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XAFS Study on Various Metal Catalysts for Hydrogen Evolution and CO_2 Reduction Reactions Incorporated with Organic Molecular Layer on Si(111) Surface

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1 Introduction

Multielectron transfer reactions at semiconductors are generally slow and a catalyst is required to efficiently promote these reactions. Many groups have examined the modification of the semiconductor surface by catalytic metals. It was, however, found that direct contact of a metal leads to the formation of a Schottky junction and recombination center, resulting in a reduced efficiency.

Recently, we have demonstrated that very efficient photoelectrochemical hydrogen evolution reaction (HER) can be achieved at a Si(111) electrode modified with a highly ordered organic molecule layer containing viologen moieties as electron mediators and Pt complexes as the "confined molecular catalysts".[1],[2] Subsequently, we have attempted to apply this concept for the CO_2 reduction. Not only $PtCl_4^{2-}$, but also $AuCl_4^-$ and $PdCl_4^{2-}$ were chosen as metal catalysts because Pd and Au metal electrodes are efficient electrocatalysts for CO_2 reduction. In the present study, we determined oxidation state and local structure of those metal catalysts before and after the electrochemical HER and CO_2 reduction reaction by polarization-dependent total reflection fluorescence (PTRF)-XAFS measurements.

2 Experiment

Si(111) electrode was modified with five layers of viologen moiety with $PtCl_4^{2-}$, $AuCl_4^-$ and $PdCl_4^{2-}$ to yield a $(Pt\text{-}V^{2+})_5$-Si(111), $(Au\text{-}V^{2+})_5$-Si(111) and $(Pd\text{-}V^{2+})_5$-Si(111), respectively, as previously reported.[1],[2],[3]

Pt L_3, Au L_3 and Pd K edge XAFS measurements were performed at BL9A of the Photon Factory (PF) and NW 10A of the Photon Factory-Advanced Ring (PF-AR). X-rays were monochromated using a Si(111) double-crystal monochromator for the Pt L_3 and Au L_3 edges at the BL9A and Si(311) double-crystal monochromator for the Pd K edge at the NW10A. The fluorescence signals were detected using a 19-element pure Ge solidstate detector (GL0110S; Canberra, USA). The EXAFS analyses were carried out using REX 2000 (Rigaku, Japan).

3 Results and Discussion

At the $(Pt\text{-}V^{2+})_5$-Si(111) electrode just after metal incorporation, the shapes of white line and EXAFS oscillation are almost the same as those of K_2PtCl_4, showing the insertion of $PtCl_4^{2-}$ into the molecular layers. After the electrochemical HER and CO_2 reduction, the period of EXAFS oscillation was changed and ligand exchange of Cl^- to oxygen species was found by curve fitting of the Fourier transform. In addition, no Pt-Pt bond was detected, showing that metallic particles were not formed and the actual catalyst for HER and CO_2 reduction is the "confined Pt complex" within the molecular layer.

At the $(Au\text{-}V^{2+})_5$-Si(111) electrode just after metal incorporation, XANES and EXAFS oscillation were similar to those of Au foil, rather than those of $NaAuCl_4$, showing that the Au complexes were reduced to Au metallic particles during metal incorporation, indicating that the actual catalyst for HER and CO_2 reduction is Au metallic particle.

The XANES spectrum of the $(Pd\text{-}V^{2+})_5$-Si(111) electrode just after metal incorporation was distinct from both those of K_2PdCl_4 and Pd foil but the EXAFS oscillation was almost identical to that of K_2PdCl_4 pellet, suggesting that the insertion of $PdCl_4^{2-}$ into the molecular layers as was the case of $PtCl_4^{2-}$. After the electrochemical HER and CO_2 reduction, the period of EXAFS oscillation was changed by the formation of Pd-Pd bond, showing that the Pd complexes incorporated within the molecular layer were gradually reduced to Pd metallic particle during HER and CO_2 reduction. Thus, both Pd complex and Pd metallic particle can be the actual catalysts for HER and CO_2 reduction reaction.

References

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