

**in situ XAFS Study on Pt Complex Embedded in Organic Molecular Layer**

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**Introduction**

Photoelectrochemical reaction at semiconductor surfaces is a key technology in the new energy scheme because it can synthesize storable Gibbs energy with relatively high efficiency by using solar energy. In the past 40 years, both theory and experiment have been dramatically developed[1]. Semiconductors such as Si, GaAs and CdSe have a suitable band gap for visible light induced various electrochemical reactions. However, those semiconductors are corrosive in contact with aqueous solutions. In addition, very large over potential is required to drive such multi-electron processes because semiconductor electrodes do not have catalytic activity. Recently, we constructed an organic molecular layer of ethyl benzylchloride, which serves as corrosion protection layer and linker groups for additional functional moieties, on hydrogen-terminated Si(111) surface, and grafted viologen multilayer on the linker groups by sequential surface reactions. After anionic Pt complex was embedded in the molecular layer by electrostatic interaction between Pt complex and viologen moieties, very efficient photoelectrochemical hydrogen evolution reaction (HER) was achieved due to electron mediation capability of viologen groups and catalytic activity of Pt complex. In the present work, local and electronic structure of Pt catalyst embedded in the molecular layer was investigated by in situ XAFS measurements during photoelectrochemical HER.

**Experimental**

Surface modification was performed as reported previously[2]. A freshly prepared H-Si(111) substrate was illuminated with 254-nm light for 8 h in deaerated 4-vinylbenzylchloride in the Ar-filled glovebox to yield a 4-ethylbenzylchloride (EBC)-modified Si(111) surface. The EBC-Si(111) substrate was kept in a 4,4'-bipyridine-saturated benzene solution at reflux temperature for 12 h and then placed in 1,4-dibromobutane at 80°C for 12 h. After repeating these modification steps alternately for 4 times so that the monolayer was terminated with bipyridine group, the substrate was kept in 1-bromobutane at 80°C for 12 h to yield a 5L-V<sup>2+</sup>-Si(111) surface. The 5L-V<sup>2+</sup>-Si(111) substrate was immersed in an aqueous solution of 10 mM K<sub>2</sub>PtCl<sub>4</sub> for 20 min to ion

exchange the halide ions of the viologen groups by PtCl<sub>4</sub><sup>2-</sup>.

XAFS measurements were performed at BL12C of the Photon Factory (KEK-PF) in total reflection fluorescence mode by using a 19-element pure Ge solid state detector (GL0110S; Canberra, USA). The sample was mounted on a six-axis goniometer to achieve total reflection configuration. XANES and EXAFS of 5L-PtV<sup>2+</sup>-Si(111) surfaces at Pt L3 edge were measured in air and under electrochemical condition.

**Results**

A peak around 11.56 keV corresponding to the Pt L3 absorption was observed in all the XANES spectra. In air, normalized white line (WL) intensity is identical to that of K<sub>2</sub>PtCl<sub>4</sub> and a shoulder which is characteristic of Pt-Cl bond was observed around 11.58 keV, confirming incorporation of PtCl<sub>4</sub><sup>2-</sup> into the molecular layer. Bond length and coordination number obtained by curve fitting of EXAFS oscillation were in reasonable agreement with previous report on K<sub>2</sub>PtCl<sub>4</sub>. When the surface was immersed in aqueous electrolyte solution, WL intensity increased and the shoulder around 11.58 keV attributed to Pt-Cl bond disappeared, suggesting ligand exchange reaction. Based on curve fitting of EXAFS oscillation, Cl<sup>-</sup> is exchanged with oxygenated species in solution such as OH<sup>-</sup> and H<sub>2</sub>O. At -0.6 V, WL intensity further increased and Cl<sup>-</sup> was completely exchanged by oxygenated species. Although this potential is much more negative than reduction potential of Pt complex to Pt metal, XANES shows characteristic feature of Pt complex and no change due to formation of Pt-Pt bond was observed in EXAFS. Even at -0.8 V which is onset of HER, no change due to formation of Pt metal cluster was observed, showing that not Pt metal but Pt complex acts as a catalyst for HER.

**References**

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