

*In-situ* PTRF-XAFS study about the monolayer Pt on Au(111)

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### 1 Introduction

Platinum has been proved to possess an outstanding catalytic performance in fuel cell technology, especially in catalyzing the cathode reaction, while the high price of Pt has greatly limited wide spreading of fuel cell. Previous reports have revealed that the metal (M) core- Pt shell (M@Pt) structure not only increases the utilization of Pt upto 100%, but also greatly enhances the overall catalytic activity<sup>[1]</sup>. There are two possibilities for the enhancement. One is charge transfer between Pt and M, and the other one is modification of the density of state (DOS) for electrons caused by Pt-Pt bond distance change. When Pt monolayer is deposited on Au(111), the Pt-Pt bond distance is expected to be elongated because of epitaxial growth of pt layer. However, the Au@Pt nanoparticles showed shorter Pt-Pt bond distance than that of Pt nanoparticle. In this research, in order to examine the Pt-Pt bond distance of Pt overlayer deposited on the flat Au(111) directly, we carried out *in-situ* polarization dependent total reflection fluorescence X-ray absorption fine structure spectroscopy (PTRF-XAFS), which could provide the three-dimensional surface structure.<sup>[2]</sup>

### 2 Experiment

An Au(111) substrate was obtained by electropolishing and furnace annealing at 900 °C for 10 hours. Before Pt deposition experiment, Au(111) was annealed by butane gas to reveal the characteristic surface. Submonolayer of Pt species was deposited by so-called Surface Limited Redox Replacement (SLRR) reaction in a N<sub>2</sub>-filled glovebox. The fresh Pt/Au(111) sample was set on a homemade electrochemical cell system with 0.1 M HClO<sub>4</sub> filled. The PTRF-XAFS of Pt L<sub>3</sub>-edge was measured at BL12C, Photon Factory using a Si(111) double crystal monochromator. Total reflection condition was adjusted by a 5-axis goniometer. The fluorescence signal was detected by a 7 channels SDD. Due to the interference from the Au L<sub>3</sub> edge, the measurement stopped at  $k = 7 \text{ \AA}^{-1}$ .

### 3 Results and Discussion

We measured Pt L<sub>3</sub> edge spectra at reduced condition. (+0.4 V vs RHE.) To determine the Pt-Pt bond distance, we did the model fitting of raw data by feff 8 and thorough search for both s- and p-polarization<sup>[4-6]</sup>. We proposed the model structure of Pt layer deposited in a two-dimensional way (Fig.1). Fig.2 shows the thorough search result for s-pol EXAFS data. The Pt-Pt bond distance was found to be 2.87 Å in average. For p-pol, we found the Pt-Au bond distance at 2.80 Å.

In the present research, we have concluded that the submonolayer of Pt deposited on Au(111) surface results in the Pt-Pt bond distance expansion. We have found the discrepancy in Pt-Pt distances between the flat surface and nanoparticle surface.

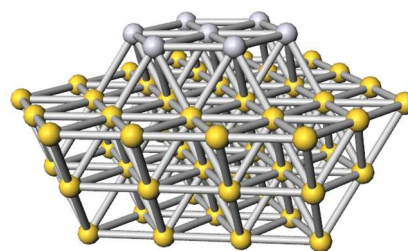


Fig.1 Pt/Au(111) model.

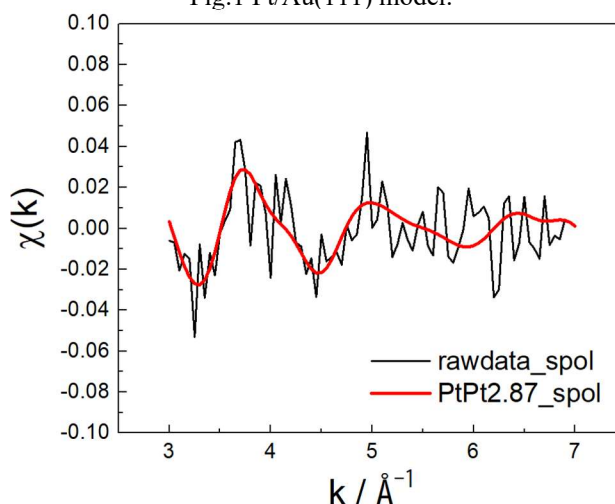


Fig.2 Simulation result.

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