Multi-Scale, Structure-Reactivity Modeling of Nanowire-Based Single Site Catalysts for Small-Molecule Reactions

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Heterogeneous catalysis underlies a number of key industrial processes, yet the catalysts that enable these to work remain poorly understood. Nevertheless, for conventional metal-based catalysts, there is a seemingly unavoidable compromise between low activation barriers and weak binding, which hinders catalytic performance. Single atom alloys (SAAs) represent emerging material systems with the ability to circumvent this limitation and deliver enhanced catalytic performance; indeed, SAAs combine dopant-like activation energy with intermediate adsorption strength. However, to a large extent, given the relative novelty of these materials in addition to pressure and materials gaps within their studies, the understanding of SAA behavior is primarily phenomenological. Therefore, rationally designing SAAs with tailorable and superior activity and selectivity represents a 'holy grail' outcome. We propose to combine innovative synthesis (i.e. using metal nanowire - supported SAAs as a new type of an SAA catalyst), advanced in situ characterization, and robust theoretical calculations to enable rational tuning of their activity, selectivity, and stability.

By designing and investigating several exemplary SAA catalysts and reactions, the seed proposal seeks to address the following key, fundamental points: - What are (i) the geometrical configuration, (ii) electronic structure, and (iii) metal-adsorbate interactions, characteristic of nanowire-supported SAA catalysts under reaction conditions? - What is the nature of the reaction mechanism, active sites, and descriptors that control the activity, selectivity, and stability of catalysts, during the catalytic process? - Can we optimize the catalytic performance of SAA by using strategies such as (i) increasing numbers of surface sites and (ii) controlling where the catalytically active dopants reside?

The anticipated result of this proposal will be the rational development of the new type of a catalytic system that combines single atom catalysts with a low-dimensional support.

Indeed, the focus of this project involves the directed development of methods to enable the rational design of new nanowire catalysts. The bulk of the effort will be the integration of multi-scale computational methods and machine learning with a synthesis, characterization, and design feedback cycle. The proposal describes how, as a coordinated team, we will computationally screen for new catalysts, synthesize well-defined, novel nanowire-supported catalysts, use new computational methods to aid in their characterization, and then evaluate the catalytic performance, so we can test and improve upon reactivity descriptors and figures of merit to acquire functional, mechanistic understanding with the following proposed deliverables.

Synthesis: Controlled experimental synthesis and large-scale production of new, pure, and active ultrathin metal nanowire-based single-atom alloys (i.e., SAA).

Characterization: Development of techniques, that are capable of not only interrogating the geometry of the active metal site in SAAs but also monitoring its change in operando conditions.

Theory and Computation: Construction of an internally consistent and validated multi-scale model, which can be employed to understand and optimize the system operating under a range of operating conditions, and to enable the search for novel, tunable SAAs for other reactions.

Broader Impacts: Our proposed work will be impactful and far-reaching in that it should yield valuable insights not only into the mode and strength of reactant, intermediate, and/or product adsorption via realistic modeling of the active sites but also into the basis of relevant in situ reaction pathways and associated activation barriers that underlie heterogeneous catalysis reactions, in general. With the emphasis on the synergy between theory and experiments in this proposal, students in PI/co-PI-led teams will be expected to interact with each other and develop a close understanding of how close interaction between theory and experiments can be implemented in order to best achieve the desired outcomes. To increase the participation of underrepresented and minority groups in our research, we plan to partner with the Center for Inclusive Education (CIE) at Stony Brook University through a host of complementary initiatives.