High Efficiency Solar-based Catalytic Structure for CO₂ Reforming

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By: Dr. Hisham Menkara
Principal Investigator
PhosphorTech Corporation
Kennesaw, Georgia

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National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Infrastructure for Carbon Capture and Storage
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Outline

• Benefits to the Program
• Project Goals and Objectives
• Technical Status
  – Conventional vs hybrid heterojunction systems
  – Solution-based synthesis of photocatalyst materials & structures
  – Glancing Angle Deposition (GLAD) of metal oxides by IAD
  – Chemical products selectivity and detection
  – CO₂ reforming results and concept feasibility using biomass
• Accomplishments to Date
• Summary
• Appendix
Benefits to the Program

- **Benefit Statement**: Critical challenges identified in the utilization focus area include the cost-effective use of CO₂ as a feedstock for chemical synthesis or its integration into pre-existing products. The efficiency of these utilization processes represents a critical challenge. This research is developing a set of materials and systems useful in converting CO₂ into other useful chemicals using sunlight as energy.

**Inorganic Photocatalyst**

**Organic Photocatalyst**
Program Goals

• The goal of this project is to develop and demonstrate a novel photocatalytic structure and solar-based reactor having high CO\textsubscript{2} reforming potential, and high utilization of solar solar energy.
  
  - **Phase I**: Development & optimization of low-cost solution-based coating processes
    
    • **Objectives**: to develop solution-based thin-film coating processes for controlled and uniform coating of TiO\textsubscript{2} and NBG semiconductors on various substrates. Optical and physical properties will be measured and optimized.
  
  - **Phase II**: Development, fabrication, & characterization of p-n structures for CO\textsubscript{2} reduction
    
    • **Objectives**: to develop and fabricate p-n structures using optimized thin-films and demonstrate CO\textsubscript{2} reforming potential into fuels and chemicals
  
  - **Phase III**: Refinement of CO\textsubscript{2} reactor and prototype demonstration
    
    • **Objectives**: to build a CO\textsubscript{2} reactor prototype and refine p-n structure for maximum yield and energy conversion efficiency
### Photocatalyst Technology Challenge

<table>
<thead>
<tr>
<th>photocatalyst</th>
<th>band-gap energy (eV)</th>
<th>photocatalyst</th>
<th>band-gap energy (eV)</th>
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<tr>
<td>Si</td>
<td>1.1</td>
<td>TiO$_2$ rutile</td>
<td>3.02</td>
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<tr>
<td>WSe$_2$</td>
<td>1.2</td>
<td>Fe$_2$O$_3$</td>
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<td>$\alpha$-Fe$_2$O$_3$</td>
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<td>SnO$_2$</td>
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<tr>
<td>SiC</td>
<td>3.0</td>
<td>ZnS</td>
<td>3.5</td>
</tr>
</tbody>
</table>

**Photo-synthetically Active Radiance (PAR)**

![Photo-synthetically Active Radiance (PAR)](image)

**Terrestrial Spectral Irradiance (AM1.5)**

(Total available from 280-2500 nm ~ 992 W/m$^2$)

- Available UV Energy ~ 46 W/m$^2$
- Available Vis Energy ~ 430 W/m$^2$
- Available IR Energy ~ 516 W/m$^2$

![Terrestrial Spectral Irradiance (AM1.5)](image)
Conventional vs Hybrid Photocatalysts

**Conventional System**
- High recombination rate of photo-generated electron-hole pairs
- Excess metal loading leads to increased light reflection
- Hydrogen is formed by competing reduction reactions

**Hybrid System (Patent-pending)**
- PN junction acts as an efficient e-h separator
- Metal-free surfaces lead to increased light absorption
- Semiconductors with different band gaps can be used to harvest more solar energy

**Competing reduction reaction leads to hydrogen formation**

\[ 4H^+ + 4e^- \rightarrow 2H_2 \]

- Methane formation: \( CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \)
- Carbon monoxide formation: \( CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \)
- Methanol formation: \( CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \)
- Formic acid formation: \( CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H \)
- Formaldehyde formation: \( CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O \)
Photocatalytic Reactor Designs – Commercialization Perspective

**Radiator-Type Design**

![Diagram of Radiator-Type Design](image1)

**Solar-Thermal Design**

![Diagram of Solar-Thermal Design](image2)

**Planar Reactor Design**

![Diagram of Planar Reactor Design](image3)

Prototype radiator-type solar reactor built using modular quartz tubing & mylar reflector (Tube unit: 0.5in diameter X 15 in long)

Chemical Products

- $\text{CO}_2$
- $\text{H}_2\text{O}$
- $\text{CO}_2 + \text{e}^- \rightarrow \text{CO}_2$
- $2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{O}_2 + 4\text{H}^+$

Reactors Unit

- Cross Section

- PN Nanostructure
- Metal Substrate
- Glass Tube

Photocatalyst Structure

- H$_2$O
- CO$_2$
- Reflectors

Prototype radiator-type solar reactor built using modular quartz tubing & mylar reflector (Tube unit: 0.5in diameter X 15 in long)

PhosphorTech Corporation – 3645 Kennesaw North Industrial Pkwy, Kennesaw, Ga  30144

www.phosphortech.com - (770) 745-5693 (phone) - (770) 828-0672 (Fax)
Product(s) Detection by FTIR (Gas Phase)

Fourier Transform Infrared Spectroscopy (FTIR)

Continuous flow closed system CO₂ reforming reactor coupled to FTIR gas cell for real-time analysis
CO₂ Reforming using TiO₂/Cu Photocatalyst Structure & UV Light

- CO₂ concentration decreases, while methane increases
- Reforming yield slows over time due to Cu oxidation and formation of graphitic carbon

Time evolution data measured by FTIR of gas composition inside a TiO₂/copper photocatalytic reactor system under UVA radiation - 6W UVA bulb (340-400 nm) with intensity of ~8 mW/cm²] - Atmospheric pressure & room temperature)
Fuel Product(s) Selectivity through Multilayer Structures

- Formaldehyde

![Graph showing absorbance vs wavenumbers for different reactor types](image)
FTIR spectrum of gas composition in photocatalytic reactor with TiO$_2$ nanorod on Ti substrate after UVA radiation of 168 hours (7 days) at 8 mW/cm$^2$. 

**Wavenumbers (cm$^{-1}$)**

- CO$_2$
- CH$_4$
- Formic compound
- H$_2$O
- 3330 ppmV
- 25 µl
Various TiO$_2$ nanoporous films grown with glancing angle $\alpha = 95^\circ$
Ion-assisted Deposition (IAD) of Thin-film Nanostructures

Thin-film processing at Georgia Tech:
- Process development for wide bandgap TiO₂ and narrow bandgap thin-films
- Multilayer deposition/optimization
- Investigation of “3D” nano-structures for improved light harvesting and catalytic properties
Glancing Angle Deposition

- GLAD is a thin film deposition technique that enables growth of porous, nano-structured films

- Thin films grown by physical vapor deposition (PVD) with e-beam evaporation system

- Substrate oriented so that flux arrives at substrate at highly oblique angles of incidence, determined by $\alpha$ and $\alpha_{\text{tilt}}$

- Typically $\alpha \sim 70^\circ$ or higher

- Substrate can be rotated about axis, $\phi$

- Use low-pressure PVD as atoms must travel in a linear trajectory and create shadow effect

High Selectivity Structure for Formic Acid Production

• Exclusive formate formation using stable metal alloy and hybrid metal oxide semiconductors:
  • High long-term stability
  • IPA used as a hole scavenging agent
  • Implementation near semiconductor industry?
  ➔ high IPA concentration in waste water

• Formic acid is an important preservative and industrial chemical and is used in some fuel cells:
  - 720,000 tonnes/yr (relatively small market)
  - Current production involves high pressures and temperatures and the use of methyl formate, formamide, and hydrolysis processes
  - Ammonium sulfate byproduct, which is difficult to dispose of

Energy Efficiency ~ 0.20%
Example: Dairy Industry

• Production of certain dairy products such as Greek yogurt and cheese create a waste byproduct of whey acid:
  – The US Northeast alone produces about 150 million gallons of acidic whey a year
  – Whey acid is hazardous to the environment & waterways
  – Some whey acid can be mixed with livestock feed, fertilizers, and some food groups but with limited use due to high acidity

→ *Whey acid seems to work as a good organic hole scavenger for CO₂ reforming into fuels and chemicals under sunlight*

→ *Experiments were performed using unmodified whey acid solution from yogurt*
FTIR Analysis of Liquid & Gas Phase Compositions

Following 3hrs of solar simulator radiation ~350 mW/cm²; T= 60°C

Liquid Phase FTIR

Gas Phase FTIR

Wavenumbers (cm⁻¹)

Absorbance

Absorbance

Gas phase

CO₂

Methanol

Formaldehyde

Formic compound

H₂O vapor

Lactic Acid

CO₂

Wavenumbers (cm⁻¹)

Absorbance

Absorbance

Lactic Acid

CO₂ (dissolved)

Water

Lactose+

Sample in contact with evanescent wave

Infrared Beam

ATR Crystal

To Detector

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CO₂ Reforming by Sunlight using Whey Acid as Sacrificial Agent

- 50% drop in CO₂ gas concentration inside closed reactor in under 3 hours!
- Energy Efficiency ~ 0.4% (considering only formic compound)

A Fresnel lens was used with an Oriel solar simulator to focus light to ~350 mW/cm². Reactor temperature increased to 60°C by infrared portion of (simulated) solar spectrum.

Produced Chemicals

- Methanol
- Carbon Monoxide
- Formic Acid
- Formate

H₂O
Accomplishments to Date

• Completed all project milestones planned for Years 1-3 and achieved 16X higher efficiency than proposed target
• Achieved the highest reported CO₂ to CH₄ reforming yields (382 uL/h.g-catalyst) using TiO₂/Ti reactor and sunlight
• Achieved the highest reported CO₂ to CH₄ reforming yields (1823 uL/h.g-catalyst) using non-TiO₂ narrow-bandgap PN structure and sunlight
• Demonstrated a highly stable WBG-NBG CO₂ mini-reactor with energy efficiency under natural sunlight equivalent to 3X higher than what was reported by Nishimura in a cylindrical reactor
• Nanorods and thin-films of narrow-bandgap materials synthesized with absorption up to 650nm
• Demonstrated thin-film PN structure with average VIS/NIR light absorption at 27%
• Demonstrated improved optical and thermal performance from 3-dimensional narrow bandgap nanocrystal structures
• Improved solution-based process for fabricating large bandgap nanorod structures
• Demonstrated continuous CO₂ reforming into CH₄ and CH₂O₂ using a stable TiO₂/Ti nanorod structure
• Demonstrated new metal-oxide PN structures for CO₂ reforming into formic acid (CH₂O₂) under sunlight conditions
• First time demonstration of fast CO₂ reforming into several fuels and chemicals under sunlight using environmentally toxic acid whey as a hole scavenger with 50% drop in CO₂ levels in under 3 hours
• Presented and published (proceedings) at the 242nd ACS conference in September 2011
• Delivered an invited presentation at the Energy Materials Nanotechnology Meeting in Orlando, FL, April 16-20, 2012
• Invited to present at Heterogeneous Catalysis Symposium, ACS Philadelphia Meeting in August 2012
• Presented at the 2013 International Conference on Carbon Dioxide Utilization (ICCDU XII), Alexandria, VA, June 23-27
Summary

• Fabricated and demonstrated various nanostructures suitable for solar-based CO$_2$ reforming in sunlight conditions
• Achieved high CO$_2$ to CH$_4$ reforming yields (1.8 ml/h.g-catalyst) using narrow-bandgap Cu$_2$O oxide structure and sunlight.
  – Problems with Cu$_2$O stability could prevent successful commercialization
• Chemical product selectivity can be achieved by choice of structure
• Demonstration of highly stable CO$_2$ reforming under sunlight using an un-modified industrial biomass waste as a sacrificial agent
  ➔ > 50% drop in CO$_2$ gas concentration in less than 3 hours
• Low-cost active semiconductors, abundant stable metals, and biomass waste source are key for successful commercialization of photocatalytic technology
• It is possible to use low-cost semiconductors/metals, and biomass waste source for long-term photocatalytic CO$_2$ conversion by sunlight
  ➔ Competing with nature’s photosynthetic efficiency is now within reach
  ➔ Energy efficiency can be increased by > 20X with a photo/electrochemical hybrid
Thank You!

Georgia Tech: Z. Kang, J. Nadler
Coal & Energy Industry Consultant: R. Minkara (VP of Technology at Headwaters)

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Program Manager: William O'Dowd
**PhosphorTech**
- Solution-based Processes
- Nanocrystal Synthesis
- Catalyst Evaluation
- PN Structure Modeling
- CO₂ Reforming Reactor

**GeorgiaTech**
- Thin-film Vacuum Deposition
- Alternative Nano-structures
- Material & Film Characterization
<table>
<thead>
<tr>
<th>Task Name</th>
</tr>
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<tbody>
<tr>
<td>1. High Efficiency Solar-based Catalytic Structure for CO2 Reforming</td>
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<tr>
<td>1.1 Project Management &amp; Planning</td>
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<tr>
<td>1.2 Development &amp; Optimization of Solution-based Thin-film Processes</td>
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<tr>
<td>1.2.1 Preparation of NBG Precursors and Solutions</td>
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<td>1.2.2 Acquire and Evaluate Commercial TiO2 Nanocatalysts</td>
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<td>1.2.3 Develop Solution-based Deposition Techniques</td>
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<td>2. Development &amp; Fabrication of PN Structure</td>
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<td>2.1 Simulation and Optimization of PN Structures</td>
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<td>2.3 Comparison of PN Structure with Conventional Photocatalysts</td>
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<td>3. Refined of CO2 Reactor Components</td>
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<td>3.1 Develop Thin-film Deposition Process</td>
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<td>3.2 Investigate Alternative Structures and Surface Morphologies</td>
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<td>4. Build and Demonstrate CO2 Reactor Prototype</td>
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<tr>
<td>4.1 Build and Demonstrate CO2 Reactor Prototype</td>
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<tr>
<td>4.2 Demonstrate CO2 Reforming</td>
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Gantt Chart

- Milestone
- Decision Point
- Milestone
- Decision Point
- Milestone


