

High thermal stability of Au clusters on a Nb-doped TiO₂(110) Surface

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Introduction

It is a common sense that Gold is inert and noble metal with no catalytic applications. Haruta et al. have reported pioneering works on the nanoscale Au clusters showing CO oxidation reaction below zero degree.^[1] "Nano" makes gold active and variable. However, why "Nano" performs the miracle is one of the biggest mystery in the catalyst field. To obtain the further insight of Au-TiO₂ interaction at an atomic level, preparation and characterization of well-defined model catalysts using single crystal surfaces are indispensable.

In this work, small Au clusters were deposited on a Nb-doped TiO₂(110) surface by vacuum deposition, and the structure of the deposited Au clusters on the TiO₂(110) surface was investigated by using the polarization-dependent total reflection XAFS (PTRF-XAFS) technique.^[2] The effect of high temperature treatment on the structure of the Au clusters on the TiO₂(110) surface was also examined to see thermal stability of them.

Experimental

Nb-doped (0.05 wt%) TiO₂(110) surface was cleaned by immersing 10% HF solution and annealing at 650°C in air for 1h according to the previous reports.^[3] The TiO₂ sample was transferred into the ultra-high vacuum (UHV) PTRF-XAFS chamber and annealed at 700°C for 1 h to remove residual adsorbed water and reduce carbon contaminant. Then Au was vacuum-deposited on the sample surface and the Au coverage was estimated to be ca. 0.2 ML by XPS (1 ML was defined as 1.4×10¹⁵ atoms/cm²). PTRF-XAFS was carried out with the UHV PTRF-XAFS chamber. XAFS analysis was carried out using REX 2000 and FEF9.0.

Results and Discussion

Fig. 1(a)-(c) shows the observed Au L₃-edge PTRF-EXAFS spectra of the vacuum-deposited Au on a Nb-doped TiO₂(110) surface. There was no significant difference in all three orientations, indicating that the structure of the Au species should be a symmetric one. The characteristic oscillation due to Au-Au interaction was observed for all spectra, but the periodicity was longer than that of Au foil while the amplitude was smaller. These results indicated that Au-Au bond length was shorter than that of Au foil and coordination number was smaller, which suggested the formation of small Au clusters.

The sample was then annealed at 500°C for 1 h in UHV and the PTRF-EXAFS measurement of the annealed sample was done at RT as shown in Fig. 1(d)-(f). No significant change was observed before and after the high temperature treatment, showing that no significant aggregation of the Au clusters occurred even at 500°C and they were thermally stable.

Previous results reported that Au was easily aggregated on undoped TiO₂(110) surfaces, which were prepared by cycles of ion sputtering and high temperature annealing in UHV.^[4] The high thermal stability of the Au clusters, which were observed in this study, might be related to the difference of electronic states of the substrate TiO₂ between Nb doping and undoping.^[5] We are now planning to perform similar experiments using an undoped TiO₂(110) substrate.

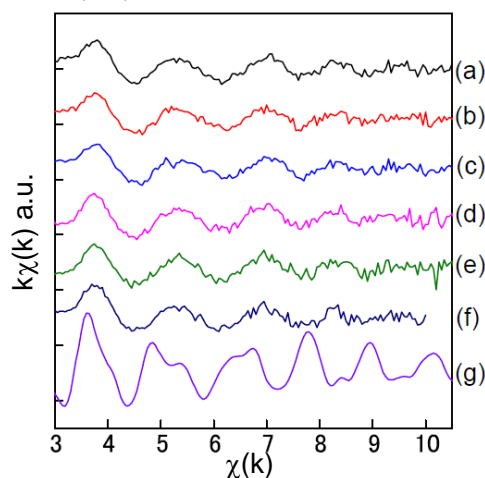


Figure 1 (a)-(c) PTRF-EXAFS spectra of the vacuum-deposited Au on a Nb-doped TiO₂(110) surface. (d)-(f) were the PTRF-EXAFS spectra obtained after annealing at 500°C for 1 h. (a) and (d) E//[001], (b) and (e) E//[1-10], (c) and (f) E//[110]. (g) EXAFS spectrum of Au foil.

References

- [1] M. Haruta et al., *Gold Bulletin*, **37** (2004) 27.
- [2] W.-J. Chun et al., *J. Synchrotron Rad.*, **8** (2001) 168.
- [3] Yamamoto et al., *Jpn. J. Appl. Phys.*, **44** (2005) L511, Nakamura et al., *J. Phys. Chem. B*, **109** (2005) 1648.
- [4] C.E.J. Mitchell et al., *Surf. Sci.*, **490** (2001) 196.
- [5] D. Morris et al., *Phys. Rev. B*, **6** (2000) 13445.

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