XAFS Characterization of Size-controlled Pt Nanoparticles Prepared from Pt₄ Complex and Polypyrroles for Enhanced Oxygen Reduction Reaction

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1 Introduction
We prepared size-controlled Pt nanoparticles on multi-wall carbon nanotubes (MWCNTs) decorated with polypyrrole matrix overlayers from newly prepared Pt₄ complex and pyrrole monomers. The oxidation states and the local coordination structures of the prepared Pt nanoparticles with/without polypyrrole matrix overlayers were investigated by Pt L₃-edge XAFS. The prepared Pt nanoparticles with polypyrrole matrix overlayers exhibited superior oxygen reduction reaction (ORR) performance as electrocatalysts compared with Pt nanoparticles without polypyrrole matrix overlayers and commercial Pt/C catalysts.[1]

2 Experimental
Pt nanoparticles with polypyrrole matrix overlays (A), and Pt nanoparticles without polypyrrole matrix overlayers (B) were prepared according to the literature, respectively.[1]

Pt L₃-edge XAFS was measured in a transmission mode at 20 K at the BL-12C station with a Si(111) double-crystal monochromator. Ionization chambers filled with pure N₂ and pure Ar were used to monitor incident and transmitted X-rays, respectively. EXAFS spectra were analysed using ATHENA and ARTEMIS programs. k³-Weighted EXAFS oscillations were Fourier transformed into R-space, and curve-fitting analysis was performed in R-space with coordination number (CN), interatomic distance (R), Debye-Waller factor (σ²), and correction-of-edge energy (ΔE₀). Phase shifts and backscattering amplitudes were calculated by the FEFF8 code.

3 Results and Discussion
The oxidation state of the Pt nanoparticles with/without polypyrrole matrix overlayers (A and B) were analyzed by Pt L₃-edge XANES (Figure 1(A)). The white line heights of A and B were very similar to that of Pt foil, indicating that the oxidation state of A and B were both zero.

The local coordination structures of A and B were analyzed by Pt L₃-edge EXAFS (Figure 1(B)). The bond distances of the Pt-Pt coordination in A and B after the reduction were fitted as 0.276 ± 0.001 nm and 0.277 ± 0.001 nm, respectively, whose values were identical to Pt⁰ foil (R = 0.277 ± 0.001). On the contrary, the coordination number (CN) of Pt-Pt bond in A was 5.4 ± 1.0, while the larger CN of 7.3 ± 0.7 was observed in B. This result supports the formation of smaller Pt nanoparticles on A, which was confirmed by TEM analysis. TEM images of A exhibited small Pt nanoparticles of 1.5 ± 0.5 nm with polypyrrole matrix overlayers, while the size control of Pt nanoparticles was not possible without polypyrrole matrix overlayers with large Pt nanoparticles of >3 nm. The Pt-O/N contribution (CN = 0.8 ± 0.4, R = 0.216 ± 0.002 nm) was also observed in A.

The size-controlled Pt nanoparticles in A exhibited better activity and durability than non-regulated Pt nanoparticles in B without polypyrrole matrix overlayers and a commercial Pt/C catalyst during the ORR at the fuel cell cathode without substantial aggregation of the size-controlled Pt nanoparticles.

Figure 1: (A) Pt L₃-edge XANES spectra of A, and B. (B) k³-Weighted Pt L₃-edge EXAFS Fourier transforms of A, and B.


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