

Electron Microscopy Studies of P Doped PtNi Concave Octahedral Nanoparticles as Highly Active Oxygen Reduction Reaction Electrocatalysts in Alkaline Electrolyte

Wang, S.¹, Yang, S.¹ and Yang, G.²

¹ Xi'an Jiaotong University, China, ² Thermo Fisher Scientific, China

The oxygen reduction reaction (ORR) in alkaline electrolyte is important for clean energy technologies, such as alkaline anion exchange membrane fuel cells, microbial fuel cells, and alkaline metal–air batteries. To date, platinum (Pt) and PtM (where M=Fe, Co, Ni) electrocatalysts with various composition and shapes have been developed to improve the ORR activity and durability. However, the low activity and lack of efficiency of ORR on the surface limits the commercialization of this clean energy technologies. Introduction of phosphorus (P) dopants into catalyst can efficiently modify the electronic structure and electron transport properties of the active site and therefore tailor the physical-chemical properties of catalysts to enhance their activity and stability. In this study, P doped PtNi (P-PtNi) concave octahedron nanoparticles (NPs) were successfully prepared by phosphorizing the starting material PtNi concave octahedrons using NaH₂PO₂ in oil bath and used as ORR electrocatalysts in alkaline electrolytes.

Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) characterizations demonstrate that the P-PtNi octahedron NPs have concave structure in their eight {111} facet with average edge length of about 8 nm. High angle annular dark field scanning transmission electron microscopy (HAAD-STEM) characterization and energy-dispersive X-ray spectroscopy (EDS) mapping analysis (shown in Fig. 1) reveal that P uniformly distributes throughout the whole concave octahedron, Pt mainly locates at the edges and corners rather than the inner part of the concave octahedron, while Ni situates the center and forming the core of octahedron, suggesting the formation of P doped quasi core-shell PtNi concave octahedral NPs. X-ray photoelectron spectroscopy (XPS) spectra further imply the successful doped P in PtNi NPs. The as-prepared P-PtNi concave octahedra exhibit improved ORR activity and stability. The specific activity of P-PtNi/C catalyst at 0.9V was 2.75 mA/cm, which was 2 times greater than that of PtNi/C catalyst (1.35 mA/cm) and 11 times greater than that of commercial Pt/C (0.25 mA/cm). The mass activity showed by P-PtNi/C catalyst (0.68A/mg) at 0.9V was 1.5 times higher than that of PtNi/C catalyst (0.46 A/mg) and 5.7 times higher than that of commercial Pt/C (0.12 A/mg). The improved electrocatalytic performance for ORR of P-PtNi/C can be mainly attributed to the P dopant in the PtNi concave octahedral NPs which could adjust the electronic structures of Pt and Ni followed by Pt–OH_{ad} formation. The present results on the synthesis of P doped PtNi concave octahedron NPs and their improved ORR activity and stability to provide a new insight into the development of ORR catalysts with low utilization of Pt.

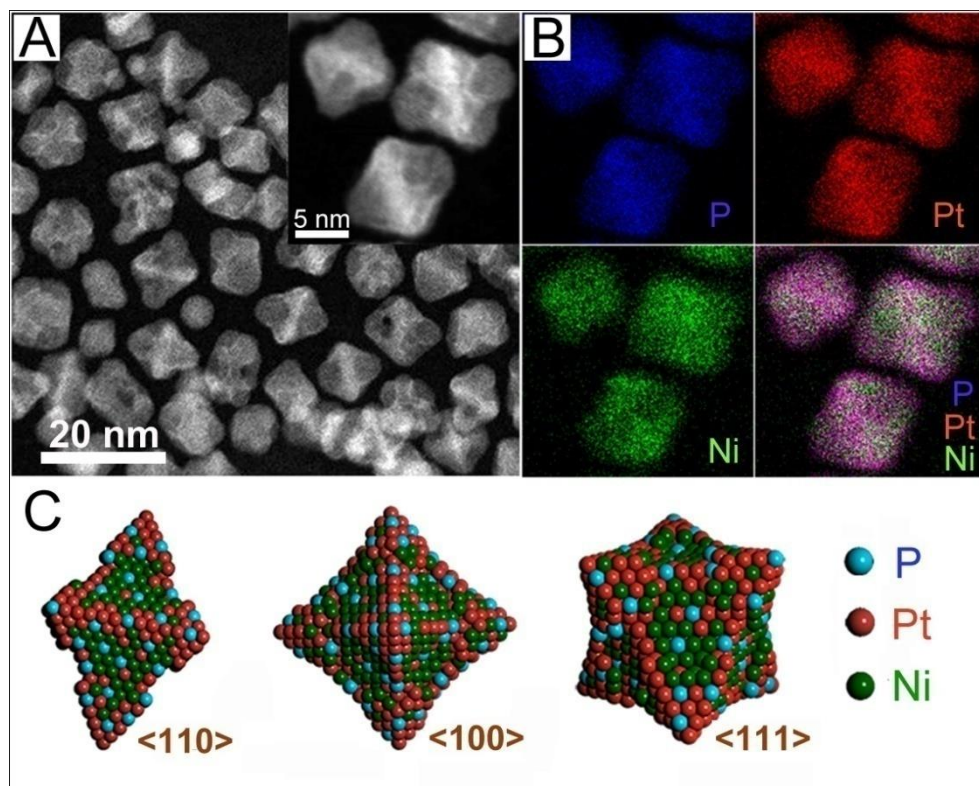


Fig 1. (A) HAADF-STEM images of P-PtNi octahedra. The inset is enlarged HAADF-STEM image corresponding EDS mapping in B. (B) EDS mapping of P-PtNi octahedral. (C) Atomic structural model of P-PtNi NPs.