

PTRF-XAFS study of structures of Pt species deposited on Thiol-terminated Organic Monolayer Formed on Si(111) Surface

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Introduction

Deposition of metallic layer onto an ultra-thin organic layer formed on a solid surface has attracted much attention because of its potential applications for sensors, catalysts, and electronic devices. Recently, a novel method to form a uniform metallic layer on top of an organic monolayer formed on a solid substrate has been proposed, where metal complex ions were pre-adsorbed on top of the ω -functional organic monolayer formed on a solid surface and then reduced to metallic state [1-2]. However, structures of the adsorbed metal complex ions and the metallic layers have not been characterized well, which makes the formation mechanism unclear. Polarization-dependent total reflection fluorescence (PTRF)-XAFS [3] is one of the powerful method because it can determine definite three-dimensional structure of metal species dispersed on a flat surface at sub-Å resolution.

In this work, the structures of Pt species immobilized on thiol-terminated organic monolayer formed on Si(111) surface via Si-C covalent bond were determined by measuring Pt L₃ edge PTRF-XAFS.

Experimental

A hydrogen-terminated Si(111) surface, which was obtained by dipping the Si(111) sample in NH₄F aqueous solution, was illuminated with 254 nm UV light in the decene solution containing CH₂=CH(CH₂)₉SH to form the organic monolayer with thiol group at its end. The monolayer-covered Si(111) sample was then immersed into 5 mM K₂PtCl₄ solution to immobilize the Pt complex ions selectively to the thiol group. Finally, the adsorbed Pt complex ions were reduced by immersing the sample in 0.1 M NaBH₄ aqueous solution. The Pt L₃ edge PTRF-XAFS measurements were carried out in air at BL12C. EXAFS analysis was performed using REX 2000 (Rigaku Co., Japan).

Results and Discussion

Figure 1(A) shows the Pt L₃ edge XANES spectra of Pt species formed on the monolayer-covered Si(111) surface. The XANES spectra of Pt foil and K₂PtCl₄ aqueous solution were also shown as references. In (c) of Fig.1(A), the position of the absorption edge was observed in the higher energy region than that of the K₂PtCl₄ reference

((b)), suggesting that the adsorbed Pt complex ion was more oxidized probably due to the interaction with the thiol group of the monolayer. The substitution of the -Cl ligand of the Pt complex ion with other ligands such as -OH might also occur. After reduction ((d) of Fig. 1(A)), the characteristic peaks observed in Pt foil were observed, but the intensity was weaker than that of Pt foil. It suggests that the small Pt nanoclusters should be formed on the surface.

Fig. 1(B) shows the EXAFS region. The spectra of Pt species before and after reduction showed similar features with those of K₂PtCl₄ and Pt foil, respectively. Curve fitting analysis revealed the presence of Pt-Pt interaction after reduction with coordination number of ~5, which was less than that of bulk Pt. This result is in good agreement with the XANES results. No significant differences between s- and p-polarization were detected, indicating that the adsorbed Pt complex ions were not oriented and that sphere-shaped Pt nanoclusters were formed after reduction.

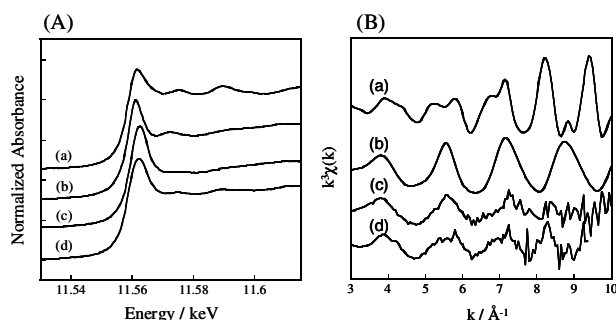


Figure 1 Pt L₃ edge XAFS spectra of (a) Pt foil, (b) K₂PtCl₄ aqueous solution and the Pt complex ions adsorbed on thiol-terminated monolayer formed on Si(111) (c) before and (d) after reduction. (A): XANES; (B) EXAFS.

References

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