

## PTRF-XAFS on Various Metal Catalysts for CO<sub>2</sub> Reduction Incorporated with Organic Molecular Layers on Si(111) Surfaces

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### 1 Introduction

Si has a suitable bandgap for solar-to-chemical energy conversion. However, multi-electron transfer reactions such as hydrogen evolution, oxygen evolution and carbon dioxide reduction reactions at Si electrodes are very slow and a catalyst is required to efficiently promote these reactions. Although many groups have attempted the modification of the semiconductor surface with various catalytic metals, direct contact of those metals often leads to the formation of a Schottky junction and recombination center, resulting in a reduced efficiency.

Recently, we have constructed organic molecular layers with viologen moieties as electron transfer mediators and Pt complexes as confined molecular catalysts on a hydrogen terminated Si(111) surfaces and demonstrated its very high photoelectrochemical hydrogen evolution activity.<sup>[1],[2]</sup> More recently, we have applied this concept for the CO<sub>2</sub> reduction by incorporating not only Pt complexes but also Au and Pd complexes into the molecular layers because Pd and Au metal electrodes are efficient electrocatalysts for CO<sub>2</sub> reduction.<sup>[3]</sup> In the present study, we characterized oxidation state and local structure of those metal catalysts before and after the CO<sub>2</sub> reduction reaction by polarization-dependent total reflection fluorescence (PTRF)-XAFS measurements to determine the actual catalytic species for CO<sub>2</sub> reduction.

### 2 Experiment

Si(111) electrodes were modified with multi-viologen-layers, and then immersed into aqueous solutions containing K<sub>2</sub>PtCl<sub>4</sub>, NaAuCl<sub>4</sub> and K<sub>2</sub>PdCl<sub>4</sub> to yield a (Pt-V<sup>2+</sup>)<sub>5</sub>-Si(111), (Au-V<sup>2+</sup>)<sub>5</sub>-Si(111) and (Pd-V<sup>2+</sup>)<sub>10</sub>-Si(111), respectively, as previously reported.<sup>[1],[2],[3]</sup>

Pt L<sub>3</sub>, Au L<sub>3</sub> 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<sub>3</sub> and Au L<sub>3</sub> 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 multi-element Ge solid-state detector. The EXAFS data were analysed using REX 2000 (Rigaku, Japan).

### 3 Results and Discussion

In the XANES spectrum of the modified Si(111) electrode just after immersion in a NaAuCl<sub>4</sub> aqueous solution, white line observed for NaAuCl<sub>4</sub> pellet was absent. XANES spectrum and EXAFS oscillation were similar to those of Au foil, rather than those of NaAuCl<sub>4</sub> pellet, showing that the Au complexes were spontaneously reduced to form Au metallic particles on the molecular layer. Almost no change was observed in the XANES and EXAFS oscillation after CO<sub>2</sub> reduction, indicating that the actual catalysts for CO<sub>2</sub> reduction is Au metallic particles.

The XANES spectrum and the EXAFS oscillation of the modified Si(111) electrode just after immersion in a K<sub>2</sub>PdCl<sub>4</sub> aqueous solution are similar to those of K<sub>2</sub>PdCl<sub>4</sub> pellet, suggesting that the PdCl<sub>4</sub><sup>2-</sup> was successfully inserted into the molecular layers as Pd complex. After the CO<sub>2</sub> reduction, formation of the Pd-Pd bond was identified by curve fitting of the Fourier transform of EXAFS oscillation, showing that the Pd complexes incorporated within the molecular layer were reduced to Pd metallic particle as potential was made more negative for CO<sub>2</sub> reduction. Thus, Pd metallic particles are the actual catalysts for CO<sub>2</sub> reduction reaction.

In the XANES spectrum of the modified Si(111) electrode just after immersion in a K<sub>2</sub>PtCl<sub>4</sub> aqueous solution, the shape of white line and EXAFS oscillation were almost identical to those of K<sub>2</sub>PtCl<sub>4</sub> pellet, suggesting that PtCl<sub>4</sub><sup>2-</sup> was successfully inserted into the molecular layers. After the CO<sub>2</sub> reduction, the white line intensity rather increased despite the negative potential holding for CO<sub>2</sub> reduction. Moreover, no Pt-Pt bond was detected and formation of Pt-O bond was identified by

curve fitting of the Fourier transform, showing that metallic particles were not formed but ligand exchange from chlorine to oxygenated species took place. Thus, the actual catalysts for CO<sub>2</sub> reduction are Pt complexes.

References

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