1. 57503-DNI6
2. Developing the Photocatalytic Properties of Zeolitic Imidazolate Frameworks
3. Jier Huang, Marquette University

In the second year of the grant, we have made progress in the following projects:

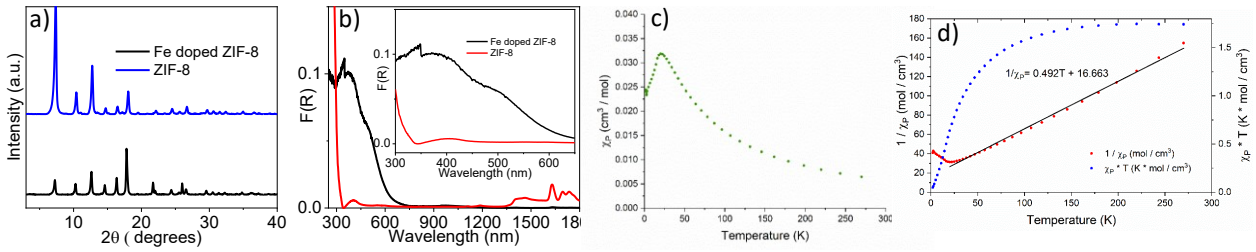

Figure 1. XRD patterns (a) and diffuse reflectance spectra (b) of ZIF-8 and 25%-Fe-doped ZIF-8; The inset of b shows the zoomed spectral region from 300-650 nm; c) Plot of the paramagnetic susceptibility for 6%-Ni-ZIF-67. This data is representative of the paramagnetic susceptibility plots for both Ni-doped ZIF-67 derivatives. Magnetic susceptibility curve plotted as $\chi_P \bullet T$ vs. T (blue) and Curie plot (red) for a) 6%-Ni-ZIF-67. The least-squares fits over the quasi-linear region of the Curie plots are superimposed on the red traces.

1) In last year's progress, we reported mixed-metal ZIF films with different ratios of Co/Zn and Co/Cu, which was published at *J. Am. Chem. Soc.* **2018,** *140*, 11573-11576. In the second year of the project, we continued this project and have synthesized the mixed-metal ZIFs based on Co/Ni, Zn/Fe, and Co/Fe. We have carried out the studies on their excited state dynamics in Zn/Fe and Co/Ni as well as their magnetic properties (Figure 1) through the collaboration with Prof. John Berry at University of Wisconsin at Madison. We found that the excited state in Fe doped ZIF-8 shows ligand to charge transfer nature, and Ni doped ZIF-67 show antiferromagnetic ordering below the Néel temperature. A manuscript on these results is under preparation.

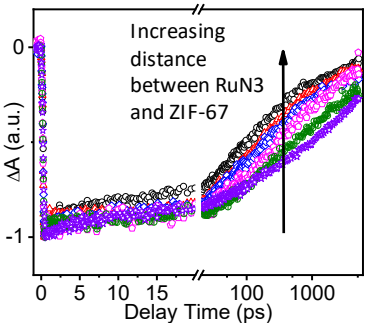

Figure 2. The recovery of ground state bleach of RuN3 with different thickness of Al_2O_3 layer on ZIF-67, which illustrates that ENT efficiency decreases with increasing thickness of Al_2O_3 layer.

2) In the first year of the project, we observed energy transfer (ENT) from RuN3 to ZIF-67 and electron transfer (ET) from $[Ru(bpy)_3]^{2+}$ to ZIF-67. In this year's effort, we investigated the dependence of these dynamics on distance between the photosensitizer and ZIF-67 with a goal toward unravelling the factors that control ENT and ET dynamics in ZIFs. For example, we found that ENT efficiency decreases with increasing distance between RuN3 and ZIF-67, which is controlled by depositing different thickness of Al_2O_3 layer via atomic layer deposition method (Figure 2).

3) In addition to the continuous work from last year's project, we also initiated a new project by introducing a different ligand (i.e. 5-methyltetrazole) to ZIF-67. It is interesting to note that the introduction of 5-methyltetrazole not only changed the Co center from tetrahedral to octahedral geometry, which results in change of optical properties, but also altered the spin nature of Co center (Figure 3).

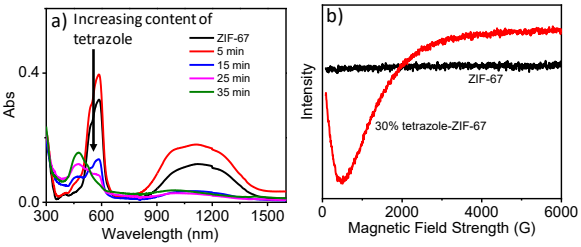

Figure 3. a) The diffuse reflectance spectra of ZIFs change with different ratios of 5-methyltetrazole and 2-methylimidazole. b) The EPR spectra of ZIF-67 and ZIF-67 with 30% 5-methyltetrazole.

4) One of the proposed objects for this grant is to incorporate nanoparticles to ZIFs to enhance the light harvesting and charge separation properties of ZIFs, which represent the key properties that determine their application in photocatalysis. Therefore, we also examined the excited

state and photocatalytic properties of nanoparticles such as $CuInS_2$/ZnS quantum dots and Co_3O_4 hollow nanostructure spheres. The results from these studies have been summarized and submitted to peer-reviewed journals (See publication #1 and #2).

5) Through collaboration with Prof. Jing Gu's group, we have investigated the catalytic mechanism of 1H-MoS_2 using in situ X-ray absorption spectroscopy under the standard catalytic conditions. We not only identified a reversible Ni dopant in the basal plane which serves as the active sites for catalysis but also captured the intermediate structures that determines the catalytic performance of 1H-MoS_2 (Figure 4). These results are unprecedent and have been recently submitted to *Angewandte Chemie* (Publication #4).

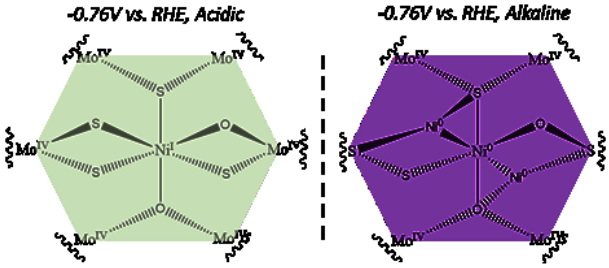

Figure 4. The proposed catalytic mechanism of Ni doped 1H-MoS_2 under acidic (left panel) and basic (right panel) conditions according to the in situ X-ray absorption spectroscopic studies.

The impact of research on PI's career and the students

1) This award allows the PI and her research group to perform the fundamental studies on the optical and magnetic properties of ZIFs and supports her participating professional activities including mentoring graduate and undergraduate students, participating outreach program and community service, scientific meetings etc. The PI has given 4 invited talks in two international scientific conference/workshop and two universities, including International MOF 2018 (New Zealand, December 10-13, 2018), Photocatalysis Workshop (China Petroleum University, July 5, 2019), University of Miami (October 19, 2018), and Lanzhou University (June 20, 2019).

2) One graduate student has been trained on this project and submitted a few peer-reviewed papers.

3) One undergraduate student has been trained on this project. Nick has presented his work at Marquette Summer Poster Session on July 23, 2019.

4) One postdoc researcher has been trained on this project since April 1st, 2018.

Publications that acknowledged this grant

1) Hu, W.; Yang, S.; **Huang, J.*** "Composition Effect on the Carrier Dynamics and Catalytic Performance of $CuInS_2$/ZnS Quantum Dots for Light Driven Hydrogen Generation ", Submitted to *J. Chem. Phys.* **2019** (invited submission for special issue of quantum dots).

2). He, P.; Yang, S.; Hu, W.; Lee, S.; **Huang, J.*** "Unravelling the Active Sites of Co_3O_4 Hollow Spheres for CO_2 Photoreduction." *Submitted to ACS Applied Energy Materials.* **2019**.

3) Zhou, Y.; Hu, W.; Yang, S.; Nyakuchena, J.; Duisenova, K.; Lee, S.; Fan, D.; **Huang, J.*** "Unravelling the Catalytic Active Site in Mixed-Node Metal Organic Frameworks using In Situ X-ray Absorption Spectroscopy", *submitted to Journal of Catalysis,* **2019**.

4) Pattengale, B.; Huang, Y.; Yang, S.; Younan, S.; Hu, W.; Li, Z.; Lee, S.; Fu, J.; **Huang, J.*** "Direct Evidence of Reversible Ni Dopant Active Sites in 1T-MoS_2 Electrocatalysts for Hydrogen Generation", *Submitted to Angewandte Chemie,* **2019.**

5) Pattengale, B.; SantaLucia, D.; Yang, S.; Hu, W.; Liu, C.; Zhang, X.; Berry, J.*; **Huang, J.*** "Direct Observation of Node-to-Node Communication in Zeolitic Imidazolate Frameworks", *J. Am. Chem. Soc.* **2018**, *140*, 11573-11576.

6). Pattengale, B.; **Huang, J.*** "Photoinduced Interfacial Charge Separation Dynamics in Zeolitic Imidazolate Framework." *Phys. Chem. Chem. Phys.* **2018**, *20*, 14844-14888.