

Revisit of Pt Deposition via Surface Limited Redox Replacement of Copper UPD Layer on Au(111) by EXAFS

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1 Introduction

Two-dimensional (2D) Pt thin films have been used in variety of applications in recent years. A new deposition method, called as SLRR (Surface Limited Redox Replacement) was developed based on UPD monolayer serving as a reducing sacrificial template in a galvanic displacement reaction with more noble Pt ions[1]. The deposition protocol involves several steps in which the Au surface (substrate) is first covered with a UPD layer of Cu which plays a role as sacrificial metal and was displaced with Pt under open circuit potential (OCP).

We reported that $[\text{PtCl}_4]$ was a main and initial product after the SLRR which was totally different from the original pictures[1]. After the critical discussion we revisited the XAFS analysis and now we proposed another new model structure that satisfied all characterization results including XAFS[2].

2 Experiment

A $\phi 15$ mm Au(111)(5 mm thick) single crystal (SPL) was used as substrate. The Au(111) was electrochemically polished and flame-annealed and then transferred into an Ar filled glovebox for further deposition. A monolayer of Cu was underpotentially deposited which was then replaced with Pt by immersing the sample into 0.1 M HClO_4 + 1 mM H_2PtCl_6 for 30 s. sample was then transferred to the in-situ XAFS cell. 6 μm Mylar film was used as X-ray window. The XAFS cell was assembled inside the glovebox filled with N_2 , and then transferred to a 5-axis goniometer for total reflection adjustment. XAFS spectra were measured at BL12C and BL9A, PF. A 19-element Ge solid state detector (MSSD; Canberra) was used as the fluorescence detector. A Zn filter ($\mu\text{t} = 3$) was placed in front of the MSSD to remove the elastic scattering from the solution and Au substrate.

3 Results and Discussion

Previous EXAFS analysis clearly showed that PtCl_4 complex was present with Pt-Cl = 0.226 nm parallel to the Au surface[2]. However, we assumed the mixture model of PtCl_4 and Pt nanoclusters as shown in Fig .1 where Pt-Pt was wqual to 0.288 nm, Pt-Au was 0.282 nm and total particle size was 2.2 nm. Figure 2 shows the comparison between the observed and

calculated EXAFS oscillations in parallel and perpendicular directions. This structure was consistent with XPS, AFM and cyclic voltammetry results. We concluded the mixture Pt species present on the Au surface after the SLRR.[3]

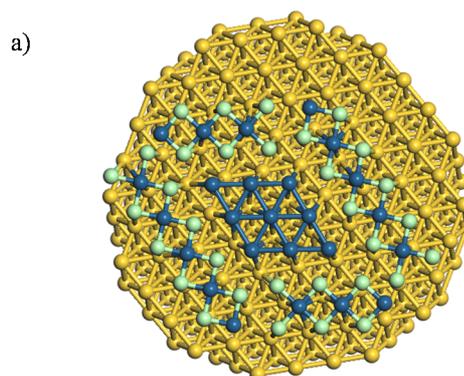


Fig. 1: Proposed model structure

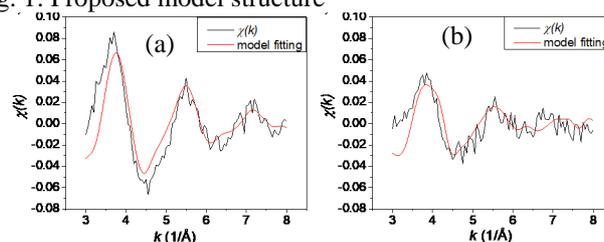


Fig.2 XAFS oscillations (a) $\vec{E} \parallel$ surface (b) $\vec{E} \perp$ surface

[1] Brankovic, S. R., Wang, J. X. & Adzic, R. R. (2001). *J.Serb.Chem.Soc.* **66**, 887-898.

[2] Yuan, Q., Takakusagi, S., Wakisaka, Y., Uemura, Y., Wada, T., Ariga, H. & Asakura, K. (2017). *Chem. Lett.* **46**, 1250-1253.

[3] Yuan, Q., Wakisaka, Y., Uemura, Y., Wada, T., Ariga-Miwa, H., Takakusagi, S., Asakura, K. & Brankovic, S. R. (2017). Submitted to *J.Phys.Chem, C*.

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