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 CO₂-reducing PECs that can generate formate and methanol at neutral pH. These cells were composed of CdS/NiOx photoanodes and NiO/CdTe or CuFeO₂/CuO cathodes (Figure 1). UV-Vis absorbance measurements showed that the CdS/NiOx and CuFeO₂/CuO electrodes strongly absorb in the visible. Next, the photoelectrochemical responses of the CdS/NiOx and CuFeO₂/CuO electrodes were measured under CO₂ 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 CuFeO₂/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 CuFeO₂/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 CO₂ reduction. The photoelectrochemical responses of the NiO/CdTe electrodes were also measured under Ar or CO₂ 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 CuFeO₂/CuO or NiO/CdTe photocathodes, PECs were next fabricated with the CdS/NiOx photoanodes. In order to test the PECs for CO₂ reduction, ¹²C or ¹³C labeled CO₂ 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 ¹H NMR was utilized to analyze the products formed. In the first studies, in the presence of ¹²C CO₂, after photoirradiation, we were able to determine from NMR analyses that 60 μM formate could be produced from the CuFeO₂/CuO/CdS/NiOx PEC. By biasing the CuFeO₂/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 CuFeO₂/CuO cathode with the NiO/CdTe led to lower amounts of CO₂ 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).
Next, in order to study the use of an organohydride with the PECs, we tested the utilization of CpRh(bpy)Cl₂ as a co-catalyst. By using CpRh(bpy)Cl₂ as a co-catalyst, much higher amounts of CO₂ reduction were observed from the NiO/CdTe photocathodes as compared to the CuFeO₂/CuO which is summarized in Table 1. As demonstrated, NMR analysis showed that the unbiased PECs in the presence of CpRh(bpy)Cl₂ could yield 400 µM and 187 µM formate from the NiO/CdTe and CuFeO₂/CuO respectively. Therefore, in the presence of CpRh(bpy)Cl₂, the unbiased NiO/CdTe PEC showed a 40-fold increase in product yield as compared to the unbiased NiO/CdTe PEC with no organocatalyst. In direct contrast, the CuFeO₂/CuO system showed little improvement with only a 3-fold increase in formate. Furthermore, with the biased NiO/CdTe/CpRh(bpy)Cl₂ PECs we could also detect 10 µM methanol being generated in addition to the 2.3 mM formate. This work was published in *ChemSusChem* in 2016.

In the second year of funding, we developed methods to self-assemble photoactive donor-acceptor semiconductor nanoparticles to build Z-scheme systems for CO₂ 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 (TiO₂) and acceptor (CdS) nanocrystals were self-assembled (Figure 3) using DNA and these yielded a 5.25-fold improvement in CO₂ 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 CO₂ was observed for DNA lengths of 10 to 80 bases, which separate the donor andacceptor nanocrystals by 3 to 24 nm (Figure 4). More significantly, an interparticle distance of 9-10 nm yielded the highest conversion of CO₂. When the amount of 30mer DNA linking the photocatalysts was lowered, a corresponding decrease in CO₂ 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 CO₂ 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.