High Efficiency Solar-based Catalytic Structure for CO_2 Reforming

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National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Building the Infrastructure for CO_2 Storage
August 21-23, 2012

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Outline

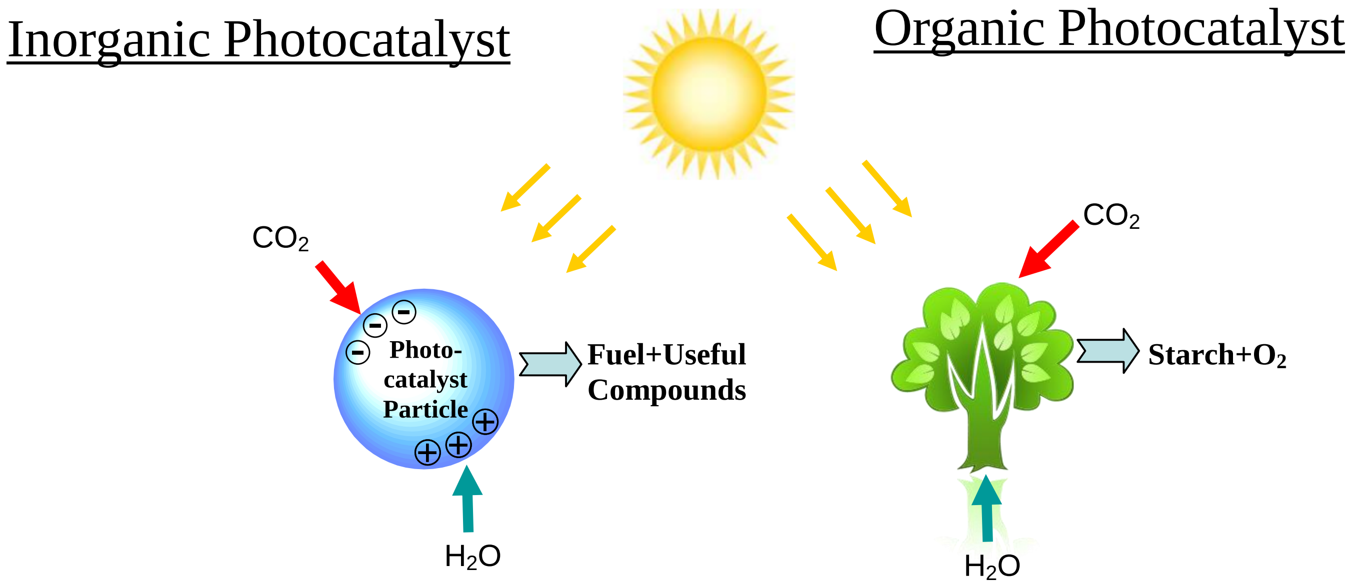
- Benefits to the Program
- Project Goals and Objectives
- Technical Status
  - Conventional vs hybrid heterojunction systems
  - Solution-based synthesis of photocatalyst materials & structures
  - Glancing Angle Deposition (GLAD) of metal oxides by IAD
  - Bandgap simulations of heterojunctions
  - CO_2 reforming results and success criteria
- Accomplishments to Date
- Summary
- Appendix

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

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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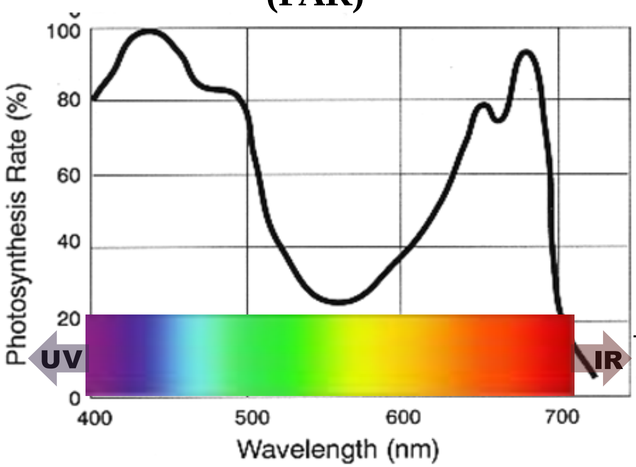
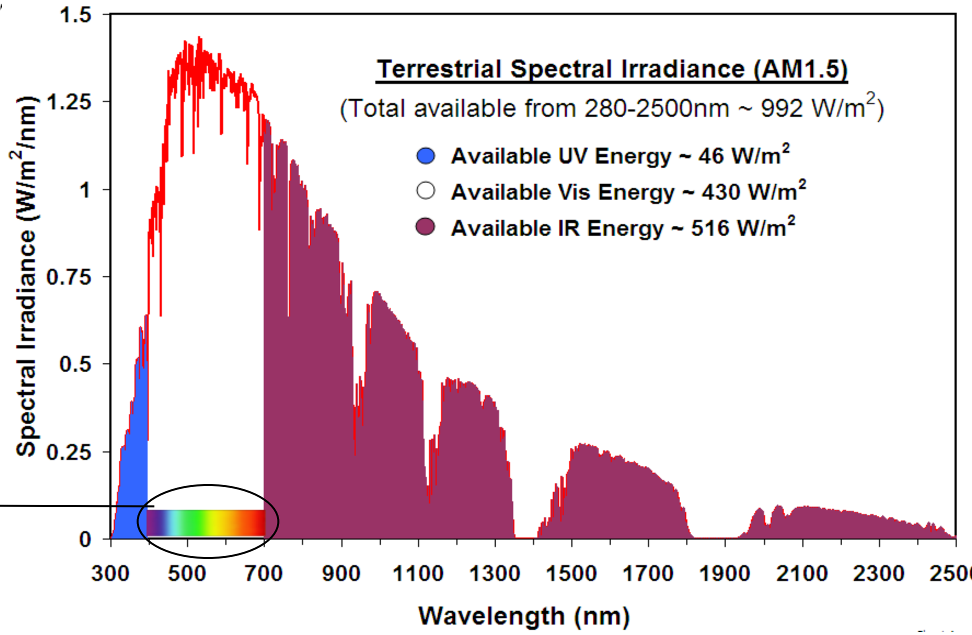
Photocatalyst Technology Challenge

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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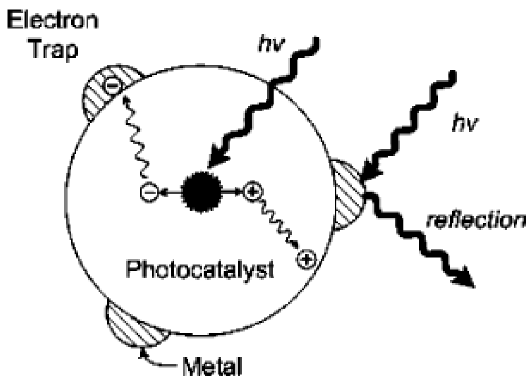
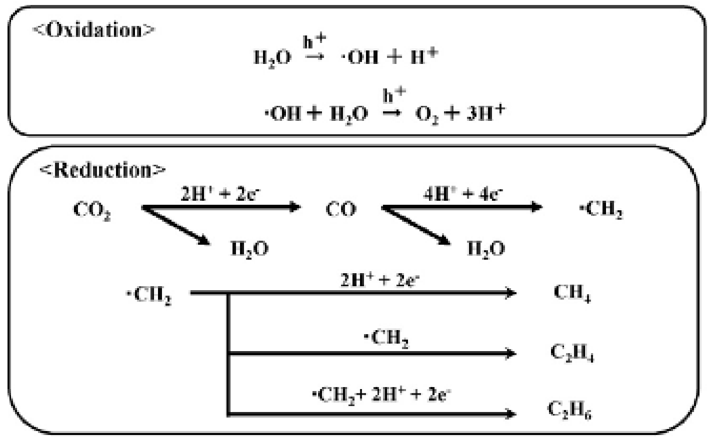
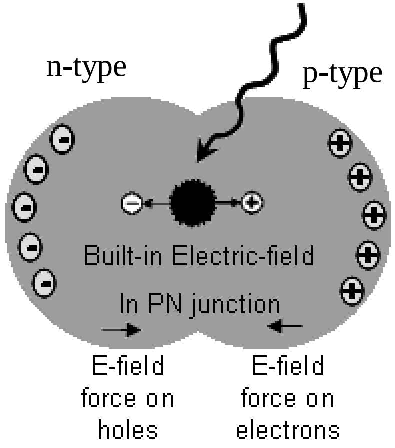
Conventional vs Hybrid Photocatalysts



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

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

Carbon monoxide formation

$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$

Methanol formation

$CO_2 + 2H^+ + 6e^- \rightarrow CH_3OH + H_2O$

Formic acid formation

$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$

Formaldehyde formation

$CO_2 + 2H^+ + 4e^- \rightarrow CH_2O$

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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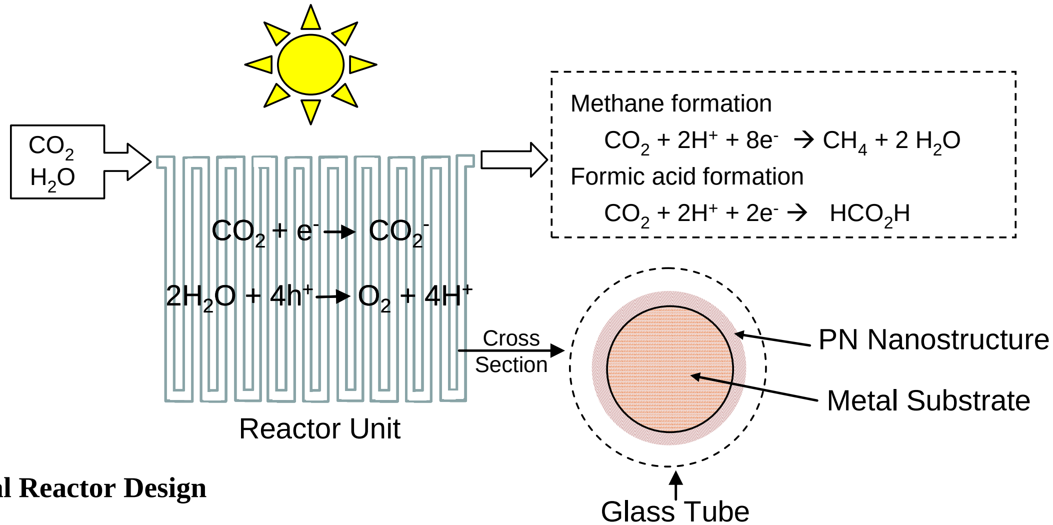
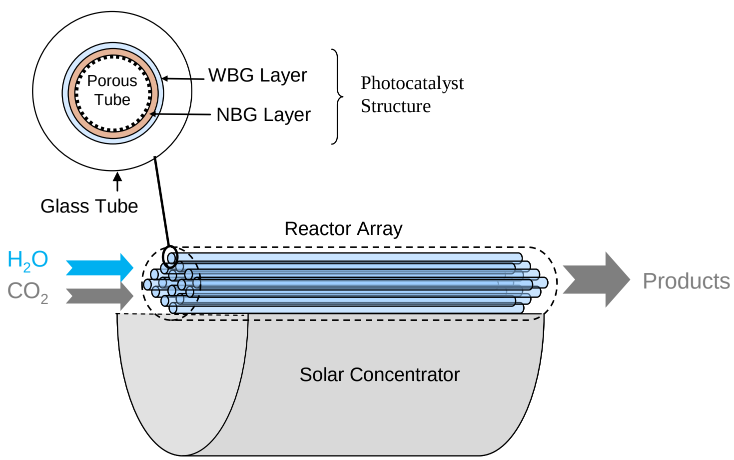
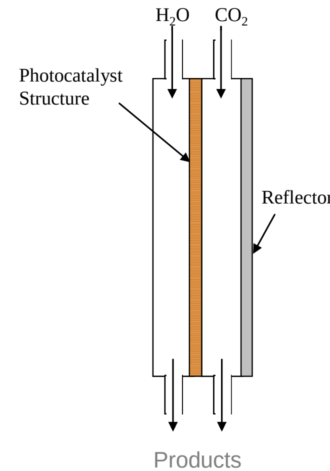
Possible Photocatalytic Reactor Designs



Cylindrical Reactor Design



Planar Reactor Design



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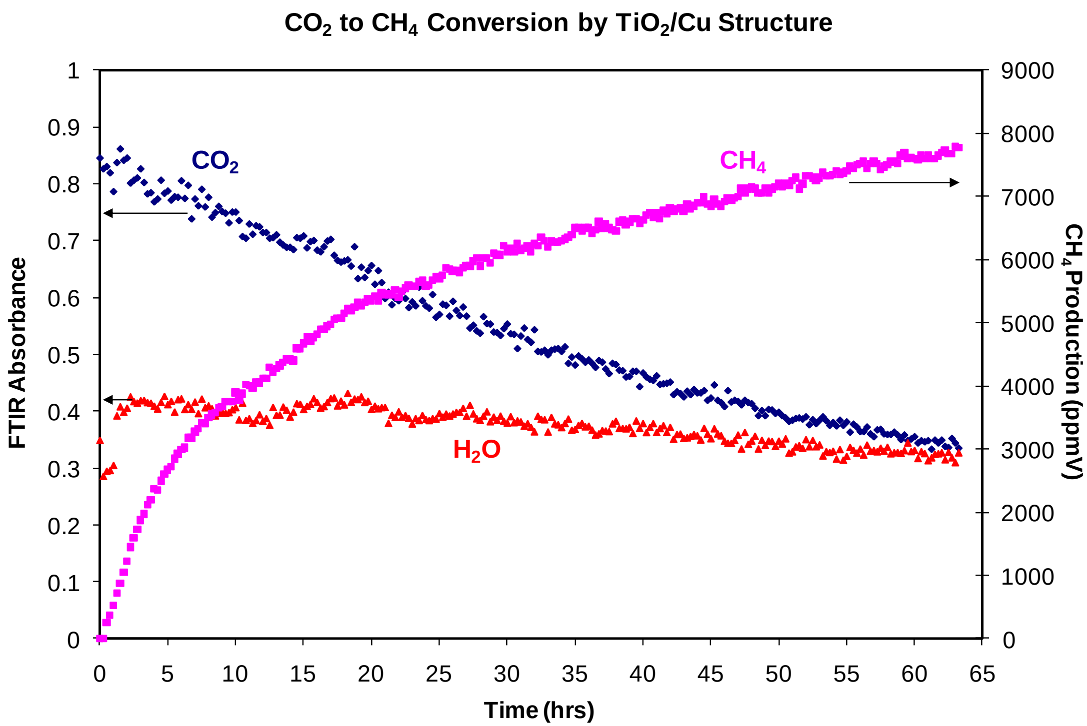
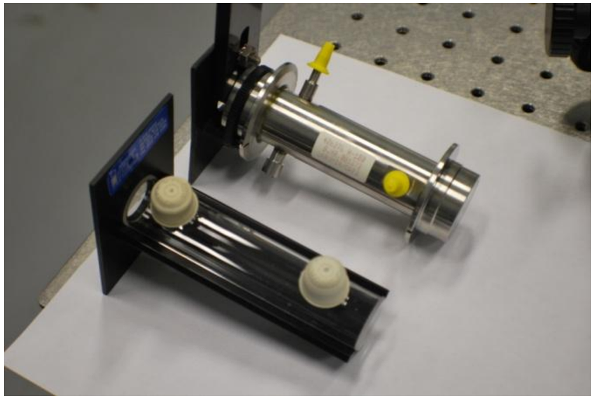
CO_2 Reforming using Photocatalyst Structure & Light



- 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 titania/copper photocatalytic reactor system under UVA radiation (UV wavelength of 340-400 nm with intensity of ~8 mW/cm^2)

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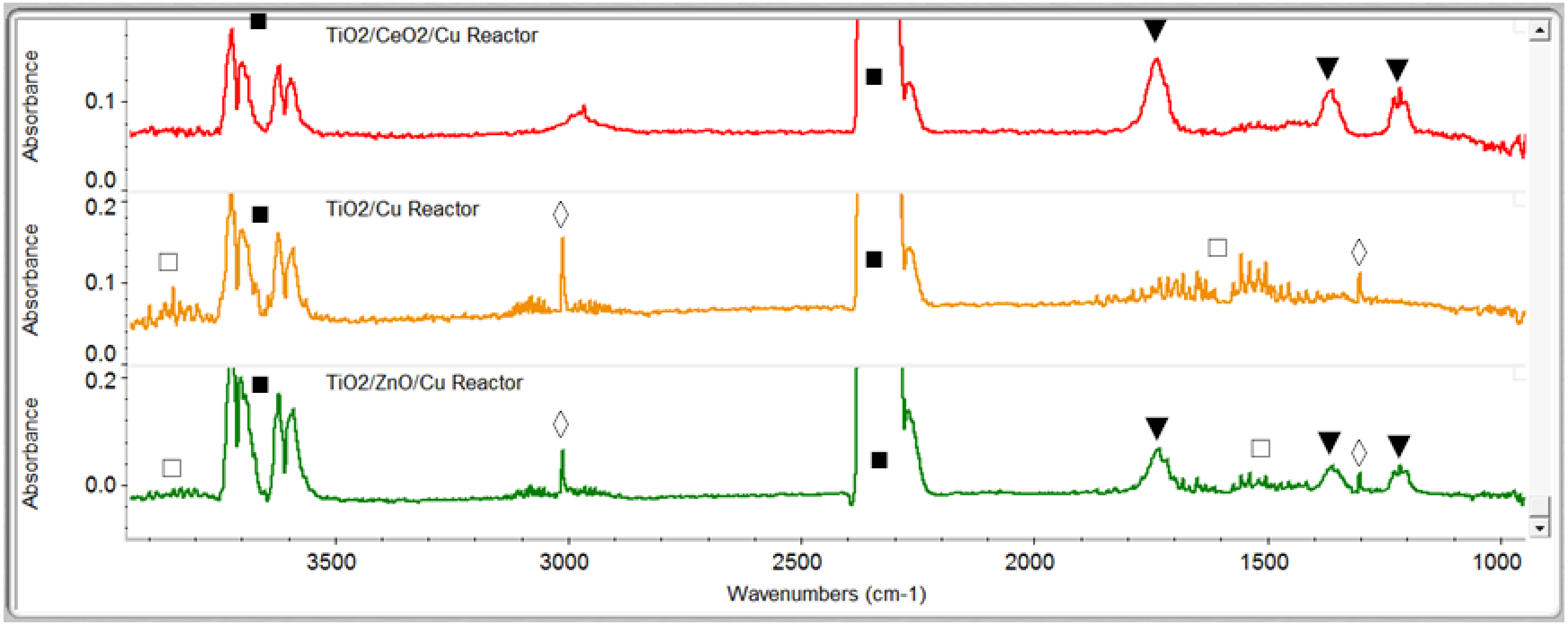
Fuel Product(s) Selectivity through Multilayer Structures

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



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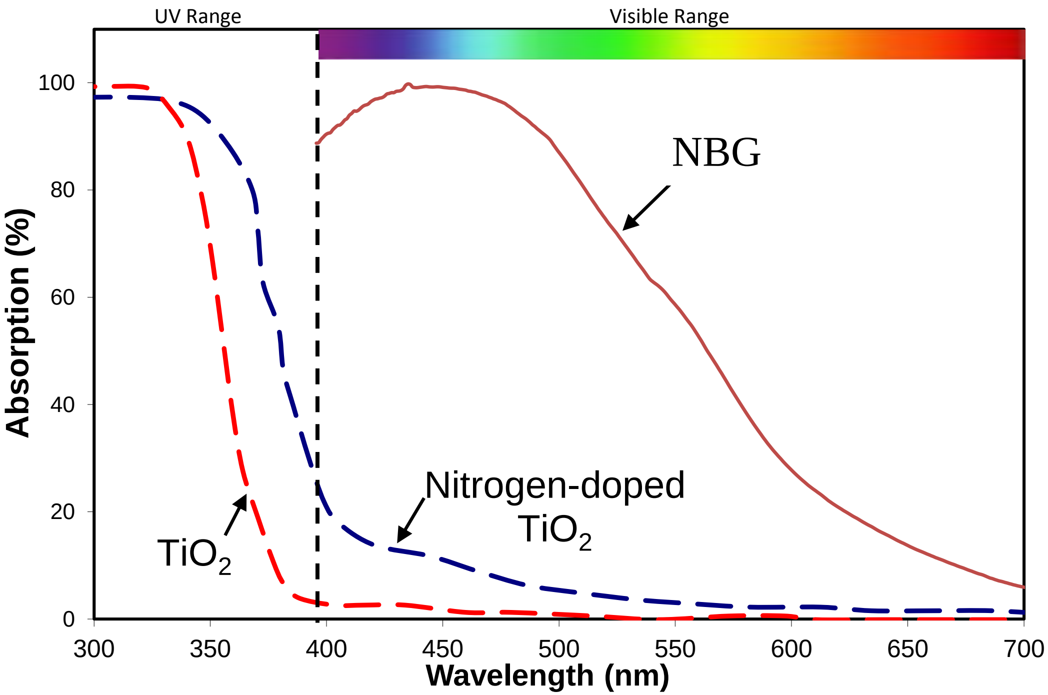
Optimized Properties and Absorption of NBG Layer

Average absorption is around 27%



Investigated various heat treatment methods and optimized solution properties, annealing time, and temperature conditions

Before heat treatment

After heat treatment

VIS/NIR absorption spectrum of 50nm NBG thin-film grown on at 180^{o}C

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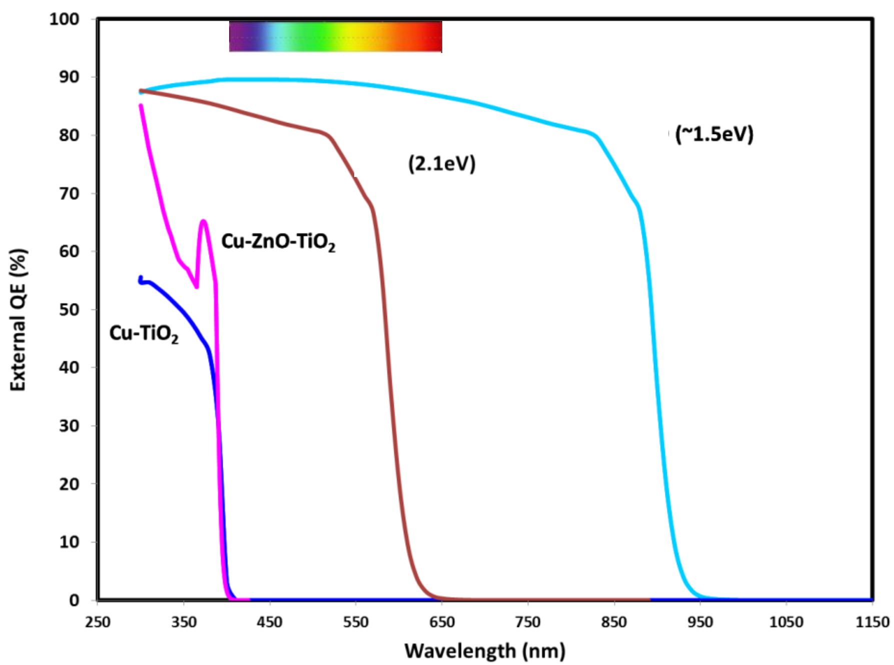
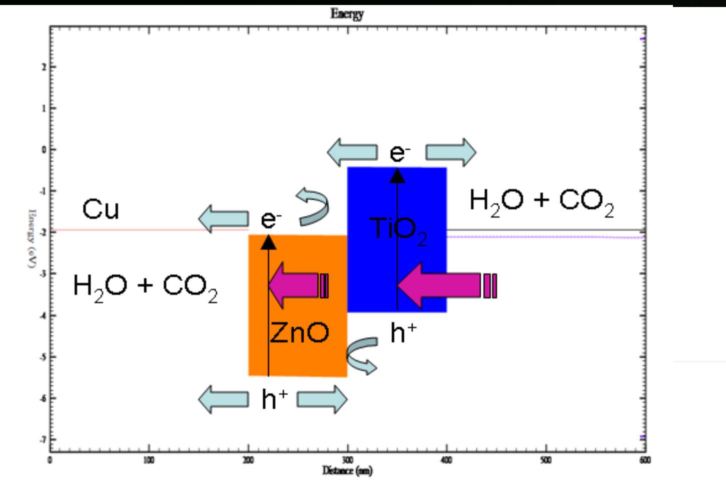
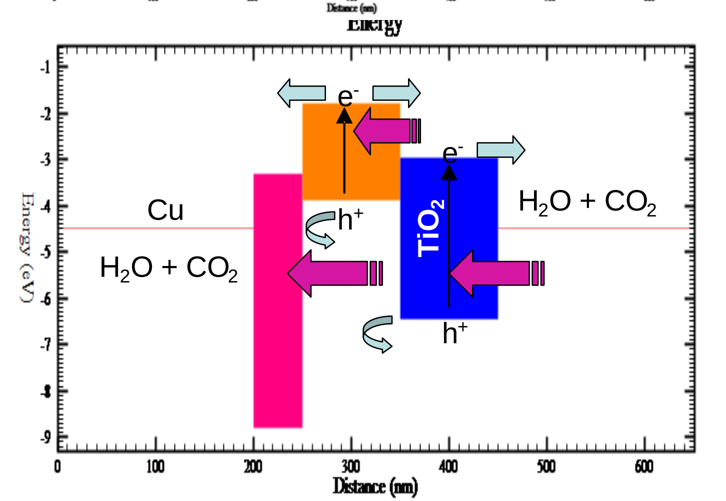
Energy Bandgap & Efficiency Simulations

- Bandgap simulations were performed to understand the mechanisms involved in various heterojunctions
- Simulations helped develop optimized structures for Cu-based systems







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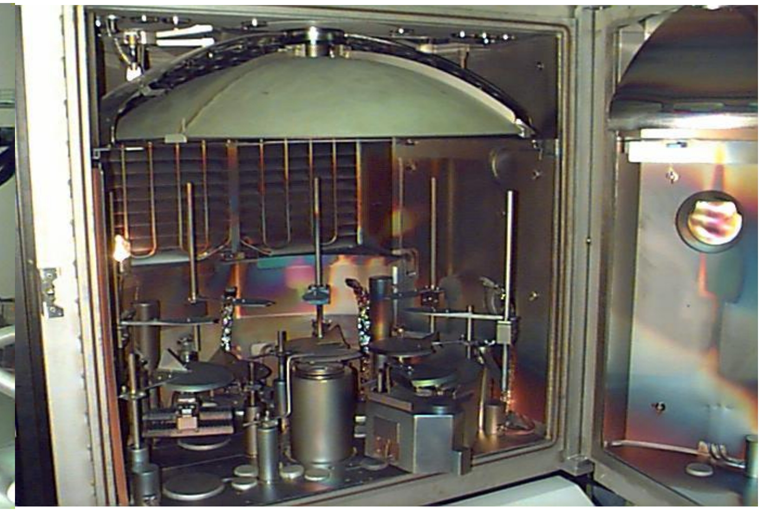
Ion-assisted Deposition (IAD) of Thin-films



- Process development for wide bandgap TiO_2 and narrow bandgap (Zn/CdSe) thin-films
- Multilayer deposition/optimization
- Investigation of “3D” nano-structures for improved light harvesting and catalytic properties

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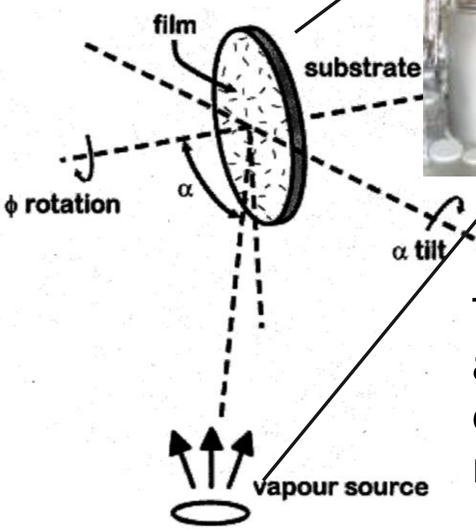
Glancing Angle Deposition

- 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 at Georgia Tech (GT)
- 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

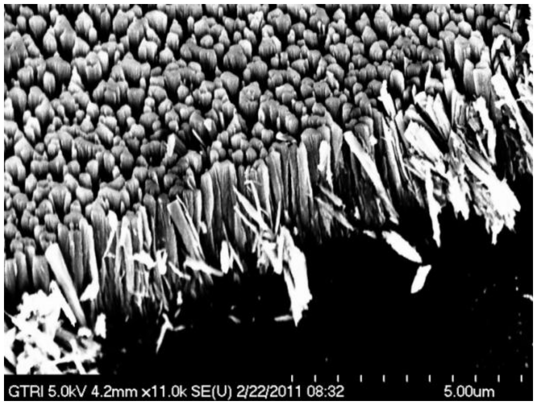
IAD E-beam Section

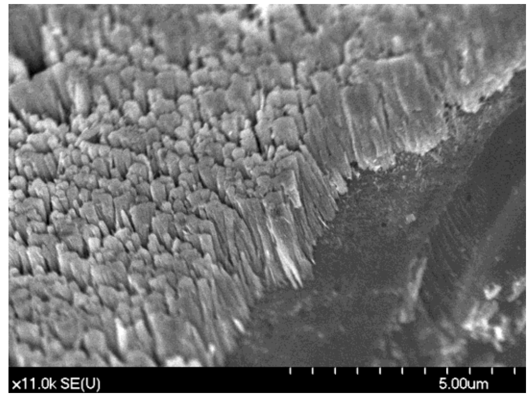


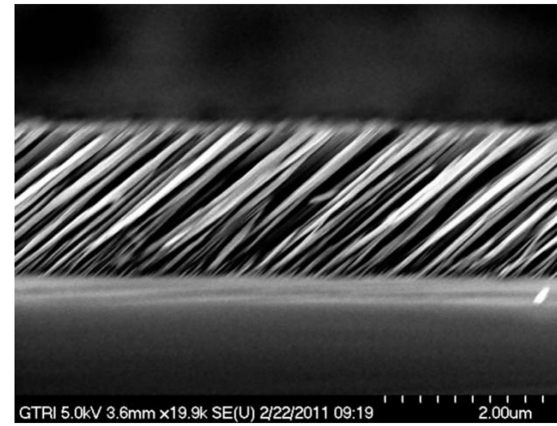
TiO$_2$, Cd/ZnSe, etc. are used as the e-evaporation source materials

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

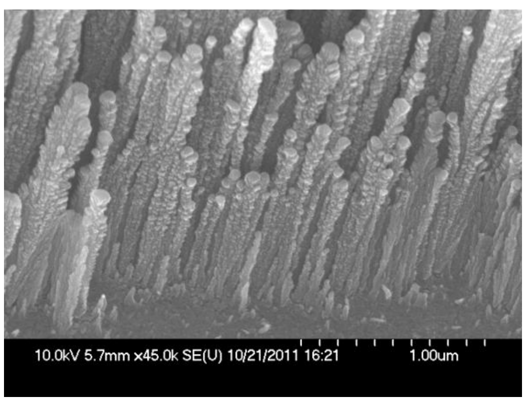
Metal Oxide Nano-Structures Grown by GLAD

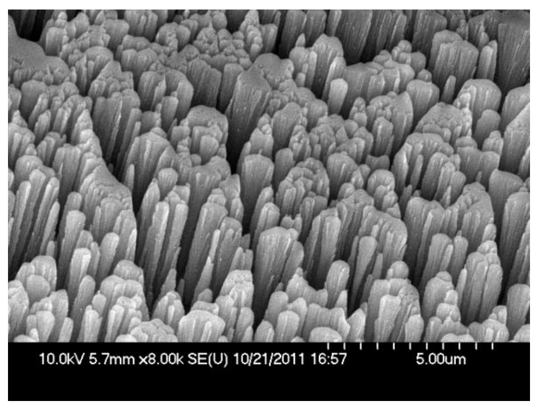


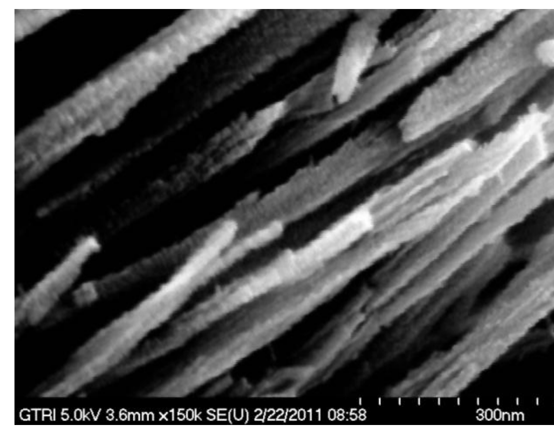




TiO_2 nanoporous film grown with glancing angle α = 95° and observed from a tilted angle.







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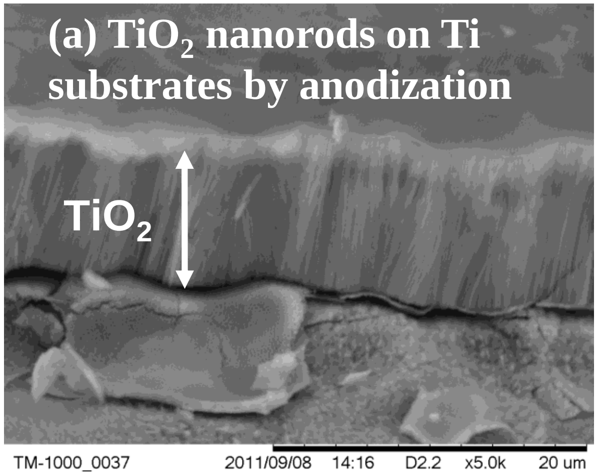
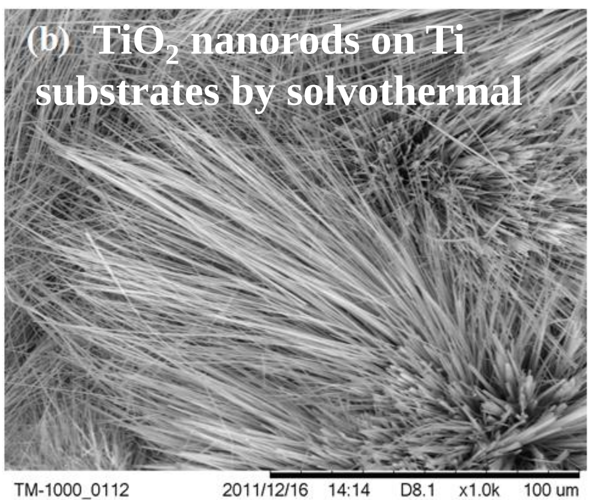
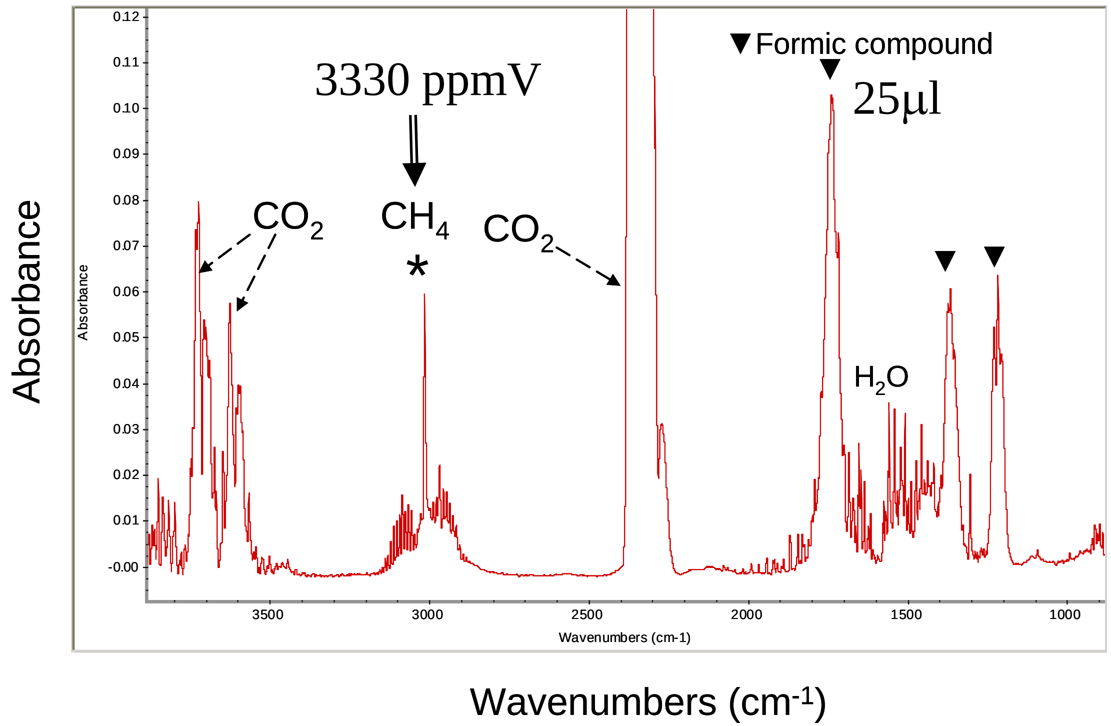
Nano-Structures Grown by Solution Processing



(a) TiO$_2$ nanorods on Ti substrates by anodization



(b) TiO$_2$ nanorods on Ti substrates by solvothermal



FTIR spectrum of gas composition in photocatalytic reactor with TiO$_2$ nanorod on Ti substrate after UVA radiation of 168 hours (7 days) from a 6W bulb.

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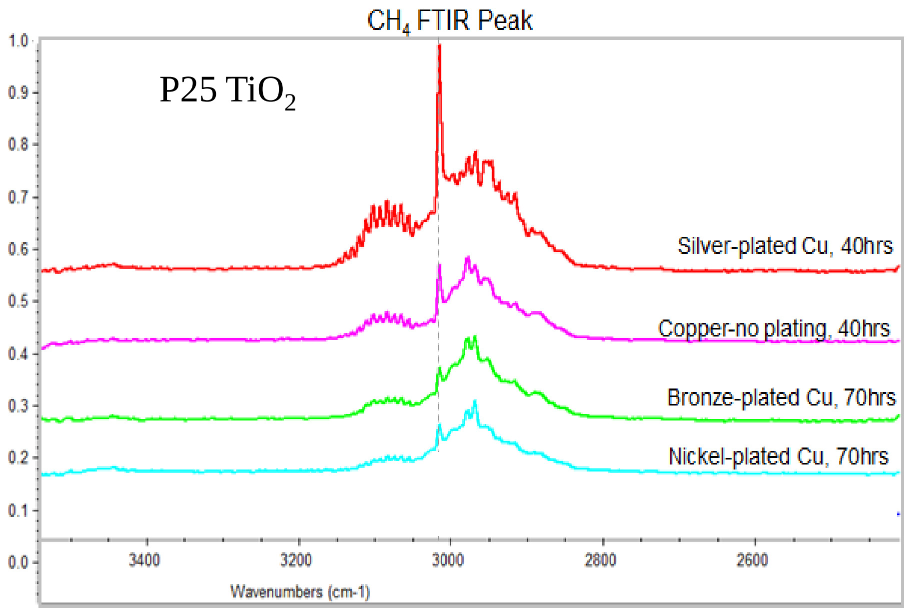
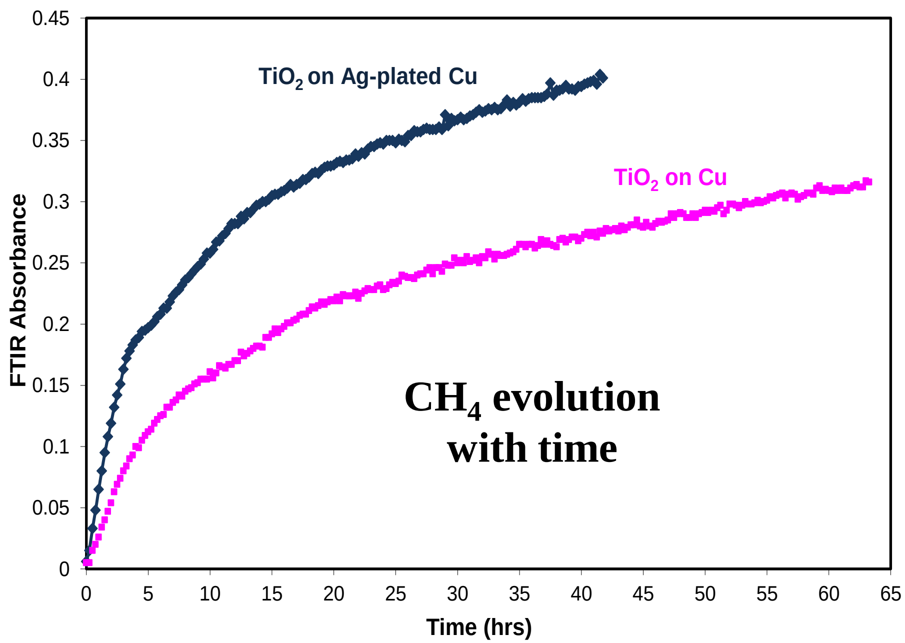
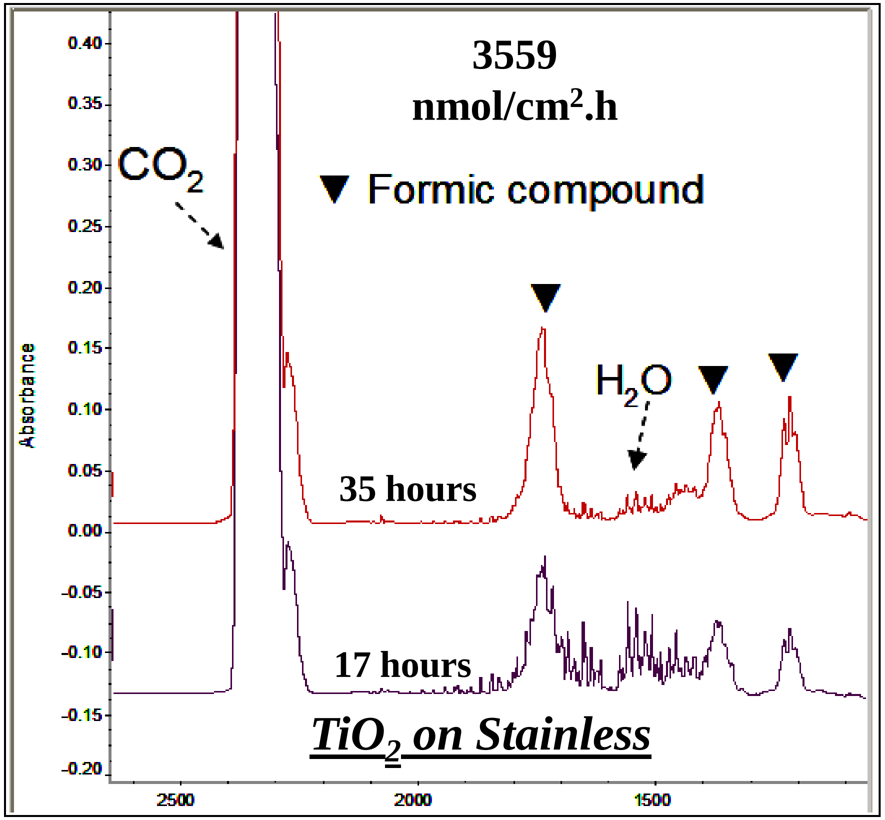
Metal Layer Deposition by Electroplating

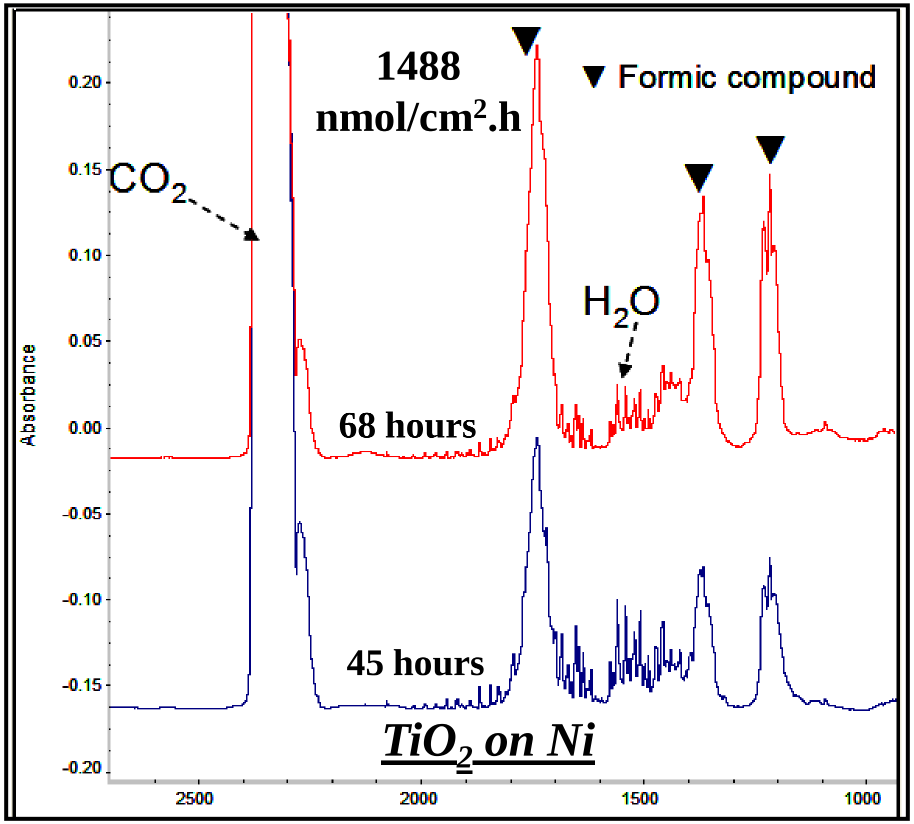




- **Electroplating provides the means to use precious metals without significantly altering system cost**
- **Ag-plating appears to enhance CO_2 to CH_4 reforming yields and offers some protection against oxidation**

Alternative Substrate Materials

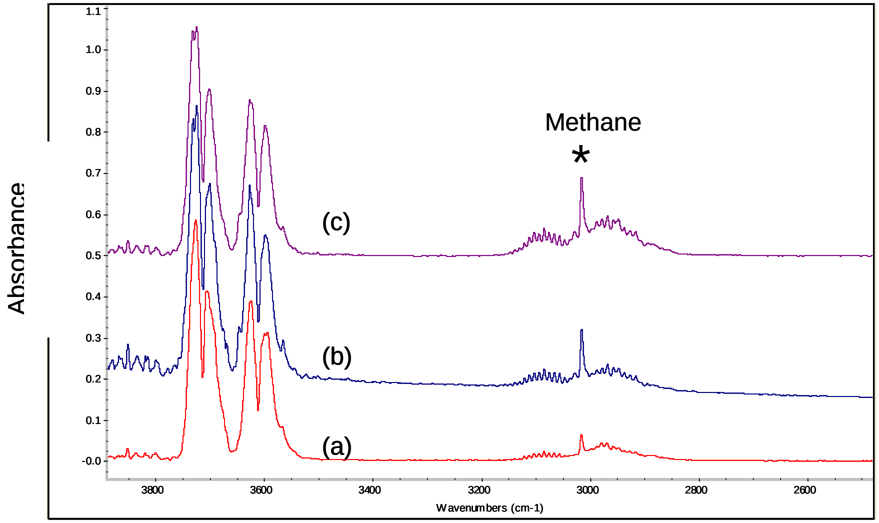




~0.34 g anatase titania on stainless steel under 6W UVA radiation

~0.34 g anatase titania on nickel under 6W UVA radiation

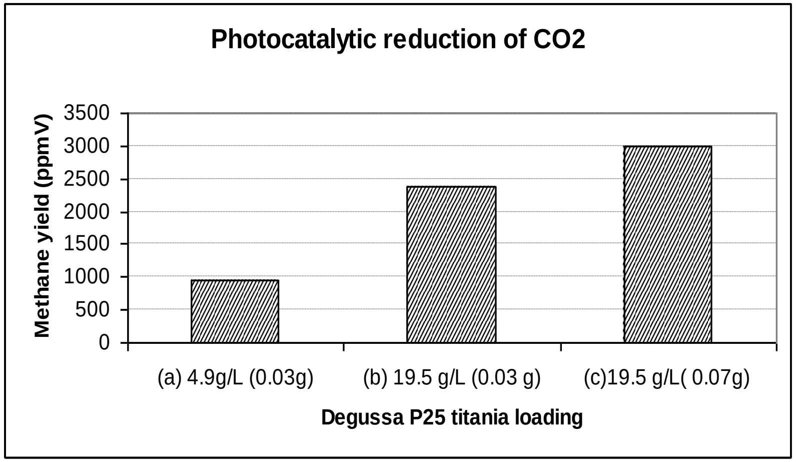
Effect of TiO_2 Loading on CO_2 Reforming

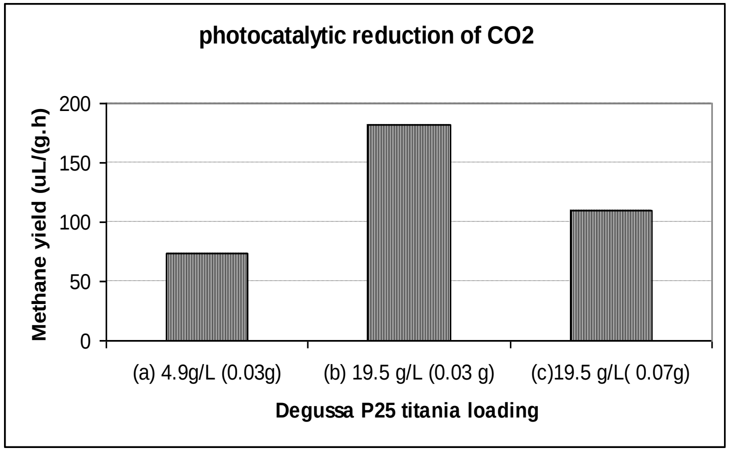


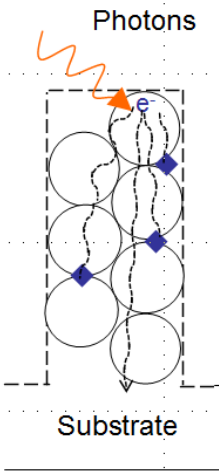
(a) 0.03 g TiO_2 from a suspension with 4.9g/L

(b) 0.03g TiO_2 from a suspension with 19.5 g/L

(c) 0.07g TiO_2 from a suspension with 19.5 g/L







Accomplishments to Date

- Completed all project milestones planned for Years 1&2
- 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 techniques for enhanced oxidation resistance of copper substrates for photocatalytic applications
- Demonstrated new metal-oxide PN structures for CO_2 reforming into formic acid (CH_2O_2) under sunlight conditions
- Investigated low-cost structures for long-term CO_2 to CH_2O_2 reforming activity using stainless steel substrates
- 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

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Summary

- Demonstrated CO_2 to CH_4 and CO_2 to CH_2O_2 reforming in sunlight conditions
- Achieved high CO_2 to CH_4 reforming yields (1823 uL/h.g-catalyst) using narrow-bandgap metal oxide structure and sunlight.
- High selectivity for CH_4 and CH_2O_2 was achieved using various metal oxide PN structures and metal substrates
- WBG TiO_2 nanorods/nanowires successfully grown on Ti substrates by electrochemical deposition and solvothermal techniques
- Various wide-bandgap thin-films and nanorods were grown by Glancing Angle Deposition (GLAD) on metal substrates

Thank You!

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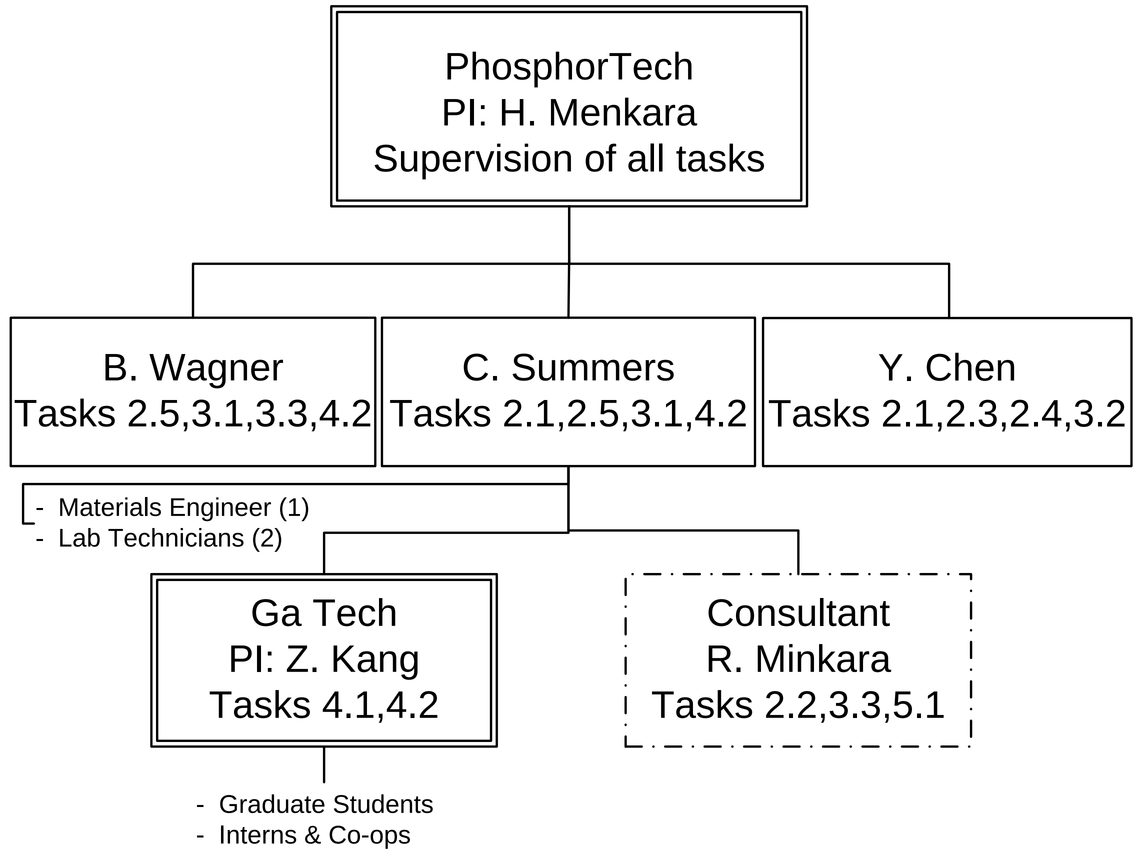
DOE NETL Award: DE-FE0004224

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



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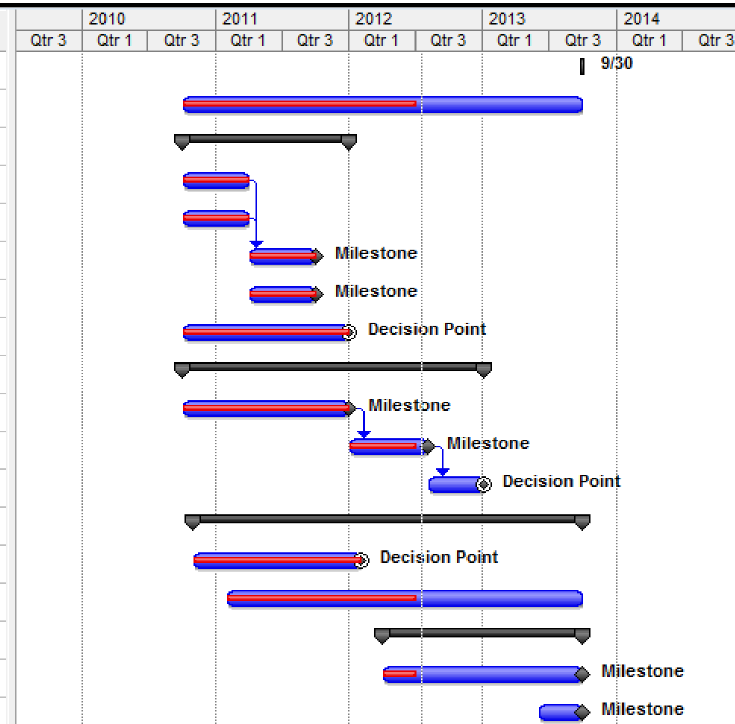
Gantt Chart

	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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- (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.