ガルバニック交換反応による1値原子層成長の偏光全反射蛍光XAFSによるその場観測

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1. Q. Yuan, Y. Wakisaka, Y. Uemura, T. Wada, H. Ariga-Miwa, S. Takakusagi, K. Asakura and S.R. Brankovic. *J.Phys,Chem, C. 122,16664-16673(2018).10.1021/acs.jpcc.8b02218*

2. Q. Yuan, S. Takakusagi, Y. Wakisaka, Y. Uemura, T. Wada, H. Ariga and K. Asakura, *Chem Lett. 46,1250-1253(2017).10.1246/cl.170423*

What is Galvanic Replacement Reaction and UPD?

M（solid) +M' $^{2+}$(sol) → M' (solid) + M^{2+} (sol)

If the M' is more noble.

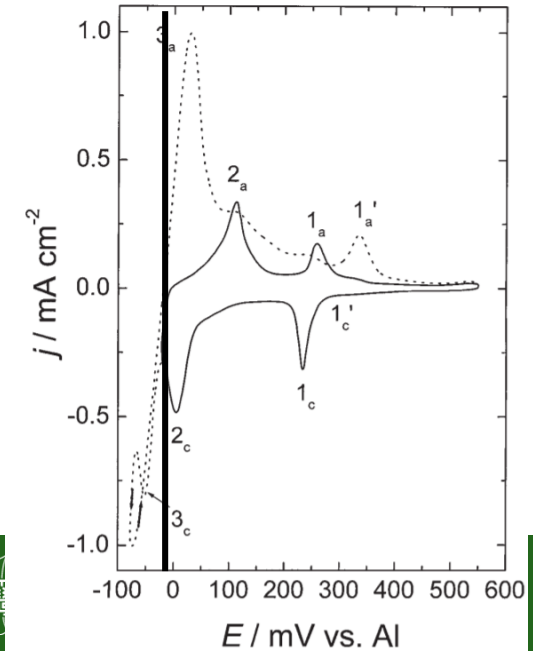
Ag (solid) + Au^{+}(sol) → Au(solid) + Ag^{+}(sol)

Zn(solid) +Cu^{2+}(sol) → Cu(solid) +Zn^{2+}(sol)

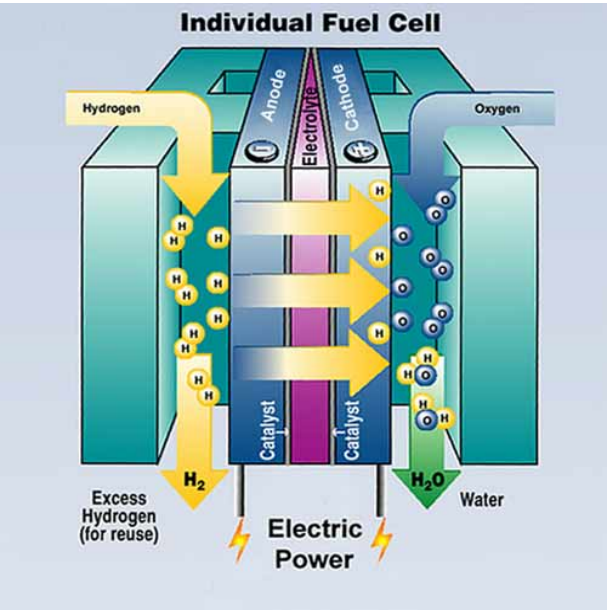
UPD(underpotential deposition)

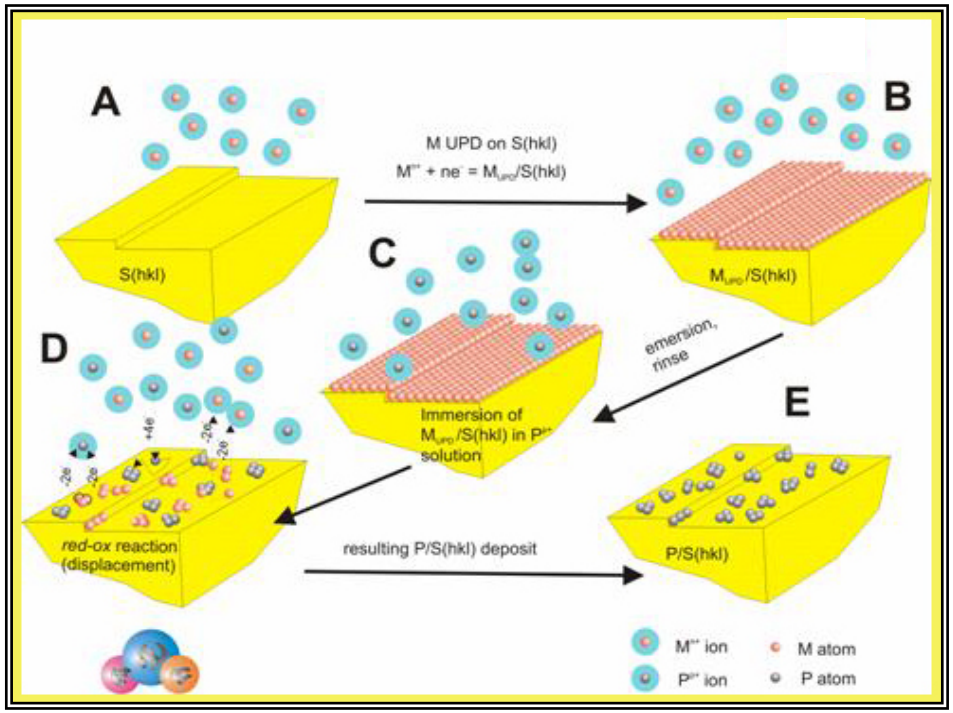
Due the strong interaction of substrate, deposition occurs at more positive potential than the deposition potential.

Al ↔Al^{3+}+3e^{-} ΔG=0

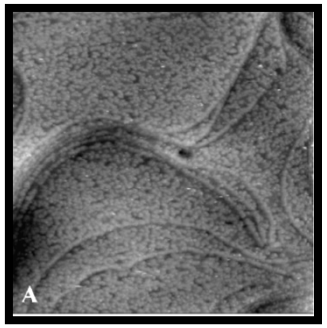


Background: galvanic replacement reaction

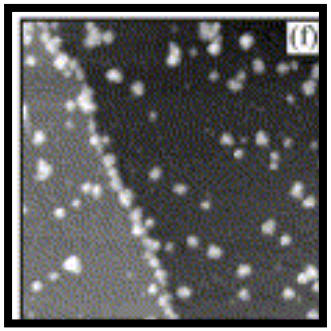




Morphology comparison:



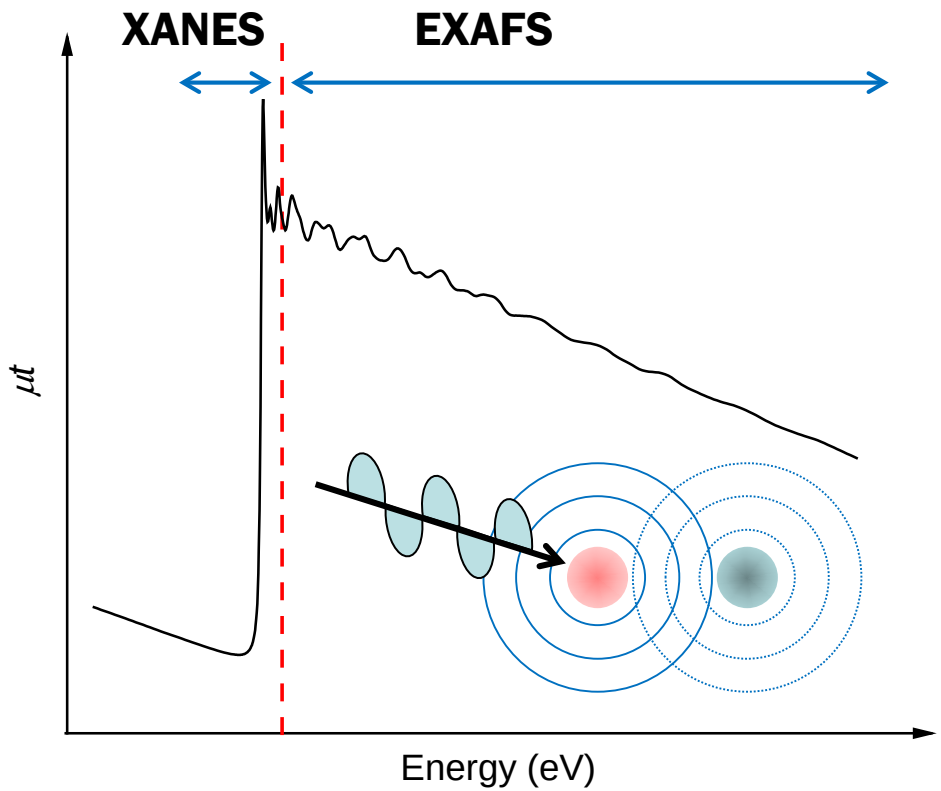
vs.



S.R. Brankovic *et. al. Surf. Sci.*, 474, L173, (2001)

D.M. Kolb *et. al. Electrochimi. Acta.*, 47, 1461, (2002)

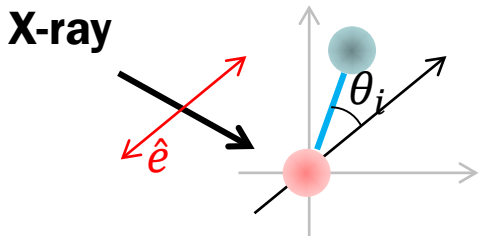
Polarization Total Reflection Fluorescence X-Ray Absorption Fine Structure



Absorbing atom

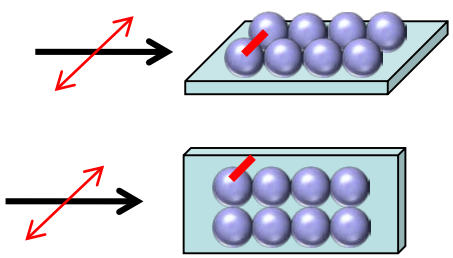
Scattering atom

Polarization dependence



K-edge: $$\chi(k) = 3\sum_{i}^{N} cos^2\theta_i\chi_i(k)$$

L_3-edge: $$\chi(k) = \frac{1}{2}\sum_{i=1}^{N^i}\chi_i(k)(1.2 + 2.4\cos^2\theta_i)$$



s-polarization

p-polarization

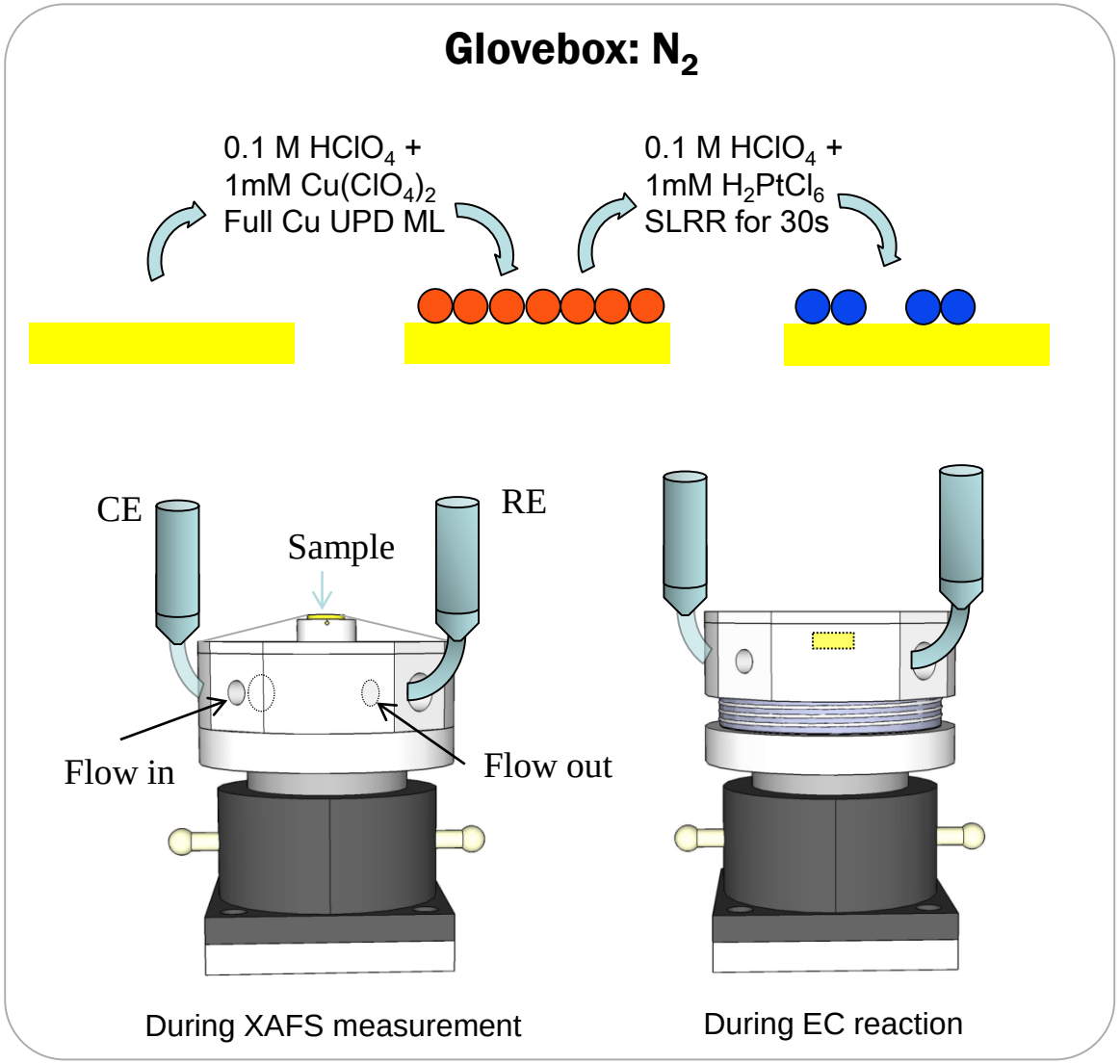
Fluorescence XAFS: diluted/thin

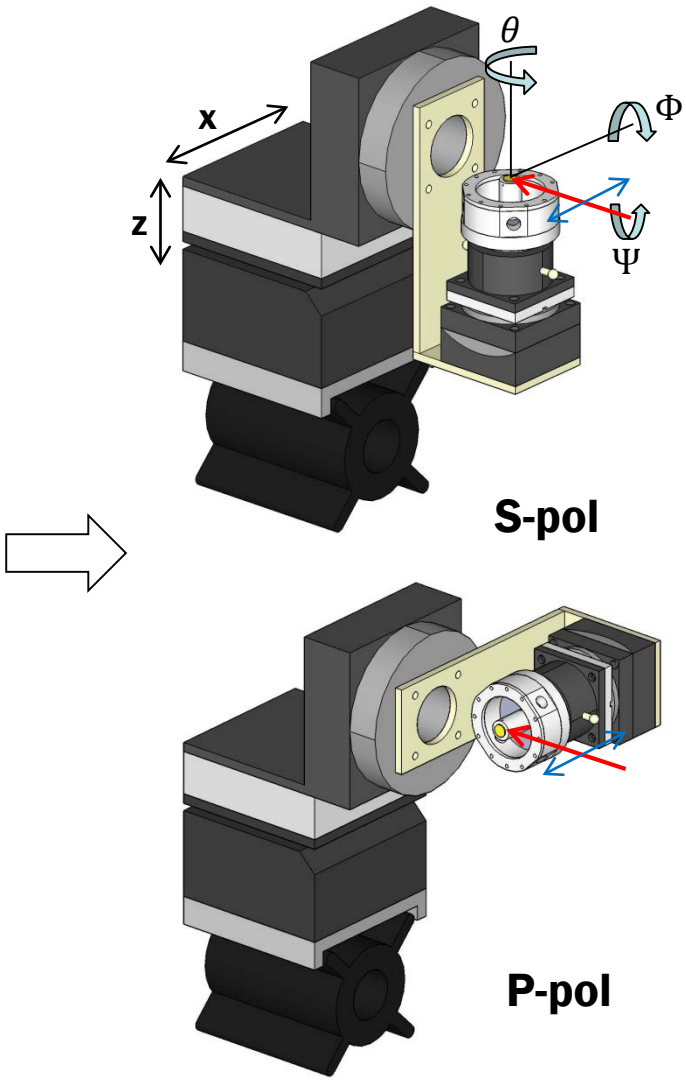
Total Reflection: X-ray depth is only a few nm

PTRF-XAFS: highly dispersed sample on atomically flat surface

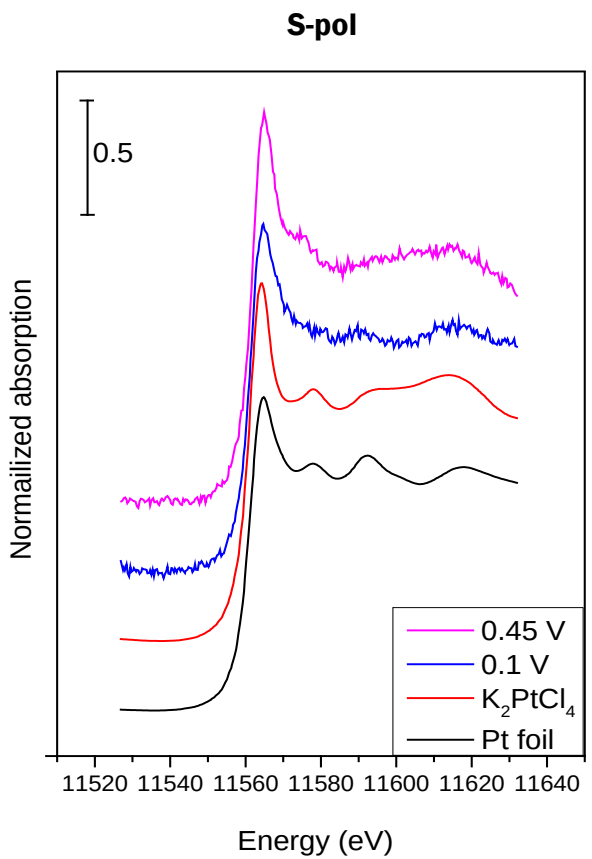
Asakura, K. In *Catalysis* Spivey, J. J., Gupta, M., Eds.; RSC publishing: Cambridge

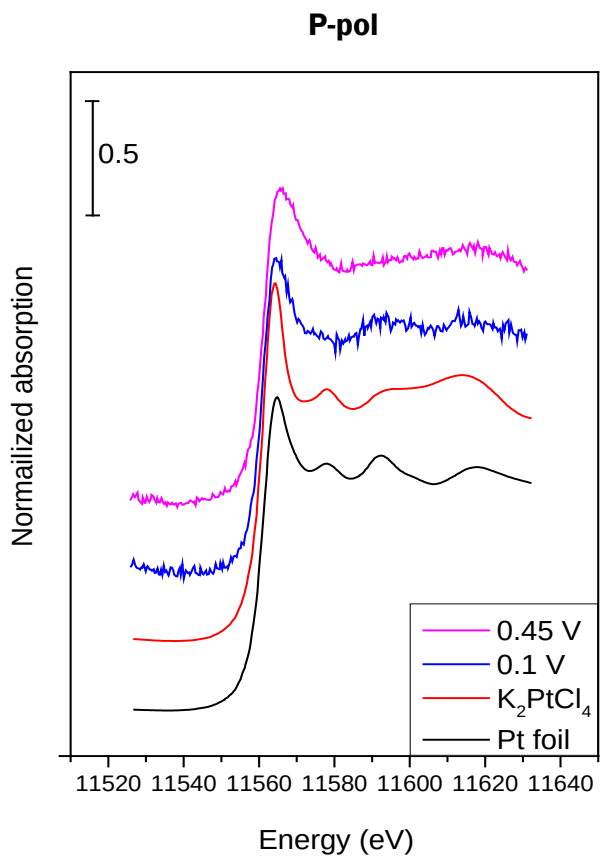
Experimental setup

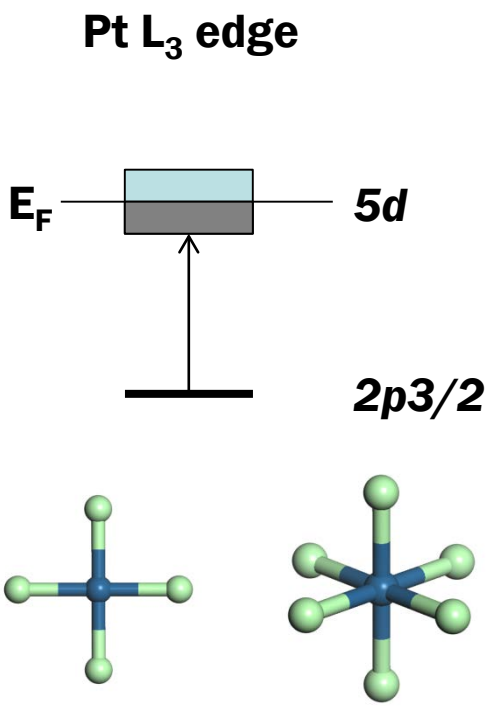




XANES results







Pt was not fully reduced to metal state after replacement reaction

Pt complex structure =$PtCl_4^{2-}$

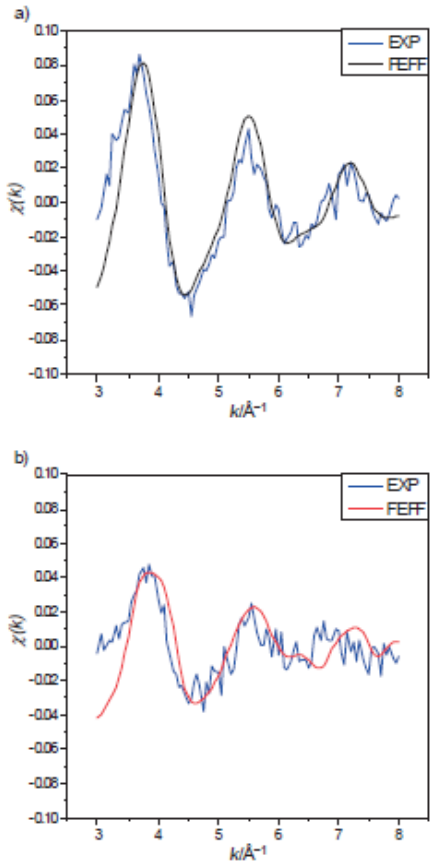


Figure 2. EXAFS comparison between the experimental data and FEFF calculation for the Pt/Au(111) at $E = 0.45$ V. a) s-Polarization and b) p-polarization.

$PtCl_4^{2-}$

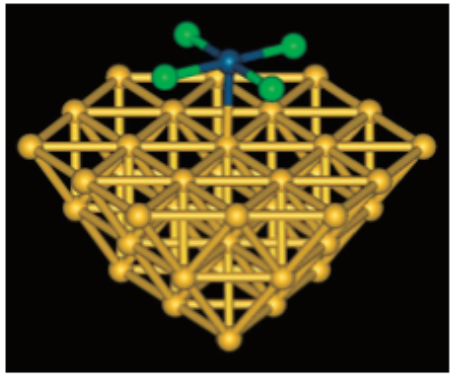
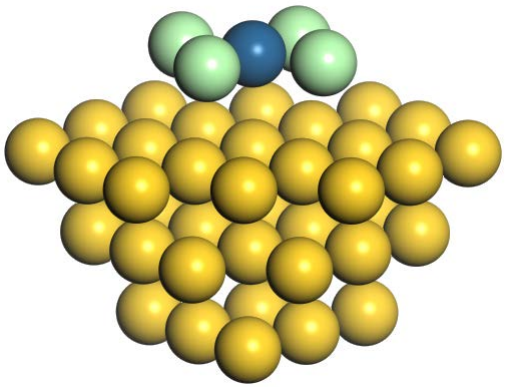
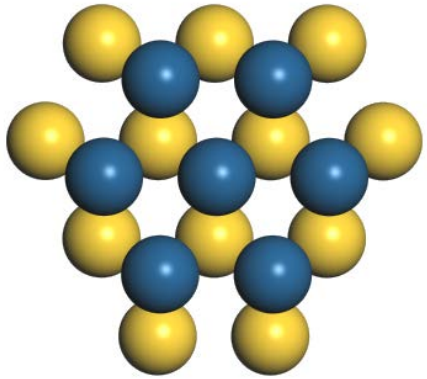


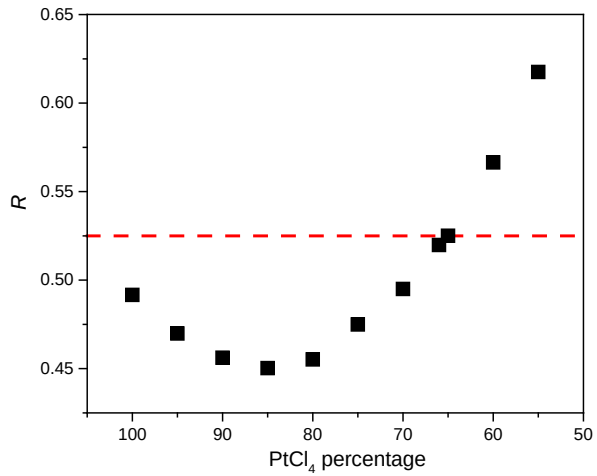
Figure 3. A $PtCl_4$ complex model on Au(111) used in the FEFF simulation. Yellow, green, and blue balls are Au, Cl, and Pt atoms, respectively. The Pt–Cl complex preserved the square planar $[PtCl_4]^{2-}$ structure with Pt on top of the Au atom. The Pt–Cl bond length is 0.226 nm for all four bonds, while the Pt–Au distance is 0.270 nm.

EXAFS simulation using FEFF code – Mixed model of $PtCl_4$ and Pt-Pt bond





F-test for $PtCl_4$ and Pt metal mixture model

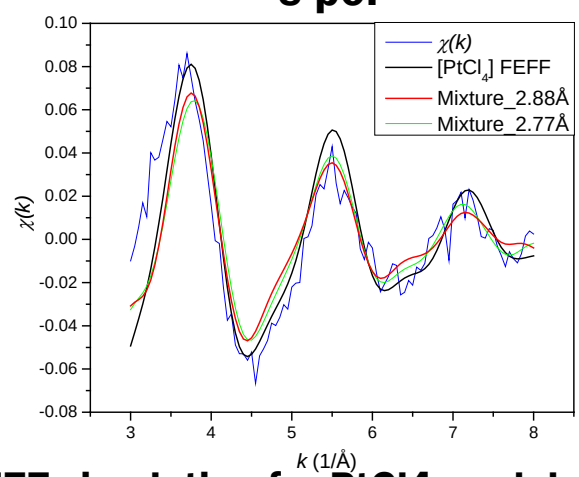


$$R_{avg}^2 = \frac{R_s^2/\varepsilon_s^2 + R_p^2/\varepsilon_p^2}{1/\varepsilon_s^2 + 1/\varepsilon_p^2}$$

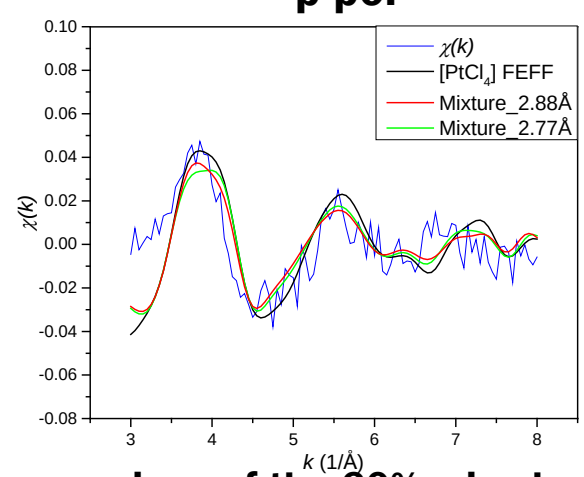
$R_{2.88} < R_{2.77}$

Pt-Pt bond length: 2.88 Å

s-pol



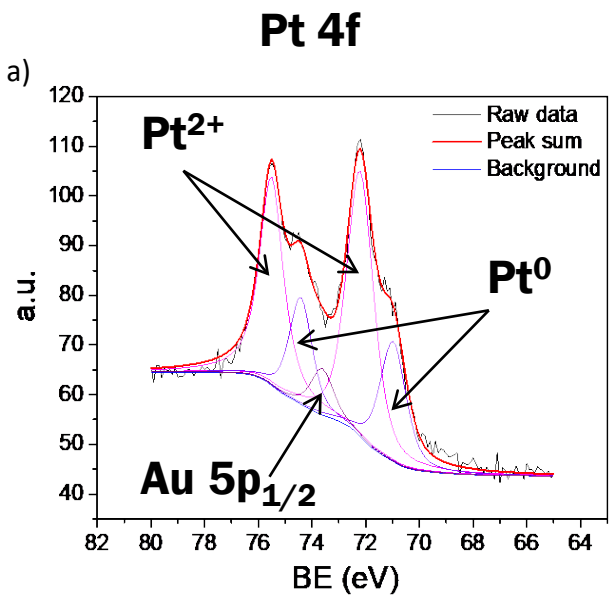
p-pol

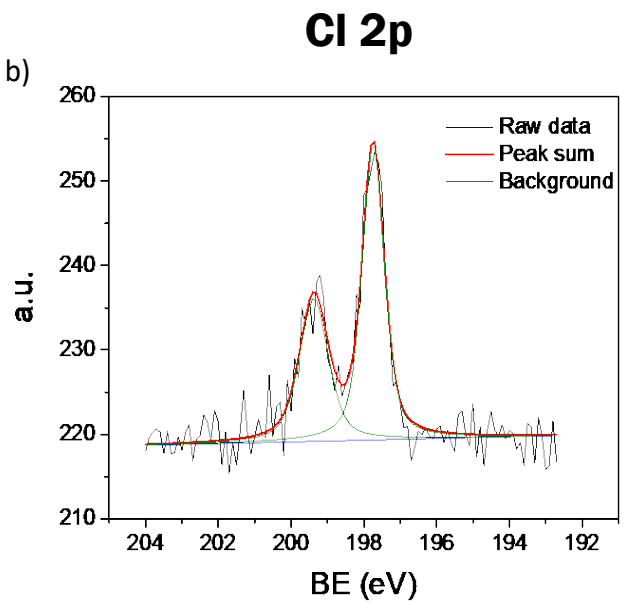


Acceptable range for PtCl4 complex: 100% to 57%

FEFF simulation for PtCl4 model with comparison of the 60% mixed model.

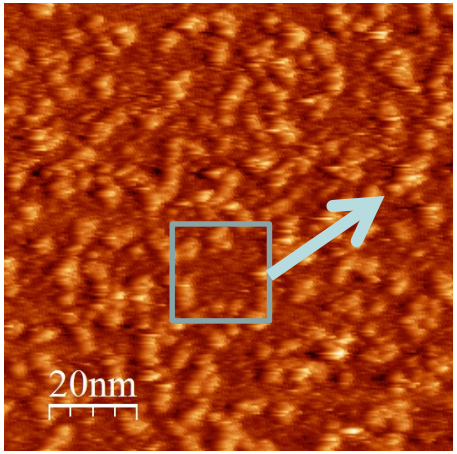
Ex-situ methods: XPS and STM

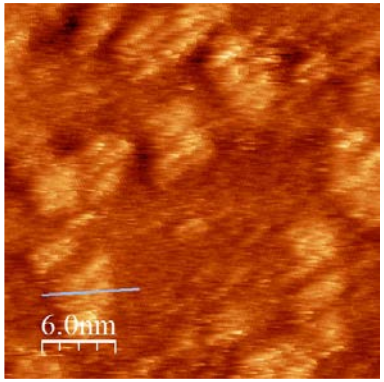


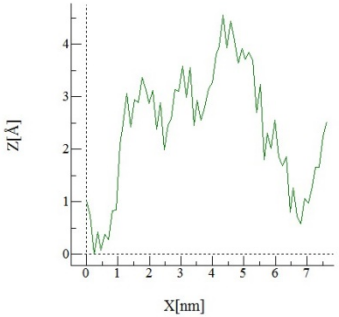


Pt coverage:
0.34±0.04 ML

40 ± 6 %

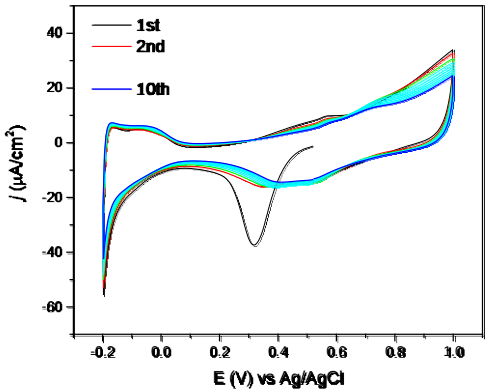






$PtCl_4^{2-}$ =± 0.22
Pt^{0} =0.12

Reaction stoichiometry



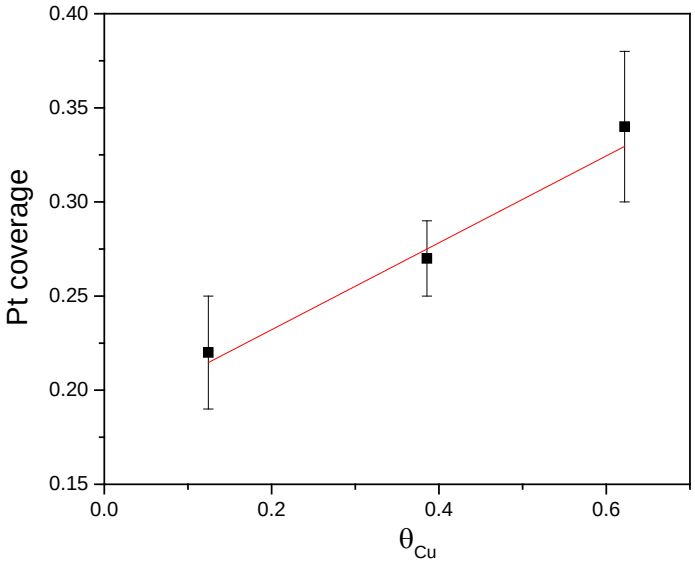
$$Pt^{2+} + 2e^- \rightarrow Pt$$

	CV	EXAFS
$PtCl_4$ percentage	**60%**	**100 to 57%**

$$\begin{cases} [PtCl_6]^{2-} + Cu^0 \rightarrow [PtCl_4]^{2-} + Cu^{2+} + 2Cl^- \\ [PtCl_6]^{2-} + 2Cu^0 \rightarrow Pt^0 + 2Cu^{2+} + 6Cl^- \end{cases}$$

$$[PtCl_6]^{2-} + 4Cu^0 + 2Cl^- \rightarrow Pt^0 + 4[CuCl_2]^-$$

Pt coverage vs. Cu coverage



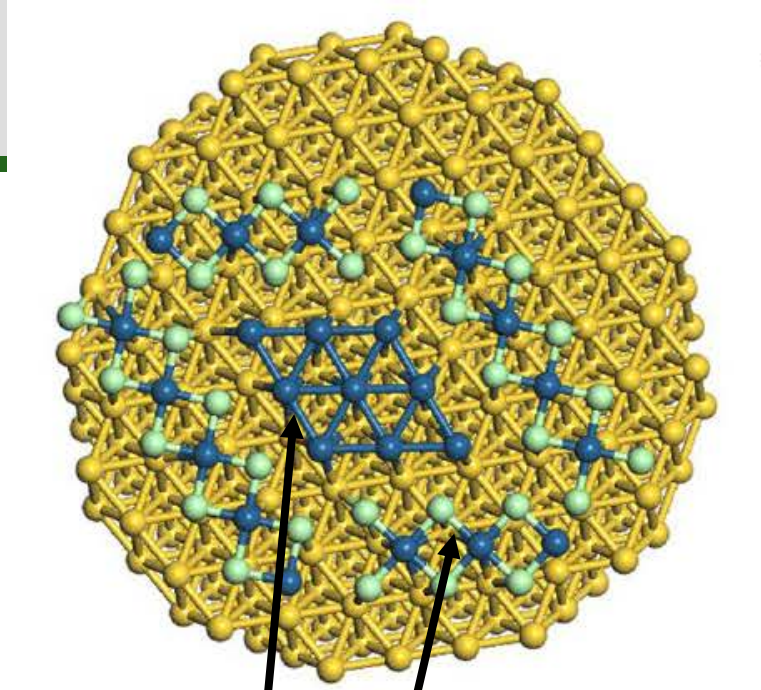
Slope: 0.23±0.04

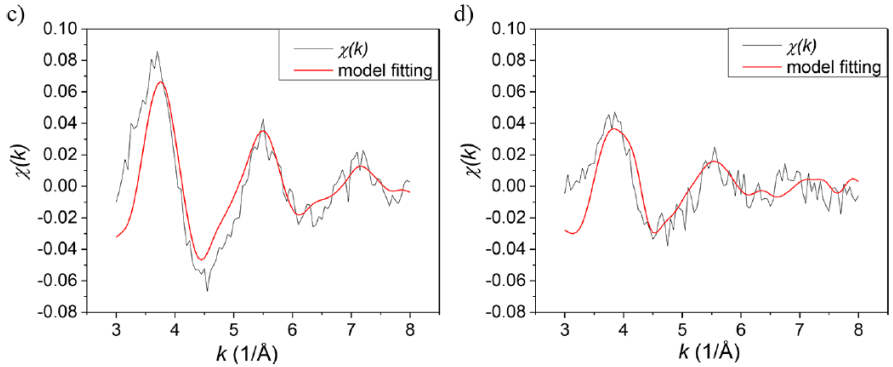
$PtCl_4$ percentage: 59%

0.62 ML Cu oxidation: 136.5 μC/cm²

Reduction of $[PtCl_6]^{2-}$ to Pt^0: 126 μC/cm²
Pt 0.14 ML

Proposed model





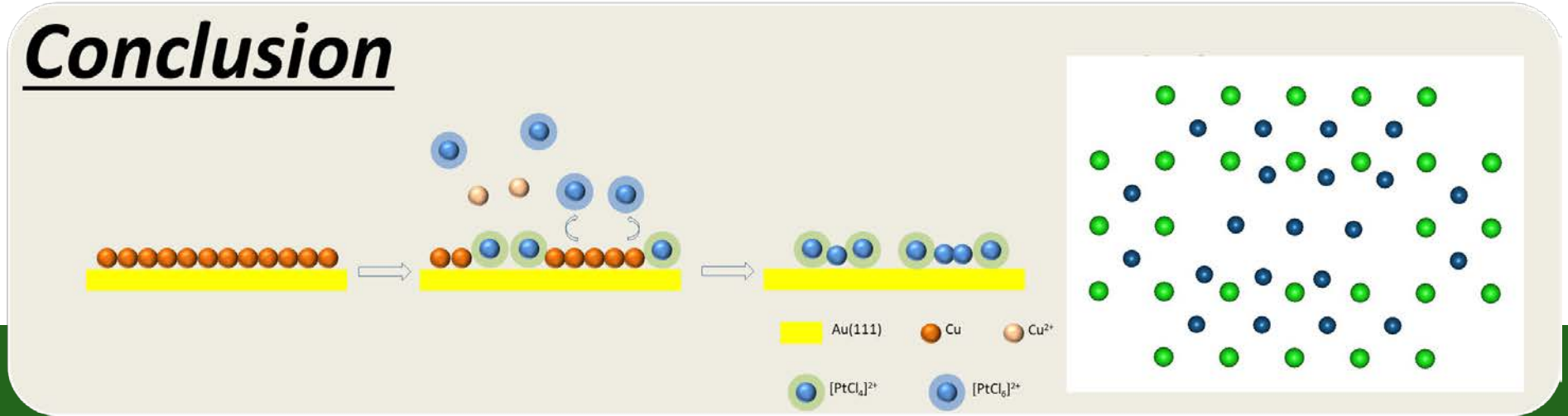
$[PtCl_2] = 0.60$

$Pt^0 = 0.40$

Conclusion

- Pt-Cl complex was observed after SLRR of Cu UPD layer, using *in-situ* PTRF-XAFS.
- $PtCl_4$ model was proposed based on FEFF calculation.
- The oxidation state of Pt was nearly 2+ based on XANES analysis.
- This Pt-Cl complex represented a shorter bond length comparing to $[PtCl_4]^{2-}$, which may coming from the charge transfer from Pt to Au substrate. Pt-Pt bond distance of 2.88 Å showed smaller R factor.
- 60% $[PtCl_4]^{2-}$ + 40% Pt metal model was proposed based on XAFS, XPS and CV.

$\mu_{\mathrm{unpol}} = (2\mu_{s,\mathrm{PtCl_4}} + \mu_{p,\mathrm{PtCl_4}})/3$ $[PtCl_4]^{2-}$ percentage: 59% + spontaneous deposition of Pt on Au(111)



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2016G035

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Yuan, Q.; Takakusagi, S.; Wakisaka, Y.; Uemura, Y.; Wada, T.; Ariga, H.; Asakura, K., Polarization-Dependent Total Reflection Fluorescence X-Ray Absorption Fine Structure (Ptrf-Xafs) Studies on the Structure of a Pt Monolayer on Au(111) Prepared by the Surface-Limited Redox Replacement Reaction. *Chem Lett.* ***2017, 46, 1250-1253.***

Thank you for your attention!