

# Preparation of Dimeric Cu Species on a TiO<sub>2</sub>(110) Surface Premodified with Mercaptobenzoic Acid

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## 1 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. An oxide surface is first precovered with an organic molecule possessing functional groups which can strongly coordinate to a metal atom and fix to oxide surface [1-3]. Then metals are deposited. We have already succeeded in preparing atomically dispersed Cu and Au species on the TiO<sub>2</sub>(110) surfaces premodified MBA (mercaptobenzoic acid, HS-C<sub>6</sub>H<sub>4</sub>-COOH) molecules, where mercapto group acts as a coordinating site to the metal atoms and carboxylic group as a binding part to the substrate TiO<sub>2</sub>(110) surface [2,3]. In this study, we attempted to prepare dimeric Cu species on a TiO<sub>2</sub>(110) surface premodified with *ortho*-MBA (*o*-MBA), and the structure of the Cu species was examined by polarization dependent total-reflection fluorescence (PTRF) EXAFS.

## 2 Experimental

Nb-doped (0.05 wt%) TiO<sub>2</sub>(110) surface was cleaned by HF etching and annealing in air at 973 K for 1h. The cleaned surface was immersed in 2 mM *o*-MBA ethanol solution to modify the TiO<sub>2</sub>(110) surface with *o*-MBA monolayer. Cu was vacuum-deposited on the *o*-MBA-modified surface, and the coverage was estimated to be 1.05 ML by XPS measurements (1 ML=5.2×10<sup>14</sup>/cm<sup>2</sup>).

PTRF-XAFS measurements were carried out at BL9A with *in-situ* PTRF-XAFS chamber (base pressure 8 × 10<sup>-8</sup> Pa). XAFS analysis was carried out using REX2000 and FEFF8.40.

## 3 Results and Discussion

Fig. 1(a)-(c) shows the observed Cu K-edge PTRF-EXAFS spectra of the Cu/*o*-MBA/TiO<sub>2</sub>(110) in three different polarization orientations. No significant difference was found in the three polarization dependent spectra. Preliminary curve fitting analysis of the observed spectra revealed main contribution from Cu-Cu (2.58 Å) and Cu-S (2.29Å) bonds.

FEFF simulation was performed to obtain information on a more detailed structure of the Cu species. We tested various structure models, and Fig. 2(a) shows one of the possible model structures (triangle Cu<sub>2</sub>S). FEFF

simulation (without polarization) using this model structure is illustrated in Fig. 2(b) (red curve) together with the experimental spectrum (*E*//[001], black curve), indicating a fair agreement of the calculated spectrum with the observed one. These results suggested that Cu was nucleated at the S atom of the *o*-MBA molecule and dimeric Cu species was formed on a TiO<sub>2</sub>(110) surface.

We are now trying to determine a more detailed 3D structure of the dimeric Cu species.

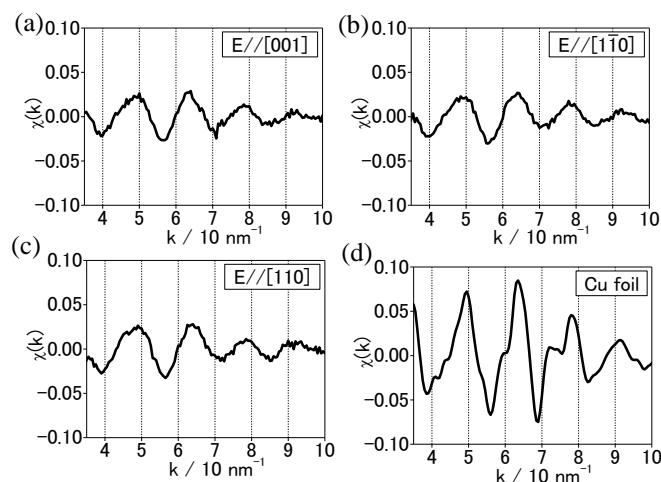


Fig. 1: (a)~(c) PTRF-EXAFS spectra of Cu/*o*-MBA/TiO<sub>2</sub>(110), respectively; (a) *E*//[001], (b) [110], (c) [110]. (d) EXAFS spectrum of Cu foil.

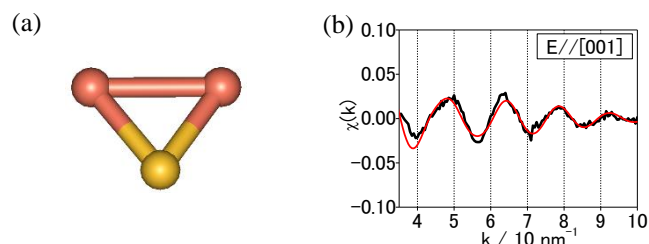


Fig. 2 (a) A possible model structure (brown ball: Cu, yellow ball: S). (b) FEFF simulation (*E*//[001]).

## References

- [1] W.J. Chun et al., *Chem. Phys. Lett.* **433**, 345 (2007).
- [2] S. Takakusagi et al., *Phys. Chem. Chem. Phys.* **15**, 14080 (2013).
- [3] K. Asakura et al., *Faraday Discuss.* **162**, 165 (2013).

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