PhosphorTech

High Efficiency Solar-based Catalytic Structure for CO_2 Reforming

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

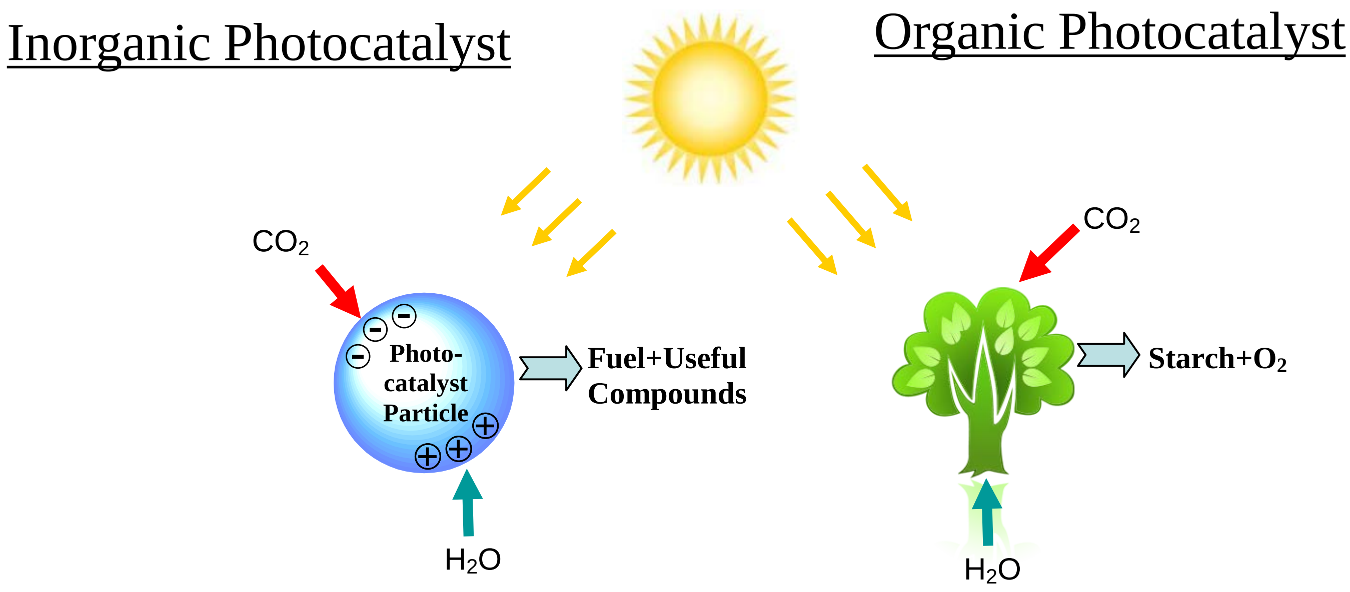
U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Infrastructure for Carbon Capture and Storage
August 20-22, 2013

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
  - CO_2 reforming results and concept feasibility using biomass
- Accomplishments to Date
- Summary
- Appendix

Benefits to the Program

- **<u>Benefit Statement</u>**: Critical challenges identified in the utilization focus area include the cost-effective use of CO_2 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 CO_2 into other useful chemicals using sunlight as energy.



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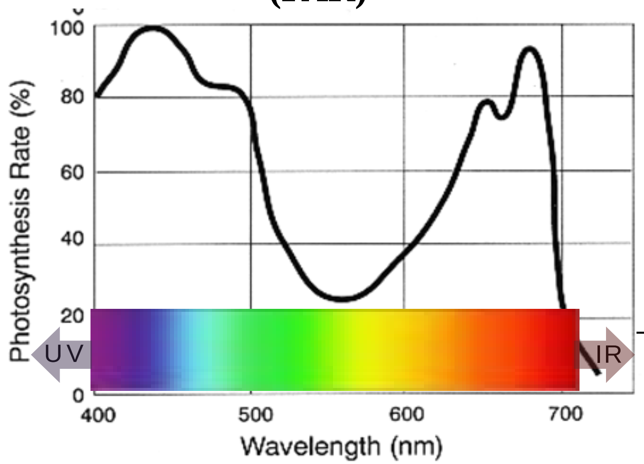
Program Goals

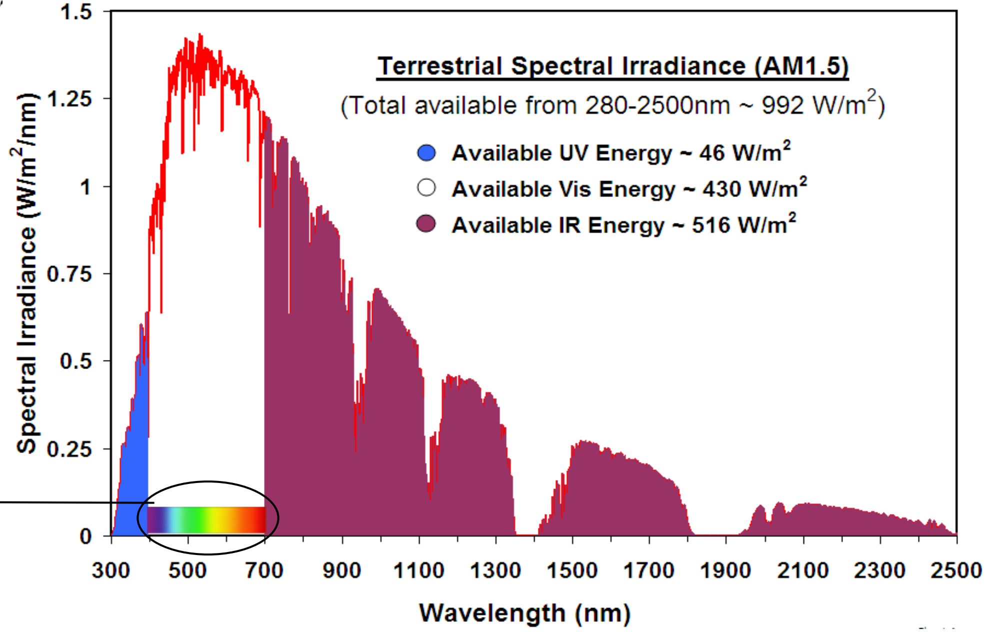
- The goal of this project is to develop and demonstrate a novel photocatalytic structure and solar-based reactor having high CO_2 reforming potential, and high utilization of solar solar energy.
  - **Phase I**: Development & optimization of low-cost solution-based coating processes
    - Objectives: to develop solution-based thin-film coating processes for controlled and uniform coating of TiO_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_2 reduction
    - Objectives: to develop and fabricate p-n structures using optimized thin-films and demonstrate CO_2 reforming potential into fuels and chemicals
  - **Phase III:** Refinement of CO_2 reactor and prototype demonstration
    - Objectives: to build a CO_2 reactor prototype and refine p-n structure for maximum yield and energy conversion efficiency

Photocatalyst Technology Challenge

photocatalyst	band-gap energy (eV)	photocatalyst	band-gap energy (eV)
Si	1.1	TiO_2 rutile	3.02
WSe_2	1.2	Fe_2O_3	3.1
α-Fe_2O_3	2.2	TiO_2 anatase	3.23
CdS	2.4	ZnO	3.2
V_2O_5	2.7	$SrTiO_3$	3.4
WO_3	2.8	SnO_2	3.5
SiC	3.0	ZnS	3.[illegible]

Photo-synthetically Active Radiance (PAR)





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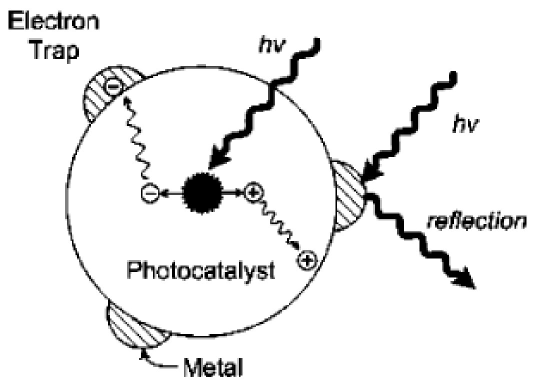
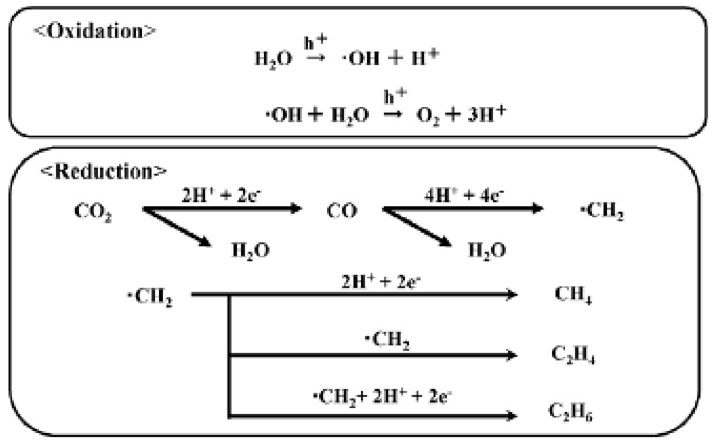
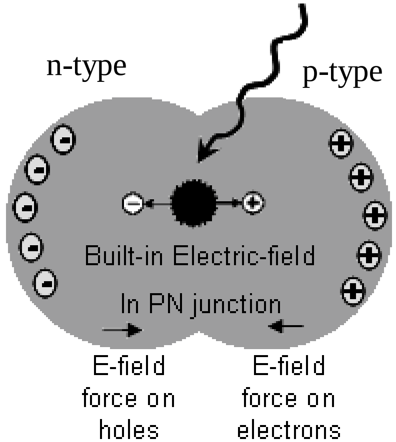
Conventional vs Hybrid Photocatalysts



A. Nishimura, Catalysis Today 148 (2009)341–349





Competing reduction reaction leads to hydrogen formation

$4H^+ + 4e^- \rightarrow 2\ H_2$

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

Methane formation

$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2\ H_2O$

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

$CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O$

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

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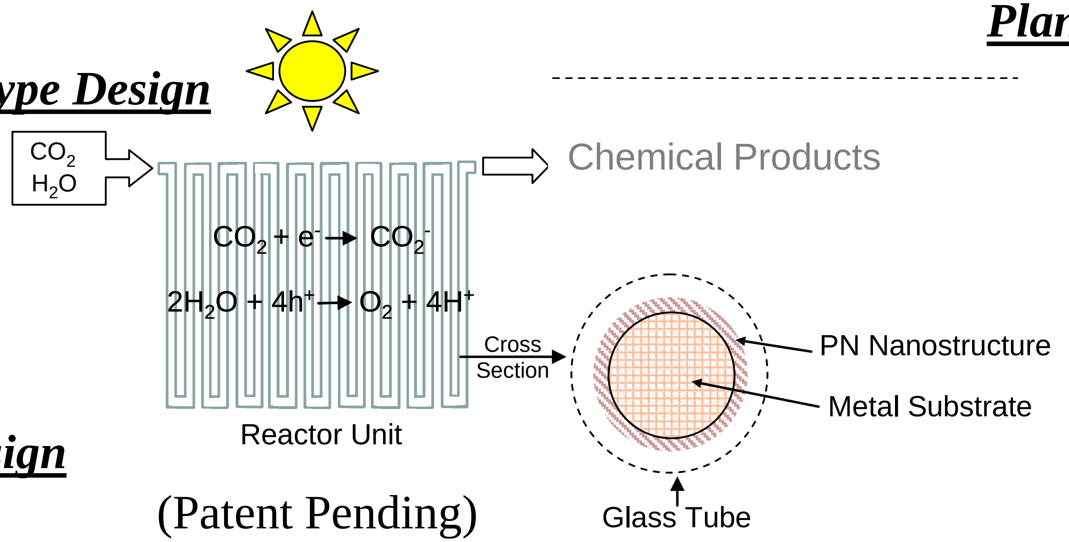
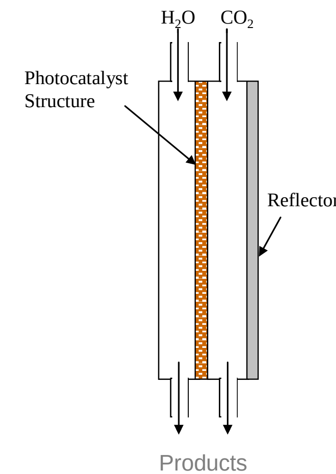
PhosphorTech Photocatalytic Reactor Designs – Commercialization Perspective

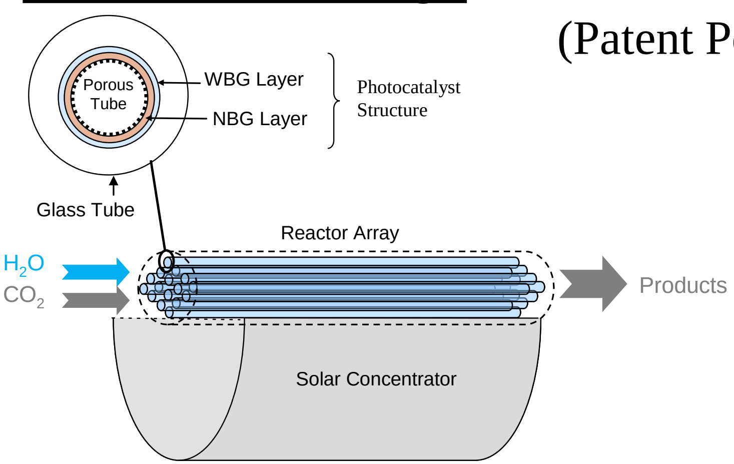
Radiator-Type Design



Planar Reactor Design



Solar-Thermal Design



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

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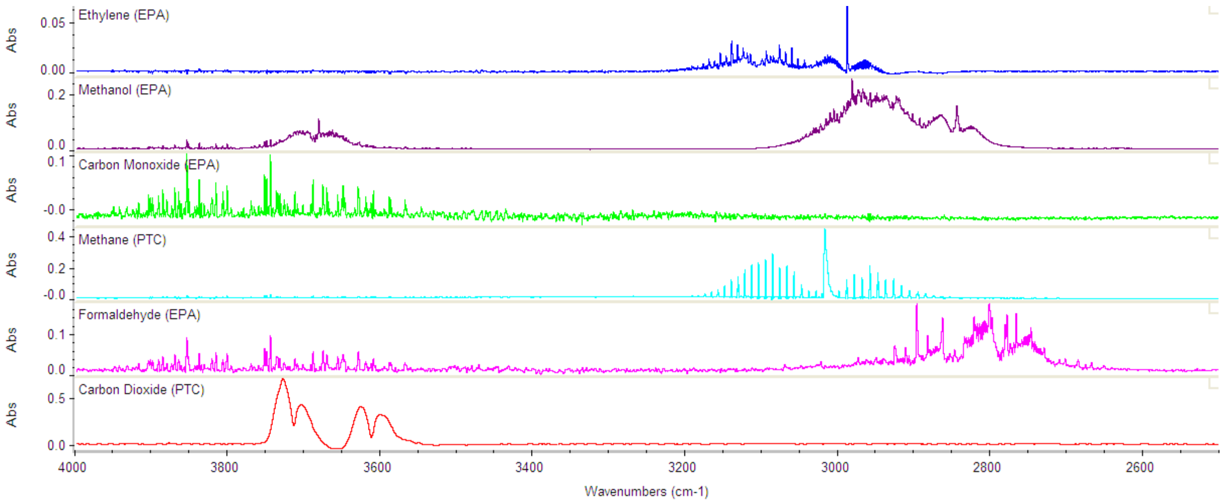
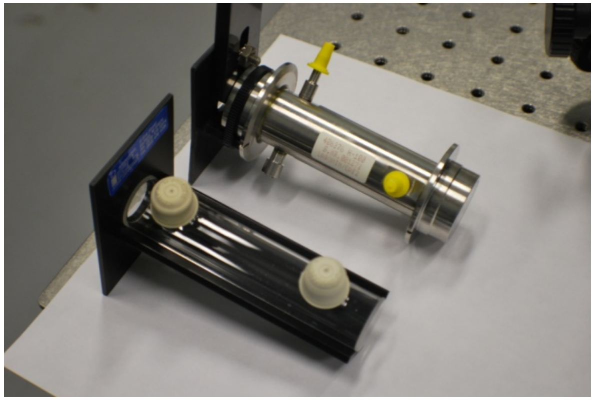
Product(s) Detection by FTIR (Gas Phase)



Fourier Transform Infrared Spectroscopy (FTIR)

Continuous flow closed system CO_2 reforming reactor coupled to FTIR gas cell for real-time analysis



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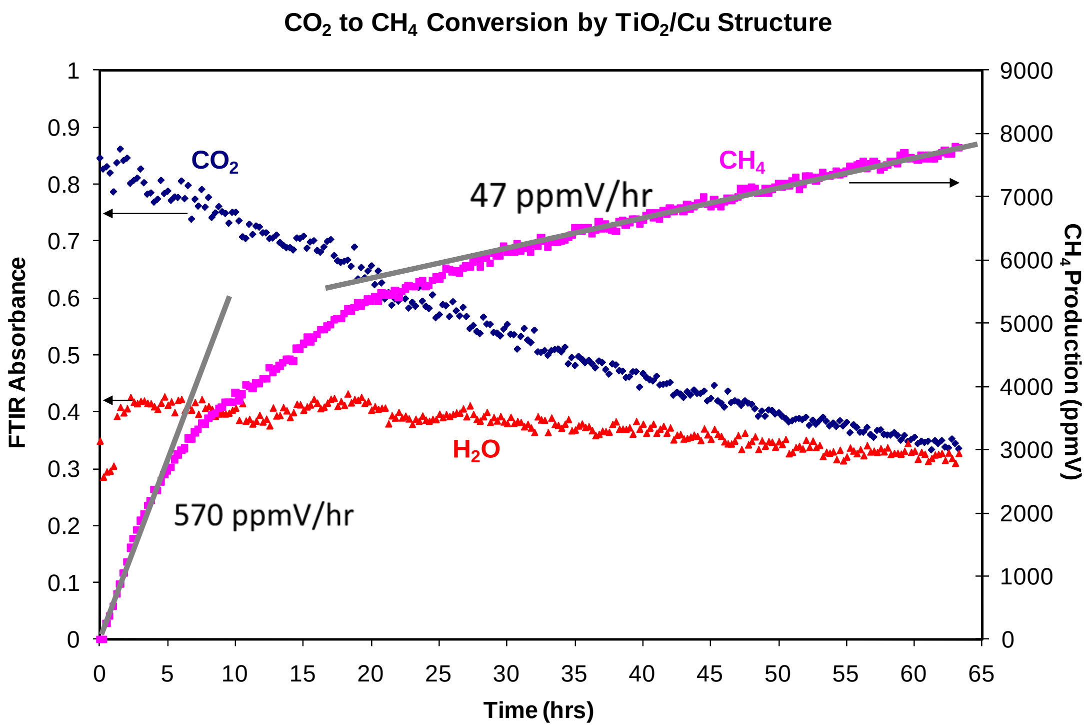
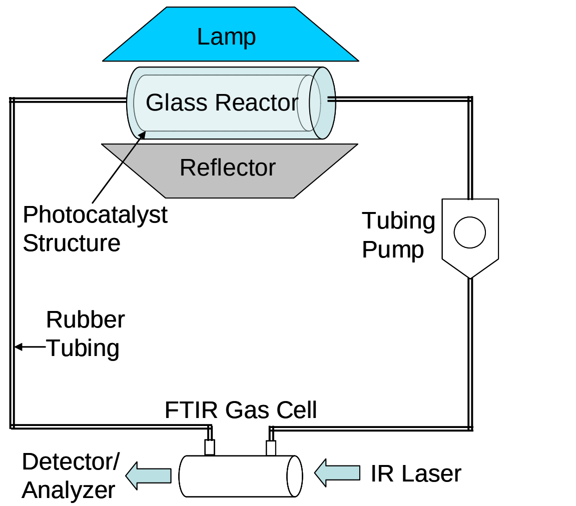
CO_2 Reforming using TiO_2/Cu Photocatalyst Structure & UV Light



- CO_2 concentration decreases, while methane increases
- Reforming yield slows over time due to Cu oxidation and formation of graphitic carbon



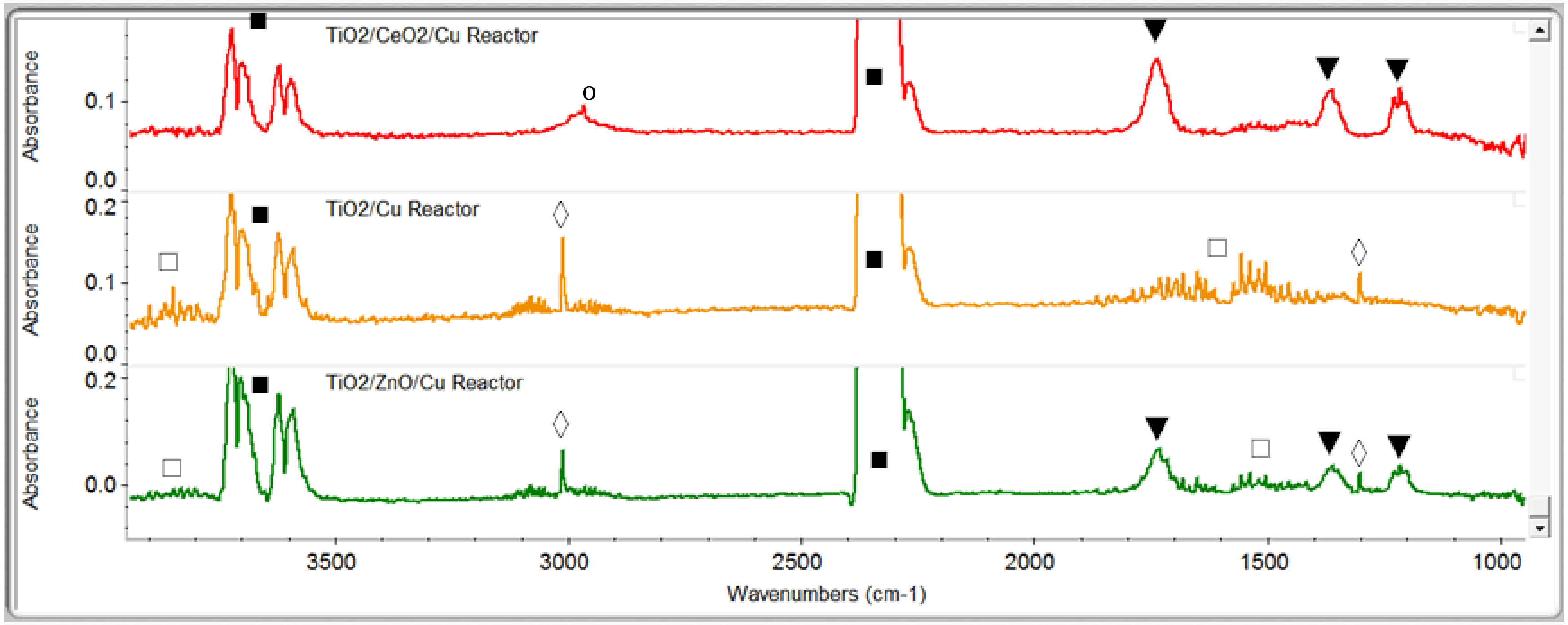
Time evolution data measured by FTIR of gas composition inside a TiO_2/copper photocatalytic reactor system under UVA radiation

- 6W UVA bulb (340-400 nm) with intensity of ~8 mW/cm^2]
- Atmospheric pressure & room temperature)

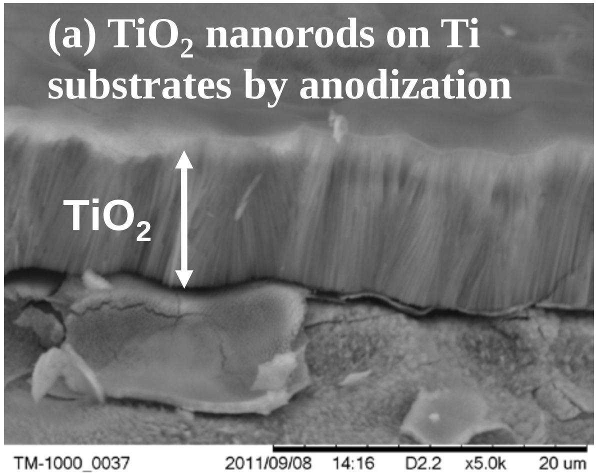
Fuel Product(s) Selectivity through Multilayer Structures

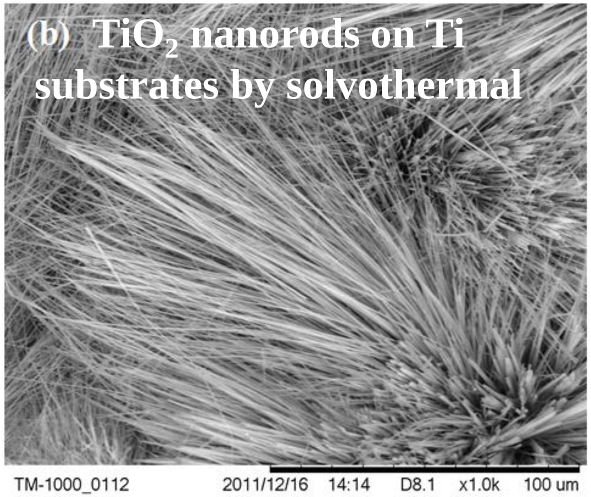
o **Formaldehyde**

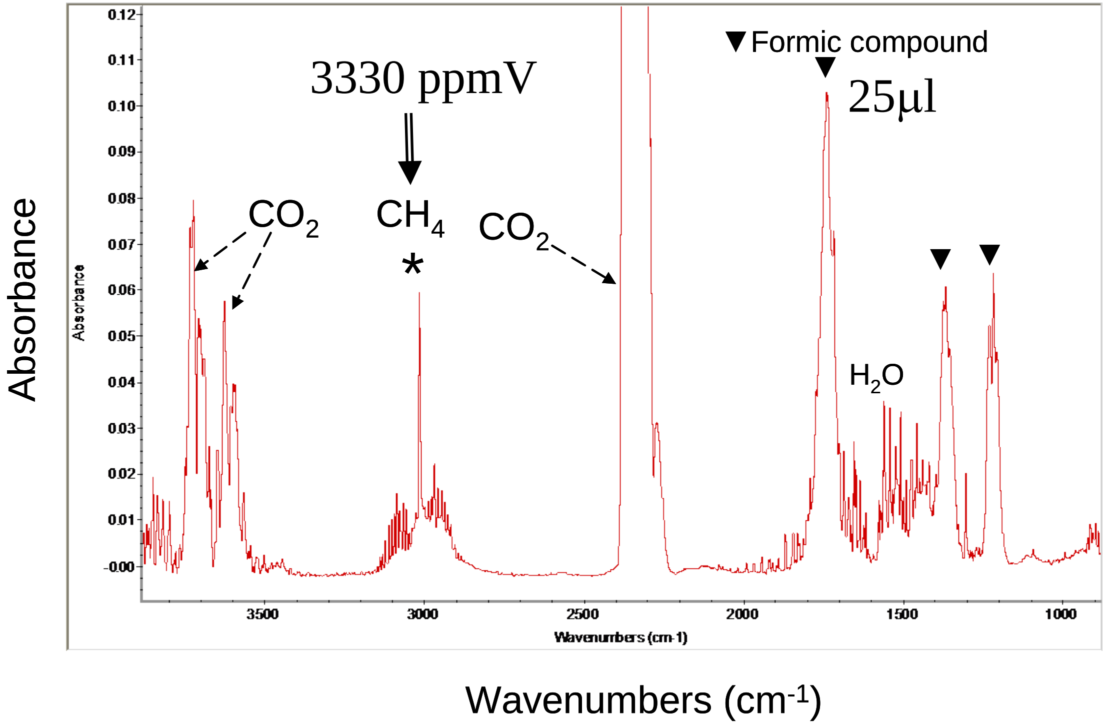
▼ **Formic Acid – CH_2O_2** ◊ **Methane – CH_4** ■ **Carbon Dioxide – CO_2** □ **H_2O Vapor**



Nano-Structures Grown by Solution Processing

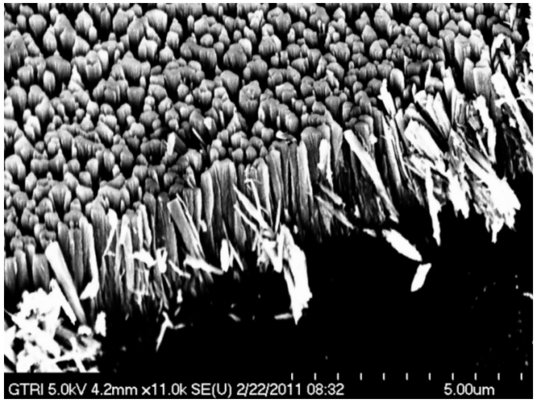


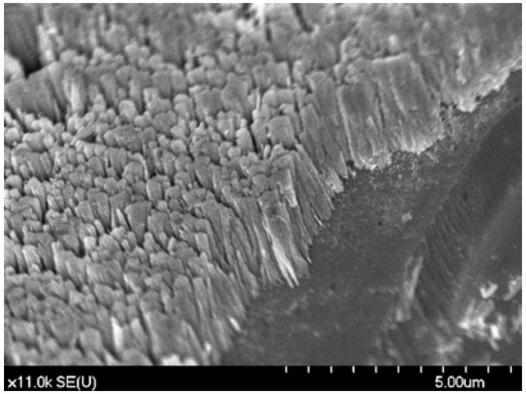


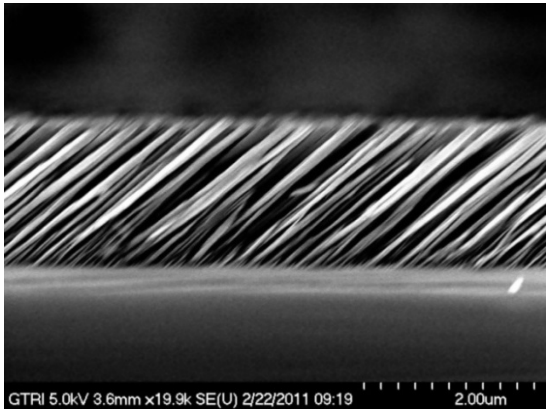


FTIR spectrum of gas composition in photocatalytic reactor with TiO_2 nanorod on Ti substrate after UVA radiation of 168 hours (7 days) at 8 mW/cm^2

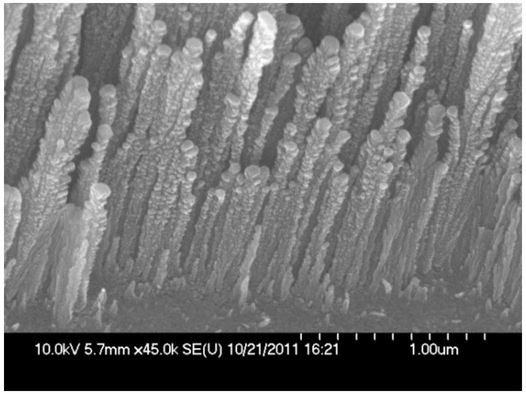
TiO_2 Nano-Structures by Glancing Angle Deposition (GLAD)

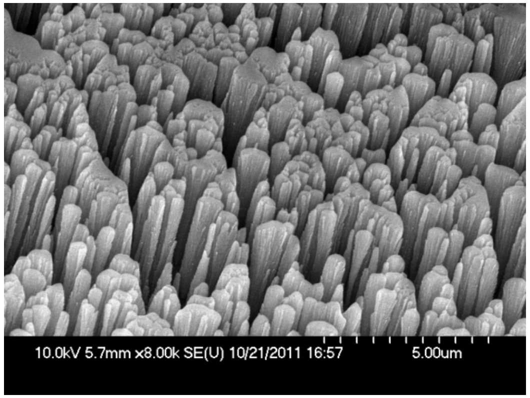


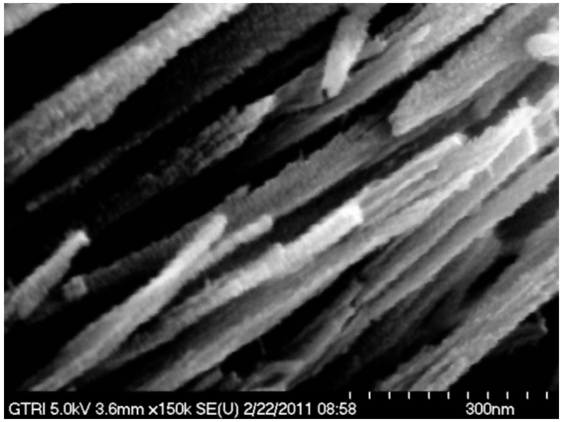




Various TiO_2 nanoporous films grown with glancing angle α = 95°







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Ion-assisted Deposition (IAD) of Thin-film Nanostructures

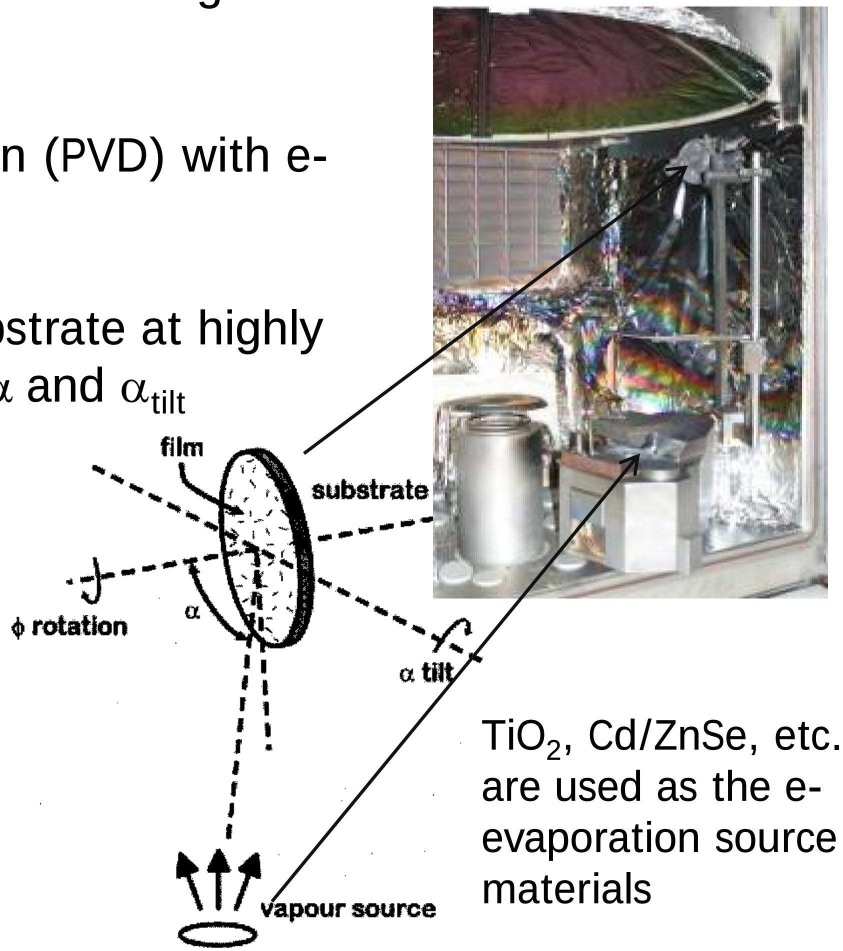
Thin-film processing at Georgia Tech:

- Process development for wide bandgap TiO_2 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 α and α_{tilt}
- Typically $\alpha \sim 70^o$ or higher
- Substrate can be rotated about axis, ϕ
- Use low-pressure PVD as atoms must travel in a linear trajectory and create shadow effect

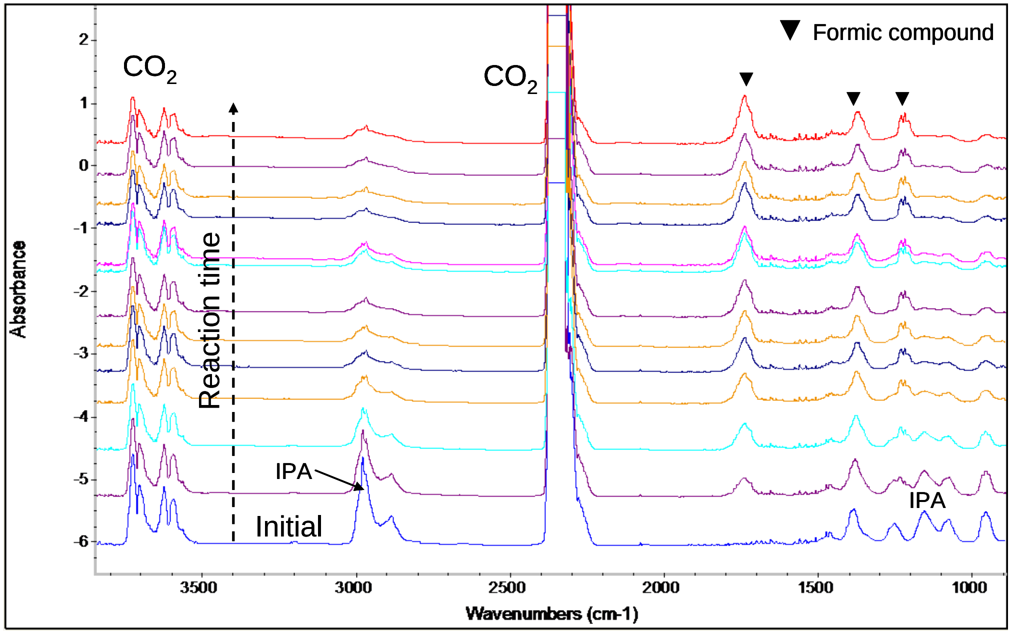
IAD E-beam Section



TiO$_2$, Cd/ZnSe, etc. are used as the e-evaporation source materials

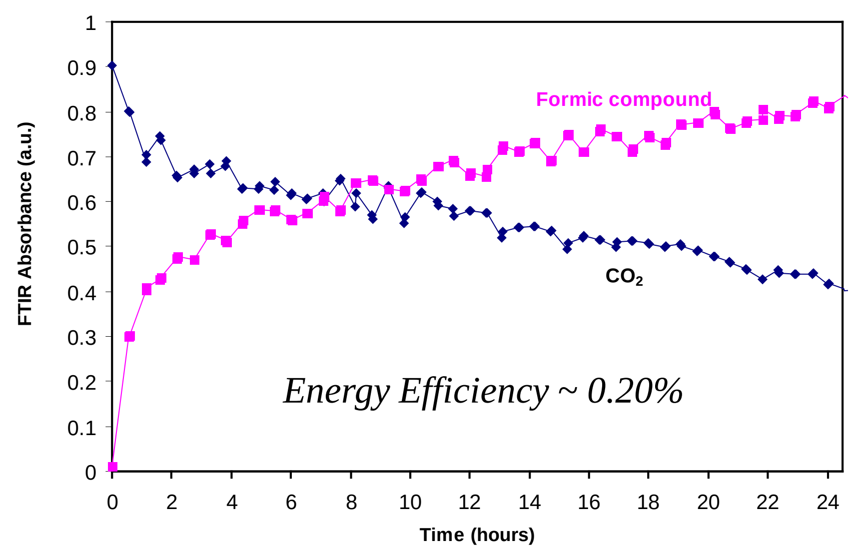
Robbie & Brett, J. Vac. Sci. Technol. A 15, 1460 (1997)

PhosphorTech High Selectivity Structure for Formic Acid Production



• 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



• 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

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Concept Feasibility Using a Common Waste Byproduct

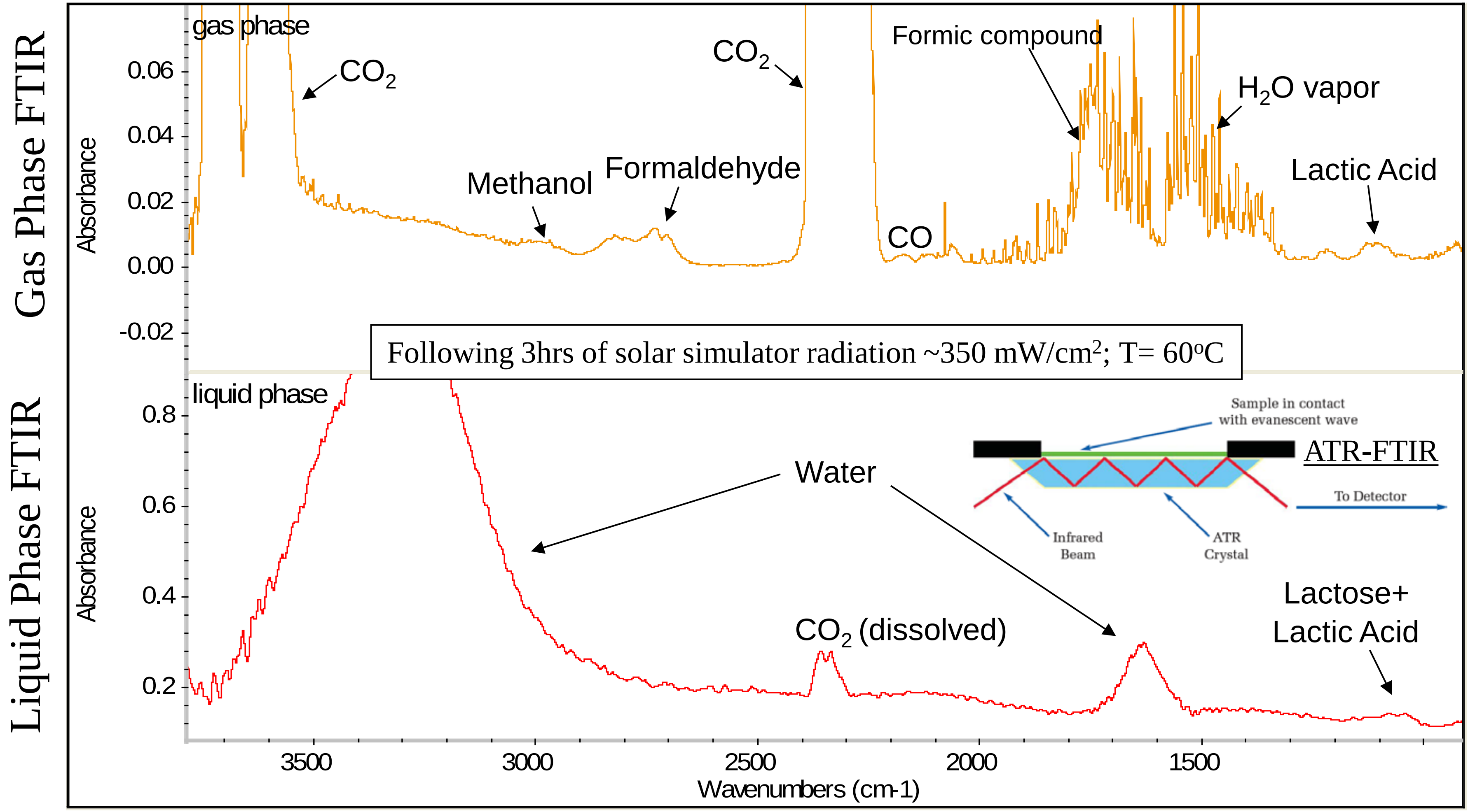
Example: Dairy Industry

- 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 CO_2 reforming into fuels and chemicals under sunlight***

➔ ***Experiments were performed using unmodified whey acid solution from yogurt***

FTIR Analysis of Liquid & Gas Phase Compositions



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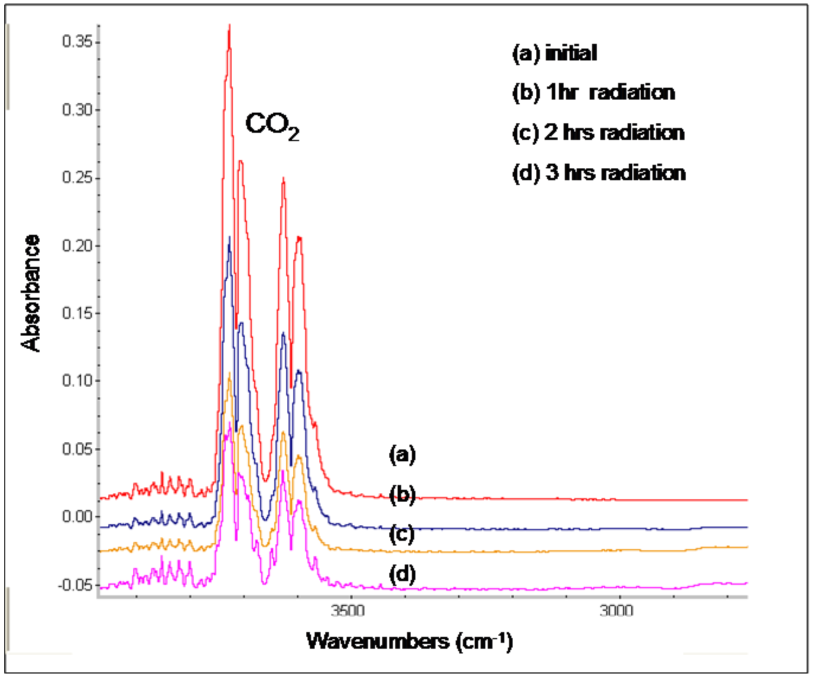
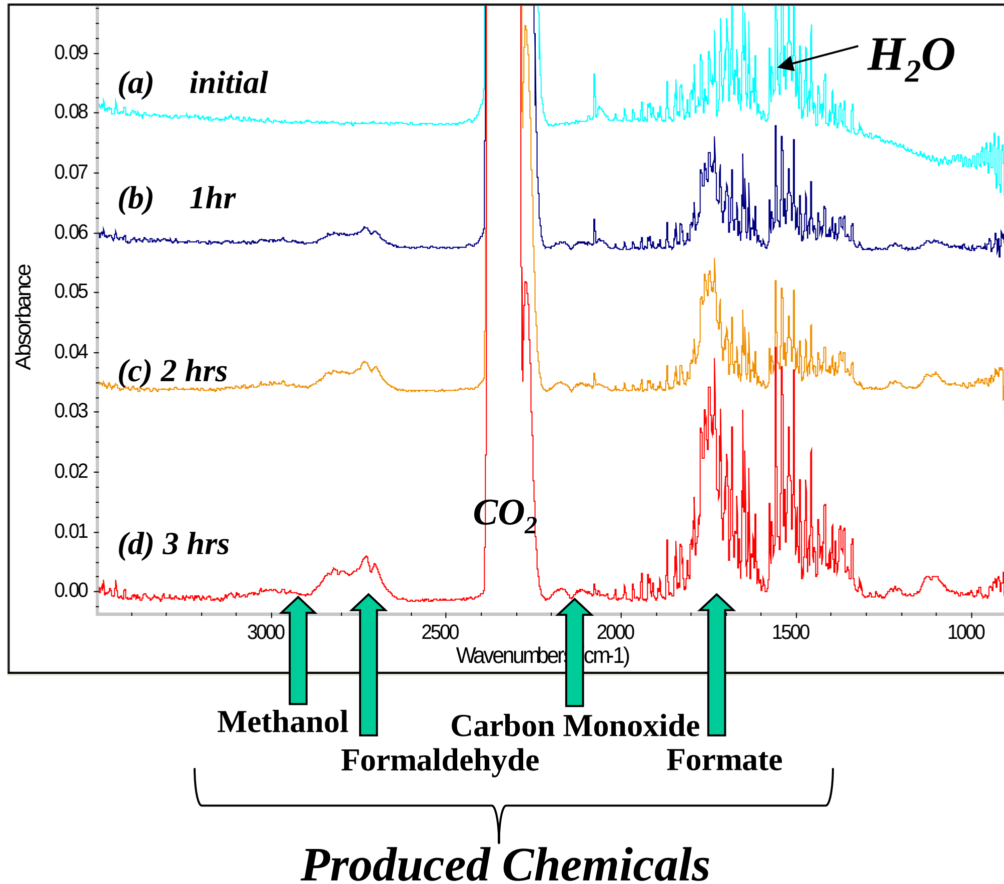
CO_2 Reforming by Sunlight using Whey Acid as Sacrificial Agent

- 50% drop in CO_2 gas concentration inside closed reactor in under 3 hours !
- Energy Efficiency ~ 0.4% (considering <u>only</u> formic compound)





A Fresnel lens was used with an Oriel solar simulator to focus light to ~350 mW/cm^2. Reactor temperature increased to 60°C by infrared portion of (simulated) solar spectrum

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Accomplishments to Date

- Completed all project milestones planned for Years 1-3 and achieved 16X higher efficiency than proposed target
- Achieved the highest reported CO_2 to CH_4 reforming yields (382 uL/h.g-catalyst) using TiO_2/Ti reactor and sunlight
- Achieved the highest reported CO_2 to CH_4 reforming yields (1823 uL/h.g-catalyst) using non-TiO_2 narrow-bandgap PN structure and sunlight
- Demonstrated a highly stable WBG-NBG CO_2 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 CO_2 reforming into CH_4 and CH_2O_2 using a stable TiO_2/Ti nanorod structure
- Demonstrated new metal-oxide PN structures for CO_2 reforming into formic acid (CH_2O_2) under sunlight conditions
- First time demonstration of fast CO_2 reforming into several fuels and chemicals under sunlight using environmentally toxic acid whey as a hole scavenger with 50% drop in CO_2 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_2O oxide structure and sunlight.
  – Problems with Cu_2O 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!

PhosphorTech: Y. Chen, A. Thamban, M. Nguyen, B. Schupeta, C. Summers, B. Wagner
Georgia Tech: Z. Kang, J. Nadler
Coal & Energy Industry Consultant: R. Minkara (VP of Technology at Headwaters)

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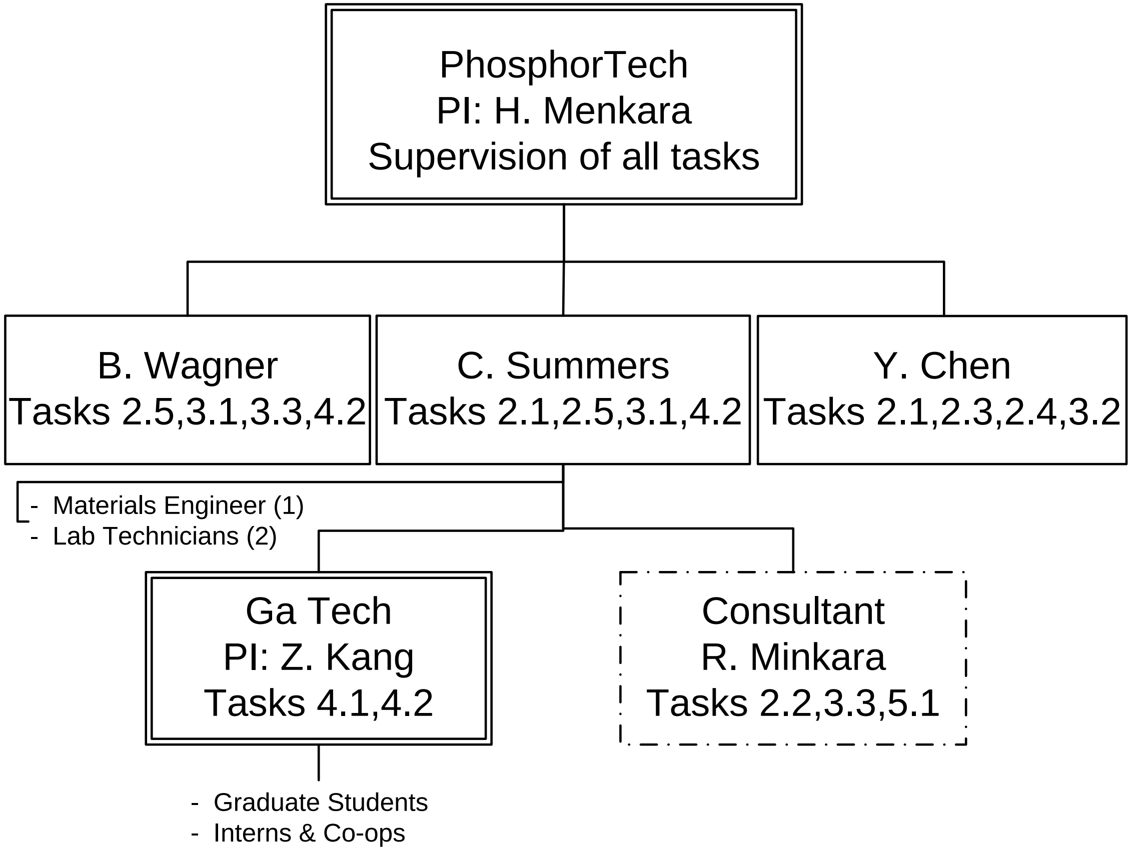
under

DOE NETL Award: DE-FE0004224

Program Manager: William O'Dowd

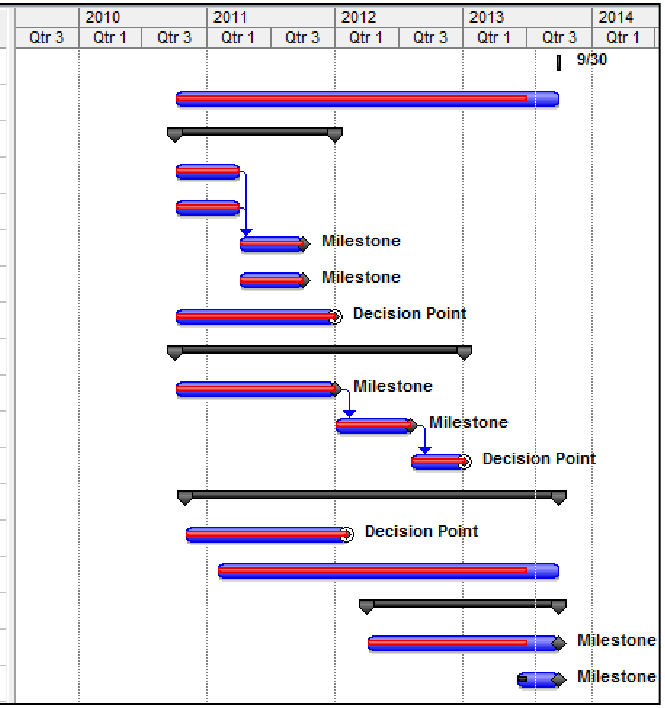
Organizational Chart

- **PhosphorTech**
  - Solution-based Processes
  - Nanocrystal Synthesis
  - Catalyst Evaluation
  - PN Structure Modeling
  - CO_2 Reforming Reactor
- **GeorgiaTech**
  - Thin-film Vacuum Deposition
  - Alternative Nano-structures
  - Material & Film Characterization



Gantt Chart

	Task Name
1	**High Efficiency Solar-based Catalytic Structure for CO2 Reforming**
2	**1. Project Management & Planning**
3	**2. Development & Optimization of Solution-based Thin-film Processes**
4	2.1 Preparation of NBG Precusrsors and Solutions
5	2.2 Acquire and Evaluate Commercial TiO2 Nanocatalysts
6	2.3 Develop Solution-based Deposition Techniques
7	2.4 Develop Post-deposition Heat Treatment Process
8	2.5 Evaluation of Thin-film Quality
9	**3. Development & Fabrication of PN Structure**
10	3.1 Simulation and Optimization of PN Structures
11	3.2 Fabrication of PN Structure from Theroretical/Experimental Data
12	3.3 Comparison of PN Structure with Conventional Photocatalysts
13	**4. Refinement of CO2 Reactor Components**
14	4.1 Develop Thin-film Deposition Process
15	4.2 Investigate Alternative Structures and Surface Morphologies
16	**5. Build and Demonstrate CO2 Reactor Prototype**
17	5.1 Build and Demonstrate CO2 Reactor Prototype
18	5.2 Demonstrate CO2 Reforming



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- Y. Chen, A. Thamban, M. T. Nguyen, H. Menkara. "Highly Selective Photocatalytic Conversion of Carbon Dioxide and Water into Methane", Published in the Division of Fuel Chemistry Proceedings, 242nd ACS National Meeting, Denver, CO. Aug. 28 - Sept. 1, 2011.
- (Invited) H. Menkara, A. Thamban, M. Nguyen, Z. Kang, Y. Chen, "Solar-based CO_2 Reforming into Fuels and Chemicals using Nanostructures", 2012 Energy Materials Nanotechnology Meeting, Orlando, FL, April 16-20, 2012.
- (Invited) Y. Chen, A. Thamban, M. T. Nguyen, H. Menkara, "New Metal-Semiconductor Nanocatalyst Systems for CO_2 Reforming by Solar Energy", Heterogeneous Catalysis Symposium, ACS Philadelphia, August 22, 2012.
- H. Menkara, C. J. Summers, Method and Apparatus for Gas Reforming, U.S. Patent Application filed Sept. 2010.