Tuning Geometric and Electronic Structure of Noble Metals with Core-shell Platform as Enhanced Catalysts

by

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Technical Summary

The noble metals (NMs) are special materials satisfying the Sabatier principle which bind adsorbates neither too strongly nor too weakly. Along with the resistance to corrosion and bulk oxidation, making noble metals universal catalysts for many important industrial reactions. Despite the appealing chemical properties, noble metals are not the optimal catalysts for particular reactions based on theoretical calculations. Core-shell nanostructures are a versatile platform that has the potential to solve this problem. Recent advances have enabled the synthesis of platinum titanium tungsten carbide (Pt/TiWC) and platinum titanium tungsten nitride (Pt/TiWN) core-shell nanoparticles featuring superior Pt mass activity in oxygen reduction reaction (ORR) and CO tolerance during hydrogen oxidation reaction (HOR) which are the critical reactions to enable hydrogen fuel cell technologies. However, applications with these materials in thermal catalysis reactions and other adsorbates have not been shown. Furthermore, the use of tungsten carbide or nitride as the only backbone core material limits the tunability and core stability for the core-shell catalysts.

This thesis includes a combination of synthesis, characterization, and catalytic performance of new core-shell nanoparticles to provide a fundamental understanding of this versatile platform. Firstly, new core materials tantalum carbide (TaC) and niobium carbide (NbC) combining with platinum (Pt), rhodium (Rh), and iridium (Ir) shells will be introduced. The materials were analyzed by x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) to demonstrate the significant shell electronic and geometric structure alterations induced by the core. Next, these materials along with the conventional Pt/TiWC and Pt/TiWN materials were tested with thermal catalytic probe reactions, namely, carbon dioxide and acetylene selective hydrogenation. Core-shell catalysts featured superior selectivity towards the intermediate products compared to their parent NM catalysts owing to the modified geometric and electronic structures. Finally, the Pt/TaC core-shell nanoparticle was shown to outperform commercial Pt in methanol oxidation reaction (MOR) and methanol interfered ORR application due to the Pt shell electronic structure change which facilitates direct methanol fuel cell technologies. Overall, this work not only demonstrates methods to synthesize a broader spectrum of core-shell nanoparticles but also provides fundamental understandings of shell-core interactions in thermal-catalytic and electrochemical reactions.

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