BCLA+PTRF-XAFSによる表面Pt種の構造決定

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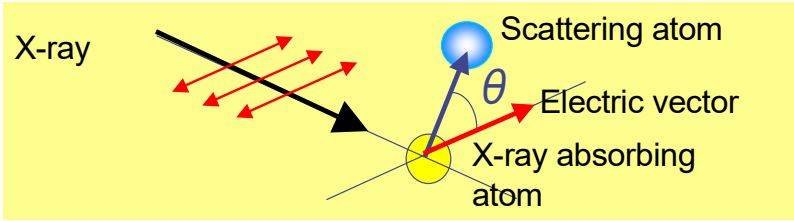
Introduction

Polarization dependent total reflection fluorescence XAFS(PTRF-XAFS) is a powerful technique to investigate the 3 dimensional structure of dispersed metal on the surface.

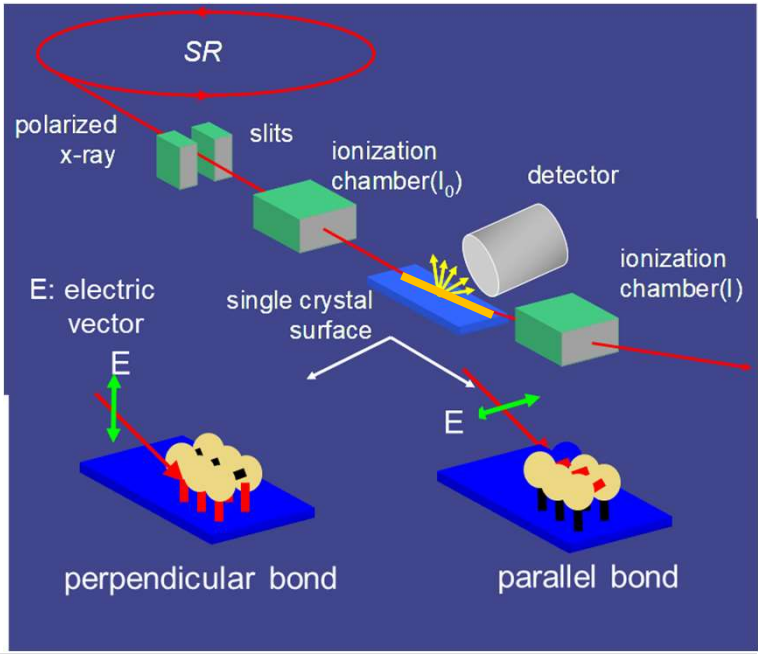


$$\chi_{obs}(k) = \sum_i \chi_i(k) 3\cos^2\theta] \quad \text{(K edge)}$$

$$\chi_{obs}(k) = \sum_i \chi_i(k)(0.7 + 0.9\cos^2\theta_i) \quad (L_{2,3}edges)$$

It is surface sensitive because penetration depth of X-ray is small in the total reflection conditions.

Demerit: Grazing angle incidence is necessary and a long footprint occurs on surface to require the large flat surface



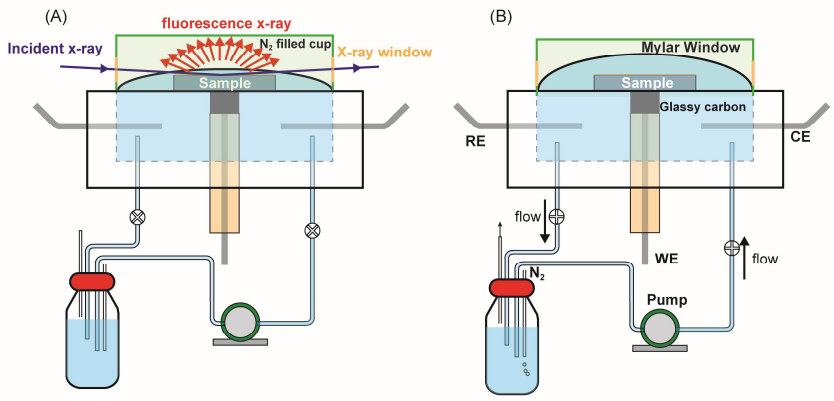
When it was applied to solution/solid interface.

Presence of water gives large scattering even under the total reflection conditions.

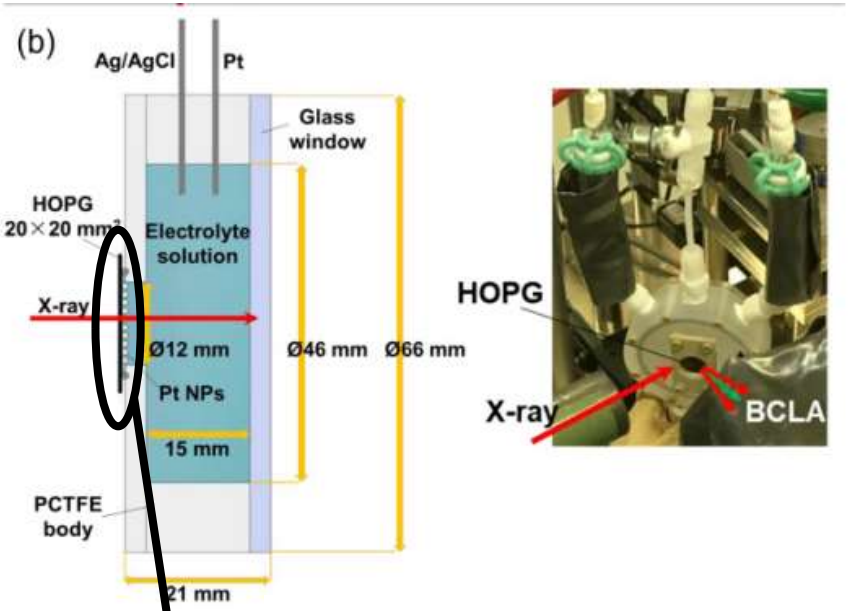
Thus we have to reduce the thickness of the solution layer.

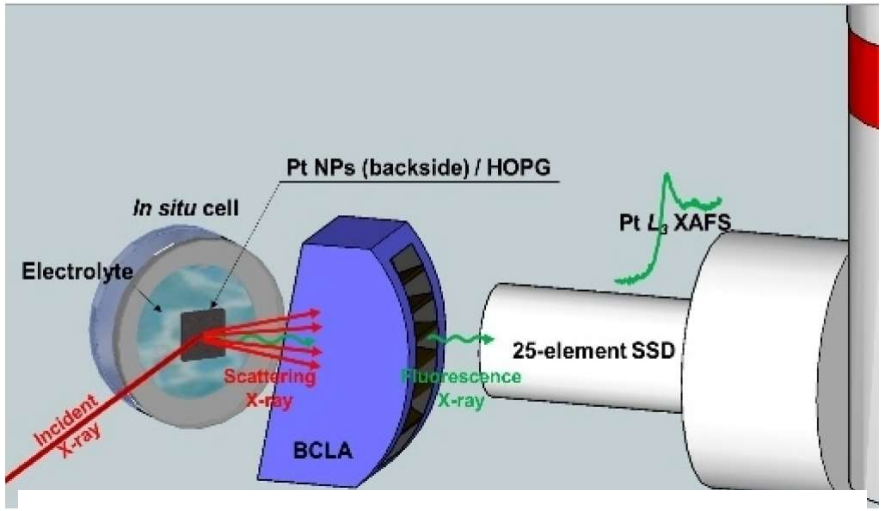
This blocks the diffusion of solution and reaction.

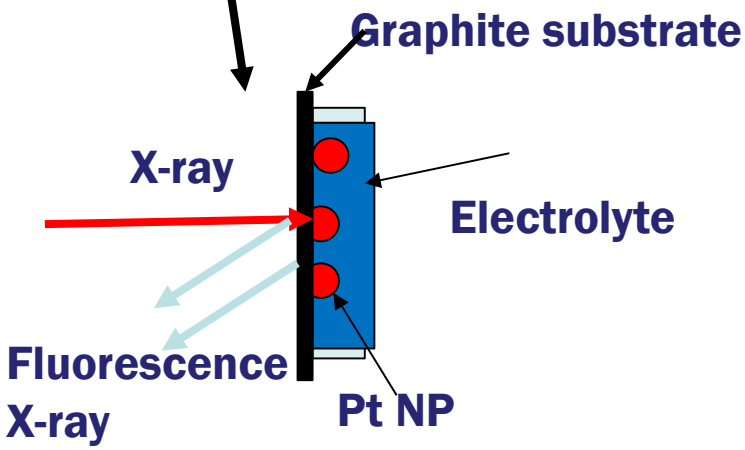
We have to remove the backscattering X-ray



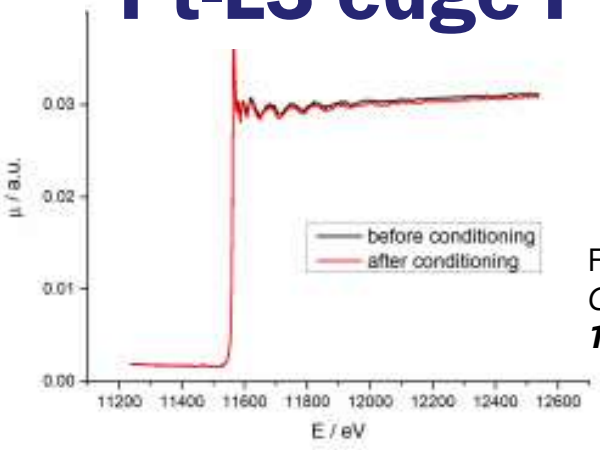
BCLA（Bent Crystal Laue Analyzer)＋BI（Back Illuminated)-XAFS







Pt-L3 edge PtAuCo/C



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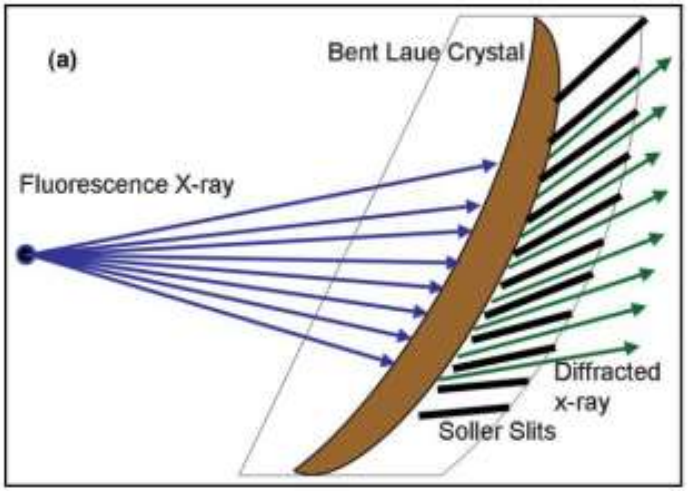
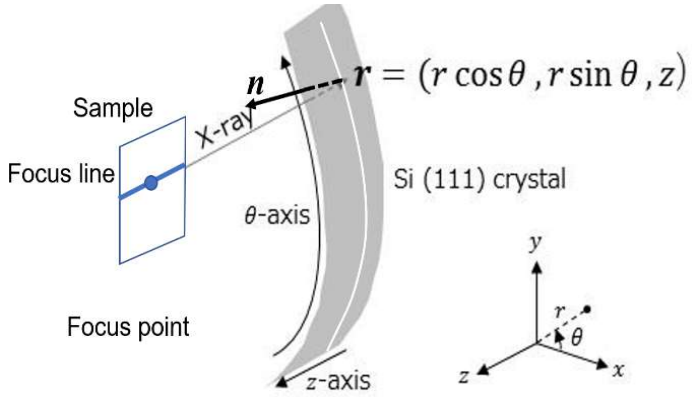
BCLA(Bent Crystal Laue Analyzer)





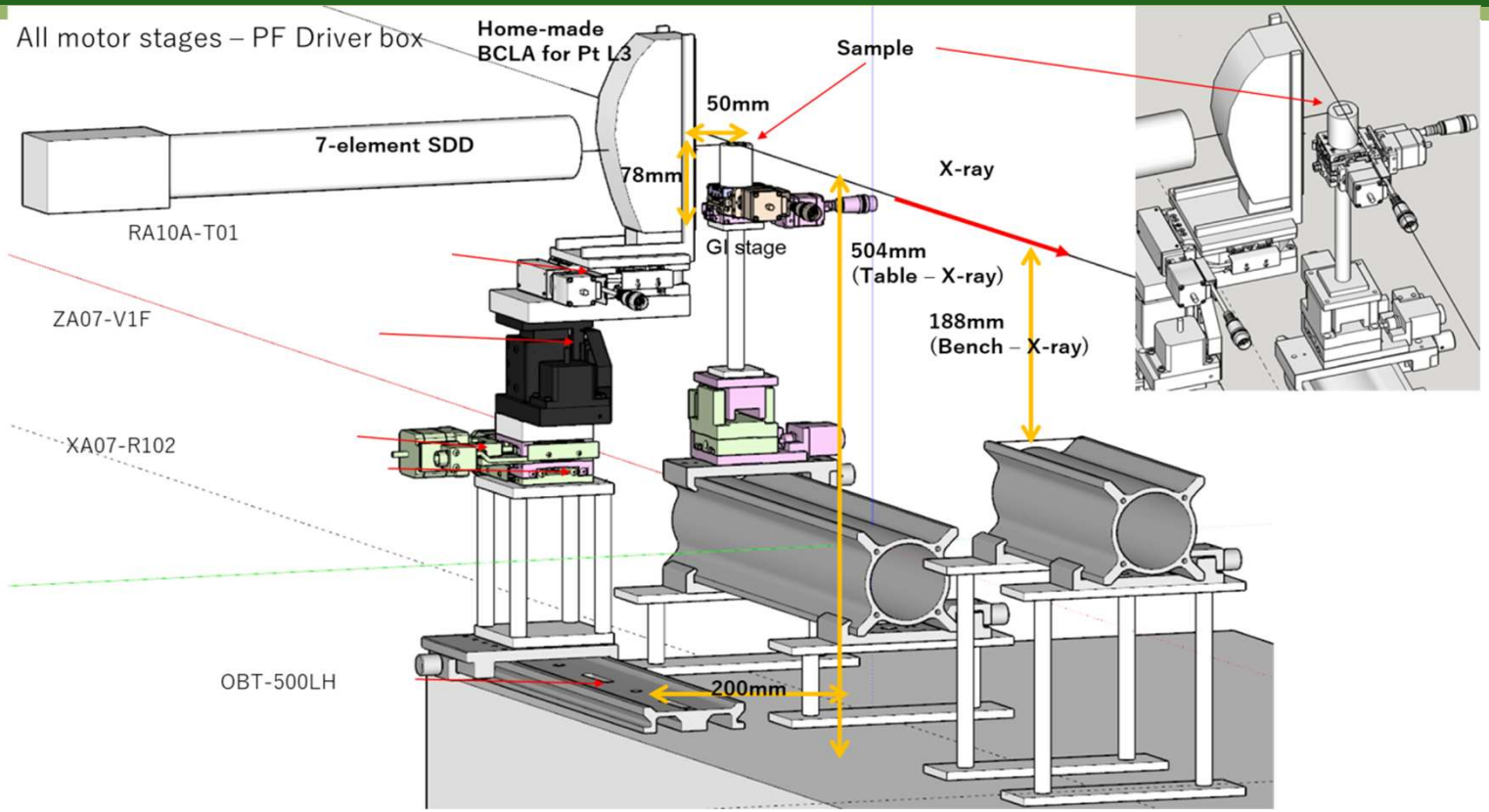
The crystal is bent in a log spiral way, the angle between the surface normal and the radial vector from the focal oint is constant over the spiral curved surface.

Sakayanagi, Y. (1982). Jpn. J. Appl. Phys. 21, L225-L226.

The BCLA requires the point focus but total reflection conditions give long footprint on the surface as shown lines. If the BCLA crystal and sample surface are parallel and focus points of BCLA and x-ray footprint are agreed, we can use whole BCLA crytal surface as a detector and we can increase the sensitivity.

But is it true?

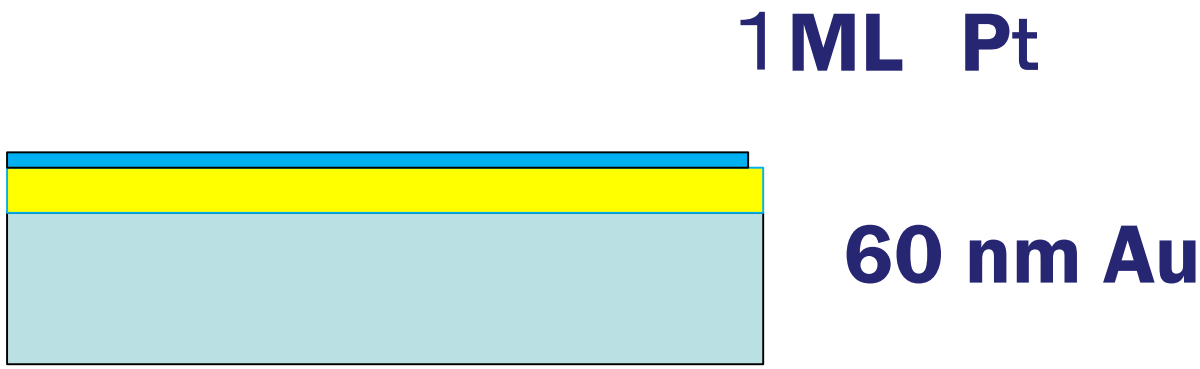
Experimental BL15 A1



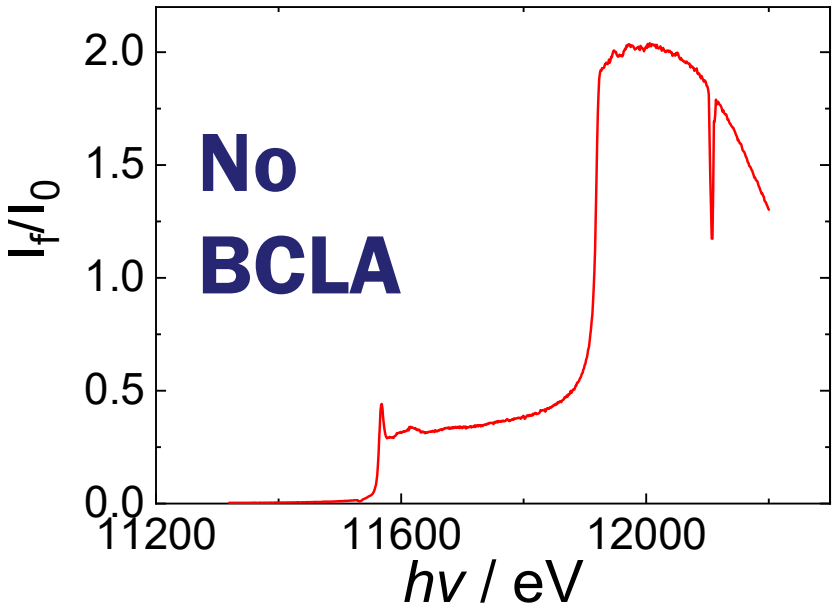
1. Schematic diagram of the TRF-XAFS system. The incident X-rays come from the left side and the fluorescent X-rays are analysed by the BCLA. The BCLA is covered with a lead sheet, except for its entrance and exit windows. Grazing angle was 4.5 ± 1.0 mrad

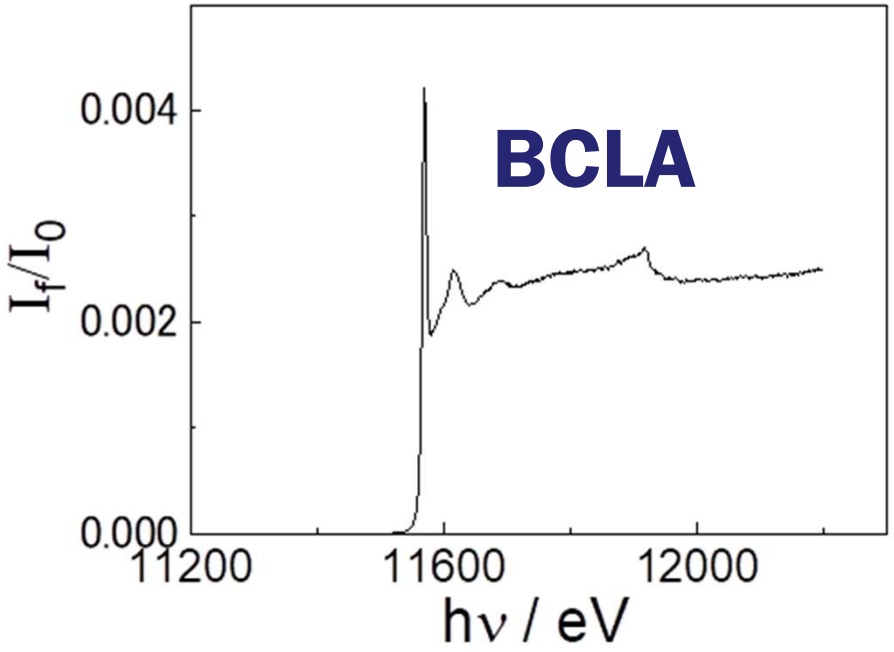
Sample

A thin Pt layer was deposited on a 60-nm-thick polycrystalline Au thin film evaporated on a 10-mm × 20-mm Si(100) wafer by self-terminating electrodeposition (Liu et al., 2012, Liu et al., 2015). Pt was electrochemically deposited on a Au polycrystal from 3 mmol K2 PtCl4–NaCl at pH = 4 with an applied voltage of −0.7 V vs. Ag/AgCl. The deposition time was 20 s. Hereafter, the sample is called Pt/Au/Si. The Pt coverage was estimated to be 1 ML thick by X-ray photoelectron spectroscopy (XPS).



XAFS Spectra without BCLA and with BCLA

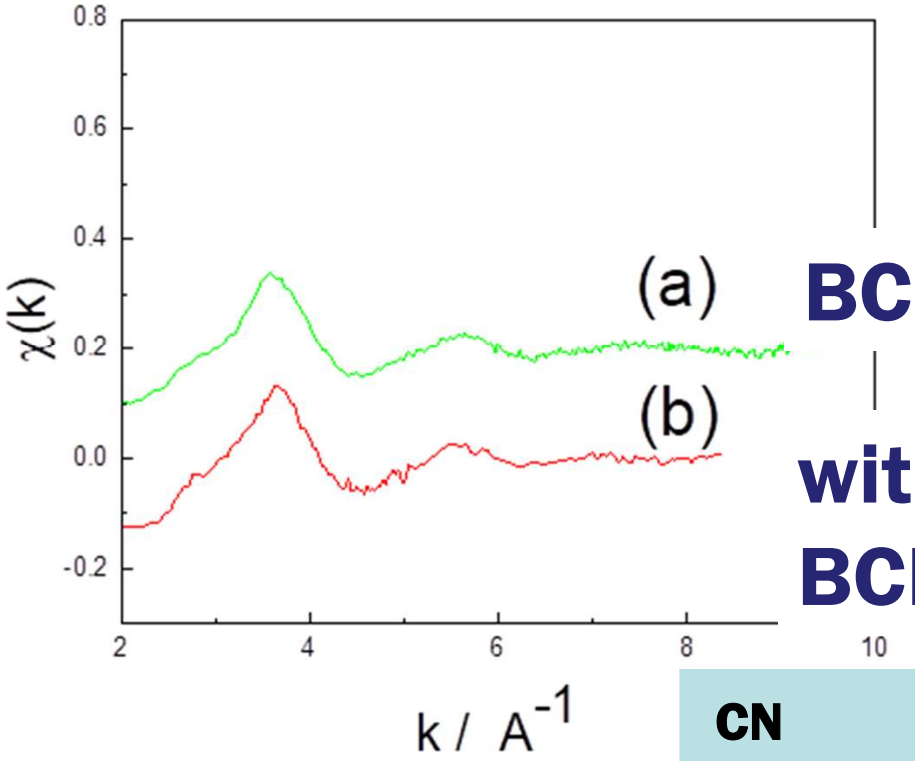




1. TRF-XAFS spectrum of Pt/Au(111) measured without the BCLA measured by the SDD. The SDD energy window was set in the range 9.1–9.5 keV.

XAFS can be measured!!

EXAFS osciilation after background extraction

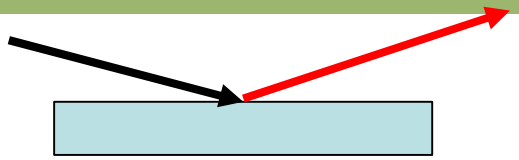


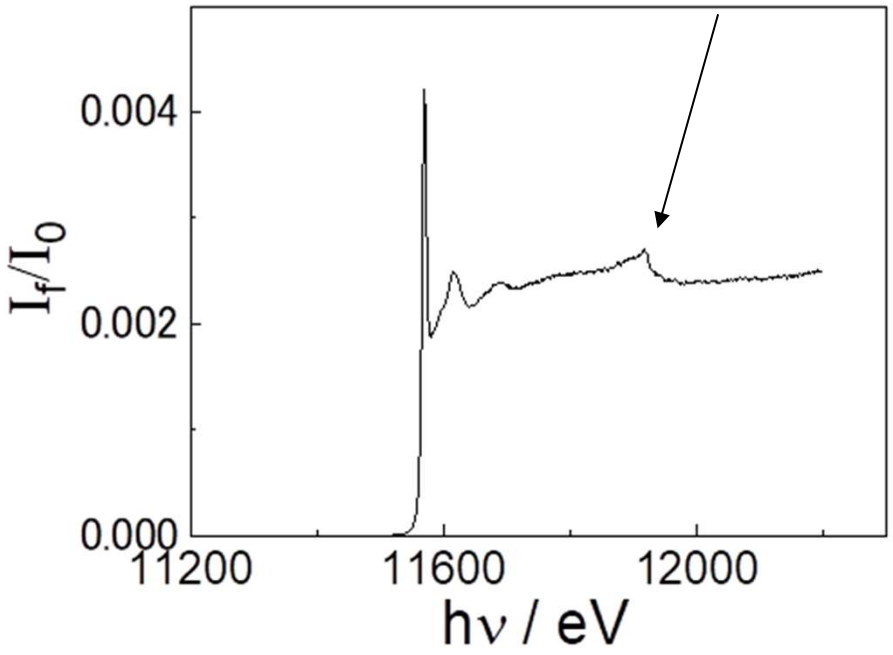
BCLA

without BCLA

CN	r / 0.1 nm	DE / eV	DW / 0.1 nm
5.5± 0.5	2.05 ± 0.03	27 ± 5	0.09 (fixed)

Spetrum abnormality





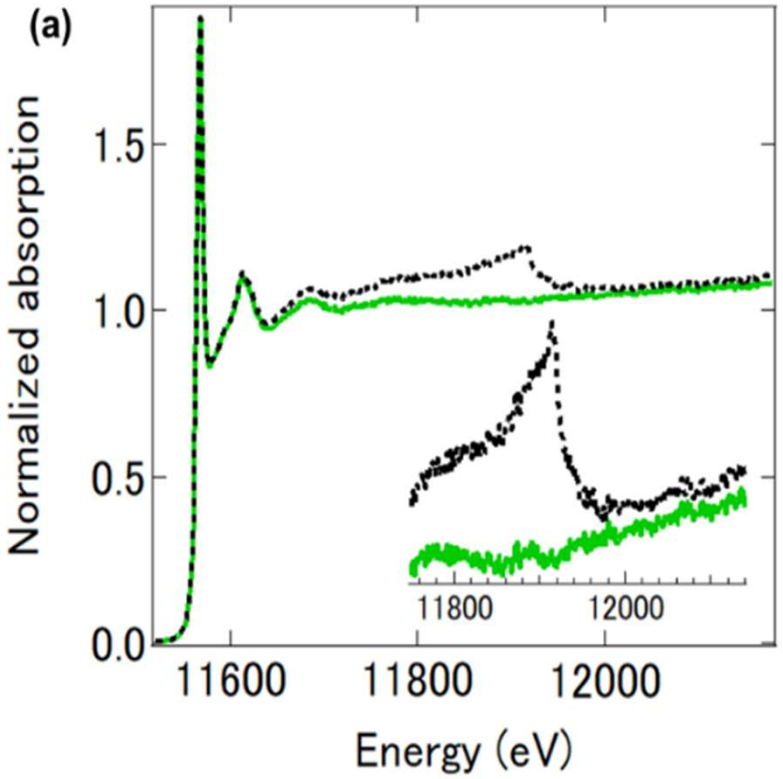
$$I_f \propto \mu_{Pt} I_t = \mu_{Pt} \left| \frac{E_0 + E_r}{E_0} \right|^2 \cdot I_0$$

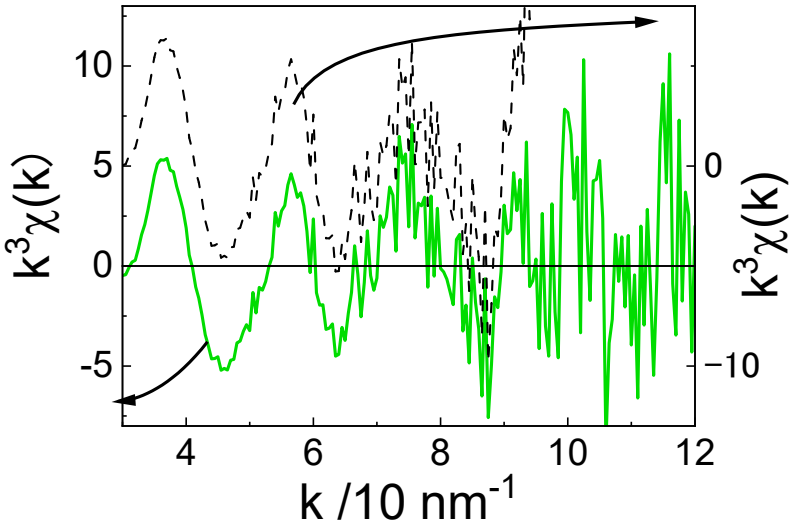
$$= \frac{4\left(\frac{\theta_0}{\theta_c}\right)^2 \mu_{Pt}}{h + \left(\frac{\theta_0}{\theta_c}\right)\sqrt{2(h-1)}} \cdot I_0$$

$$h = \left(\frac{\theta_0}{\theta_c}\right)^2 + \left[\left\{\left(\frac{\theta_0}{\theta_c}\right)^2 - 1\right\}^2 + \left(\frac{\beta}{\delta}\right)^2\right]^{\frac{1}{2}}$$

Abrupt change in absorption and in reflectivity

Correction is made at θ=4.5 mrad





After suitable correction, the abnormality can be removed.

Conclusions

We can measure PTRF-XAFS with BCLA.

It will open a new method to remove the scattering from the solution.

The BCLA can expand the energy range of measurement even if the presence of Au.

Acknowledgement

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0.1 ML Pt on Au(111) under presence of electrolyte