

**Center for Renewable Energy  
Science & Technology (CREST) at the  
University of Texas at Arlington:  
Value-Added Hydrogen Generation  
with CO<sub>2</sub> Conversion**

Project ID # PD080

**PI Names: Rick Billo and Krishnan Rajeshwar**

**Presenter Names: Krishnan Rajeshwar & Fred MacDonnell**

**May 9-13, 2011**

# Overview

## Timeline

- Project start date: 8/15/08
- Project end date: 5/31/11
- Percent complete: 90 %

## Budget

- Total project funding
  - DOE share: \$2,387,463.00
  - Contractor share: \$596,865.00
- Project is fully funded

## Barriers

- Barriers addressed
  - DOE: D, E, Y, Z, AA, AB
  - Direct photochemical reduction of H<sup>+</sup> and CO<sub>2</sub> to useful fuels, such as H<sub>2</sub> and CH<sub>3</sub>OH, still faces a number of technical challenges. Some of these include:
    - Lack of efficient photocatalysts
    - Difficulty in driving multi-electron processes
    - Coupling these reductions to useful oxidative reactions

## Partners

- Interactions/ collaborations
  - none
- Project lead : UT Arlington



# Task 1 DOE Identified Barriers:

## Oxide Semiconductors for Solar Energy Conversion

7	<p><b>Development of Semiconductor Materials for Photoelectrochemical Hydrogen Production</b></p> <ul style="list-style-type: none"> <li>▪ Develop and optimize the current state-of-the-art materials for meeting near term efficiency and durability targets.</li> <li>▪ Discover, utilizing combinatorial or other screening methods, new materials for meeting long-term efficiency, durability, and cost targets.</li> <li>▪ Develop cost-effective synthesis techniques for fabricating the most promising semiconductor materials.</li> <li>▪ Develop accelerated screening protocols to evaluate and validate long-term material efficiencies and durability.</li> </ul>	Y, Z, AB
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**Y. Materials Efficiency.** Materials with smaller bandgaps more efficiently utilize the solar spectrum, but are often less energetically favorable for hydrogen production because of the bandedge mismatch with respect to either hydrogen or oxygen redox potentials. Materials with appropriate bandedge and bandgap for hydrogen production must be developed.

**Z. Materials Durability.** Durable materials with the appropriate characteristics for photoelectrochemical hydrogen production that meet the program goals have not been identified. The high-efficiency materials currently available corrode quickly during operation, and the most durable materials are very inefficient for hydrogen production.

**AB. Bulk Materials Synthesis.** Fabrication techniques for materials identified to have potential for high efficiency, durability and low cost need to be developed on scales consistent with implementation in commercial reactors.

8	<p><b>Development of PEC Device and System Auxiliary Material</b></p> <ul style="list-style-type: none"> <li>▪ Determine the functional requirements for auxiliary materials including protective coatings, catalytic coatings, photoelectrode substrates, hydrogen impervious materials, and photovoltaic layer materials.</li> <li>▪ Discover, develop, and test materials to facilitate PEC device and systems development</li> </ul>	AA
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**AA. PEC Device and System Auxiliary Material.** The functional requirements for auxiliary materials must be determined and materials discovered, developed, and tested to facilitate PEC device and systems development. The auxiliary materials may include protective coatings, catalytic coatings, photoelectrode substrates, hydrogen impervious materials, and photovoltaic layer materials.

# Task 1 Project Objectives:

## New Oxide Semiconductors for Photocatalysis and Photoelectrochemical Catalysis

SubTask Number	Project Milestones	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1	Proof-of-concept of electrodeposition of $\text{BiVO}_4$	Dec 2009	Dec 2009	Dec 2009	100	Complete
2	Combustion synthesis of $\text{BiVO}_4$ nanoparticles	March 2010	March 2010	March 2010	100	Complete
3	Use of $\text{BiVO}_4$ for $\text{CO}_2$ photoreduction	Sept 2010	Sept 2010	Sept 2010	100	Complete
4	Combustion synthesis of $\text{Bi}_2\text{WO}_6$ and $\text{AgBiW}_2\text{O}_6$	Dec 2010	May 2011	May 2011	90	Nearly Complete
5	Photodeposition of Pt nanoislands on $\text{AgBiW}_2\text{O}_6$	Dec 2010	March 2011	March 2011	100	Complete
6	Optimizing $\text{Bi}_2\text{WO}_6$ and $\text{AgBiW}_2\text{O}_6$ for $\text{CO}_2$ photoreduction	Dec 2010	May 2011	May 2011	90	Nearly complete



# Project Objectives

## Materials for Solar Energy Conversion

- **Heterogeneous Photocatalysts**
  - **Oxide semiconductors for solar energy conversion and CO<sub>2</sub> photoreduction**
  - **Demonstrate combustion synthesis as an energy- and time-efficient synthesis method**
  - **Demonstrate its applicability to the synthesis of bismuth vanadate and silver bismuth tungstate**
  - **Demonstrate the use of silver bismuth tungstate for mild syngas generation using photo-electrochemistry**



# Advantages of Combustion Synthesis of Semiconductors

- Exothermic and fast reaction
- Products are homogenous and crystalline
- High surface area
- Simplicity of the process
  - No special equipment is required
- Possibility to incorporate “dopants” in situ in the oxide

 **Energy input for synthesis process comes from reaction exothermicity**

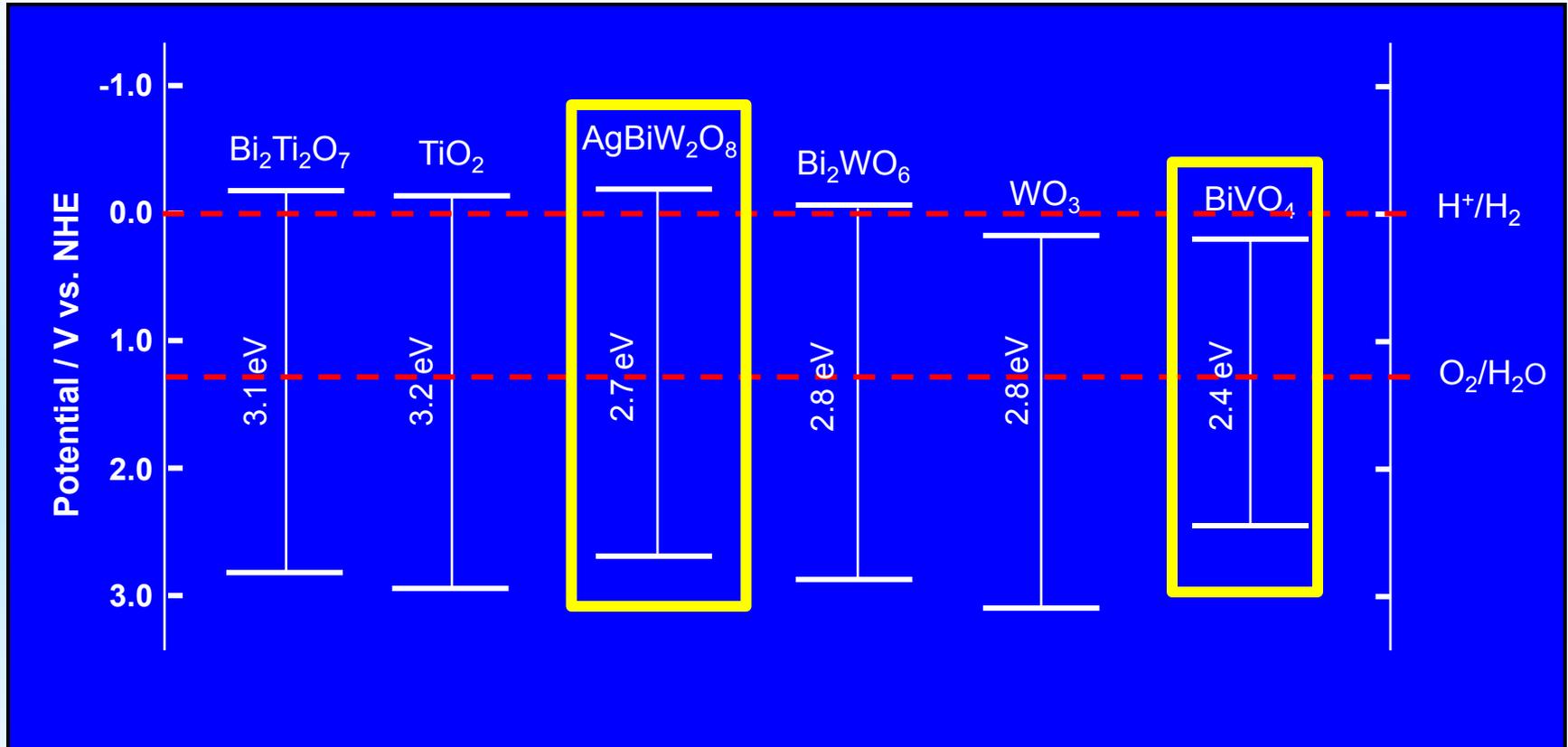




## Process Genesis and Variants

- **Self-propagating high-temperature synthesis (SHS)-name coined by A. G. Merzhanov.**
- **Synonyms: Combustion synthesis, solution combustion synthesis, gel (or sol-gel) combustion, fire or furnace-less synthesis etc.**
- **Pechini method (U.S. Patent 3,330,697, July 11, 1967) based in resin intermediates, i.e., on ignition of the resin, the organic portion is removed, leaving the mixed product behind.**
- **This method not widely used for solar applications yet.**

# Selected Semiconductor Photocatalysts



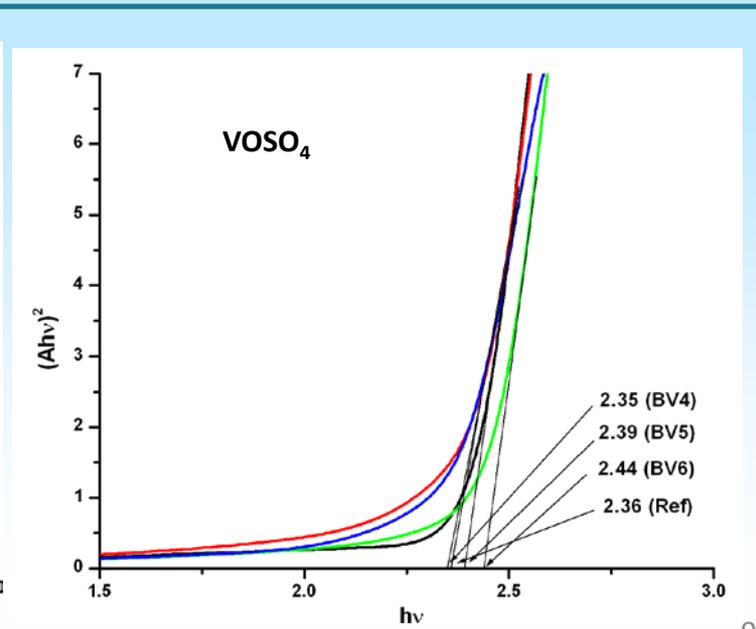
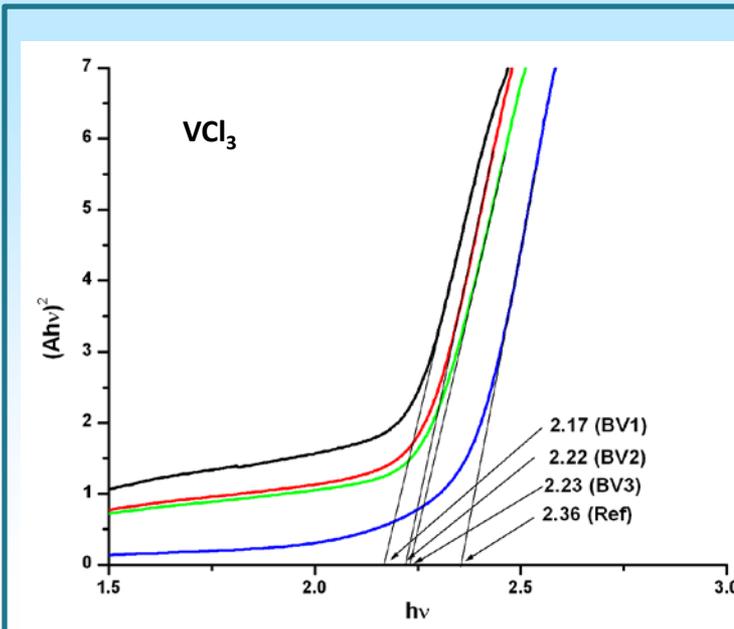
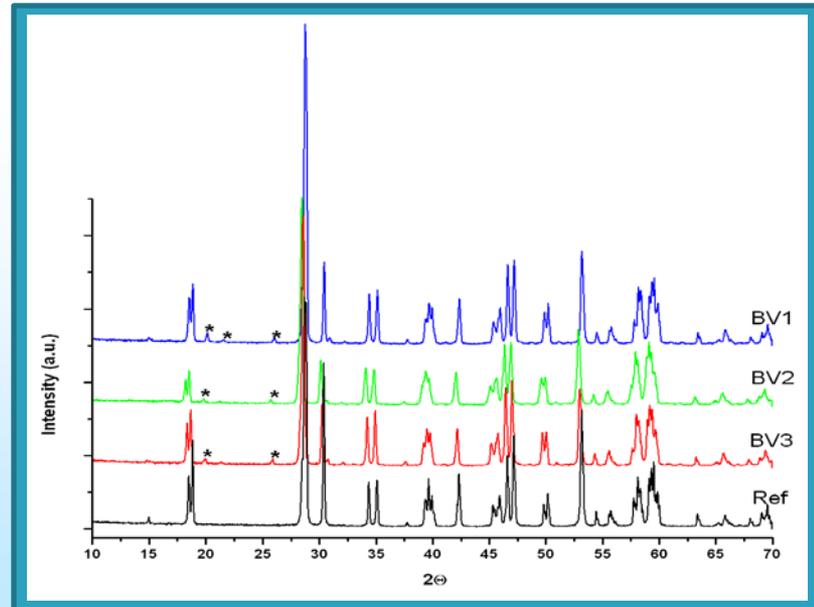
Comparison between the band edges of selected semiconductors (at pH 1) and the redox potentials for water splitting.



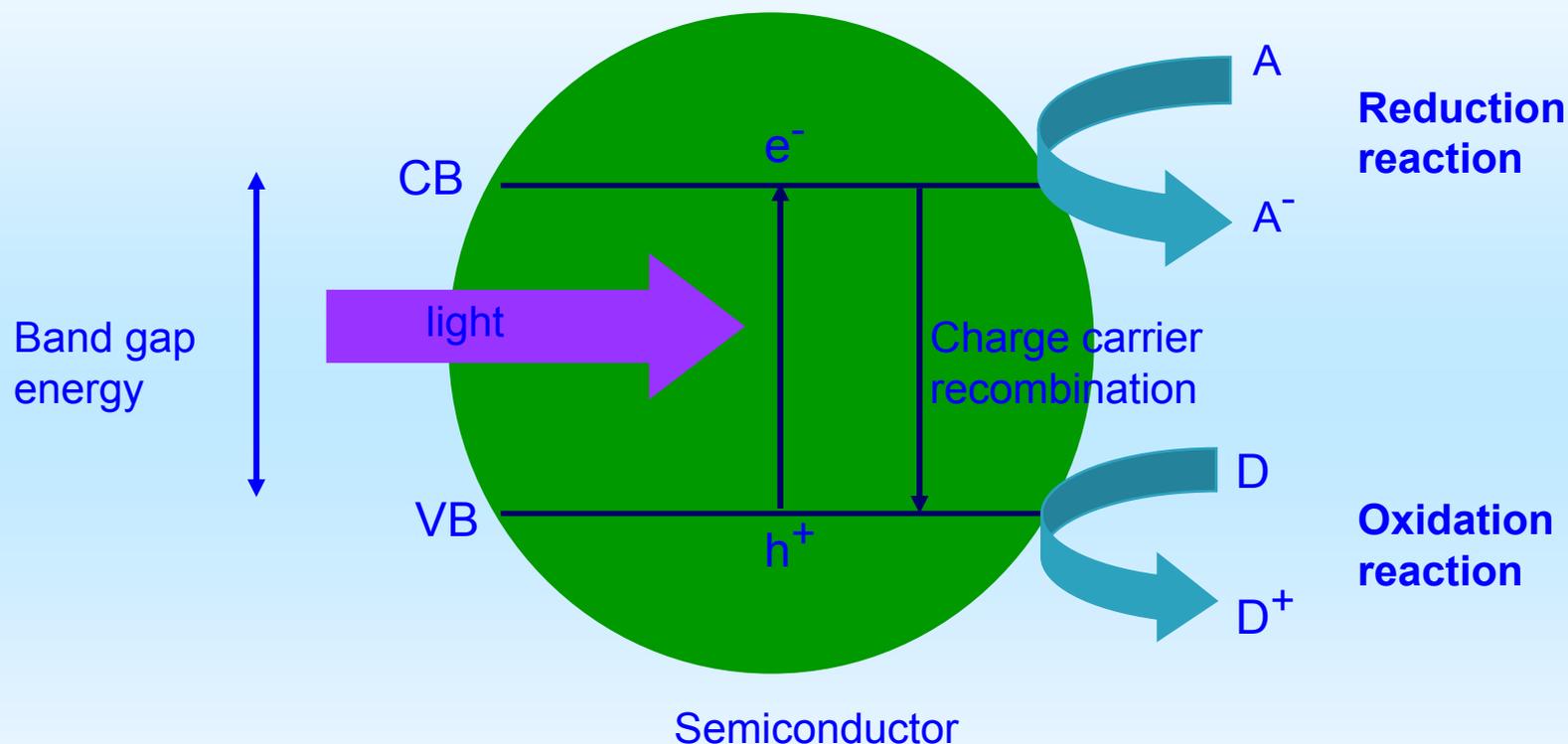
# Combustion Synthesis of Bismuth Vanadate



Sample	Precursor	Fuel
BV1	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O} + \text{VCl}_3$	Urea
BV2		Glycine
BV3		Citric acid
BV4	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O} + \text{VOSO}_4$	Urea
BV5		Glycine
BV6		Citric acid
$\text{BiVO}_4$ (R)		

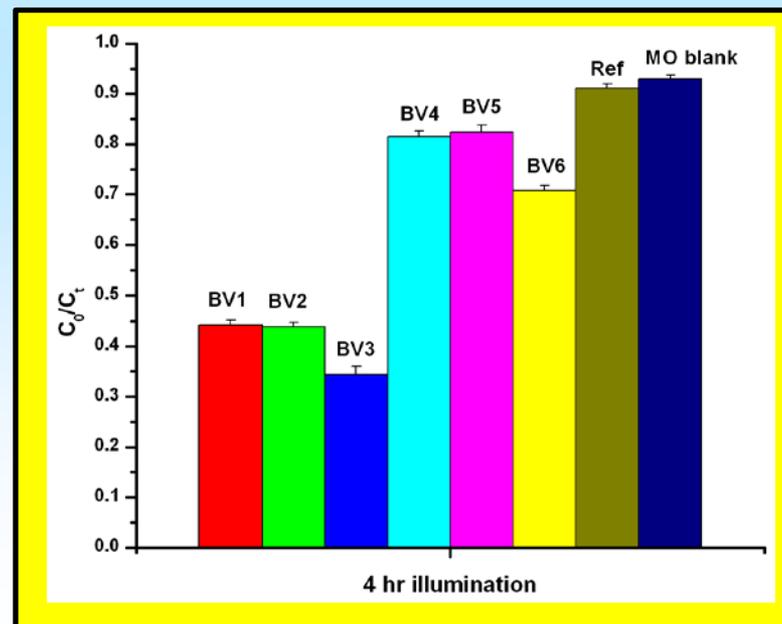
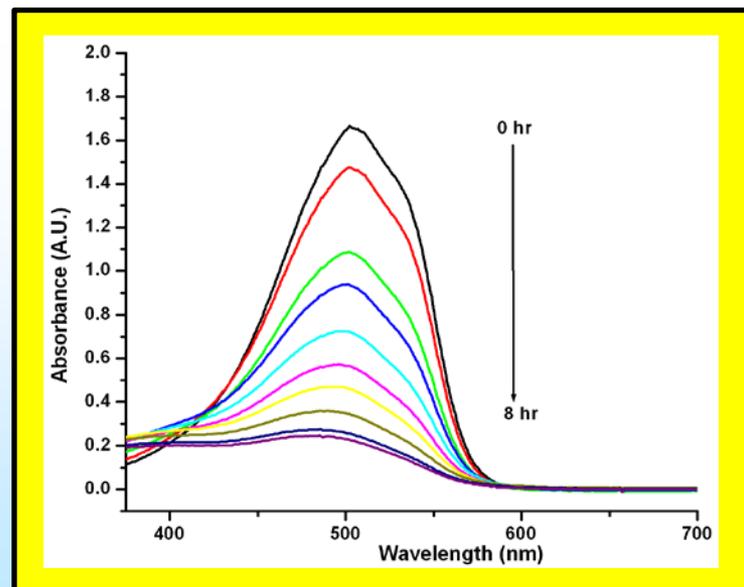
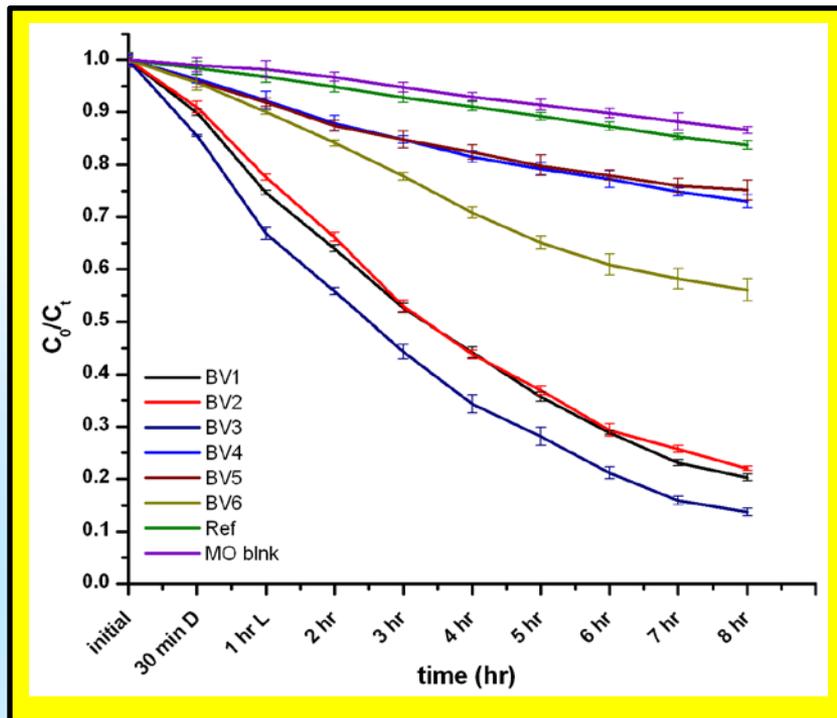


# Heterogeneous Photocatalysis



Schematic diagram of the heterogeneous photocatalytic process occurring on an illuminated semiconductor particle.

# Use of Bismuth Vanadate for Dye Photodegradation



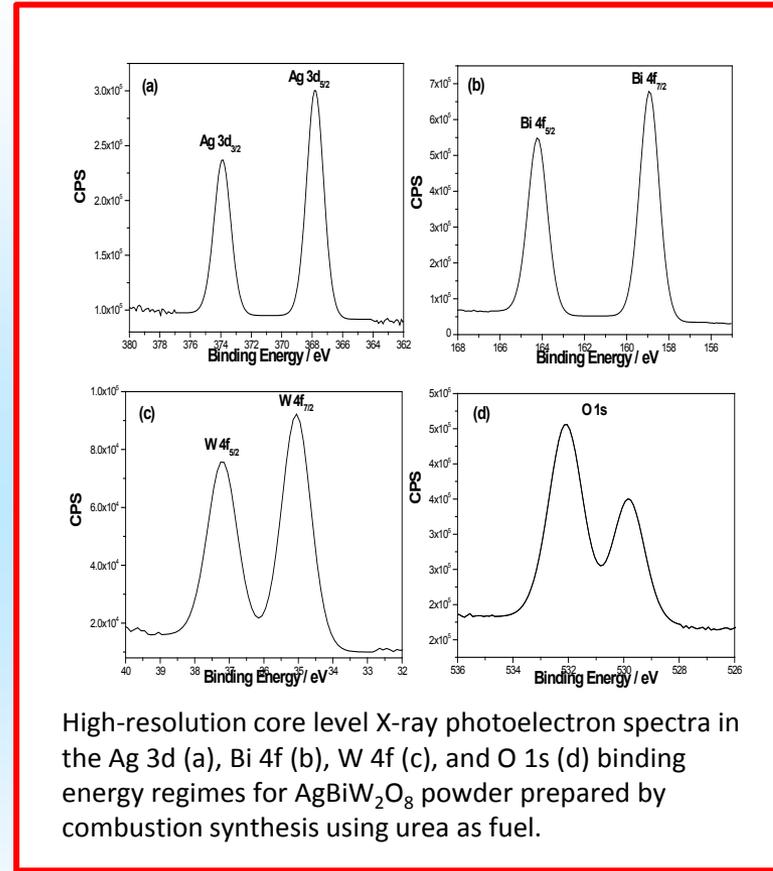
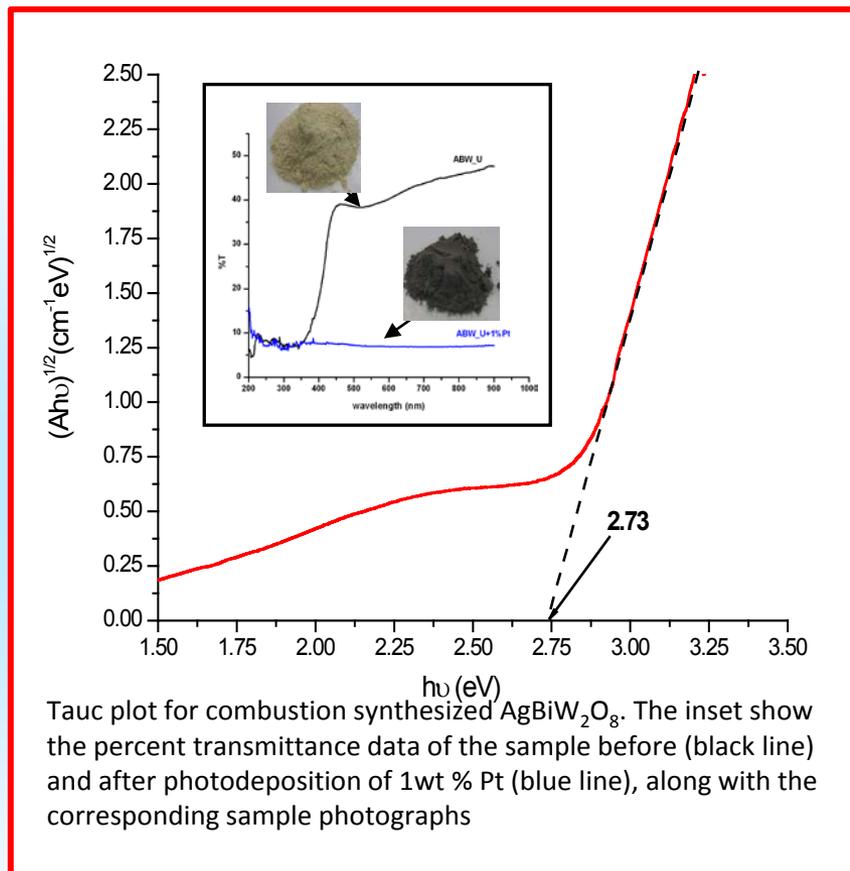
Bismuth vanadate is not suitable for hydrogen generation but is a good photocatalyst for environmental remediation.

# Combustion Synthesis of Silver Bismuth Tungstate

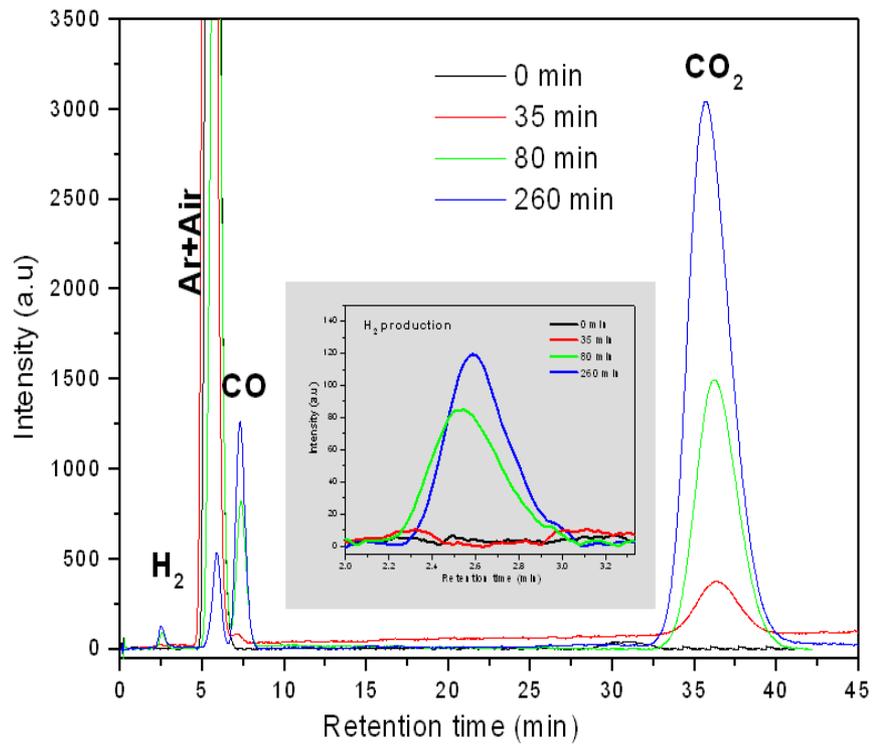
- Precursor mixture of sodium tungstate, bismuth nitrate, and silver nitrate in nitric acid
- Urea used as fuel
- Mixture of fuel and precursor dried and ignited
- Final product washed, dried, and ground to powder



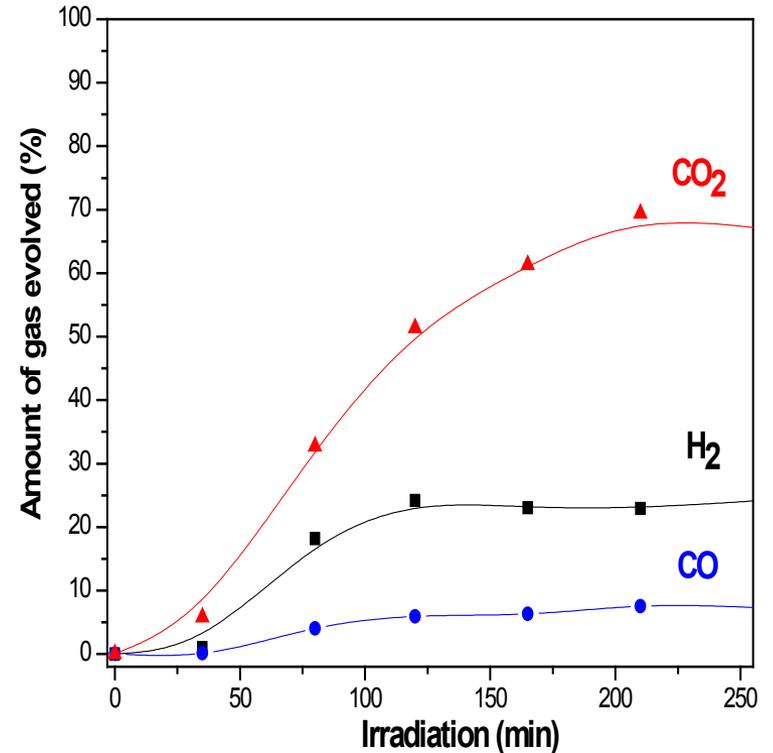
# Photogeneration of Syngas Using Combustion Synthesized $\text{AgBiW}_2\text{O}_8$



# H<sub>2</sub> and CO Photogeneration

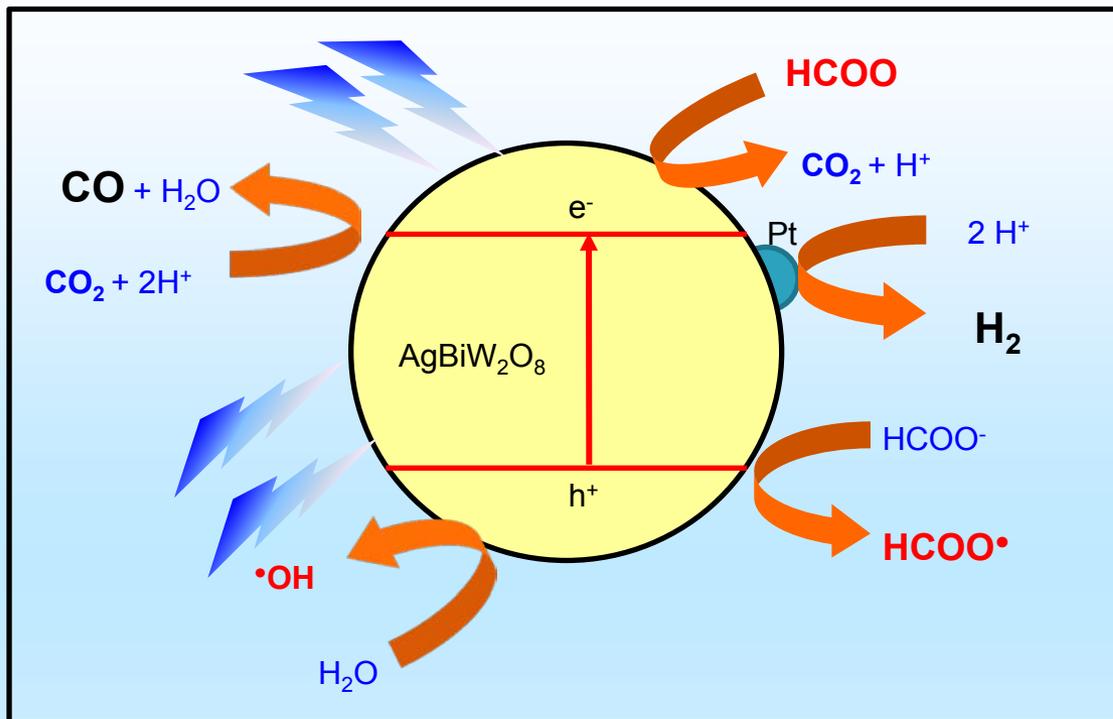


Selected GC runs for detection of gaseous products during the photocatalytic reaction of AgBiW<sub>2</sub>O<sub>8</sub> - 1 wt.% Pt in 0.1 M HCOOH



Evolution of photogenerated syngas (H<sub>2</sub>+CO) sustained by in situ formation of CO<sub>2</sub> from HCOOH.

# Syngas Photogeneration by AgBiW<sub>2</sub>O<sub>8</sub>-Pt



Quantum yields (QY %) were measured by chemical actinometry using 0.006 M K<sub>3</sub>Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·3H<sub>2</sub>O in 1 N H<sub>2</sub>SO<sub>4</sub>

**3.2 x 10<sup>-2</sup> moles of photons/h**

$$QY\% = \frac{\text{mol of product formed}}{\text{mol of photons}} \times 100$$

**QY CO<sub>2</sub> = 4.5 %**

**QY H<sub>2</sub> = 3.0 %**

**QY CO = 0.8 %**

**0.5 g AgBiW<sub>2</sub>O<sub>8</sub>/Pt in 200 mL HCOOH 0.1 M**

**PCP = Photocatalytic performance**

**PCP CO<sub>2</sub> = 14.4 x 10<sup>-3</sup> mol/g·L·h**

**PCP H<sub>2</sub> = 10 x 10<sup>-3</sup> mol/g·L·h**

**PCP CO = 2.2 x 10<sup>-3</sup> mol/g·L·h**

$$PCP = \frac{\text{mol of product}}{m V t}$$

**Cumulative: CO<sub>2</sub> = 2.8 x 10<sup>-2</sup> mol/g.L, CO = 3 x 10<sup>-3</sup> mol/g.L, H<sub>2</sub> = 1.0 x 10<sup>-2</sup> mol/g.L**

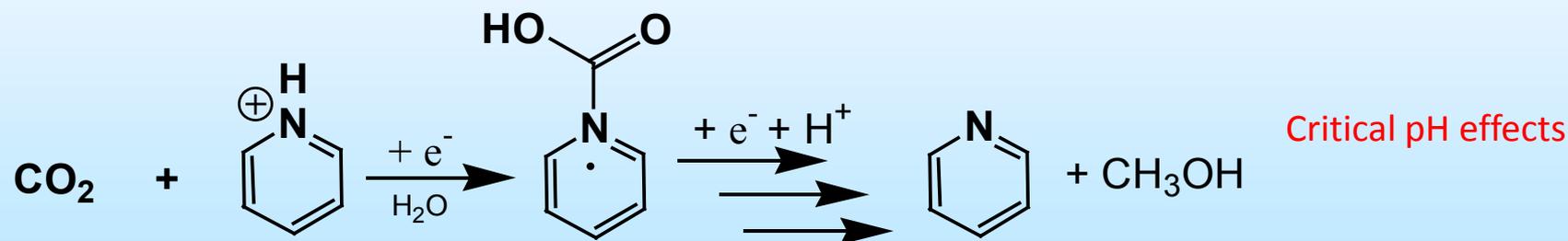


# Task 1: Summary for Heterogeneous Photocatalysis

- Time and energy-efficient method developed for two new-generation oxide semiconductor photocatalysts: bismuth vanadate and silver bismuth tungstate.
- Silver bismuth tungstate has been used for mild syngas photogeneration.
- Further materials optimization will continue.

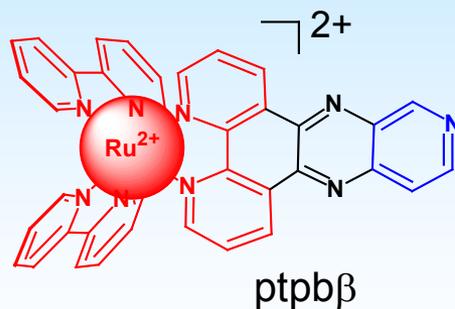
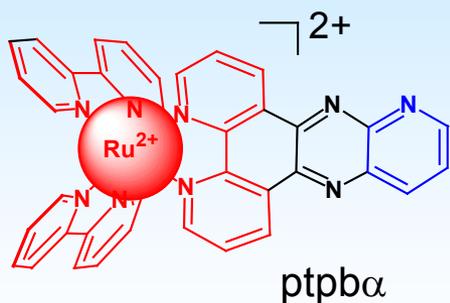
# Task 2: Molecular photocatalysts for CO<sub>2</sub> Remediation and CH<sub>3</sub>OH Formation

Inspiration: Bocarsly and coworkers demonstrate electroreduction of CO<sub>2</sub> using pyridine as a electrocatalyst



Barton CE, Lakkaraju PS, Rampulla DM, Morris AJ, Abelev E, Bocarsly AB. Using a One-Electron Shuttle for the Multielectron Reduction of CO<sub>2</sub> to Methanol: Kinetic, Mechanistic, and Structural Insights. *J. Am. Chem. Soc.* **2010**; 132: 11539-51.

Strategy: Generate reduced pyridinium ions using *the* photochemistry of Ru-polypyridyl complexes



# Task 2 DOE Identified Barriers:

## Homogeneous Photocatalytic CO<sub>2</sub> reduction and Methanol Formation

2	<b>Distributed Reforming of Renewable Liquid Feedstocks</b> <ul style="list-style-type: none"><li>Analyze and research options for alternative renewable feedstocks (e.g., ethanol, methanol, sugars, sugar alcohols, bio-oils, bio-based Fischer Tropsch liquids) for distributed production.</li><li>Utilizing the technology concepts developed for distributed natural gas reforming, develop efficient, integrated, compact, robust process technology for bio-derived liquid feedstocks.</li><li>Explore novel technology for reforming bio-derived renewable liquid feedstocks that could result in a cost breakthrough.</li></ul>	A, B, C, D, E, F
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**D. Feedstock Issues.** Availability of some feedstocks is limited in certain areas. Feedstock-flexible reformers are needed to address location-specific feedstock supply issues. Effects of impurities on the system from multiple feedstocks as well as the effects of impurities from variations in single feedstocks need to be addressed in the reformer design.

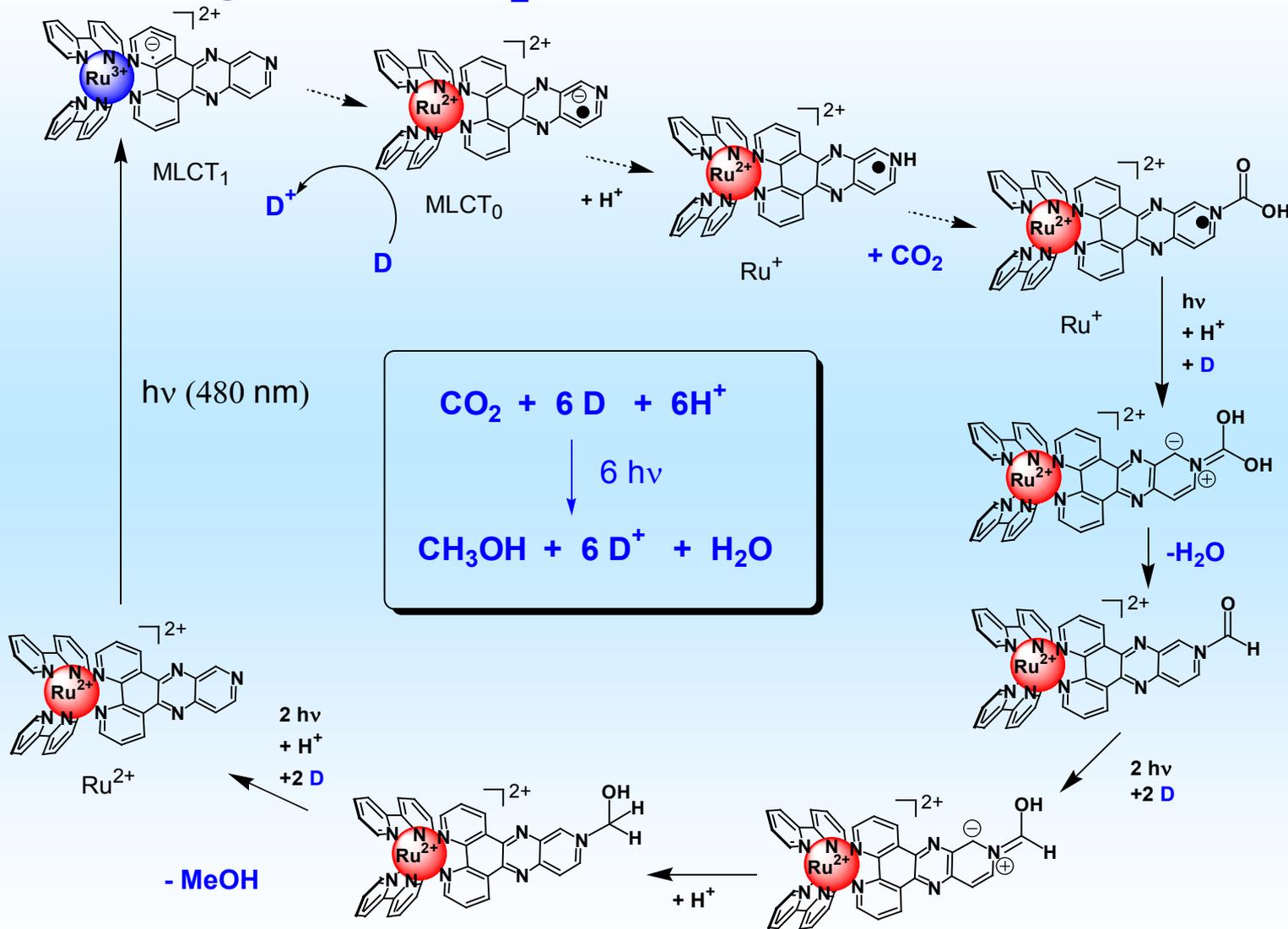
**E. Greenhouse Gas Emissions.** Distributed natural gas reformers emit greenhouse gases. Feedstocks and/or technologies that can approach near zero net greenhouse gas emissions are needed.

# Task 2 Project Objectives:

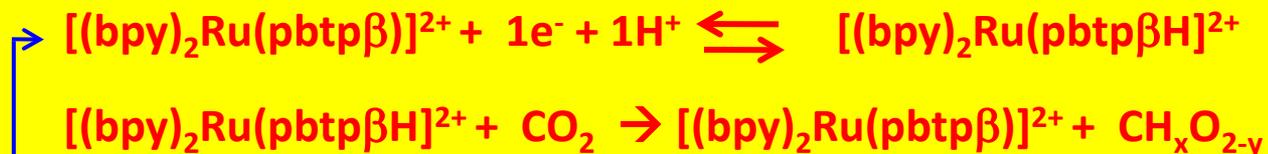
Develop Homogeneous Molecular Photocatalysis to Convert CO<sub>2</sub> to methanol

SubTask Number	Project Milestones	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1	Synthesis of three Ru-photocatalysts	Dec 2009		Dec 2009	100	complete
2	Electrocatalytic screening of three photocatalysts	March 2010		March 2010	100	complete
3	Photophysical Evaluation of the Photocatalysts	June 2010	Oct 2010	Oct 2010	100	complete
4	Demonstration of Photocatalytic CO <sub>2</sub> reduction to MeOH	Sept 2010	Dec 2010	March 2011	100	complete
5	Optimizing /Screening of Photochemical CO <sub>2</sub> reduction	Dec 2010	March 2011	May 2011	90	Nearly complete

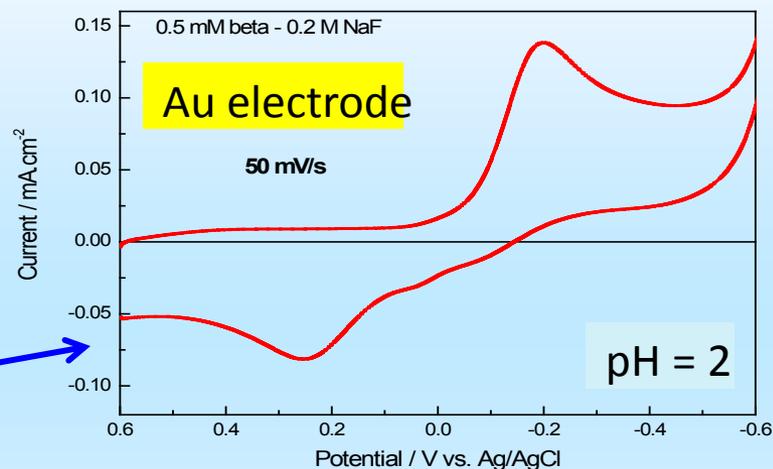
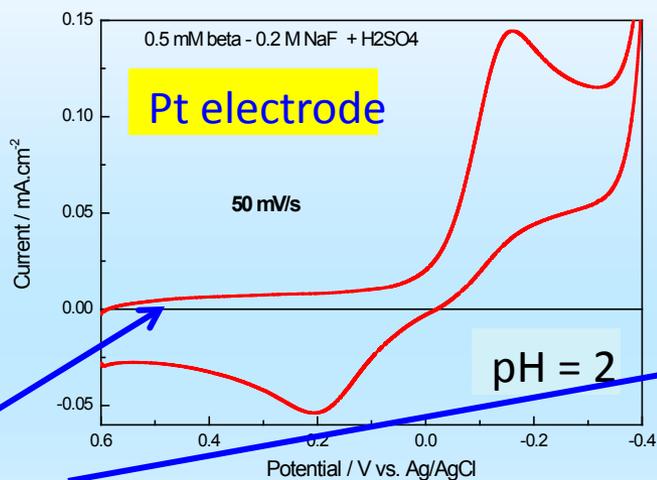
# Proposed Homogeneous Photocatalytic Cycle for CO<sub>2</sub> Reduction to Methanol



# Performance of $[(bpy)_2Ru(ptpb\beta)]^{2+}$ as Homogeneous Catalysts for $CO_2$ reduction

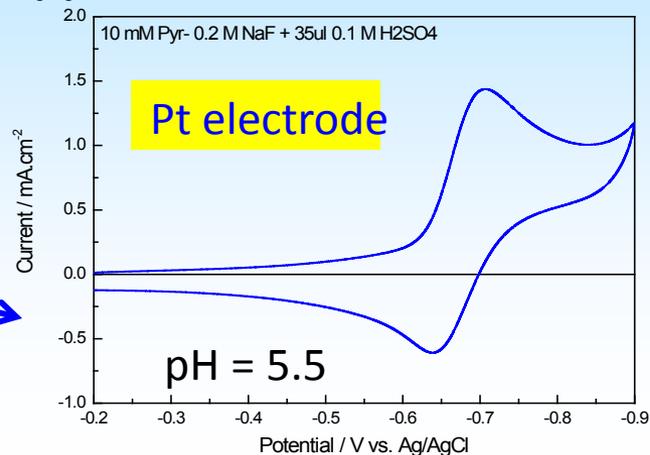


EC' mechanism: redox process followed by a catalytic chemical reaction



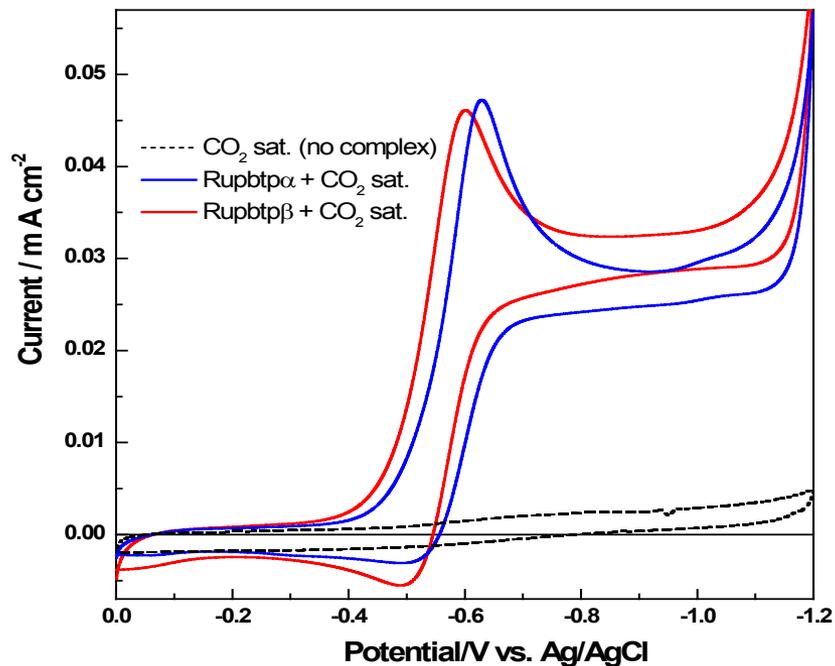
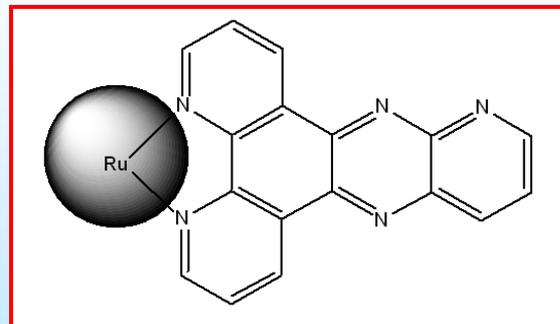
$[(bpy)_2Ru(ptpb\beta)]^{2+}$

vs. Pyridine

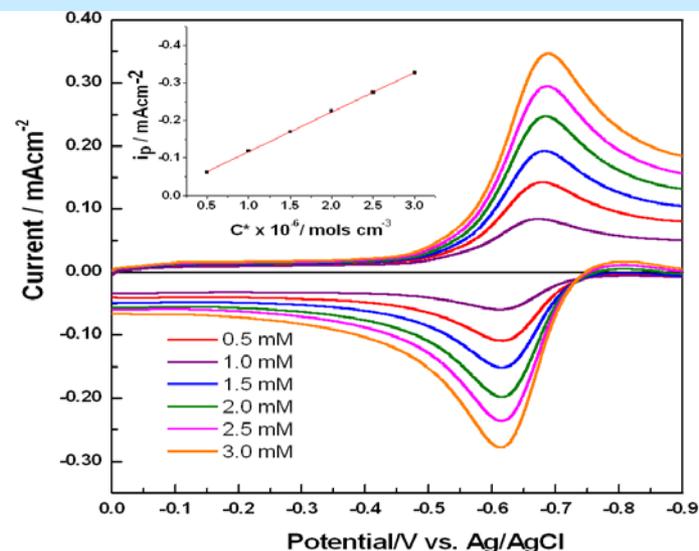


# CO<sub>2</sub> Reduction via Electrocatalysis with Ruthenium Photocatalysts

$[(bpy)_2Ru(ptpb\alpha)]^{2+}$  vs.  $[(bpy)_2Ru(ptpb\beta)]^{2+}$



Comparison of the voltammetric behavior of  $[(bpy)_2Ru(ptpb\alpha)]^{2+}$  and  $[(bpy)_2Ru(ptpb\beta)]^{2+}$  in CO<sub>2</sub> saturated solution. Scan rate = 5 mV/s. The voltammogram with CO<sub>2</sub> without any Ru complex is shown in black dot line.

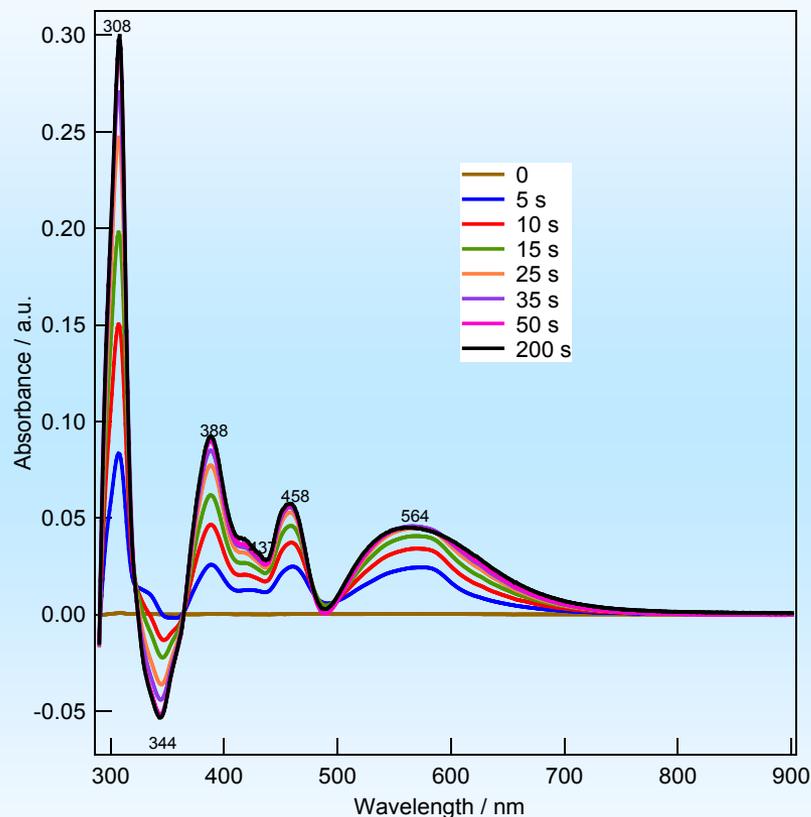


Effect of concentration on the voltammetric behavior of the first electroreduction process of  $[(bpy)_2Ru(ptpb\alpha)]^{2+}$  in DMF + 1 M buffered water (pH ~ 5.5). Scan rate = 50 mV/s. Working electrode = glassy carbon disk of 1 mm diameter.

# Photoreduction of CO<sub>2</sub> by [(bpy)<sub>2</sub>Ru(ptpbβ)]<sup>2+</sup>

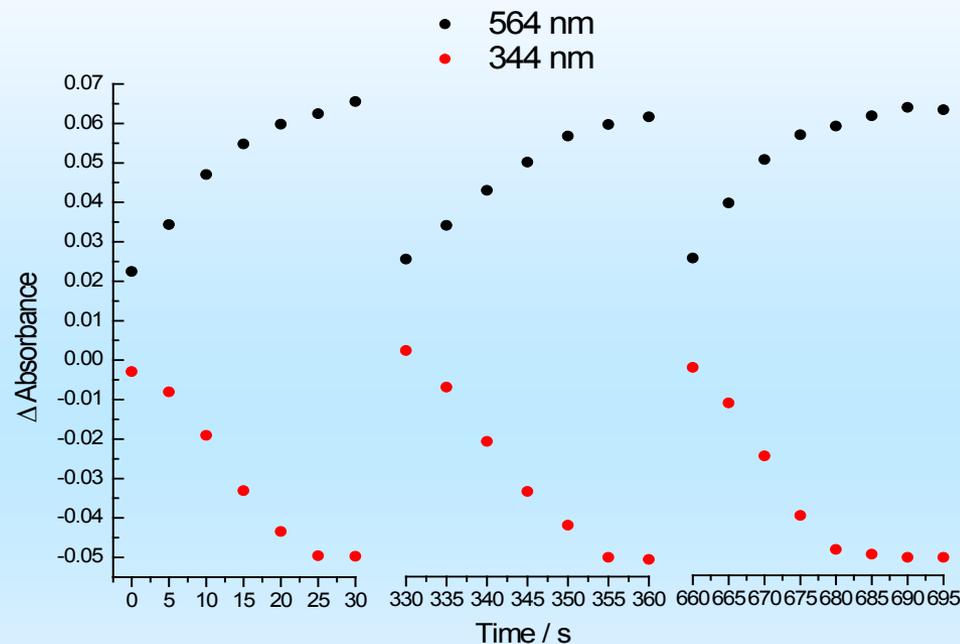


## Photochemistry of [(bpy)<sub>2</sub>Ru(ptpbβ)]<sup>2+</sup>



Difference absorbance spectra of [(bpy)<sub>2</sub>Rupbtpβ]<sup>2+</sup> (2.2 × 10<sup>-4</sup> M) in N<sub>2</sub> saturated DMF/TEA (0.25 M)/H<sub>2</sub>O (1 M) solutions during photolysis in the time domain for 0 to 200 s. Peaks pointing down indicate bands disappearing while those pointing up correspond to new bands appearing as a consequence of the photochemical reaction.

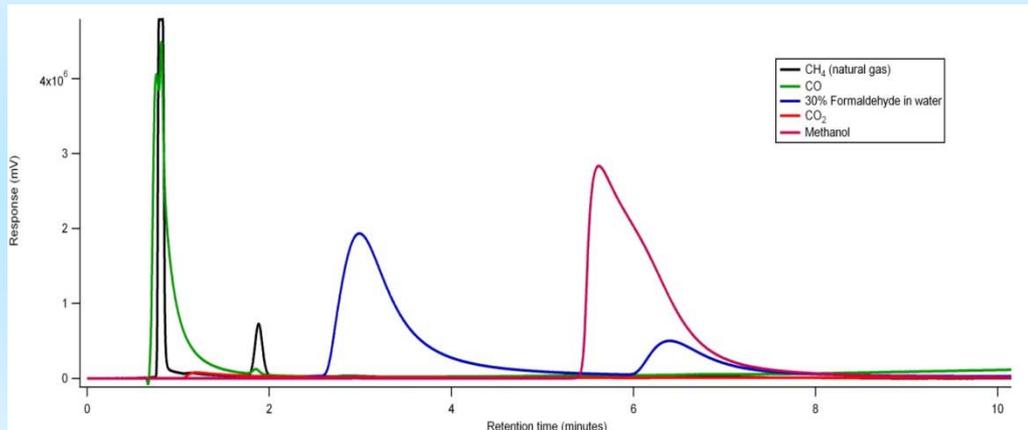
## CO<sub>2</sub> Photocatalytic Conversion



Demonstration of efficient photocatalytic cycles: The three consecutive and reversible photochemical changes of [(bpy)<sub>2</sub>Ru(pbtbβ)]<sup>2+</sup> in CO<sub>2</sub> saturated DMF/TEA (0.25 M)/H<sub>2</sub>O (1 M) are shown from left to right. The photoreduced catalyst is manifested in the growth of a band at 544 nm at expense of the 344 nm band characteristic of the unreduced photocatalyst. Each photoreduction requires 30 s to be completed and is separated from the next by a 5 min CO<sub>2</sub> bubbling under dark. The period of bubbling in the dark is provoking the removal of the reduced CO<sub>2</sub> species coordinated to the complex and thus releasing the complex to be able to work again as photocatalyst in the next irradiated cycle.

# Photochemistry of $[(bpy)_2Ru(ptpb\alpha)]^{2+}$ and $[(bpy)_2Ru(ptpb\beta)]^{2+}$ in DMF/ water or MeCN /water

**Conditions:** In a typical experiment, a water jacketed reaction vessel of 50 mL total volume was filled with ~25 mL MeCN or DMF that is 1.0 M H<sub>2</sub>O (pH 5), 0.20 M TEOA, and 100  $\mu$ M Ru complex. The solutions are degassed, saturated with CO<sub>2</sub>, and then placed in the photochemical reactor for irradiation. Samples of both the headspace and solution are collected at various time periods and subjected to gas chromatographic (GC) analysis for product detection.



GC Analysis: Standards run using 1 C/minute temperature ramp from 110 C to 150 C using a Haysep DB column. Black line is methane, domestic natural gas, green line



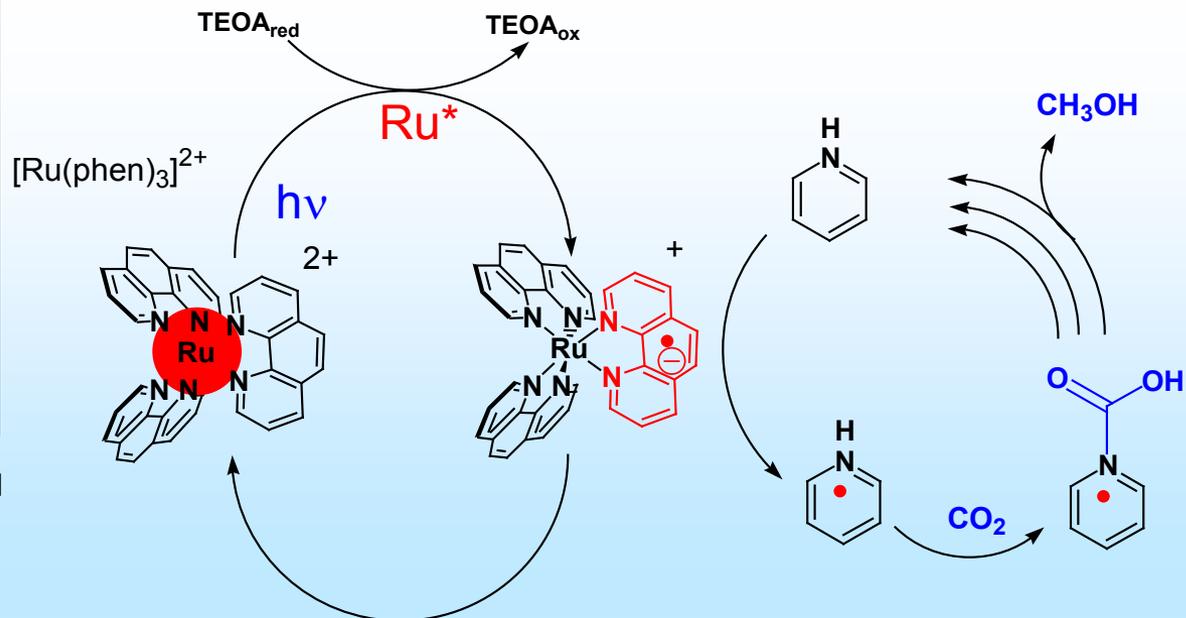
**Custom Photoreactor: Water-jacketed glass reaction vessel with optical probe, stir bar and lamp consisting of 120 ultra bright diode in circular pattern (wavelength 470 nm)**

**$\alpha$  and  $\beta$  complexes inactive at pH 5. Donor does not function below pH 5**

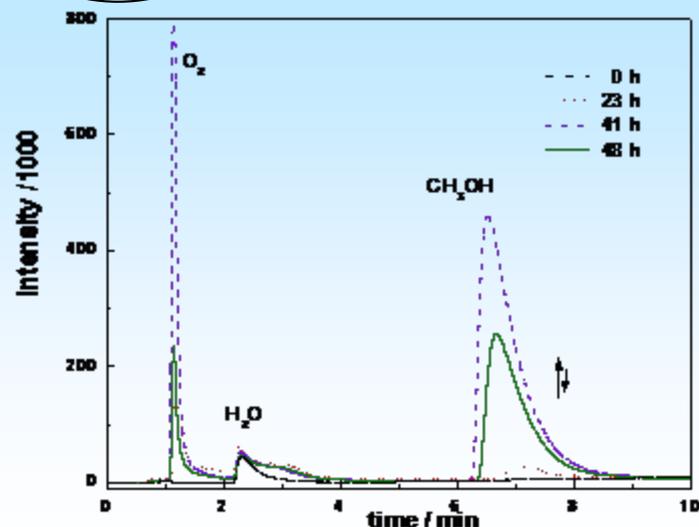
# Photochemistry of $[\text{Ru}(\text{phen})_3]^{2+}$ and Pyridine in Water at pH 5



Conditions: 100  $\mu\text{M}$   $[\text{Ru}(\text{phen})_3]^{2+}$ , 0.1M pyridine, 0.20 M TEOA, pH 5.0 then saturated with  $\text{CO}_2$  by extensive bubbling and placed under  $\text{CO}_2$  atm. We are currently working to quantify and optimize this reaction.



**MeOH detected by GC analysis!**

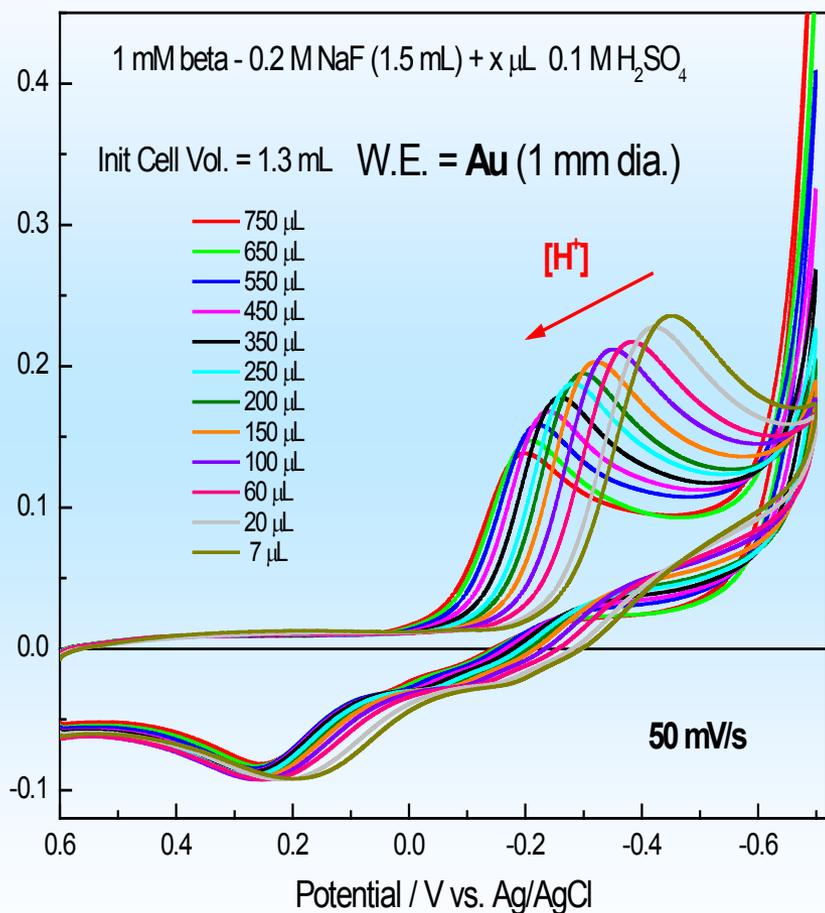


# Effect of [H<sup>+</sup>] on the Electrocatalysis

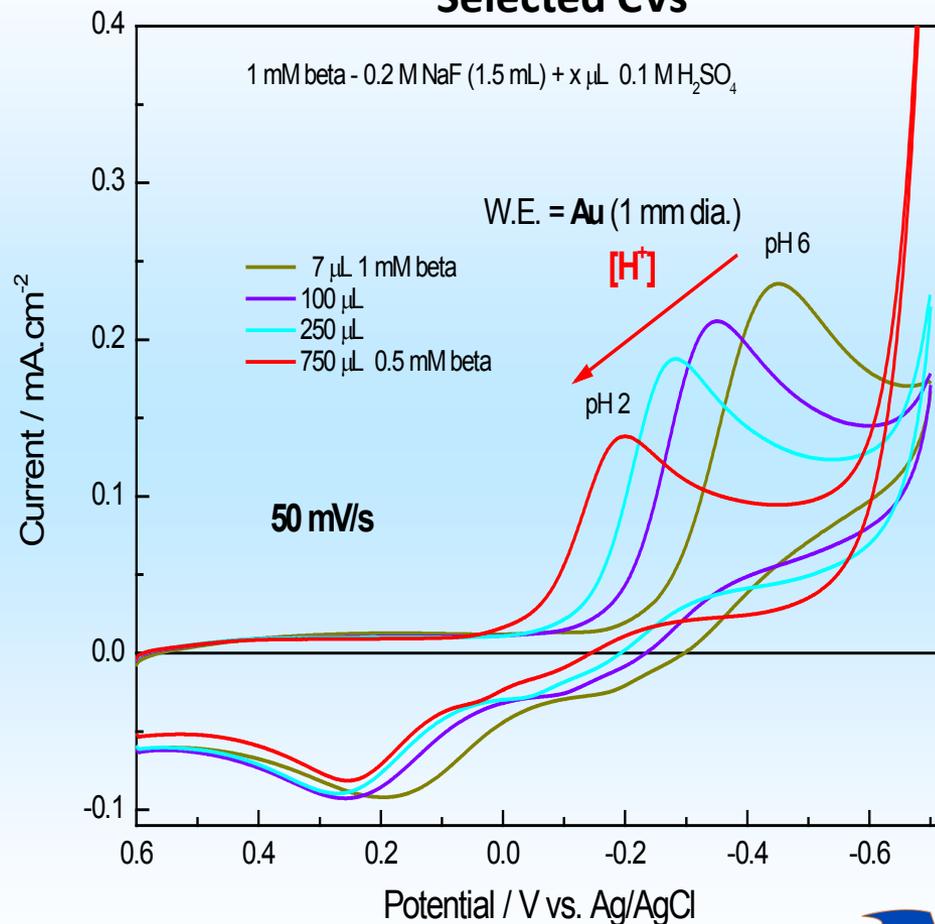
Cyclic voltammetry of  $[(bpy)_2Ru(ptpb\beta)]^{2+}$  on a Au electrode



working electrode: Au (1mm dia.)



Selected CVs

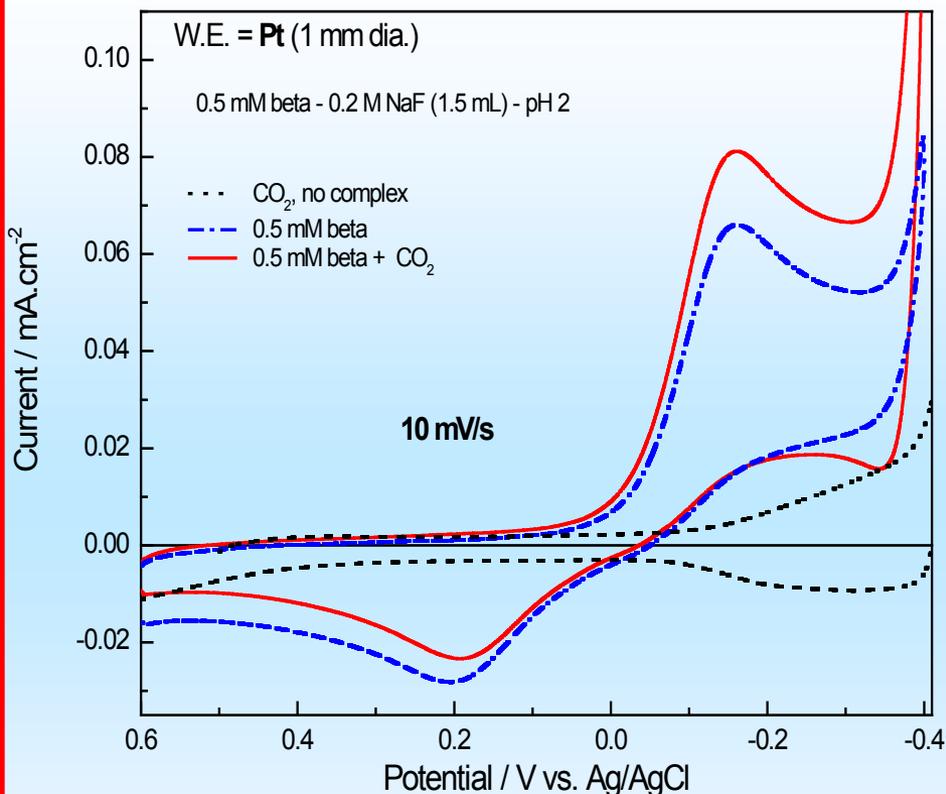


$E_p$  vs. pH shifts positively by 60 mV per unit of pH for pHs between 6 and 2



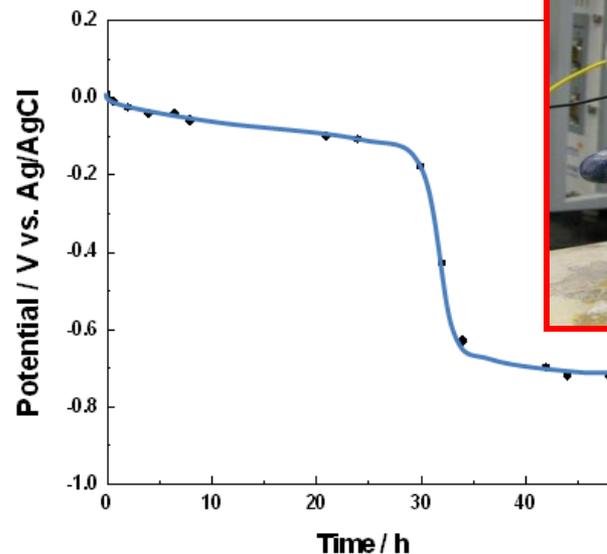
# Electrocatalytic reduction of CO<sub>2</sub> by [(bpy)<sub>2</sub>Ru(ptpbβ)]<sup>2+</sup> at pH 2

## Comparative CV runs



Voltammetric profiles of 0.5 mM [(bpy)<sub>2</sub>Ru(ptpbβ)]<sup>2+</sup> in 0.2 M NaF aq. media (adjusted to pH 2 with H<sub>2</sub>SO<sub>4</sub>) in N<sub>2</sub> (dash blue line) and CO<sub>2</sub> (b) saturated solutions respectively. Scan rate = 10 mV/s. A blank run of CO<sub>2</sub> saturated supporting electrolyte without the complex is shown in black dot line.

## Galvanostatic Electrolysis



Potential evolution during galvanostatic electrolysis of 5 mM [(bpy)<sub>2</sub>Ru(ptpbβ)]<sup>2+</sup> in 0.1 M KCl aq. solution (pH 2) under constant CO<sub>2</sub> bubbling. Applied current = 0.45 mA (cathodic).



During ~ 30 h the potential holds in the 0V/-0.2V range sustained by an EC' mechanism (1e<sup>-</sup> reduction process forming [(bpy)<sub>2</sub>Ru(ptpbβH)]<sup>2+</sup> and followed by a chemical reaction that regenerate the initial [(bpy)<sub>2</sub>Ru(ptpbβ)]<sup>2+</sup> complex). At times longer than 30 h the potential shifts to -0.7V because all the [(bpy)<sub>2</sub>Ru(ptpbβ)]<sup>2+</sup> complex has been converted to [(bpy)<sub>2</sub>Ru(ptpbβH)]<sup>2+</sup>

# CH<sub>3</sub>OH Detected as Product in Electrocatalysis

Method: Galvanostatic Electrolysis under CO<sub>2</sub> bubbling

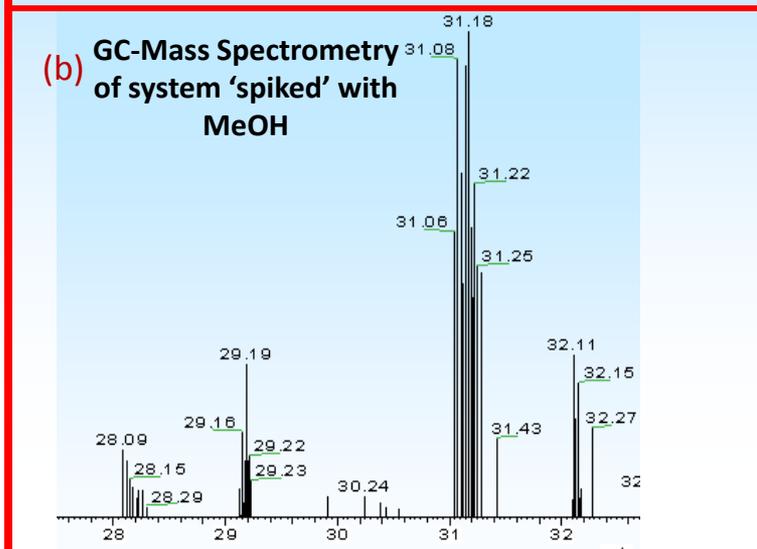
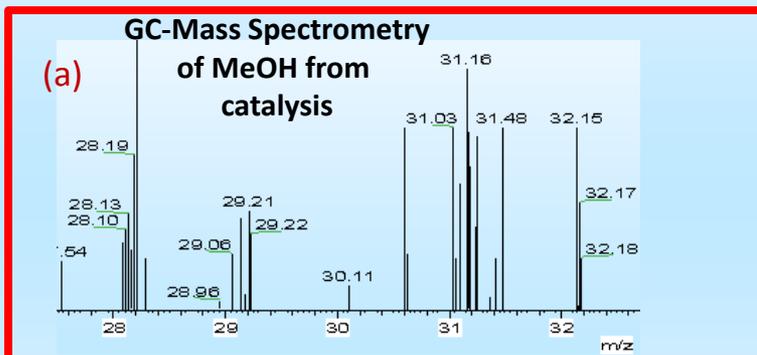
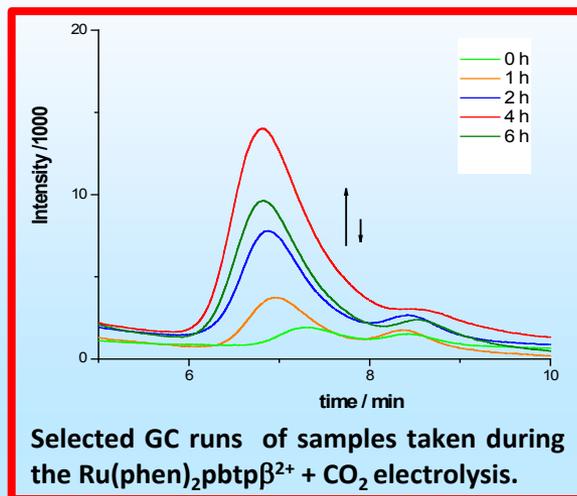
[Ru(phen)<sub>2</sub>pbtpβ] = 5 mM Electrolyte: 0.1 M KCl (@ pH 2 w/1M HCl)

Applied current : -0.45 mA

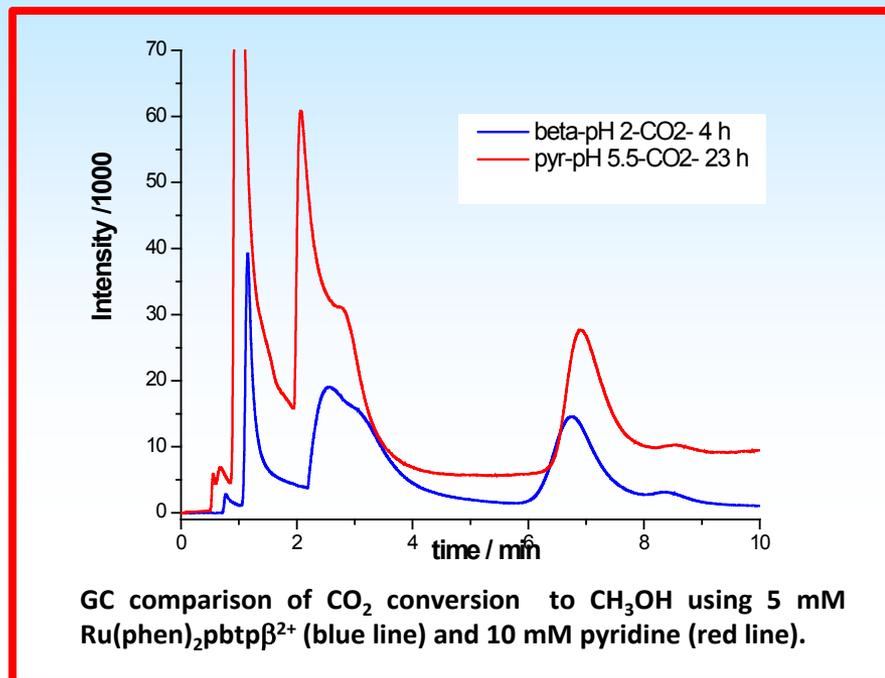
W.E.= Pt foil (8.4 cm<sup>2</sup>)

C.E.= Pt in separated compartment

Ref. E.= Ag/AgCl, KCl sat.



Comparison of GC-MS data of a 2 h electrolysis sample (a) with authentic spectra of 10 mM CH<sub>3</sub>OH(b)



# Task 2: Summary

- Ruthenium complexes with internal pyridyl functions prepared and characterized.
- **Complexes competent for electrocatalytic CO<sub>2</sub> reduction to methanol. Optimum performance at pH 2.**
- Ru  $\alpha$  and Ru  $\beta$  photocatalysts inactive for photochemical CO<sub>2</sub> reduction at pH 5 and experimental constraints precluded testing at pH 2.
- **Simple homoleptic complex, [Ru(phen)<sub>3</sub>]<sup>2+</sup>, is able to function at pH 5 with pyridine added as co-catalyst.**

**Methanol is produced photochemically!!!**

- Controlling variables including ligand isomerism (ptpb $\alpha$  vs ptpb $\beta$ ), solvent composition (DMF/MeCN/H<sub>2</sub>O), solution pH, and choice of donor, need further investigation and optimization.

