

PTRF-XAFS Study of Spontaneous Deposition of Pt on Au(111)

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1 Introduction

In order to obtain the Pt monolayer catalyst which has the potential to afford >100% Pt atom economy, surface limited redox replacement (SLRR) is a prospective method.^[1, 2] In the previous work we found that the Pt monolayer was obtained through the unique precursor state. The previous work indicated that spontaneous deposition of PtCl_4^{2-} occurred with the interaction of Au(111) and PtCl_6^{2-} , together with the SLRR of PtCl_6^{2-} with sacrificial UPD (underpotential deposition) Cu.^[3] In this work, we explored the the spontaneous deposition of PtCl_4^{2-} onto Au(111). We have applied the technique of in situ polarization-dependent total reflection fluorescent X-ray absorption fine structure (in situ PTRF-XAFS).

2 Experiment

High-quality Au(111) was obtained by flame annealing with a butane gas burner. The Au single crystal disk was transferred into a N_2 -filled glovebox and then immersed in 1 mM $\text{H}_2\text{PtCl}_6 / 0.1 \text{ M HClO}_4$ for 30 s. We call the process as “Pt spontaneous deposition (Pt SD)”, the Au(111) was rinsed in deaerated ultrapure water for 30 s. Then the Pt-deposited Au(111) disk was loaded into a homemade XAFS-electrochemical cell, through which deaerated 0.1 M HClO_4 was subsequently cycled. The cell was taken out of the glovebox for PTRF-XAFS measurement.

3 Results and Discussion

The Pt L_3 -edge XAFS spectra, especially the XANES region, of the Pt species had a large polarization – dependence as shown in Fig. 1. The white line peak intensities of the s- and p-polarization were smaller and larger than that of K_2PtCl_4 , respectively. The peak positions of EXAFS oscillations were well corresponding to that of K_2PtCl_4 . EXAFS curve fitting analysis confirmed the Pt-Cl bond length of 2.27 Å. From XPS (Fig. 2), we also confirmed the surface Pt and Cl after Pt SD.

From these evidences, we have concluded that the Pt SD on Au(111) produces PtCl_4^{2-} located on Au(111) single crystal parallel to the surface.

The current work not only provides new insight for the SLRR method to prepare Pt-skin electrocatalysts, but also serves as the pilot research for further in situ study of Pt stability and dynamic structural variation under electrochemical conditions.

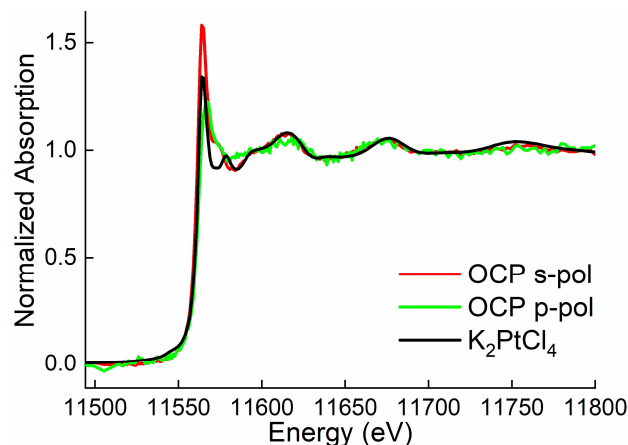


Fig. 1: PTRF XAFS of Pt/Au(111) measured in s- and p-polarization at open circuit potential in 0.1 M HClO_4 , as compared with XAFS of K_2PtCl_4 .

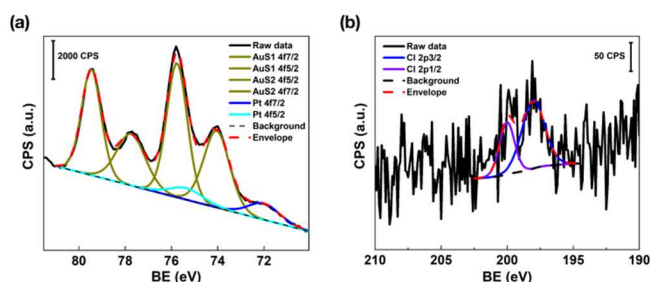


Fig. 2 (a) Pt 4f (b) Cl 2p XPS spectra of Pt/Au(111) after Pt SD.

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References

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