise which will not only work in Alberta but eventually participate in projects globally. The initial skill sets are very similar to the petro-chemical infrastructure capabilities already in place in Alberta and this project will allow development of new skills needed to transition Alberta into a lower carbon economy in the future. Manufacturing of the semiconductor subcomponents are likely to remain principally near McGill to take advantage of the expertise during the launch phase. That said, the National Institute of Nanotechnology, established as a partnership between the University of Alberta, Government of Alberta and the NRC will be an excellent source of highly

trained technical staff which would facilitate a potential technology transfer to a manufacturing location in Alberta.

# 5. Overall Conclusions

In this project, we have built a field-deployable demonstration system that can convert greenhouse gas emissions into valuable chemicals and fuels using natural sunlight as the primary energy input. The nanowire photocatalyst yield and energy conversion efficiency has been significantly improved. The selectivity of $CO_2$ conversion towards $CH_4$ and syngas generation has also been significantly enhanced. The performance of the field-deployable system has been evaluated. With the optimization of the reaction chamber, stable and efficient operation of the system under real sunlight condition has been demonstrated. The knowledge gained in the demonstration system bridges the gap between the laboratory discovery and a large-scale solar fuel production plant. To sum up, the project has been successfully completed and all the milestones have been met or exceeded. The successful completion of the project paves the way for the installation of a large-scale $CO_2$ conversion plant in the near future and its full-scale commercial deployment.

# 6. Scientific Achievements

### Patents and Patent Applications

1. $CO_2$ Reduction into Syngas, US 62/862,332, filed June 17$^{st}$ 2019
2. $CO_2$ Reduction into Methane, US 62/945,661, filed Dec. 9$^{th}$, 2019
3. $CO_2$ Conversion with Nanowire-Nanoparticle Architecture, US 62/878.607, filed July 25$^{th}$, 2019
4. Silicon Photoanode Comprising a thin and Uniform Protective Layer Made of Transition Metal Dichalcogenide and Method of Manufacturing Same, US 16/453,010, filed June 26, 2019.

### Books and Book Chapters

1. Semiconductors for Photocatalysis, Mi, Z., Wang, L. and Jagadish, C., Academic Press, 2017.
2. Chu, S., Kong, X. H., Vanka, S., Guo, H. and Mi, Z., Artificial photosynthesis on III-nitride nanowire arrays. Chapter Six in “Semiconductors for Photocatalysis", Academic Press, 2017.

### Journals

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2. Mi, Z., "Field-deployment of a carbon dioxide transformation system powered by sunlight," Lessons Learned Workshop: Carbon Capture, Utilization, and Storage (CCUS), Calgary, Canada, November 2018.
3. Keynote: Z. Mi, "Gallium nitride: A platform towards practical artificial photosynthesis," 102nd Canadian Chemistry Conference and Exhibition (CSC), Quebec City, Canada, June 3-7, 2019.
4. Invited: Zetian Mi and Srinivas Vanka, "Monolithically Integrated InGaN/Si Tandem Photoelectrodes for Efficient and Stable Photoelectrochemical Water Splitting," MRS Spring Meeting, Phoenix, AZ, April 22-26, 2019.
5. Invited: Z. Mi, "Artificial Photosynthesis on III-Nitride Nanowire Arrays," 233rd ECS Meeting, Seattle, WA, May 13-17, 2018.
6. Invited: Z. Mi, "Solar Water Splitting and CO2 Reduction on III-Nitride Nanostructures," MRS Spring Meeting, Phoenix, AZ, April 2-6, 2018.
7. Invited: Z. Mi, "Electronic structure of III-nitride nanowires for efficient light emitters and solar fuels generation," Nanowires and Nanowire Growth Workshop, Lund, Sweden, May 29 – June 2, 2017.
8. Keynote: Z. Mi, "Emerging applications of III-nitride nanostructures: From deep UV photonics to artificial photosynthesis," UK Nitrides Consortium Conference, Oxford, UK, Jan. 5-6, 2017.

# 7. Next Steps

In the next steps, we plan to further improve the efficiency of the photocatalytic system by optimizing the light-harvesting absorbers and co-catalysts. To commercially deploy the technology, we will raise funds and build a pilot scale solar refinery pilot plant that reduces tons of $CO_2$-equivalent per year. This will bridge the gap between our prototype demonstration in this project and the full-scale commercial implementation. The technology readiness of the system will be thoroughly evaluated and validated, and the commercialization feasibility of the process will be demonstrated. The goal is to evaluate this process, in the context of efficiency, feedstock requirements, durability, products, scalability and cost, and to demonstrate an integrated system with low cost, high performance, durability, and scalability. The commercialization plan will be adapted to the reality of the market conditions. To execute our development and commercialization plan, we will work with many industrial collaborators and strategic partners. We will align subcontractors, integrators and end-user for the pilot scale demonstration which will validate the production yield estimates as well as detailed techno-economic analysis of the technology. In tandem, we will discuss with private and public capital markets to attract investment and fund the product development, modular and scalable deployment in plant applications of various sizes to address the markets in and beyond Alberta. Our initial market entry is the oil sands operations in Alberta with abundant sources of both high-intensity $CO_2$ emissions as well as wastewater. It appears that in Alberta, companies like Air Products and Air Liquide would be ideal clients for the chemical outputs like $H_2$ or $O_2$. The $CH_4$ produced from the reaction could be used by the oil producer for energy in their daily operations and reduce their natural gas requirement. It is expected that the development of our technology will follow the trend of solar cells and can be readily scaled up in the near future: the installation of $CO_2$ conversion plants with capacity similar to the current solar panels (512 GW in 2018) has the potential to reduce 366 Mt $CO_2$ annually, which is more than the annual carbon emissions in Alberta (263 Mt in 2016). Our technology will position Alberta and Canada as a world-leader in the utilization of $CO_2$, which could potentially meet its international greenhouse gas emissions-reduction commitments and targets in 2030 and 2050.

# 8. Communication Plan

We will work closely with our main partner, ERA, to disseminate the results of this project and the possible demonstration of a large-scale solar refinery pilot plant in the next step. We are also interested in attending and presenting our non-confidential project results with industry, academic community, government and general public through related workshops and conferences worldwide. This may draw attention of the technology among future potential customers and partners, and solicit additional industrial investment for its further development. In addition, some major results and findings of the project will be organized into papers and submitted to major journals, which will foster interdisciplinary and international collaboration and promote additional novel developments in $CO_2$ solutions.