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XAFS Characterization of Size-controlled Pt Nanoparticles Prepared from Pt_4 Complex and Popypyrroles 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 Pt_4 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 L_{III}-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 overlayres (**A**), and Pt nanoparticles without polypyrrole matrix overlayres (**B**) and were prepared according to the literature, respectively.[1]

Pt L_{III}-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 N_2 and pure Ar were used to monitor incident and transmitted X-rays, respectively. EXAFS spectra were analysed using ATHENA and ARTEMIS programs. k^3-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 (σ^2), and correction-of-edge energy (ΔE_0). 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 overlayres (**A** and **B**) were analyzed by Pt L_{III}-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 L_{III}-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 Pt^0 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 overlayres, 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.

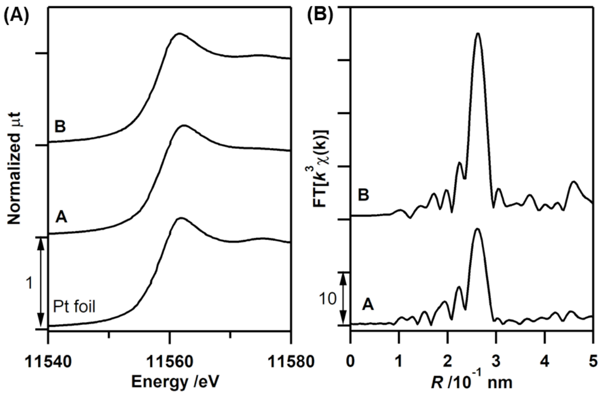

Figure. 1: (A) Pt L_{III}-edge XANES spectra of **A**, and **B**. (B) k^3-Weighted Pt L_{III}-edge EXAFS Fourier transforms of **A**, and **B**.

[1] K. Ichihashi, S. Muratsugu, S. Miyamoto, K. Sakamoto, N. Ishiguro, M. Tada, *Dalton Trans.* **2019**, *48*, 7130–7137. (**selected as inside front cover**)

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