1. PRF#: 57580-ND5
2. Project Title: A New Class of Heterogeneous Catalysts Based on Single Layer Nanosheets
3. P.I. Name, Affiliation: Luyi Sun, University of Connecticut

Heterogeneous catalysts play an important role in many petrochemical reactions because of their advantages in product separation and catalyst recycling. We aim to design and create a new class of heterogeneous catalysts supported on single-layer nanosheets, in contrast to the ones supported on porous materials or nanoparticles. Particularly, we proposed to use α-zirconium phosphate (ZrP) single-layer nanosheets as the support, which contain a high density of surface hydroxyl groups and can be easily prepared from the exfoliation of ZrP micro-crystals. Because of their unique structure and morphology, such ZrP nanosheets based heterogeneous catalysts are expected to be readily accessible and separated, and thus exhibiting advantages of both heterogeneous catalysts (recyclability) and homogeneous catalysts (high accessibility).

Based on what achieved in Year 1, during the second year of this project, we synthesized two types of catalysts supported on ZrP nanosheets: (1) ZrP supported Au nanoparticles (NPs); (2) ZrP supported Zn complex. For both catalysts, we started from the synthesis and exfoliation of ZrP to prepare ZrP single-layer nanosheets. ZrP micro-crystals were first synthesized by a hydrothermal method (6.0 g of $ZrOCl_2\cdot 8H_2O$ in 60.0 mL of 6.0 mol/L H_3PO_4 at 200 °C for 24 h). Subsequently, the synthesized ZrP micro-crystals were exfoliated by propylamine or tetra-*n*-butylammonium hydroxide to form single-layer ZrP nanosheets, as detailed in our last report as well as shown in Figure 1.

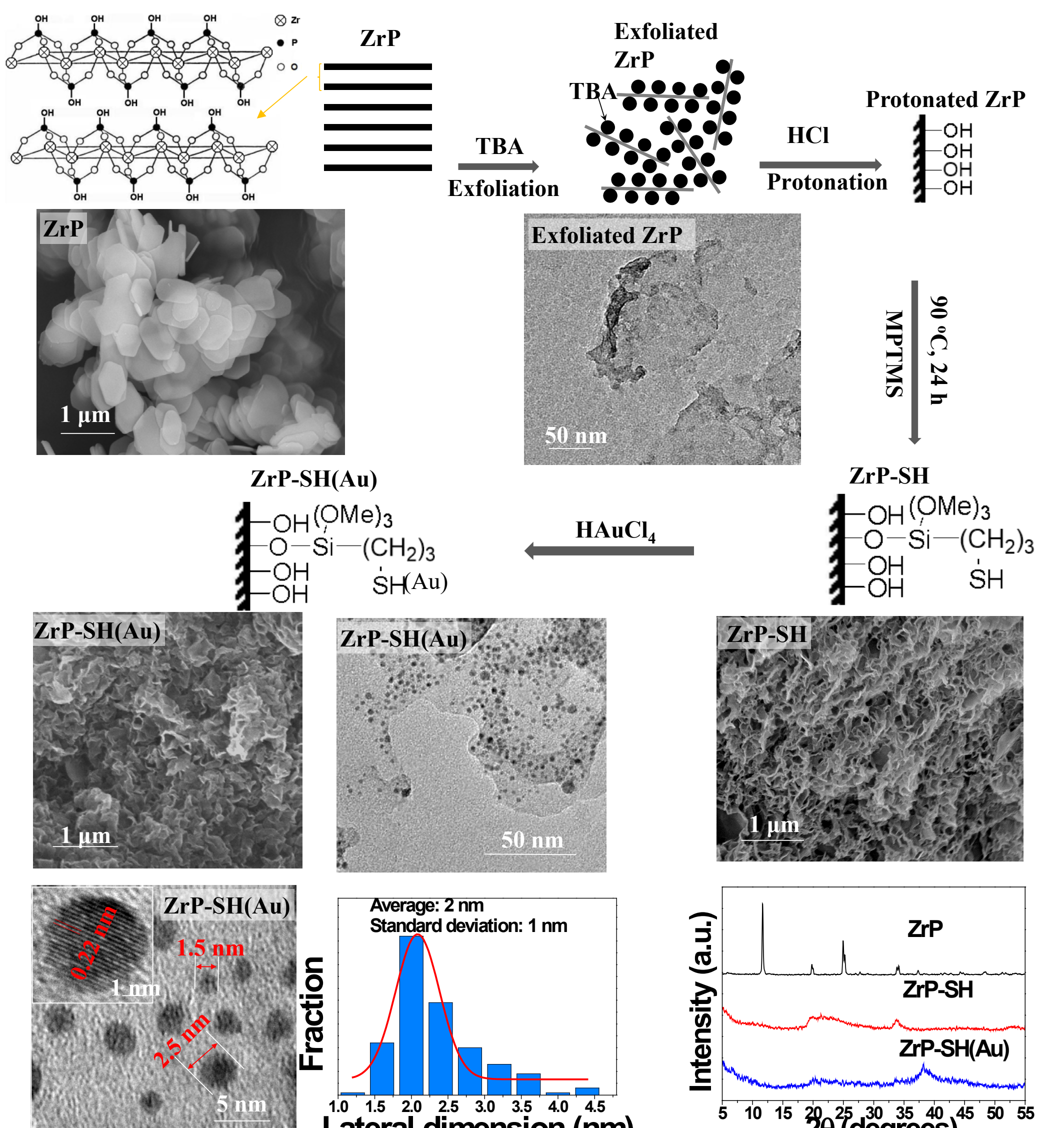

Figure 1. Procedures to immobilize Au NPs onto the thiol functionalized ZrP nanosheets and the corresponding structural characterizations.

Based on the prepared ZrP single-layer nanosheets, we managed to graft thiol groups onto the nanosheets first, and subsequently synthesized Au NPs on the ZrP nanosheet surface [ZrP-SH(Au)] thanks to the strong interactions between Au NPs and thiol groups (Figure 1).

Alternatively, we grafted amine groups onto the surface of ZrP nanosheets, which was subsequently reacted with salicylaldehyde to form salicylaldimine functionalized ZrP nanosheets (ZrP-SA). Finally, ZrP-SA was reacted with zinc acetate to form ZrP nanosheets supported Schiff-base Zn complex (ZrP-Zn, Figure 2).

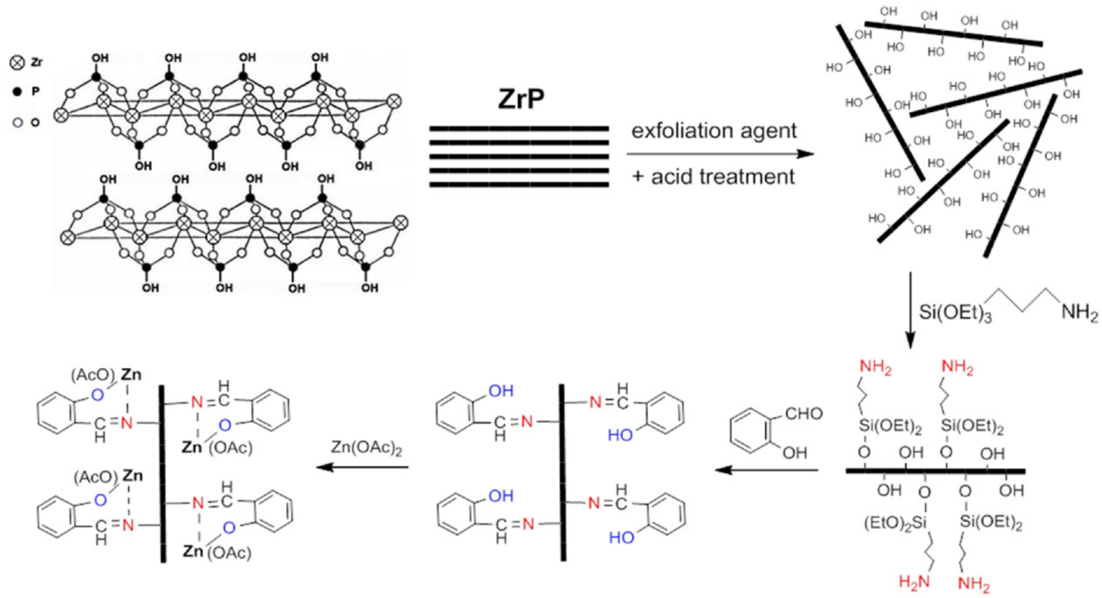

Figure 2. Procedures to synthesize ZrP nanosheets supported Schiff-base Zn complex.

Both ZrP-SH(Au) and ZrP-Zn exhibited excellent catalytic performance. ZrP-SH(Au) was demonstrated to be able to effectively reduce 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in the presence of borohydride (BH_4^-), a model reaction to evaluated Au NPs. ZrP-SH(Au) demonstrated combined advantages of heterogeneous and homogeneous catalysts as designed. ZrP-Zn was proved to be an effective catalyst to polymerize lactide to form polylactic acid (PLA), during which the catalyst support, ZrP nanosheets, can also serve as nanofillers to improve the physical properties of the synthesized PLA.

Two journal papers (*Advanced Composites and Hybrid Materials* **2019,** *2*, 520-529; *ACS Applied Polymer Materials* **2019,** *1*, 1382-1389) have been published based on the results shown above, and one is to be submitted soon.

This ACS PRF grant has had a huge impact on me and my students. When conducting the preliminary research to prepare for this proposal, I developed several new ideas on nanosheet research, which led to another two grants. Two graduate students, two visiting scholars, and seven undergraduate students benefited a lot from working on this project. Mr. Hao Ding, a PhD student, has gained significant experience and confidence in the past two and a half years when working on this project and is on his track to complete his PhD. Another PhD student, Jingjing Liu, who did not receive stipend directly from this grant but worked on this project, has obtained her PhD and now works for the University of Texas Rio Grande Valley. Seven undergraduate students were heavily involved in this project (they participated in this project through registering for a research course at the University of Connecticut and thus did not receive stipend directly from this grant). Throughout this project, these undergraduate students received a wide spectrum of training, including basic chemical synthesis and separation skills, materials preparation and processing techniques, and various chemical, mechanical, and physical characterizations. Two of the students are now working in chemical industry.