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Zero Valence Iron Nanoparticle - Metal Organic Framework Composites as Novel Separating Materials for Tc04 in Nuclear Waste Streams

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RCEU 2023 Project Proposal

Project Title

Zero Valence Iron Nanoparticle – Metal Organic Framework Composites as Novel Separating Materials for TcO_4^- in Nuclear Waste Streams

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I. Project Description

Nuclear energy, known for the high energy density and zero carbon emission, is considered as an important alternative resource for fossil fuel. However, the lack of a permanent solution for high-level nuclear waste remains a barrier to increased nuclear power generation. Within these nuclear wastes, ^{99}Tc, primarily exist as TcO_4^-, is one of the most problematic radionuclides because of its long half-life, high environmental mobility, and the lack of effective sorbents under harsh conditions.

At present, TcO_4^- is mainly treated by cationic polymer-based resins, which can absorb TcO_4^- via ion exchange. Due to their organic nature, however, those resins may lose capacity when exposed to highly alkaline solutions and high radiation doses, such as those present in the legacy tank wastes at the US Hanford site. Recently, metal-organic frameworks (MOFs) with cationic features on metal nodes or linkers have been utilized to absorb TcO_4^- via replacing the liable -OH/H_2O groups on metal nodes or free anions within the void space of frameworks. Although demonstrating promising results, the number of practical cationic MOFs is still very limited and their selectivity in the presence of competing anions, e.g., NO_3^-, SO_4^{2-}, is unsatisfying since the absorption process is governed mainly by electrostatic forces. Another common Tc absorption strategy is to reduce TcO_4^- to much less soluble Tc(IV) complexes, e.g., $TcO_2 \cdot nH_2O$, using reducing agents, such as zero-valent iron nanoparticles (ZVINs). ZVINs have better Tc absorption and reduction selectivity over competing anions, and they can be used for environmental remediation because of their nanoscale size. Unfortunately, unless contained, they tend to aggregate into large particles and react with water and oxygen and eventually lose their reactivity. To this end, this proposed project will, for the first time, develop ZVIN-MOF composites as new Tc sorbents by encapsulating ZVINs within robust MOFs. The stability and performance of ZVINs will be greatly improved by encapsulating in the long rang ordered void space of MOFs. In addition, the absorption mechanism and capacity of resultant composites are expected to be enhanced by the synergistic combination of ZVINs' reduction of TcO_4^- to Tc(IV) species with the ability of MOFs' to absorb TcO_4^-. Given the radioactivity of Tc, nonradioactive ReO_4^- with similar coordination and redox chemistry will be used in this work as a surrogate for TcO_4^-. The proposed work is significant from both fundamental and practical standpoint and the results will advance the fundamental knowledge, establishes new remediation techniques, and supports an advanced nuclear fuel cycle.

II. Student Duties, Contributions, and Outcomes

a. Specific Student Duties

Student will work 10 weeks in the PI's lab and spent 10 hours/week which can be divided into two or three days. In this first week, student will take a training on basic lab safety and skills and give a literature survey presentation on MOFs and iron nanoparticles. Between week 2 to 6, student will work on the synthesis and characterization of selected MOFs. At the same time, student will optimize the yield, size and morphology of MOFs by systematically adjusting the reaction parameters. From week 7, student will start to synthesize Fe nanoparticles under different reaction conditions and analyze their chemical composition and particle size. In addition, student will travel to UA with the PI and graduate student in the week 9 or 10 to collect TEM data. Every two weeks, student will present his/her research work in the group meeting and discuss the experimental results and research process with the PI and graduate students. In the end of this program, student

is required to write a technical report and present his/her research work at the Research Horizons Day and SERMACS as poster and/or oral presentations.

b. Tangible Contributions by the Student to the Project *(10% of Review)*

The student's work is expected to generate MOFs and iron nanoparticles with unique chemical and physical properties, including size, morphology, pore volume, surface area, stability upon heat and acid/base, etc. This work will also benefit to the understanding of the correlation between the synthesis, structure, and property of both MOFs and iron nanoparticle and lay down a solid base for the construction of ZVIN-MOF composites which is the ultimate goal of this project. The research results will be published as a part of a peer-reviewed paper or a poster presentation at a local and regional conferences.

c. Specific Outcomes Provided by the Project to the Student *(30% of Review)*

The outcomes provided by the project to the student include:

- Basic lab safety and skill training, including handing of organic and inorganic chemicals, fume hood, box furnace, solution preparation, balance, pipet, etc.
- Knowledge about MOF and iron nanoparticles and their applications in energy and environment.
- Crystal growth of MOFs using solvothermal methods.
- Synthesis of iron nanoparticles in solution.
- Hands-on experience on analytical techniques, including XRD, FTIR, BET, SEM, and TEM
- Learn to design experiment and use scientific thinking to interpret experimental results.
- Collaboration with graduate student,
- Communication and presentation skills

III. Project Mentorship *(30% of Review)*

The student will be mentored by the PI and a PhD student. During this 10-week program, student will meet with the PI and/or the graduate student in-person twice to three times per week to conduct research and discuss the results. And every two weeks, student will report his/her research work and discuss the research process with the PI and the graduate student in a group meeting. As planned, in the first week, student will be taught by the PI to do literature search and prepare a survey presentation. At the same time, student will take a training on basic lab safety and lab skills given by the graduate student. From week 2 to week 6, student will be mentored by the graduate student to synthesize MOFs (the type of MOFs will be selected by the PI) using solvothermal method. Student will work with the graduate student and analyze the prepare products using optical microscopy (crystal habit), FTIR (composition), powder XRD (structure), and BET (pore volume and surface area). During weeks 7 to 9, student will learn to prepare iron nanoparticles under inert atmosphere (i.e., nitrogen gas) and analyze these nanoparticles using PXRD and TEM with the PI. In the last week (week 10), student will prepare a scientific report and a poster under the guidance of PI. In addition, student will be provided opportunity to continue to work on the synthesis of ZVIN-MOF composites in the following fall semester.