

## Development of in-situ Angle Resolved Total Reflection Fluorescence XAFS (ARTRF-XAFS) Measurement Technique

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### Introduction

Gold has been regarded as an inert material for catalytic applications before Haruta et al., have exhibited that the Au particles below 5 nm in size supported on TiO<sub>2</sub> has unique catalytic properties in CO oxidation.[1]

For understanding the further insight of Au-TiO<sub>2</sub> interaction we attempt to determine the surface structure of Au clusters on TiO<sub>2</sub>(110) surface by the PTRF-XAFS technique[2-6]. However, it is difficult to achieve the complete picture under the PTRF-XAFS measurement using three orientations, *i.e.* x, y, and z directions because the Au L<sub>3</sub> edge absorption generally used in Au XAFS measurement shows weak polarization dependence compared to K edge absorption. To overcome the limit we developed in-situ Angle Resolved Total Reflection Fluorescence XAFS (ARTRF-XAFS) technique.

In this work we describe the ARTRF-XAFS technique and report the surface structure of Au clusters on TiO<sub>2</sub>(110) surface obtained by the new technique.

### Experimental

A TiO<sub>2</sub>(110) single crystal was cleaned by Ar ion sputtering at room temperature, followed by annealing at 1000 K. 0.05 ML Au was loaded to the cleaned surface by vacuum evaporation of Au wire. The Au coverages were monitored by XPS. PTRF-XAFS was carried out with an in-situ PTRF-XAFS measurement chamber (a base pressure of ca.  $8 \times 10^{-8}$  Pa) [6] and a Canberra 19-element SSD in a fluorescence mode at BL9A. XAFS analysis was performed with REX 2000 and FEFF 8.0.

### Results and Discussion

To overcome the weak polarization dependence in Au L<sub>3</sub> edge absorption we attempt to increase the number of XAFS measurement at the various angles between a sample surface and the electric vector (E) of X-ray. Another important point in the ARTRF-XAFS technique is to keep a total reflection condition constantly for obtaining a high signal to background ratio. We have cleared the technical difficulty by optimizing the three axes ( $\theta$ ,  $\psi$ ,  $\phi$ ) in a UHV-compatible 6-axis goniometer.[6]

Fig. 1 shows the first ARTRF-XAFS spectra of 0.05 ML Au on the clean TiO<sub>2</sub>(110) with Au foil as a reference. Due to the anisotropic surface structure of TiO<sub>2</sub>(110) surface the ARTRF-XAFS measurement was carried out from E // [1-10] to E // [110] through E // [001] orientations.

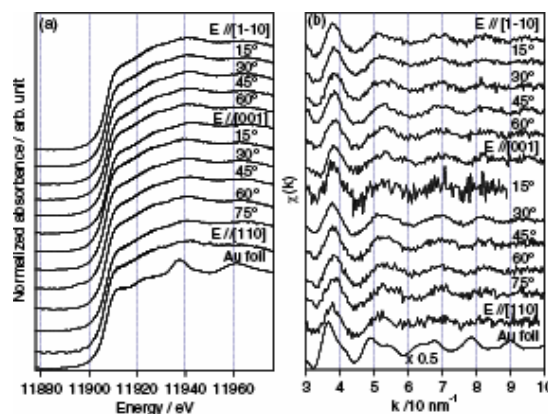


Figure 1 The ARTRF-XAFS spectra of Au / TiO<sub>2</sub>(110) surface. (a) XANES; (b) EXAFS.

First, there was no difference in all ARTRF-XANES spectra which showed small 1s→5d transition indicating the presence of metallic Au. In EXAFS region the polarization dependent spectra showed a little difference from each other and the period of the oscillations were comparable to that of Au foil. Considering these preliminary ARTRF-XAFS results we assumed that 3 dimensional small Au particles may be formed on the clean TiO<sub>2</sub>(110) surface but the detail analysis on the morphology is in progress.

### References

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