

PTRF-XAFS study of single Cu site formed on a TiO₂(110) surface covered with a nitrogen-containing molecule

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1 Introduction

Precise size control of metal species on an 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 [1-4]. In the premodified surface method, an oxide surface is first precovered with a functional organic molecule possessing functional groups which can strongly coordinate to a metal atom, and then metals are deposited on the surface. We have already succeeded in preparing atomically dispersed Cu, Ni, and Au species on the TiO₂(110) surfaces premodified with MBA (mercaptobenzoic acid, HS-C₆H₄-COOH), where mercapto group acts as a coordinating site to the metal atoms and carboxylic group as a binding part to the substrate TiO₂(110) surface [2-4].

In this study, we attempted to obtain atomically dispersed Cu on a TiO₂(110) surface by premodification with a different functional organic molecule (*ortho*-anthranilic acid, H₂N-C₆H₄-COOH) to modify and control the local Cu structure for catalytic applications. 3D structure of the Cu species was examined by polarization-dependent total reflection fluorescence (PTRF)-EXAFS.

2 Experiment

Nb-doped (0.05 wt%) TiO₂(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*-anthranilic acid (*o*-AA) ethanol solution to modify the TiO₂(110) surface with *o*-AA monolayer. Cu was vacuum-deposited on the *o*-AA-modified surface and the coverage was estimated to be 0.11 ML by XPS measurements (1 ML=5.2×10¹⁴/cm²).

PTRF-XAFS measurements were carried out at BL9A with *in-situ* PTRF-XAFS chamber (base pressure 8 × 10⁻⁸ Pa). XAFS analysis was carried out using REX2000 and FEFF8.20.

3 Results and Discussion

Fig. 1 shows the observed Cu K-edge PTRF-EXAFS spectra of Cu/*o*-AA/TiO₂(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 nitrogen or oxygen. The amplitude of EXAFS oscillations in the [110] orientation (*E*//[110]) was slightly 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 TiO₂ substrate direction. Curve fitting analysis indicated contribution from Cu-N(O) interaction (2.15 ± 0.03 Å) and Cu-N(O) interaction (1.93 ± 0.03 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.

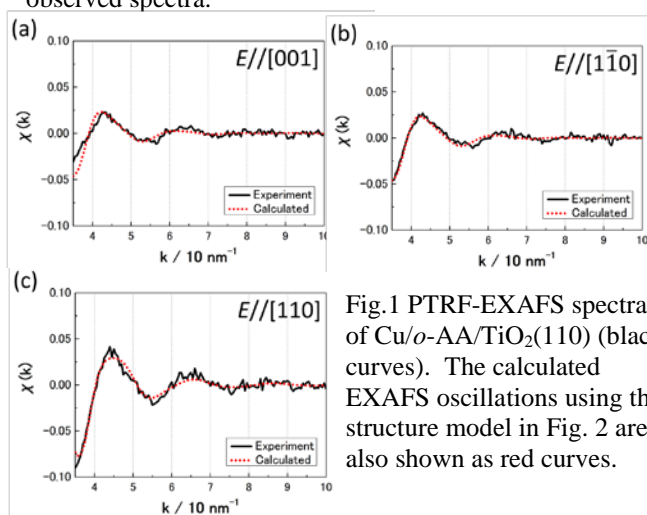


Fig.1 PTRF-EXAFS spectra of Cu/*o*-AA/TiO₂(110) (black curves). The calculated EXAFS oscillations using the structure model in Fig. 2 are also shown as red curves.

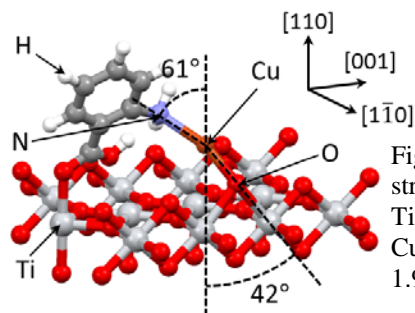


Fig.2 A proposed model structure of Cu/*o*-AA/TiO₂(110).
Cu-N: 2.15 Å, Cu-O: 1.93 Å.

References

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