II.J.3 Value-Added Hydrogen Generation with CO$_2$ Conversion

Fiscal Year (FY) 2011 Objectives

**TASK 1: Develop Homogeneous Ruthenium Photocatalysts for H$_2$ Production and CO$_2$ Reduction**
- Synthesis of ruthenium-polypridyl complexes (RPCs) as photocatalysts.
- Screen RPCs for electrocatalytic activity.
- Evaluate the photophysical properties of the RPCs.
- Demonstrate photocatalytic CO$_2$ reduction with RPCs.
- Optimize photocatalytic reaction.

**TASK 2: Develop Heterogeneous Oxide Photocatalysts for H$_2$ Production and CO$_2$ Reduction**
- Develop new oxide semiconductors for photocatalysis and photoelectrochemical catalysis.
- Demonstrate combustion synthesis of BiVO$_4$, Bi$_2$WO$_6$, and AgBiW$_2$O$_6$ nanoparticles.
- Demonstrate photoreduction of CO$_2$ using BiVO$_4$ nanoparticles.
- Develop method for photodeposition of Pt on AgBiW$_2$O$_6$.
- Optimizing Bi$_2$WO$_6$ and AgBiW$_2$O$_6$ for CO$_2$ photoreduction.

This project addresses the following technical barriers from the Production section (3.1) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

**Task 1: Technical Barriers Addressed**
- (D) Feedstock Issues
- (E) Greenhouse Gas Emissions

**Task 2: Technical Barriers Addressed**
- (Y) Materials Efficiency
- (Z) Materials Durability
- (AA) PEC Device and System Auxiliary Material
- (AB) Bulk Material Synthesis

**Technical Targets**

Progress towards meeting Technical Targets for CO$_2$ Use as a Feedstock and Greenhouse Gas Remission

**Task 1**
- Synthesis of three ruthenium polypyrindyl complexes.
- Proof-of-concept demonstration of CO$_2$ reduction to methanol using electrochemical and photochemical methods.

**Task 2**
- Combustion Synthesis of BiVO$_4$, Bi$_2$WO$_6$, and AgBiW$_2$O$_6$ nanoparticles.
- Photodeposition of Pt on AgBiW$_2$O$_6$ nanoparticles to enhance electron-hole separation under irradiation.
- Photocatalytic reduction of CO$_2$ using Pt-modified AgBiW$_2$O$_6$.

**FY 2011 Accomplishments**

**Task 1**
- Prepared two photocatalysts containing a ruthenium chromophore linked to pyridyl moiety.
- Demonstrated that these photocatalysts are competent for CO$_2$ electroreduction to methanol with an optimum performance at pH of 2.0.
- Demonstrated that the two new photocatalysts are capable of CO$_2$ photoreduction to methanol but that they require a mixed MeCN-water solvent to function.

**Task 2**
- Prepared BiVO$_4$, Bi$_2$WO$_6$, and AgBiW$_2$O$_6$ nanoparticles by Combustion Synthesis.
- Demonstrated that the combustion synthesized nanoparticles possess higher photocatalytic performance.
and larger surface area than those obtained by solid state reaction.

- Demonstrated the photocatalytic generation of H\(_2\) and reduction of CO\(_2\) using Pt-modified AgBiW\(_6\)O\(_{19}\) nanoparticles.

\[\text{\H_2 + \CO_2 \rightarrow \CH_3\OH + \CO} \]

**Introduction**

Given the current environmental concerns over CO\(_2\) as a greenhouse gas and the need for fuels derived from renewable energy sources, the capture and reduction of CO\(_2\) into fuels could help alleviate the environmental issue and turn this cheap and common feedstock into valuable fuels. The combustion of these fuels would regenerate CO\(_2\), which, in theory, be ‘recycled’ into fuel, leading to a closed carbon cycle. Of course, there is a required energy input for this carbon-based fuel cycle, and ideally this would be based on solar-energy. Task 1 of this project describes the development of molecular photocatalysts, based on the discovery of Bocarsly and co-workers that pyridine is an excellent electrocatalyst for the reduction of CO\(_2\) to methanol [1-3]. In this work, we covalently link a ruthenium chromophore to a pyridine co-catalyst to develop a homogeneous CO\(_2\) reduction photocatalyst. The project involves the design, synthesis, characterization and testing of these photocatalysts for CO\(_2\) reduction to methanol. Task 2 describes the preparation of BiVO\(_4\), Bi\(_5\)W\(_{12}\)O\(_{40}\), and AgBiW\(_6\)O\(_{19}\) semiconductor nanomaterials by a “mild” (low-temperature) combustion synthesis. This method is both energy- and time-efficient because the exothermicity of the combustion reaction provides the energy for the synthesis and the reaction times are just a few minutes. The resulting combustion synthesized nanoparticles are tested as photocatalysts for H\(_2\) generation and CO\(_2\) reduction. Sample characterization involves several techniques such as high resolution transmission electron microscopy, thermogravimetric analysis, Brunauer-Emmett-Teller (BET) surface area, diffuse reflectance spectroscopy, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

**Approach**

**Task 1**

We designed and prepared complexes in which the well-established photochemistry of ruthenium-polypyridyl coordination complexes is used to generate a reduced pyridine functional group. These complexes are characterized electrochemically and photochemically to determine optimum reaction conditions. Excitation of each Ru(II) complex with visible light in the region of 400-500 nm forms an excited \(^5\)MLCT (metal-to-ligand charge-transfer) state in which the pyridine-containing ligand is reduced by one electron. This excited state quickly relaxes to a second, long-lived, triplet excited state, \(^3\)MLCT. Reductive quenching of the Ru\(^{3+}\) center traps the electron on the pyridyl ligand and thus has ‘photogenerated’ an analogue of the pyridine radical. Reaction of this radical anion with CO\(_2\) at the proper pH leads to a sequence of photoreductions that ultimately produce methanol. We used electrochemistry to screen the photocatalysts for photocatalytic CO\(_2\) reduction activity under various pH conditions. Gas chromatography coupled with mass spectrometry was used to look for the reduced CO\(_2\) products, specifically for methanol. The complexes ability function as photocatalysts was examined in a custom designed photoreactor with 470 nm ultrabright diode lamp. Reaction conditions included the presence of a sacrificial donor, triethanolamine (TEOA) to reductively quench the photoexcited complexes.

**Task 2**

We used solution combustion synthesis (SCS) to prepare BiVO\(_4\), Bi\(_5\)W\(_{12}\)O\(_{40}\), and AgBiW\(_6\)O\(_{19}\) semiconductor nanoparticles. The selection of these three materials was based on their respective band gap energy overlapping the solar spectrum and thus making them able to perform heterogeneous photoreactions using solar light. Using SCS is convenient as compared with the traditional solid-state reaction method for nanoparticles preparation. The combustion synthesis uses a fuel (i.e. urea) that in contact with the metal precursors promotes the combustion reaction in few minutes instead of the high energy consumption associated with the solid state reaction that normally takes several hours of heating at high temperatures. Furthermore, SCS generates much smaller nanoparticles because of the gases generated during the combustion reaction. The synthesized powders were characterized in their physical shape and size (high-resolution transmission electron microscopy [HRTEM], BET), composition, crystalline structure (XRD, energy dispersive X-ray spectroscopy, XPS), and light absorption (diffuse reflectance ultraviolet-visible spectroscopy [UV-Vis]). The ability of these nanoparticles as heterogeneous photocatalysts was examined in a 200 mL photoreactor containing 0.5 g of semiconductor nanoparticles in aqueous media irradiated from a light source (xenon or tungsten halogen lamp) placed in an inner Pyrex glass compartment.

**Results**

**Task 1**

We prepared the three photocatalysts shown in Figure 1 in 90% yield and have characterized them by nuclear magnetic resonance and elemental analysis. They are isolated as the hexafluorophosphate salt for solubility in acetonitrile or as chloride salt for solubility in water.
Electrochemistry

The voltammetric behavior of [(bpy)$_2$Ru(ptpbα)]$^{2+}$ and [(bpy)$_2$Ru(ptpbβ)]$^{2+}$ complexes in the presence of CO$_2$ is compared in Figure 2. It is worth noticing that both profiles are similar in shape although [(bpy)$_2$Ru(ptpbβ)]$^{2+}$ is peaking at less negative potentials than its analog [(bpy)$_2$Ru(ptpbα)]$^{2+}$ indicating a more facile interaction with CO$_2$ for the first complex. In both cases, the formation of a reactive nitrogen site in the pbpb (either α or β) ligand for CO$_2$ adduct formation in the form of a carbamate is expected. Figure 2 also shows that a neat increase of current is occurring at potentials more negative than -1.1 V for both complexes indicating that a next electron uptake is also a possible center for photocatalytic CO$_2$ reduction. This point is important in the view of the photochemical reduction of CO$_2$ as the $^1$MLCT excitation of the Ru π→ptpb σ* band in any of the complexes and reductive quenching of the $^3$MLCT excited state by triethylamine could trap the electron on the pbpb ligand to form [(bpy)$_2$Ru(ptpb')$^+$] either in the bpy structure of the pbpb or at the farther N of the structure. The two different locations in the pbpb ligand might work properly in the photochemical reaction. In relation to the returning positive-going scan in Figure 2, it is clear that anodic currents are much smaller than those shown in the absence of CO$_2$ and pointing out to a chemical reaction of CO$_2$ with the reduced product of any of the complexes.

For the mechanistic aspects of the electrochemical reaction, the pH dependence of the electrocatalysis was examined. As shown in Figure 3, the reduction potential shifts positive as the pH is lowered as expected for a proton-coupled process. A 60 mV shift positive for every pH unit is in agreement with a one proton-one electron shift as the pH is lowered. A separate measurement of the pK$_a$ of the pyridine acid in [(bpy)$_2$Ru(ptpbβ)]$^{2+}$ revealed a pK$_a$ near 2.0 which corresponds nicely with the peak potential shift observed for the cathodic peak. Using this data and the findings by Bocarsly that pyridine electrocatalysis of CO$_2$ reduction works best at the pKa of the pyridine acid, we ran all subsequent photoreductions at pH 2 for complexes [(bpy)$_2$Ru(ptpbα)]$^{2+}$ and [(bpy)$_2$Ru(ptpbβ)]$^{2+}$ [3].

Photochemistry and Photocatalysis

We examined the ability of [(bpy)$_2$Ru(ptpbα)]$^{2+}$ and [(bpy)$_2$Ru(ptpbβ)]$^{2+}$ to serve as photocatalysts for CO$_2$ reduction under a variety of conditions. As expected from the literature, pure water solutions were not practical as the excited state lifetime is too short for photoreactions [4]. Solvent mixtures of dimethylformamide (DMF)/water and acetonitrile (MeCN)/water resulted in suitable excited-state lifetimes for the photocatalysts. In a typical experiment, a water jacketed reaction vessel of 50 mL total volume was filled with ~25 mL MeCN that is 1.0 M H$_2$O, 0.20 M TEOA, and 100 µM Ru complex. The solutions are degassed and then placed in a homemade photochemical reactor in which blue light irradiation of wavelength 470 nm is provided by ultra bright diode array setup. Samples of both the headspace and solution are collected at various time periods and subjected to gas chromatographic (GC) analysis for product detection.

GC data was collected using a Haysep DB packed column with a length of 3 m and used N$_2$ as a carrier gas (starting at 110°C, a temperature ramp of 1°C/minute...
The temperature was done immediately after sample injection to a final temperature of 150°C. Retention times were as follows: carbon monoxide, 0.80 min.; methane, 0.88 min.; methanol, 5.8 min.; formaldehyde and formic acid, 8 min.

Methanol was detected under electrolytic and photolytic conditions. Methanol production increased with electrolysis time as expected. In the electrolysis experiment, conditions were 5 mM \((\text{bpy})_2\text{Ru(pbtpβ)}^{2+}\), 0.1 M KCl electrolyte, pH 2.0, constant CO\(_2\) bubbling. Constant current at -0.45 mA was applied to a Pt working electrode using a Pt counter electrode in a separate compartment, and Ag/AgCl reference electrode in the working electrode compartment. These results are only semi-quantitative due to peak overlap in the gas chromatogram and need further refinement for yields and turnover numbers. Similarly, methanol was detected in a photochemical experiment. 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\(_2\)O (pH 2), 0.20 M ascorbic acid, and 100 mM Ru complex. The solutions are degassed, saturated with CO\(_2\), and then placed in the photochemical reactor for irradiation at 470 nm. Samples of both the headspace and solution were collected at various time periods and subjected to GC analysis for product detection. Methanol was detected by GC of the solution phase (Figure 4) and its identity confirmed by mass spectrometry. As with the electrolysis result, the results are not quantitative as overlap of the MeOH peak with another species prevents accurate quantification. Work is in progress to find conditions for clear resolution of the MeOH peak by GC.

**Task 2**

BiVO\(_4\), Bi\(_2\)WO\(_6\) and AgBiW\(_2\)O\(_6\) nanoparticles were prepared by SCS [5]. The band edges of these three semiconductor materials are shown in Figure 5 comparatively to other materials and also the redox potentials for CO\(_2\) electroreduction and water splitting are shown there. The three selected materials have band gaps in the 2.4-2.7 eV range thus overlapping the solar spectrum and in contrast with TiO\(_2\) which has served as a model workhorse for a stable and inert inorganic semiconductor although its 3.2 eV band gap is too high to be used as solar absorber.

All samples were fully characterized (by HRTEM, XPS, XRD, BET, UV-Vis and Raman spectroscopy) to ascertain
particle size, composition, crystalline structure and absence of impurities [6]. Figure 6 shows the UV-visible diffuse reflectance data on a SCS-synthesized AgBiW$_2$O$_8$ sample processed in the form of Tauc plot of the square root of the Kubelka–Munk function vs. the photon energy. The band gap value estimated from this plot is 2.73 eV and in very good agreement with the value (2.75 eV) reported for this ternary oxide in a previous study on solid-state reaction (SSR) [7]. Much higher surface areas (as determined by BET isotherm, see Table 1) are found for the SCS samples than for those prepared by SSR, thus pointing out to a better quality product obtained in a time- and energy-efficient manner by SCS.

Table 1.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Micropore Area (cm$^2$)</th>
<th>External Surface Area (cm$^2$)</th>
<th>BET Surface Area (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCS AgBiW$_2$O$_8$</td>
<td>5.488</td>
<td>28.938</td>
<td>34.44 (our work)</td>
</tr>
<tr>
<td>SSR AgBiW$_2$O$_8$</td>
<td>0.136</td>
<td>0.406</td>
<td>0.54 (our work)</td>
</tr>
<tr>
<td>SSR AgBiW$_2$O$_8$</td>
<td>-</td>
<td>-</td>
<td>0.29 (ref. 7)</td>
</tr>
</tbody>
</table>

A newly designed sealed photoreactor was then used to perform heterogeneous photocatalysis with the semiconductor particles suspended in CO$_2$ saturated water. The lamp (400 W medium-pressure Hg arc encased in Pyrex glass, photon flux: 235 mW/cm$^2$) was turned on and the gaseous products evolved were analyzed by gas chromatography (GC SRI 310) as a function of the illumination time using a Shin Carbon column and a thermal conductivity detector.

Best samples for photoreduction of CO$_2$ are the SCS-derived AgBiW$_2$O$_8$ powders which are able to perform the photocatalytic generation of syngas followed the principle outlined in Figure 7a. The rationale for using formate ions as the in situ precursor for CO$_2$ was two-fold. The direct electroreduction of CO$_2$ in aqueous media is beset both by the low partial pressure of CO$_2$ in the atmosphere (5.9 x 10$^{-4}$ atm) and by its low solubility in water (1.5 g/L at
298 K) [8]. On the other hand, formate species have high solubility in water (945 g/L at 298 K) [9]; they have high proclivity for being adsorbed on oxide surfaces and are easily photoconverted to CO$_2$ (Figure 7a). The in situ generated CO$_2$ can be subsequently reduced by the photogenerated electrons in the oxide particle. For the simultaneous photogeneration of H$_2$, the photogenerated electrons must be stored on the oxide surface in noble metal catalyst (e.g., Pt) islands [10]. Thus, the AgBiW$_2$O$_8$ particles were loaded with 1 mass% Pt using a photocatalytic procedure described elsewhere [11]. After surface modification with Pt, the color of the oxide particles changed significantly from light yellow to a grayish hue as illustrated in Figure 6 (insert). The diffuse reflectance spectra also changed consequently as also shown in Figure 6 (insert). Thus, we envision that the portion of the photogenerated electrons channeled toward the Pt catalyst islands would reduce protons to hydrogen while those that diffuse to the (naked) oxide surface would be utilized for the reduction of CO$_2$ to CO (Figure 7a).

The Pt-modified AgBiW$_2$O$_8$ particles were loaded into the photoreactor containing a de-aerated solution of 0.1 M HCOOH at a dose of 2 g/L. Figure 7b illustrates the temporal profiles of the three products of the overall photocatalytic reaction, namely, H$_2$, CO and CO$_2$. It is worth noting that the first products to be seen are the generation of CO$_2$ and H$_2$ from the oxidation of HCOOH using the photogenerated holes from the semiconductor valence band and the reduction of H$^+$ through photogenerated electrons in the conduction band of AgBiW$_2$O$_8$, respectively. The (subsequent) formation of CO tracks the in situ photogeneration of CO$_2$ at or near the particle surfaces. The run was terminated at 225 min at which time the gases accumulated were as follows: H$_2$ = 1.0 x 10$^2$ mol/gL, CO = 3.0 x 10$^{-3}$ mol/gL and CO$_2$ = 2.8 x 10$^2$ mol/gL. These data are reported as the number of moles of product divided by the photocatalyst mass and liquid volume in the photoreactor. Quantum yields for the formation of syngas (H$_2$+CO) and CO$_2$ in the formic acid solution amount to H$_2$ = 5.0 %, CO = 0.8 % and CO$_2$ = 4.5 %.

**Conclusions and Future Directions**

Our findings in Task 1 show that properly designed RPCs can act as a homogeneous photocatalyst or electrocatalyst for CO$_2$ reduction to methanol. This proof of concept now needs to be refined and optimized to determine the efficiency of the process. Ultimately, we would need to couple the reductive process with a more practical oxidative process, for example water oxidation, to construct a practical system for solar fuel generation.

Our findings in Task 2 show that among the three heterogeneous photocatalysts, the Pt-modified AgBiW$_2$O$_8$ is capable of performing CO$_2$ photoreduction. The data described is a useful proof-of-concept for the following:

(a) AgBiW$_2$O$_8$ can be simply and quickly prepared by SCS;
(b) A mild photocatalytic procedure for syngas generation can be developed based on the use of formate ions as an in situ precursor for CO$_2$, and (c) The SCS-derived AgBiW$_2$O$_8$ powder, after Pt surface modification, can generate syngas via this procedure. Ultimately, better performances can be expected by optimizing the amount of Pt on the semiconductor nanoparticles and by using solvent mixtures of DMF/water and MeCN/water to enhance CO$_2$ solubility in the liquid phase.

**References**


