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Final Report: CO_2 Reduction Using Biomimetic Photocatalytic Nanodevices

Yujiang Song, Robert M. Garcia, Zhongchun Wang, Craig J. Medforth, Haorong Wang, John A. Shelnutt and James E. Miller

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Final Report: CO_2 Reduction Using Biomimetic Photocatalytic Nanodevices

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Abstract

Nobel Prize winner Richard Smalley was an avid champion for the cause of energy research. Calling it "the single most important problem facing humanity today," Smalley promoted the development of nanotechnology as a means to harness solar energy. Using nanotechnology to create solar fuels (*i.e.,* fuels created from sunlight, CO_2, and water) is an especially intriguing idea, as it impacts not only energy production and storage, but also climate change. Solar irradiation is the only sustainable energy source of a magnitude sufficient to meet projections for global energy demand. Biofuels meet the definition of a solar fuel. Unfortunately, the efficiency of photosynthesis will need to be improved by an estimated factor of ten before biofuels can fully replace fossil fuels. Additionally, biological organisms produce an array of hydrocarbon products requiring further processing before they are usable for most applications. Alternately, "bio-inspired" nanostructured photocatalytic devices that efficiently harvest sunlight and use that energy to reduce CO_2 into a single useful product or chemical intermediate can be envisioned. Of course, producing such a device is very challenging as it must be robust and multifunctional, i.e. capable of promoting and coupling the multi-electron, multi-photon water oxidation and CO_2 reduction processes. Herein, we summarize some of the recent and most significant work towards creating light harvesting nanodevices that reduce CO_2 to CO (a key chemical intermediate) that are based on key functionalities inspired by nature. We report the growth of Co(III)TPPCl nanofibers (20-100 nm in diameter) on gas diffusion layers via an evaporation induced self-assembly (EISA) method. Remarkably, as-fabricated electrodes demonstrate light-enhanced activity for CO_2 reduction to CO as evidenced by cyclic voltammograms and electrolysis with/without light irradiation. To the best of our knowledge, it is the first time to observe such a light-enhanced CO_2 reduction reaction based on nanostructured cobalt(III) porphyrin catalysts. Additionally, gas chromatography (GC) verifies that light irradiation can improve CO production by up to **31.3%** during 2 hours of electrolysis. In addition, a variety of novel porphyrin nano- or micro-structures were also prepared including nanospheres, nanotubes, and micro-crosses.

Table of Contents

List of Figures

1.0 Introduction

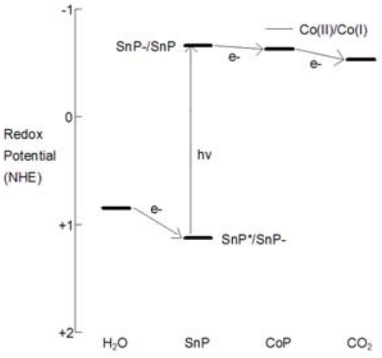

Figure 1. ***Energetics of CO_2 reduction to CO, and the cobalt porphyrin electrocatalyst and the tin porphyrin photocatalyst.***

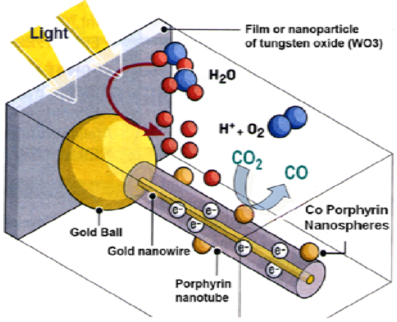

Figure 2. ***A porphyrin nanotube-metal-semiconductor composite nanodevice for conversion of CO_2 to CO as shown in Fig. 1. Several of the required components (SnP nanotubes, gold nanowire and ball, and Co-porphyrin nanospheres) have been self-assembled as separate components or nanocomposites.***

Nanotechnology offers new opportunities for harnessing solar energy to create carbon-based fuels from CO_2, a process that impacts energy production and storage as well as climate change. Bio-inspired photocatalytic nanodevices that efficiently harvest sunlight and efficiently reduce CO_2 into a single useful product or chemical intermediate were envisioned in this project. Producing such a multifunctional robust nanodevice is very challenging since it must promote and couple the multi-electron, multi-photon water oxidation and CO_2 reduction processes. We have studied a series of approaches leading to nanodevices that harvests sunlight to reduce CO_2 to CO, which is a useful intermediate that can produce liquid fuels by known reactions. A number of organometallic compounds, including metal derivatives of porphyrins and cyclams, have been shown to have activity for CO_2 reduction. The energetics of photo-assisted CO_2 reduction using the systems we have investigating (Fig. 1) involve a tin(IV) porphyrin (SnP) photocatalyst absorbing a photon of visible light and forming the triplet excited state of the porphyrin (SnP*). SnP* can be reduced at an electrode or by an electron donor such as water (producing O_2). The resulting long-lived π-anion radical of the porphyrin ($SnP^{-\cdot}$) can reduce a cobalt porphyrin (CoP) to the Co(I) species, which can then catalyze the CO_2 to CO reaction. Our target product for the reduction of CO_2 is CO for several reasons, including its versatility (*e.g.*, CO can be converted to alcohols, ethers, or used as an intermediate to produce oxygenates or H_2), it can be selectively produced, and it can be easily recovered as the gaseous product. The other half-reaction is the oxidation of water to O_2, which is a multiple electron process requiring a strong oxidant. This could for example be provided by one of a number of inorganic photocatalysts such as WO_3, a semiconductor that is known to effectively oxidize water to O_2 when photoexcited to form an electron-hole pair. Although the electrons in the conduction band of WO_3 cannot reduce CO_2, they can reduce the excited Sn porphyrin (Fig. 1). An example of a potential nanoscale device that couples WO_3 electrically to a porphyrin-based photocatalyst to yield a 2-step system for oxidizing water and reducing CO_2 is illustrated in Figure 2. Previous Sandia successes lay the groundwork to create just such devices. The photocatalytic materials used here are self-assembled porphyrin nanostructures such as nanotubes, nanofiber bundles, nanospheres, and nanosheets that have been developed at Sandia. Co or Ni porphyrin (CoP or NiP) electrocatalysts were designed, synthesized, and structurally and electrochemically characterized for the purpose of refining their electrocatalytic properties. In parallel, Sn-porphyrin photoelectrocatalytic nanostructures were developed as a light-harvesting component. The promising porphyrin-based electrocatalysts were then coupled with or incorporated into the photoactive systems and characterized for their ability to perform light-assisted reduction of CO_2 (evolve CO). For the work described here, the water-oxidation (O_2-evolution) half-reaction was decoupled initially through the use of an electrode or a sacrificial reductant. This staged and iterative approach was considered to provide the greatest possibility of achieving our ultimate goal of eventually producing a fully functional nanodevice and provided a means for achieving and measuring success along the way.

2.0 Accomplishments

The research milestones revolved around two primary interconnected activities: (a) designing and fabricating photocatalytic nanomaterials for binding and reducing CO_2, and (b) the more complex task of incorporating these nanocatalysts into a complete light-harvesting devices.

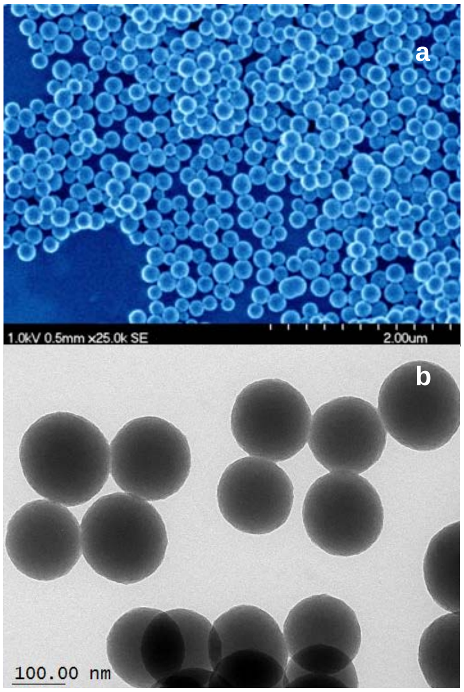

Figure 4. ***SEM image of*** **CoTPyP** ***nanospheres (a); TEM image*** **SnTPyP** ***nanospheres (b).***

2.1 Nanocatalyst Preparation

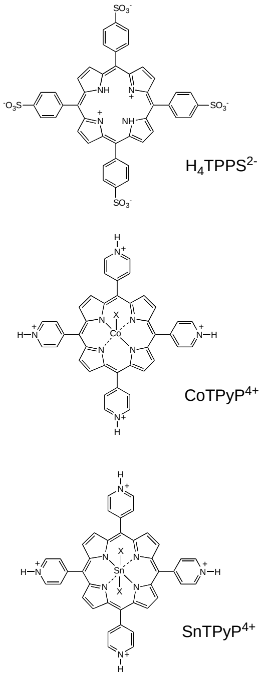

Figure 3. ***Porphyrin subunits used to prepare the nanotube electrocatalysts and photoelectrocatalysts.***

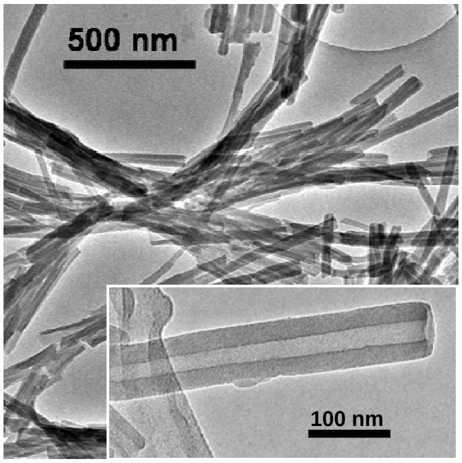

Figure 5. ***TEM image of*** **SnTPyP^{4+}-H$_4$TPPS^{2-}** ***nanotubes.***

In late FY07 and early FY08, we synthesized porphyrin-based nanostructures for use in preparing nanostructured electrodes. These first goals of this late-start project were accomplished by synthesizing new porphyrin molecules and porphyrin nanostructures. For example, the compound tetrakis(4-piperidyl)porphyrin was synthesized for the first time by John Jacobsen (UC Davis), providing a tecton for making porphyrin-based nanotubes and nanospheres that are stable over the pH range used in CO_2 reduction. Nanocatalysts for CO_2 conversion that are composed of Co porphyrin (CoP) subunits were prepared, an example being the CoP nanospheres made from CoTPyP that are shown in the SEM image of Figure 4a. These nanospheres were prepared by metal-ion-induced polymerization, *i.e.*, the porphyrin molecules are linked together through their pyridyl substituent groups by coordination to Pt^{4+} ions. The potential use of these Co nanospheres is illustrated in Figure 2, which illustrates a CO_2-reducing nanodevice. We have also prepared porphyrin nanotubes from the self-assembly of SnTPyP^{4+} and H$_4$TPPS^{2-} subunits (Fig. 5) and even hybrid porphyrin nanotubes (not shown) containing both $CoTPyP^{4+}$ and $SnTPyP^{4+}$ subunits along with H_4TPPS^{2-}; in the latter tubes, the $SnTPyP^{4+}$ photocatalyst is expected to use visible light energy to boost the reduction potential of electrons to the level necessary to reduce the $CoTPyP^{4+}$ molecules in the tubes to the catalytically active Co(I) species that does the CO_2 reduction.

In addition, we have prepared pure Sn-porphyrin nanostructures such as the SnP nanospheres in Figure 4b and the nanotube in Figure 5 with the intention of hierarchically organizing the separate Sn-porphyrin light-harvesters on the electrode with the Co-porphyrin nanocatalysts for CO_2 conversion. We have prepared additional pure Co and Sn porphyrin nanocatalysts and photocatalysts by a variety of synthetic methods (see below).

2.2 Baseline Catalytic Electrode

Co-porphyrin-modified electrodes were prepared for comparison with electrodes made with CoP nanostructures. The porphyrin (coated) electrodes were prepared by simply adsorbing Co tetraphenylporphyrin (CoTPP) onto a gas diffusion electrode (GDE) from a CoTPP solution. As the morphology of the adsorbed porphyrin material was unknown previously, the structure of the porphyrin electrode was studied by electron microscopy. Figure 6a shows the nanoscale carbon/Teflon particles of the bare electrode, and Figure 6b shows the electrode after adsorption of CoTPP. Clearly, replacing the observed crystallites of CoTPP with CoP nanostructures will greatly increase active surface area and more effectively utilize the porphyrin material.

We also obtained electrochemical data using the CoTPP-modified GDE, which shows a strong increase in current in the presence of CO_2 but not with Ar. In addition, CO is measured in the gas stream, confirming we have the desired product for the CoTPP-modified GDE. This data serves as a reference point against which the more elaborately nanostructured CoP electrocatalysts and the SnP/CoP photoelectrocatalytic systems can be evaluated.

2.3 Nanostructured Electrodes Based on SnP

The photoelectrocatalytic performance of glassy carbon electrodes modified with SnP nanospheres has been evaluated. Our early success in these experiments with the SnP nanospheres demonstrates the feasibility of photo-assisted electrocatalytic conversion using the SnP nanostructures. Although this was one of the most risky aspects of the proposed work, it turns out that successful coupling of the light-harvesting function with the catalytic production of fuel gases is possible. The SnP nanospheres were prepared by mixing an aqueous solution of 43-μM SnTPyP chloride with 200 mM chloroplatinic acid and leaving the solution undisturbed for 24 h. The SnP nanospheres were washed with water and then mixed with 0.2 M $NaBH_4$ for 4 h to reduce platinum ions near the surface to create a sparse surface layer of Pt metal nanoparticles. Figure 7 shows the platinized nanospheres that were applied to the cleaned glassy carbon electrode. The platinized porphyrin spheres were added to 200 L of a DMF solution containing anthracene-9-carboxylic acid (1 mM) as an energy-acceptor/electron-transfer mediator, and Nafion (0.25%) for casting onto a previously cleaned glassy carbon electrode and dried in air.

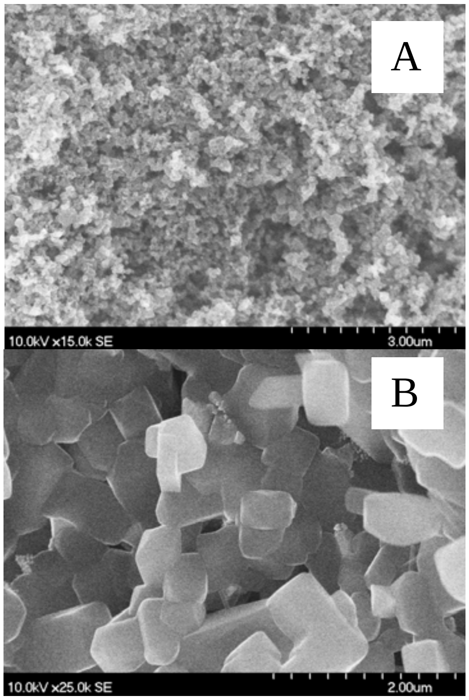

Figure 6. ***SEM images of the bare (a) and modified (b) GDE showing the CoTPP crystals on the carbon surface.***

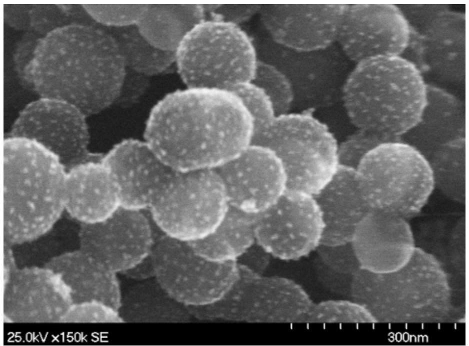

Figure 7. S***EM image of platinized Pt^{4+}-SnTPyP nanospheres showing Pt particles on surface.***

The inset in Figure 8 shows the current generated as visible light is switched on and off for this SnP-nanosphere-modified electrode. The potential of the electrode is set in the range of -0.05 V versus Ag/AgCl, a potential less negative by 0.35 V than the thermodynamic potential required to evolve H_2. Yet, when the electrode is irradiated by white light, a photocurrent is generated. Gas chromatography of the gas in the head space shows that under continuous illumination the amount of H_2 increases with time, while when left in the dark or with an unmodified electrode no H_2 is produced under these conditions. These experiments clearly demonstrate that SnP nanostructures can photoelectrochemically produce a gaseous fuel.

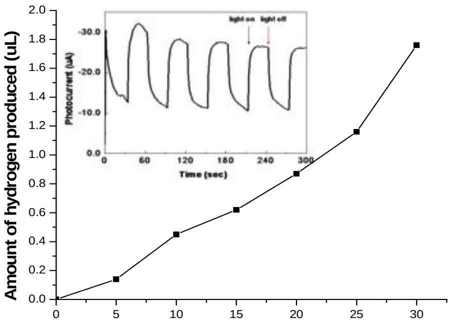

Figure 8. ***H_2 evolved by the platinized Pt^{4+}-SnTPyP nanospheres cast onto a glassy carbon electrode when irradiated by visible light. Inset: current generated when light is switched on and off.***

2.4 Nanostructured Electrodes Based on CoP

After many trials to optimize synthetic parameters, we have developed an unprecedented strategy to grow Co(III) tetraphenylporphyrin (Co(III)TPP) nanostructures on gas diffusion layer. In a typical synthesis, a porphyrin stock solution was prepared by mixing 2 mg of Co(III)TPP powder with 5 mL of ethanol under ultra-sonication. Next, the stock solution was sprayed onto a gas diffusion layer (5 cm^2 of geometrical surface area) at a rate of 10 mL/h. During the process of spraying, the gas diffusion layer was placed on a hot plate at 120 ºC to accelerate the evaporation of solvent and to avoid flooding. Figure 9 shows that Co(III)TPP nanofibers embedded in carbon nanoparticles of GDL were obtained. These nanofibers normally range from 20 to 100 nm in diameter and can be up to several microns in length. Because of the nanostructured features, the nanofibers are expected to possess a relatively high surface area and effectively catalyze CO_2 reduction. To the best of our knowledge, this is the first time nanostructured CoP capable of electrochemically reducing CO_2 (see below) was ever produced on a GDL.

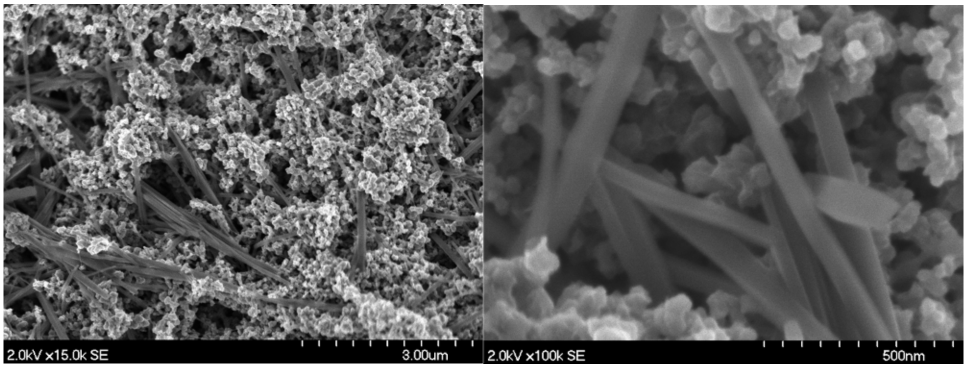

Figure 9. ***SEM images of Co(III)TPP nanofibers embedded in carbon nanoparticles of a GDL at (a) low and (b) high magnifications.***

2.5 Electrochemical Characterization of Nanostructured CoP Electrodes

The CoP nanofiber-modified GDL was examined as the working electrode in a typical three-electrode electrochemical cell (Fig. 10) with Ag/AgCl as the reference electrode and platinum wire as the counter electrode. The temperature of the electrochemical cell was maintained roughly at room temperature by continuously flowing water through the water jacket. The electrolyte used in the measurements is a freshly prepared $KHCO_3$ aqueous solution (100 mL, 0.5 M). Argon was purged through the electrolyte for at least 45 minutes before measurements to remove dissolved oxygen from the solution.

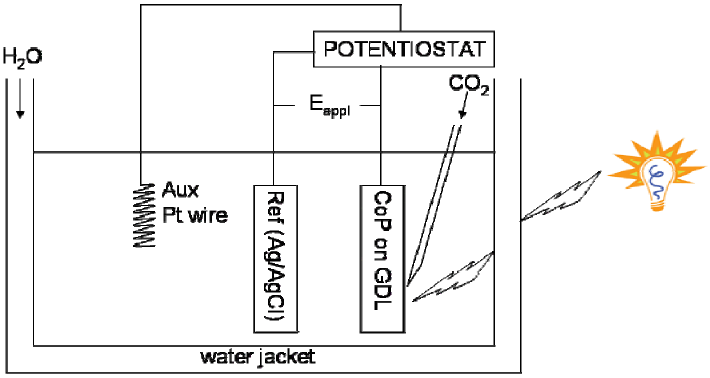

Figure 10. ***A scheme of the three-electrode electrochemical cell combined with water jacket for temperature control and light source for irradiation.***

A potential sweep (0 to -2000 mV *vs.* Ag/AgCl) was conducted at a rate of 10 mV/s in the atmosphere of argon. Following this, the electrolyte was saturated with CO_2 by purging gaseous CO_2 for at least 45 minutes. Next, a potential sweep (0 to -2000 mV vs. Ag/AgCl, 10 mV/S) was conducted with and without white light irradiation (800 nmol cm^{-2} s^{-1}).

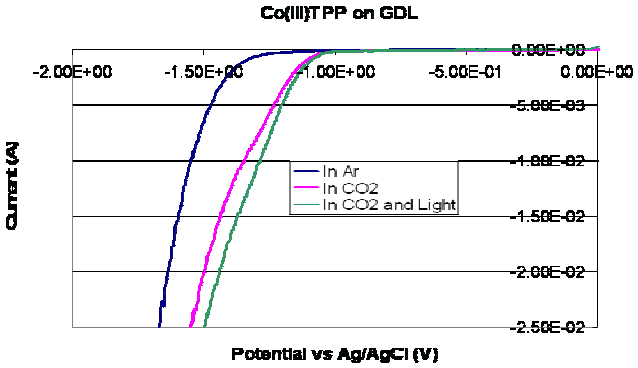

Figure 11. ***Current-potential curves for CoP nanofiber-decorated GDL in argon under room light irradiation (blue), in CO_2 under room light irradiation (pink), and in CO_2 under white light irradiation (green); (0.5 M $KHCO_3$, 10 mV/s sweep rate).***

Figure 11 shows the voltammetric response of the GDL decorated by CoP nanofibers under argon and carbon dioxide atmosphere with room light or white light irradiation. Under argon atmosphere and room light, the current remains very low at potentials below 1.4 V, consistent with the absence of CO_2 reduction. In contrast, under carbon dioxide atmosphere and room light, the current rapidly increases above 1.1 V due to electrochemical reduction of carbon dioxide catalyzed by CoP nanofibers. Surprisingly, under carbon dioxide atmosphere and white light irradiation the reduction current of CO_2 can be significantly enhanced. This phenomenon of light-enhancement for CoP has not been observed before. Our observation demonstrates that visible light is able to enhance the electrochemical reduction of CO_2, indicating an alternative avenue of solar energy conversion and storage. It is worth noting that the temperature of the cell is controlled by flowing water through the water jacket so that the improvement of CO_2 reduction current may not be related to a plausible temperature effect. However, it is not clear what the mechanism is causing the photo-enhancing effect. Additional studies will be required to gain more understanding on the mechanism of light-enhancement.

2.6 Verification of Light Response

The observed light enhancement may lead to a new type of solar technology; we determined to further confirm that this is clearly a light effect. To accomplish this task, we applied a constant voltage (-1.3 V *vs.* Ag/AgCl) to the CoP nanofiber-modified GDL using the same three-electrode electrochemical cell under carbon dioxide atmosphere. The black GDL is made of carbon nanomaterials and is subject to heating through light adsorption. To minimize the temperature variation during light irradiation, water was continuously flowed through the water jacket. As shown in Figure 12, the CO_2 reduction current rapidly increased by more than 2.5 mA when the light source was switched from diffuse room light to intense white light. Conversely, when the light was switched from intense white light to diffuse room light, the CO_2 reduction current rapidly decreased by the same amount. In other words, the current fluctuation is reversible and controllable by white light irradiation. This is evident that the CO_2 reduction based on CoP nanofibers-modified GDL is photo-responsive and can be significantly enhanced by white light irradiation. There are several factors that may contribute to the light effect, including better CO_2 adsorption and CO desorption, easier axial ligand dissociation from the central cobalt, more efficient formation of intermediate state of CoP necessary for CO_2 reduction, lowered resistance of CoP nanofibers. A heating effect from light absorption by carbon can also not entirely be ruled out, although we believe that it would have to be a very localized effect. Experiments to quantify a potential temperature effect are planned.

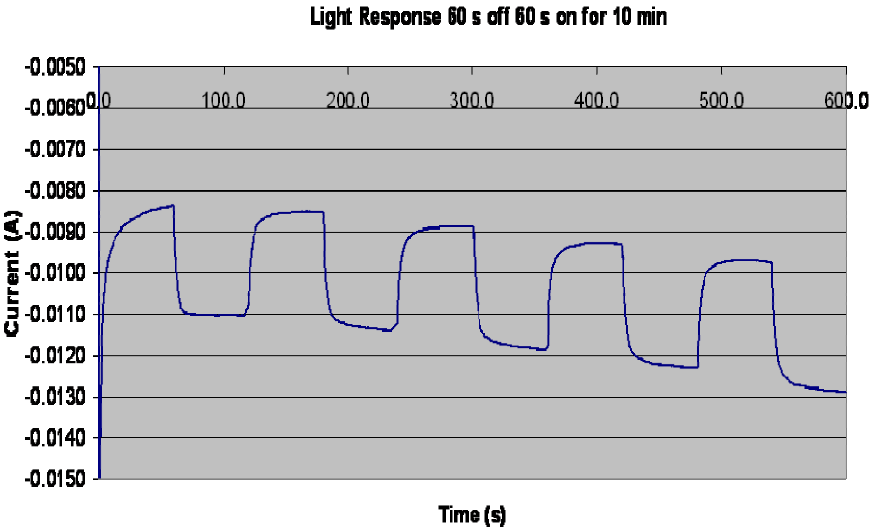

Figure 12. ***Current response to alternating room light (0.5-2.0 nmol cm^{-2} s^{-1}) and white light irradiation (800 nmol cm^{-2} s^{-1}) for ten minutes.***

2.7 Enhanced CO production

Given the fact that white light can enhance the CO_2 reduction in terms of reduction current, we expect to produce more CO under white light irradiation compared with room light irradiation. After bubbling of CO_2 for saturation, all the ports of the three-electrode electrochemical cell were well sealed to create a closed system. With and without white light irradiation, a constant voltage (-1.3 volts vs. Ag/AgCl) was applied to the CoP nanofibers-decorated GDL for electrocatalytic reduction of CO_2 for 2 hours. Gas chromatography (GC) (HP 5890 Series II instrument controlled by HP ChemStation, version A0701 software, Gaithersburg, MD) was used to quantify the CO gas produced electrocatalytically by the CoP nanofibers. The GC instrument was calibrated before the measurements by adding known amounts of CO. All gas samples (typically 500 µL) were extracted from the head space of reaction vessel and were manually injected with a syringe onto a 45/60 Mode SIEVE 5A column (9 feet length, 1/8 inch width) and carried by helium at a constant flow rate of about 70 cm^3 min^{-1} to a thermal conductivity detector operating at 170 °C. The retention time for hydrogen was about 2.1 min.

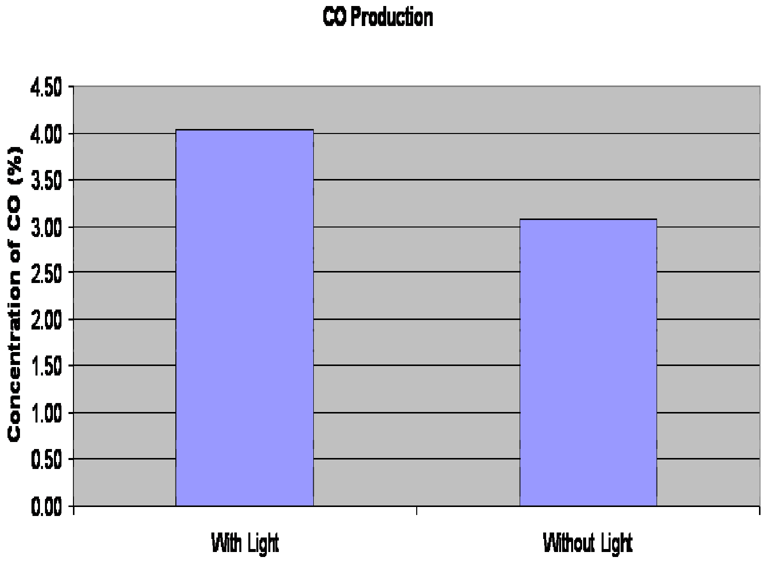

Figure 13. ***Concentration of CO in the head space of the electrochemical cell with and without white light irradiation.***

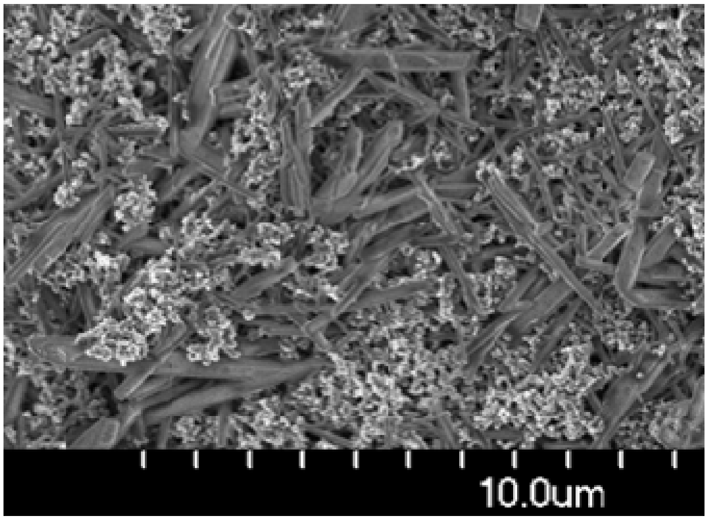

Figure 14. ***SEM image of CoP nanofibers after more than 4 hours of electrolysis.***

Figure 13 shows that under white light irradiation the CO production can be enhanced by 31.3% as expected. This may be a new way to store solar energy and a more efficient way to reduce CO_2 to CO. It is worth noting that after more than 4 hours of electrolysis, the CoP nanofibers appear to be structurally stable as shown in Figure 14. If possible, the structural stability will be further investigated in an elongated electrolysis time period in that the stability/durability of electrocatalyst is a key feature that should be paid attention to.

2.8 Ionic Co-assembly of Positively Charged CoP with Negatively Charged ZnP

It is well known that physical and chemical properties of nanomaterials are closely related to their size, shape, and composition. In this regard, we have successfully applied a novel ionic self-assembly strategy recently developed in our group to create micro-crosses composed of positively charged Co(III)N(EtOH)PyP and negatively charged Zn(II)TPPS4 at 1:1 molar ratio (Fig. 15). Remarkably, these micro-scale crosses possess interesting nanofeatures with pores in the range of 30- to 300 nm separated by typical 30-nm wide walls among one another.

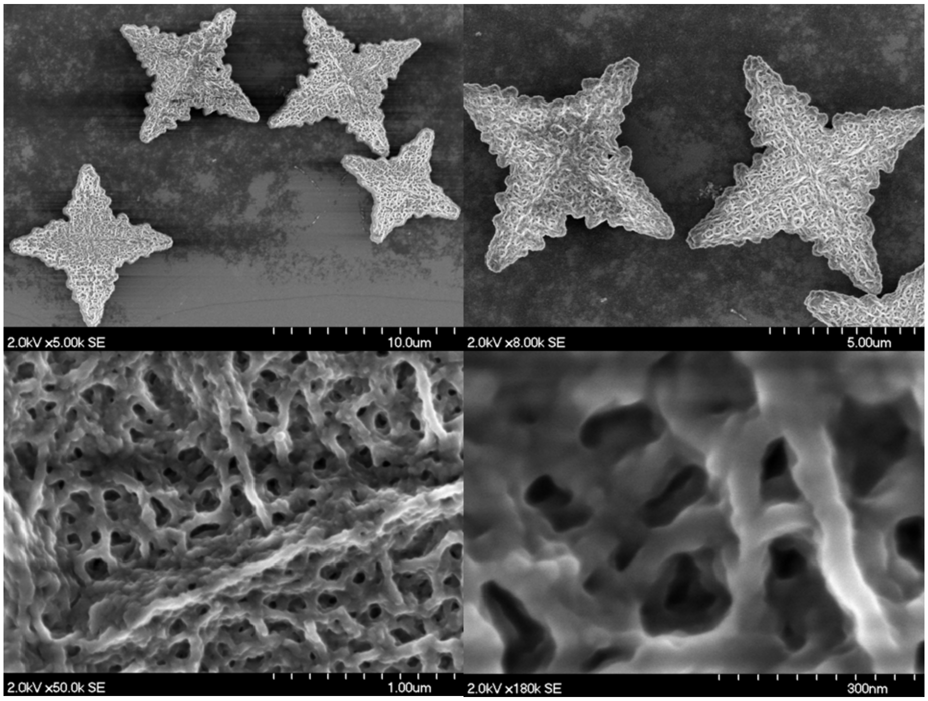

Figure 15. ***SEM images of micro-crosses with nano-features prepared by ionic co-assembly of positively charged Co(III)N(EtOH)PyP and Zn(II)TPPS4 at different magnifications .***

The nanofeatures are expected to lead to a relatively high surface making the micro-crosses efficient electrocatalyst. Since one porphyrin component of the crosses is CoP that is active for electro-catalytic reduction of CO_2, the micro-crosses should be also active for catalytic conversion of CO_2 to CO. Additionally, the other porphyrin species in the crosses is ZnP that is photocatalytic and can be excited by UV or visible light and gives out an electron as an electron donor. It is anticipated that under UV or visible light irradiation the onset potential of CO_2 reduction by CoP would be shifted from -895 mV (*vs.* RHE) to a more positive value, since the excited ZnP* molecules may reduce Co(III)P to Co(I)P instead of electrons provided by an electrode.

3.0 Educational Activities

In addition to the scientific achievements, we engaged in interactions with educational institutions throughout the project. These interactions were essential to the successful outcome of this project and to foundational efforts associated with Sandia's National Institute for Nano-Engineering initiative. High school, undergraduate, graduate, and post-doctoral students were hired to work on the synthesis and electrochemical studies of porphyrin-nanostructure-based electrocatalysts and photo-electrocatalysts. Many of these students have used this experience as a bridge to greater achievement. Kathleen Martin began working on this project as a high school student at Albuquerque Institute of Mathematics and Science (AIMS) and is now an undergraduate at UNM. Students from UNM include Leslie Lybarger who is now a graduate student at Georgia Tech, Robert Garcia who became a graduate student at UNM and is now employed directly by Sandia, and Rachel Dorin who is now a graduate student at Cornell. John Jacobsen began working with Sandia as an undergraduate at UC-Davis in the laboratories of Dr. Neil Schore and is now a graduate student at UC Davis; his thesis work is based on this project. Another UC-Davis graduate student (Christine Beavers) has worked with Professor Medforth on the synthesis and characterization of novel Co and Ni porphyrins for use in making nanostructures for the project. Others include Folusho Ajayi (now at Gwangju Institute of Science and Technology, Dr. Zhongchun Wang (now at Soladigm), and Dr. Haorong Wang (now employed in California).

4.0 Publications

The following peer-reviewed publications resulted in part from this project. Additional publications are in preparation.

Self-Assembled Porphyrin Nanostructures, Medforth, C. J.; Wang, Z.; Martin, K. E.; Song, Y.; Jacobsen, J. L.; Shelnutt, J. A., *Chem. Commun.* **2009**, DOI:10.1039/B914432C.

Monodisperse Porphyrin Nanospheres Synthesized by Coordination Polymerization, Wang, Z.; Lybarger, L. E.; Wang, W.; Medforth, C. J.; Miller, J. E.; Shelnutt, J. A., *Nanotechnology* **2008**, *19*, 395604.

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