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# PTRF-XAFS Study of Atomically Dispersed Cu Species on a $TiO_2$(110) Surface Premodified with Functional Organic Molecules

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## Introduction

Precise size control of metal species on oxide surfaces, especially in the range of <1 nm, is now highly important to develop the next-generation catalysts, sensors, and electronic devices. However this is not easy since metal atoms are easily aggregated to form large particles on oxide surfaces.

Our group has developed the "premodified surface method" to obtain a highly dispersed metal species, where before metal deposition an oxide surface is precovered with a functional organic molecule possessing a substituent atom which can strongly coordinate to a metal atom [1-2].

Here, Cu was vacuum-deposited onto the $TiO_2$(110) surface premodified with *ortho*-mercaptobenzoic acid molecules (*o*-MBA), and the structure of the deposited Cu species was determined by Polarization dependent Total-Reflection Fluorescence (PTRF) XAFS.

## Experimental

Nb-doped (0.05 wt%) $TiO_2$(110) surface was cleaned by HF etching and annealing in air at 1000 K. The cleaned surface was immersed in 1mM *o*-MBA ethanol solution to modify the $TiO_2$(110) surface with *o*-MBA monolayer. Cu was vacuum-deposited on the *o*-MBA-modified surface, and the coverage was estimated to be 0.42 ML by XPS measurements (1 ML=$5.2\times10^{14}$/cm$^2$).

PTRF-XAFS measurements were carried out at BL9A with in-situ PTRF-XAFS chamber (base pressure $8 \times 10^{-8}$ Pa). XAFS analysis was carried out using REX2000 and FEFF8.40.

## Results and Discussion

Fig. 1 shows the observed Cu K-edge PTRF-EXAFS spectra of Cu/*o*-MBA/$TiO_2$(110) in three orientations. The envelopes of the PTRF-EXAFS oscillations damped quickly compared with the EXAFS spectrum of Cu foil. This means that the nearest neighbor atom of Cu is not Cu, but a lighter atom like sulfur or oxygen. The amplitude of EXAFS oscillations in the [110] orientation (*E* // [110]) was stronger than that for the other two parallel directions, which originates from the Cu-substrate interaction because the [110] orientation corresponds to the electric vector pointing to the $TiO_2$ substrate direction. Curve fitting analysis indicated contribution from Cu-S interaction (2.17±0.02 Å) and Cu-O interaction (1.85±0.02 Å)

To determine a detailed structure of the Cu species, an iteration method using a FEFF code and a real space model structure was employed. Fig. 2 shows the proposed model structure, and polarization dependent FEFF simulation using this model structure is illustrated in Fig. 1 for comparison with the experimental spectra. The calculated EXAFS oscillations originating from the proposed model showed a good agreement with the observed spectra.

We have succeeded in preparing highly dispersed monatomic Cu species on a $TiO_2$(110) surface by using the premodified surface method.

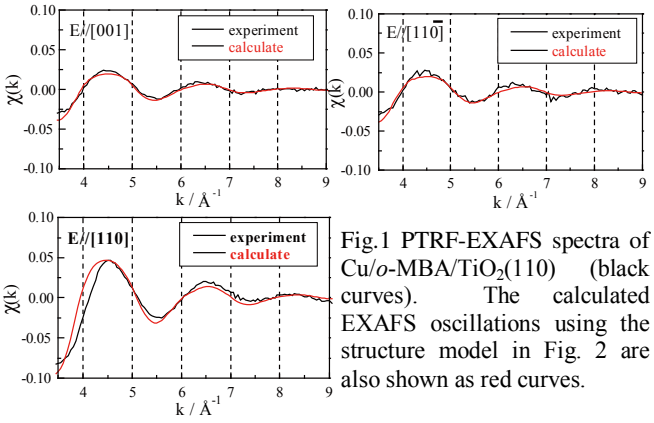


Fig.1 PTRF-EXAFS spectra of Cu/*o*-MBA/$TiO_2$(110) (black curves). The calculated EXAFS oscillations using the structure model in Fig. 2 are also shown as red curves.

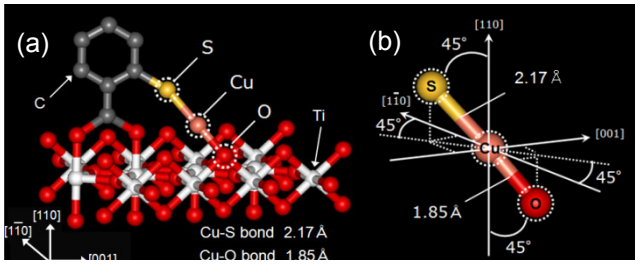


Fig. 2 (a) A proposed model structure of Cu/*o*-MBA/$TiO_2$(110). (b) Detailed local structure around Cu atom in (a).

## References

(1) Chun et al., *Chem. Phys. Lett.* **433** (2007) 345.
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