

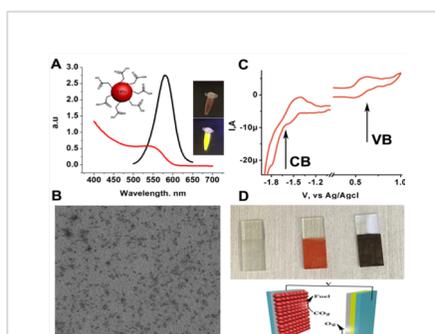
PRF #: 56999-ND10

Title: Developing Photocatalytic Assemblies for CO<sub>2</sub> Reduction

PI: Jennifer N. Cha, University of Colorado, Boulder

Co-PI: Charles B. Musgrave, University of Colorado, Boulder

The focus of the proposed research is to design, engineer, and evaluate reaction cascades to produce alternative chemicals for petroleum technologies from carbon dioxide and water. In the first year we demonstrated a simple method to construct CO<sub>2</sub>-reducing PECs that can generate formate and methanol at neutral pH. These cells were composed of CdS/NiOx photoanodes and NiO/CdTe or CuFeO<sub>2</sub>/CuO cathodes (Figure 1). UV-Vis absorbance measurements showed that the CdS/NiOx and CuFeO<sub>2</sub>/CuO electrodes strongly absorb in the visible. Next, the photoelectrochemical responses of the CdS/NiOx and CuFeO<sub>2</sub>/CuO electrodes were measured under CO<sub>2</sub> atmosphere. The CdS/NiOx electrodes showed an anodic photocurrent with onset at -0.8 V vs. Ag/AgCl, with a maximum current at -0.35 V while the CuFeO<sub>2</sub>/CuO electrode showed an onset cathodic current at 0.1 V with maximum current at -0.4 V vs Ag/AgCl. PECs were next built from the CdS/NiOx and



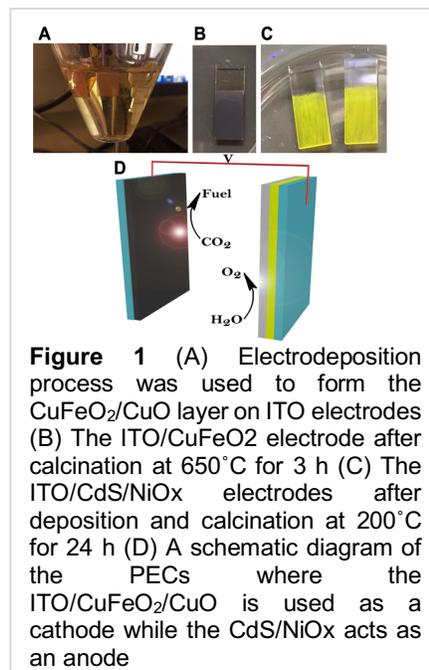
**Figure 2.** CdTe photocathode fabrication (A) UV/Vis absorbance and fluorescence of the 3.5nm thioglycolic acid capped CdTe nanoparticles (B) TEM of the as prepared CdTe NPs showed an average size of 3.5 nm (C) Band gap edges of the CdTe nanoparticles were determined to be approximately +0.56 V and -1.53 V vs. Ag/AgCl respectively. (D) Optical images of the prepared NiO/CdTe electrode

CuFeO<sub>2</sub>/CuO photoelectrodes and upon photoillumination with 465 ± 30 nm light emitting diode light for each electrode, an open circuit voltage of ca. 1 V was observed. A second photocathode of NiO/CdTe was also fabricated and tested with the CdS/NiOx

photoanode (Figure 2). The NiO/CdTe photocathodes were then coupled with the CdS/NiOx photoanodes to form the second type of autonomous PEC tested for CO<sub>2</sub> reduction. The photoelectrochemical responses of the NiO/CdTe electrodes were also measured under Ar or CO<sub>2</sub> atmosphere which showed a cathodic photocurrent onset at 0 V vs. Ag/AgCl, with a maximum current at -0.5 V. By assembling the NiO/CdTe cathode with the CdS/NiOx anode an OCV of ca. 0.7 V was obtained. The semiconductor electrodes showed limited stability, which effected the total fuel conversion gained.

Using either the CuFeO<sub>2</sub>/CuO or NiO/CdTe photocathodes, PECs were next fabricated with the CdS/NiOx photoanodes. In order to test the PECs for CO<sub>2</sub> reduction, <sup>12</sup>C or <sup>13</sup>C labeled CO<sub>2</sub> was introduced under vacuum into

a single or 3-electrode compartment PEC chamber. After 17 h photoirradiation with 465 nm light, a combination of electrospray ionization (ESI) and <sup>1</sup>H NMR was utilized to analyze the products formed. In the first studies, in the presence of <sup>12</sup>C CO<sub>2</sub>, after photoirradiation, we were able to determine from NMR analyses that 60 μM formate could be produced from the CuFeO<sub>2</sub>/CuO//CdS/NiOx PEC. By biasing the CuFeO<sub>2</sub>/CuO PEC by using Pt as counter electrodes and passing 17C through the cathode, a significantly higher amount of formate could be produced reaching 0.4 mM which equals to approximately 6.81% electron to formate efficiency. Replacing the CuFeO<sub>2</sub>/CuO cathode with the NiO/CdTe led to lower amounts of CO<sub>2</sub> photoreduction, where in unbiased experiments, the NiO/CdTe photocathodes generated ~5-10 μM of formate. Biasing the NiO/CdTe electrode could only slightly increase the total amount of formate to ~27 μM which equals to 0.5% efficiency (Table 1).

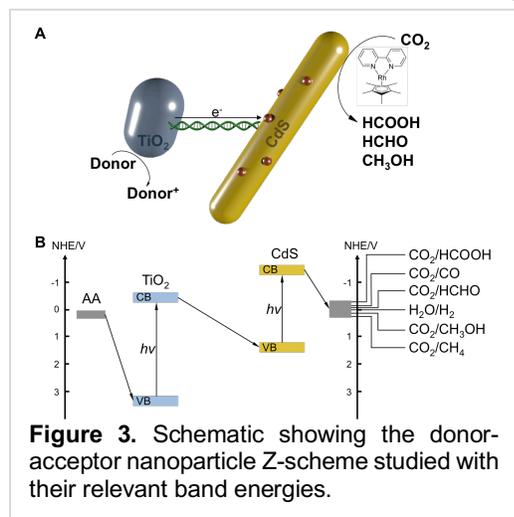


**Figure 1** (A) Electrodeposition process was used to form the CuFeO<sub>2</sub>/CuO layer on ITO electrodes (B) The ITO/CuFeO<sub>2</sub> electrode after calcination at 650°C for 3 h (C) The ITO/CdS/NiOx electrodes after deposition and calcination at 200°C for 24 h (D) A schematic diagram of the PECs where the ITO/CuFeO<sub>2</sub>/CuO is used as a cathode while the CdS/NiOx acts as an anode

Electrode	Unbiased	Biased	Unbiased+CpRhbpPyCl <sub>2</sub>	Biased+CpRhbpPy
NiO/CdTe	~5-10μM	27μM	400μM	2.3mM+10μM methanol
CuFeO <sub>2</sub> /CuO	60μM	400μM	180μM	812μM

**Table 1.** Data showing the amounts of formate and methanol produced from the photoelectrochemical cells.

Next, in order to study the use of an organohydride with the PECs, we tested the utilization of  $\text{CpRh}(\text{bpy})\text{Cl}_2$  as a co-catalyst. By using  $\text{CpRh}(\text{bpy})\text{Cl}_2$  as a co-catalyst, much higher amounts of  $\text{CO}_2$  reduction were observed from the  $\text{NiO}/\text{CdTe}$  photocathodes as compared to the  $\text{CuFeO}_2/\text{CuO}$  which is summarized in Table 1. As demonstrated, NMR analysis showed that the unbiased PECs in the presence of  $\text{CpRh}(\text{bpy})\text{Cl}_2$  could yield  $400 \mu\text{M}$  and  $187 \mu\text{M}$  formate from the  $\text{NiO}/\text{CdTe}$  and  $\text{CuFeO}_2/\text{CuO}$  respectively. Therefore, in the presence of  $\text{CpRh}(\text{bpy})\text{Cl}_2$ , the unbiased  $\text{NiO}/\text{CdTe}$  PEC showed a 40-fold increase in product yield as compared to the unbiased  $\text{NiO}/\text{CdTe}$  PEC with no organocatalyst. In direct contrast, the  $\text{CuFeO}_2/\text{CuO}$  system showed little improvement with only a 3-fold increase in formate. Furthermore, with the biased  $\text{NiO}/\text{CdTe}/\text{CpRh}(\text{bpy})\text{Cl}_2$  PECs we could also detect  $10 \mu\text{M}$  methanol being generated in addition to the  $2.3 \text{ mM}$  formate. This work was published in *ChemSusChem* in 2016.



**Figure 3.** Schematic showing the donor-acceptor nanoparticle Z-scheme studied with their relevant band energies.

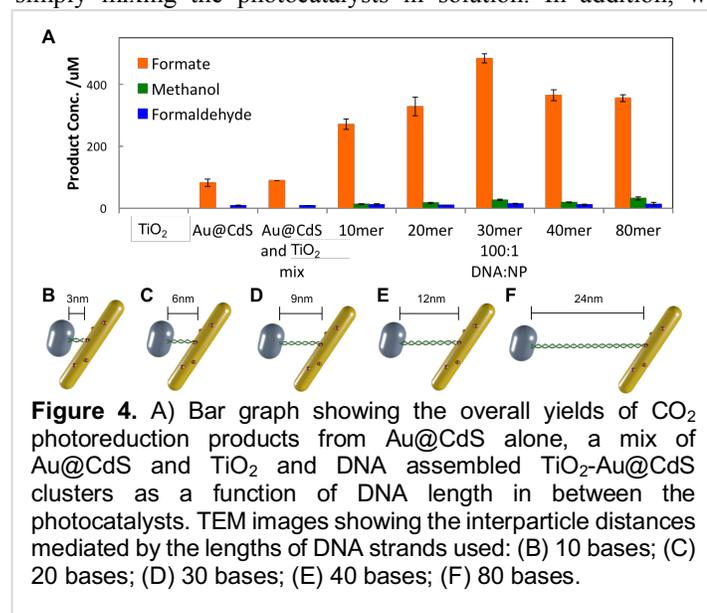
reduction reactions are run on separate catalytic sites, the stability of each photoactive nanoparticle increases. In this work, donor ( $\text{TiO}_2$ ) and acceptor ( $\text{CdS}$ ) nanocrystals were self-assembled (Figure 3) using DNA and these yielded a 5.25-fold improvement in  $\text{CO}_2$  reduction over simply mixing the photocatalysts in solution. In addition, we demonstrated that electron transfer occurs over distances far greater than those achieved with other spacers such as polymers. Efficient Z-scheme photocatalytic reduction of  $\text{CO}_2$  was observed for DNA lengths of 10 to 80 bases, which separate the donor and acceptor nanocrystals by 3 to 24 nm (Figure 4). More significantly, an interparticle distance of 9-10 nm yielded the highest conversion of  $\text{CO}_2$ . When the amount of 30mer DNA linking the photocatalysts was lowered, a corresponding decrease in  $\text{CO}_2$  reduction yields was seen, showcasing the role of DNA in mediating electron transfer. These results demonstrate the highly unique attributes of DNA as both a templating agent for precise nanoscale assembly and for enabling charge transport. This work was published in early 2018 in *Advanced Sustainable Systems*.

#### Impact on students and career

The funding provided by the ACS PRF NDI award allowed my group to explore new research directions in photocatalytic reduction of  $\text{CO}_2$  to usable fuels. Because the processes developed in this work are dependent primarily on the use of solar energy, these studies can have substantial impact on generating usable fuels from renewable sources. In addition, our studies have shown that in order to improve photodriven redox reactions, a balance is required to drive electrons in a forward direction between photoactive nanosystems with minimal back electron transfer. This work has supported in part two graduate students in obtaining experience in the areas of photocatalysis and sustainable engineering. One of the graduate students funded through the grant obtained a PhD in 2017 while another will be defending his thesis in October 2018.

In the second year of funding, we developed methods to self-assemble photoactive donor-acceptor semiconductor nanoparticles to build Z-scheme systems for  $\text{CO}_2$  reduction. In this particular work, we investigated the use of small molecule ligands and nucleic acids as structure directing agents. While single nanoparticle photocatalysts can drive oxidative polymerization, they often suffer from three major drawbacks: (1) semiconductor degradation due to oxidation of surface ions and ligand instability, (2) insufficient energy levels for running both oxidation and reduction, and (3) competing recombination events. To overcome these challenges, donor-acceptor photoactive nanocrystals were utilized simultaneously, also known as Z-schemes. Because oxidation and

reduction reactions are run on separate catalytic sites, the stability of each photoactive nanoparticle increases. In this work, donor ( $\text{TiO}_2$ ) and acceptor ( $\text{CdS}$ ) nanocrystals were self-assembled (Figure 3) using DNA and these yielded a 5.25-fold improvement in  $\text{CO}_2$  reduction over simply mixing the photocatalysts in solution. In addition, we



**Figure 4.** A) Bar graph showing the overall yields of  $\text{CO}_2$  photoreduction products from  $\text{Au@CdS}$  alone, a mix of  $\text{Au@CdS}$  and  $\text{TiO}_2$  and DNA assembled  $\text{TiO}_2$ - $\text{Au@CdS}$  clusters as a function of DNA length in between the photocatalysts. TEM images showing the interparticle distances mediated by the lengths of DNA strands used: (B) 10 bases; (C) 20 bases; (D) 30 bases; (E) 40 bases; (F) 80 bases.