PTRF-XAFS on Various Metal Catalysts for CO₂ Reduction Incorporated with Organic Molecular Layers on Si(111) Surfaces

Takuya Masuda,¹² Hiromitsu Uehara,¹ Satoru Takakusagi,³ Wang-Jae Chun,⁴ Toshihiro Kondo,⁵ Kiyotaka Asakura¹ and Kohei Uosaki¹A⁷

¹Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN), National Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan
²Japan Science and Technology Agency, PRESTO, Kawaguchi, Saitama 332-0012, Japan
³Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan
⁴Chemistry Department, International Christian University, Mitaka 181-8585, Tokyo, Japan
⁵Graduate School of Humanities and Sciences, Ochanomizu University, Ohtsuka, Bunkyo-ku, Tokyo 112-8610, Japan
⁶International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan
⁷Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-0810, Japan

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 activity. 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. More recently, we have applied this concept for the CO₂ 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 CO₂ reduction. Thus, Pd metallic particles are the actual catalysts for CO₂ reduction. Moreover, no Pt-Pt bond was 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 NaAuCl₄ aqueous solution, white line observed for NaAuCl₄ pellet was absent. XANES spectrum and EXAFS oscillation were similar to those of Au foil, rather than those of NaAuCl₄ 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 CO₂ reduction, indicating that the actual catalysts for CO₂ reduction is Au metallic particles.

The XANES spectrum and the EXAFS oscillation of the modified Si(111) electrode just after immersion in a K₂PtCl₄ aqueous solution are similar to those of K₂PdCl₄ pellet, suggesting that the PdCl₄²⁻ was successfully inserted into the molecular layers as Pd complex. After the CO₂ 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 CO₂ reduction. Thus, Pd metallic particles are the actual catalysts for CO₂ reduction reaction.

In the XANES spectrum of the modified Si(111) electrode just after immersion in a K₂PtCl₄ aqueous solution, the shape of white line and EXAFS oscillation were almost identical to those of K₂PdCl₄ pellet, suggesting that PtCl₄²⁻ was successfully inserted into the molecular layers. After the CO₂ reduction, the white line intensity rather increased despite the negative potential holding for CO₂ 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$_2$ reduction are Pt complexes.

References

* masuda.takuya@nims.go.jp