Professional Development Assignment (PDA) Report

Xuan Zhao

Dept. of Chemistry, Spring 2017

During my professional development assignment (PDA) for the spring semester of 2017, I have conducted research and established collaborations with colleague in both US and China, including Professor Peng Cheng's lab in the Department of Chemistry at Nankai University (Tianjin, China), and with Professor Claudio Verani at Wayne State University (Detroit, MI). I also worked on campus for student mentoring, served as committee member, and seminar presentation around Memphis during the spring term of 2017.

My research in Professor Cheng's lab focused on the incorporation of cobalt complexes into MOFs to investigate the effects of MOF on the activity and lifetime of catalysts for water splitting. Our lab has reported molecular cobalt catalysts for highly efficient production of hydrogen via electrolysis and photolysis in purely aqueous solutions. However, the stability and the deactivation of metal catalysts during hydrogen production remains a significant challenge for future applications. Working with a graduate student, Ms. Jing Liu, we first incorporated the free ligand DPA-Bpy into the cavity of MOF MIL-125-NH2, followed by addition of Co(II) ions. The formation of Co(DPA-Bpy)Cl_2 complex inside the cavity of MIL-125-NH_2 (Co@MOF) has been confirmed by electrochemical analysis of the cobalt complex before and after its incorporation into MIL-125-NH_2. We have tested the catalytic activity of hydrogen production under different conditions in the presence of photosensitizer and sacrificial reagent. The evolution of H_2 was observed under different pHs upon irradiation of the reaction flask containing 10 mg Co@MOF, 1 mM $Ru[(bpy)_3]^{2+}$, and 100 mM ascorbic acid. While the reaction is more active at lower pHs, the stability of Co@MOF increased at neutral conditions, and there is little change in activity after three cycles (~ 2 h each) of catalysis. Compared to the cobalt complex in the absence of MOF, its activity for H_2 production can last for about 2 hours. Therefore, there is significant improvement in catalyst stability when trapped inside the cavity of MOF. We will test other forms of MOF and catalysts and prepare a manuscript for publication.

With the availability of Bruker SMART 1000 CCD diffractometer in Professor Cheng's lab, we are going to send single crystals to Dr. Cheng's lab for crystal structure determination in early September. The single crystals were prepared by visiting professor, Dr. Lian Duan, who conducted research in my lab for one year (Mar 2016 – Mar 2017).

My PDA time at Nankai University (Tianjin, China) also allowed me to meet and recruit high-quality students to the graduate program in our chemistry department. I have visited and established collaboration with other chemistry departments in China. I have given seminar talks on my research at Tianjin University (02/27/2017), Shanxi Normal University (Taiyuan, 02/23/17), Tianjin Institute of Technology (02/25/17). I have also recruited one graduate student, Mr. Xiangquan Hu, who is currently a new graduate student in our department. My interaction with Chinese universities has also provided opportunities for visiting professors supported Chinese government to conduct research in my lab. Currently, Prof. Pinjiang Li from Xuchang University is doing research in my lab. Another professor, Dapeng Jiang from Xuchang University, has also applied for funding from Chinese government for research opportunity in my lab.

During the spring of 2017, I also did research at Professor Claudio Verani's lab at Wayne State University. Prof. Verani's research is about cobalt-based electro-catalysts for proton/water reduction, with similar research interest to my lab. Although there have been numerous reports of hydrogen production catalyzed by molecular cobalt complexes, the exact mechanisms for hydrogen production still remains to be resolved, and several key intermediates have been proposed during catalysis. We have reported the identification of Co(I) and Co(III)-H species from pulse radiolysis and flash photolysis during the electro- and photocatalytic hydrogen production process. Prof. Verani's lab has reported crystal structure of reduced Co(I) species for his project. We aim to identify the crystal structures of reduced Co species from our catalyst during my PDA. Working with a graduate student at Dr. Verani's lab, Mr. Habib Baydoun, I conducted research for my PDA focusing on identification of reaction intermediates during proton reduction process. We have tested a number of reductants to reduce the Co(II) and Co(III) complexes prepared in my lab to create reduced forms of Co(I), which may be responsible for hydrogen production. The reduction of Co(II) complex with Na/Hg or KC_8 produced a dark brown complex, the NMR spectrum of the resulting solution showed the formation of NMR active Co(I) species and the disappearance of paramagnetic Co(II) signal, although not completely. The formation of Co(III)-H species has been proposed as a key intermediate during Co catalyzed H_2 production. In order to identify the possible formation of Co(III)-H species, we have added a different amount of methanol as proton source to induce the formation of Co(III)-H species. NMR monitor of the reaction process showed the presence of signal at high magnetic field region (~ -10 ppm), which is indicative of the possible formation of Co(III)-H species. Further confirmation and structure determination of the proposed Co(III)-H species is under investigation, and the results will be submitted for publication. From results from our collaboration, we may submit joint grant proposals to federal funding agencies such as DOE.

During my PDA, I stayed on campus for about one month to guide my graduate student, and participated the committee for second year conferences of graduate students in my department. I also presented a seminar talk on solar energy conversion at Rust College and recruited two students to work in the summer as part of my Career education activity.

I will present a seminar talk at Wayne State University on October 19, and below is a list of four presented seminar talks during my PDA:

Electro- and photocatalytic H_2 production by molecular Co complexes with pentadentate ligands. Tianjin University (02/27/2017); Shanxi Normal University (Taiyuan, 02/23/17); Tianjin Institute of Technology (02/25/17)

Solar energy conversion: the conversion of sunlight into chemical fuels. Rust College, 04/24/17.

In summary, the PDA has allowed me to advance my research progress and to establish new national and international collaborations. This experience also provides the instrumentation and expertise not available at UofM to complete the ongoing research projects in my lab. The expanded research capabilities to my own lab and new opportunities for joint grant applications from the proposed PDA has already and would continue to benefit the Department of Chemistry, the College of Arts and Sciences, and the University of Memphis.