Transition Metal Carbide and Nitride Nanoparticles with Noble Metal Shells as Enhanced Catalysts

by

Aaron R. Garg

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ABSTRACT

Core-shell nanostructures represent a promising and versatile design platform for enhancing the performance of noble metal catalysts while reducing the cost. Early transition metal carbides (TMCs) and nitrides (TMNs) have been identified as ideal core materials for supporting noble metal shells owing to their earth-abundance, thermal and chemical stability, electrical conductivity, and their ability to bind strongly to noble metals while still being immiscible with them. Unfortunately, the formation of surface oxides or carbon on TMCs and TMNs presents a difficult synthetic challenge for the deposition of atomically thin, uniform noble metal layers. Recent advances have enabled the synthesis of TMC core nanoparticles with noble metal shells (denoted as NM/TMC), although applicability toward TMN cores has not been previously demonstrated. Furthermore, the complete properties of these unique materials are still unknown.

This thesis conducts a detailed investigation of the synthesis, characterization, and catalytic performance of NM/TMC and NM/TMN core-shell nanoparticles to provide a comprehensive understanding of their material properties and the underlying phenomena. First, in-situ studies yielded insight into the mechanism behind the high temperature self-assembly of NM/TMC particles, indicating the presence of a metallic alloy phase preceding the formation of the core-shell structure upon insertion of carbon into the lattice. Next, the synthesis of NM/TMN nanoparticles was demonstrated via nitridation of a parent NM/TMC, and the structural and electronic properties of both core-shell materials were examined through in-situ X-ray absorption spectroscopy (XAS). The analysis revealed significant alterations to the electronic structure of the noble metal shell due to bonding interactions with the TMC and TMN cores, which led to weakened adsorbate binding energies. Finally, the materials displayed improved performance for the oxygen reduction reaction (ORR), a critical challenge for fuel cell technologies. Notably, particles with complete, uniform shells exhibited unprecedented stability during electrochemical ageing at highly oxidizing conditions, highlighting the great potential of core-shell architectures with earth-abundant TMC and TMN cores for future ORR applications. Overall, this work will provide new opportunities toward the design of enhanced noble metal catalysts and enable further optimization of their performance.

Thesis Supervisor: Yuriy Román-Leshkov
Title: Associate Professor of Chemical Engineering