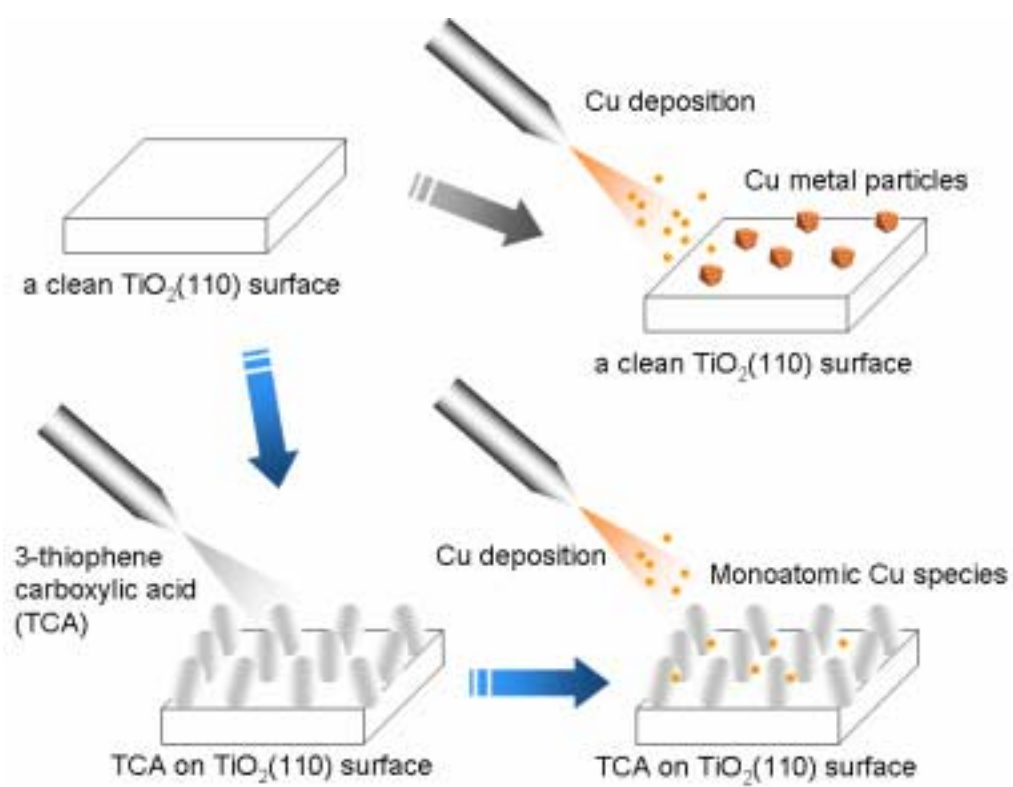




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Title	Preparation of atomically dispersed Cu species on a TiO <sub>2</sub> (110) surface premodified with an organic compound
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On a bare  $\text{TiO}_2$  (110) surface Cu easily aggregates to Cu particles by vacuum evaporation while on the  $\text{TiO}_2$  (110) surface premodified with 3-thiophene carboxylic acid provide monoatomically dispersed Cu species which will lead to small nanocluster with less than 1 nm in size.

# Preparation of Atomically Dispersed Cu Species on a TiO<sub>2</sub>(110) Surface

## Premodified with an Organic Compound

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### Keywords

Premodified surface method; Cu; TiO<sub>2</sub>(110); 3-Thiophenecarboxylic acid; X-ray absorption fine structure; Polarization-dependent total reflection fluorescence XAFS; Atomically-dispersed Cu

### Abstract

Highly dispersed monoatomic Cu species on a TiO<sub>2</sub> (110) surface were

successfully prepared by a new method in which the  $\text{TiO}_2(110)$  surface was premodified with a 3-thiophenecarboxylic layer. Polarization-dependent total reflection fluorescence-X-ray absorption fine structure (PTRF-XAFS) showed the three dimensional structure of the monoatomic Cu species which were stabilized on the surface through the formation of Cu-S (adsorbate) and Cu-O (bridging oxygen) bonds.

## 1. Introduction

Metal oxides are widely used as substrates for obtaining highly dispersed metal clusters with their size less than a few nm which are stabilized by a metal-oxide chemical interaction. A well-defined single crystal oxide is used as a model substrate to investigate the metal-oxide interaction[1]. Cu on a rutile  $\text{TiO}_2(110)$  surface is one of the most widely investigated surfaces [2-10] because supported Cu on oxides has important catalytic properties[11-13]. These studies have demonstrated that it is usually quite difficult to obtain fine clusters less than 1 nm in size by simple vacuum evaporation of Cu on the  $\text{TiO}_2(110)$  [6, 8]. Therefore, another approach is required to obtain Cu metal clusters smaller than 1 nm. Highly dispersed  $\text{Cu}_3$  triangle and  $\text{Cu}_6$  prism clusters have been prepared by using the

organometallic compound  $\text{Cu}(\text{DPM})_2$  (DPM= dipivaloylmethanate = 2,2,6,6-tetramethyl-3,5-heptadione) [9]. It has been suggested that the DPM ligands play an important role in preventing Cu aggregation, by stabilizing the Cu monomer on the surface. However, this method requires an elaborate chemical synthesis or the purchase of an expensive precursor. We expected that when a  $\text{TiO}_2(110)$  surface was covered with an organic molecule possessing a substituent atom which can coordinate to Cu, the adsorbed organic molecule would stabilize the Cu species and block their diffusion. This new approach (which can be called a premodified surface method), if successful, would be much easier than the organometallic compound method for obtaining a highly dispersed metal species, and is also of interest with respect to understanding the metal-support interaction. The organic molecules we have focused on are carboxylic acids which are adsorbed stably on a  $\text{TiO}_2(110)$  surface and create a well-ordered monolayer with a  $(2 \times 1)$  superstructure at room temperature[14-20]. In this study, we used the 3-thiophene carboxylic acid (TCA) because TCA has a thiophene ring containing a sulfur atom which can coordinate to a Cu atom. In this work, the surface structure of Cu species on the modified  $\text{TiO}_2(110)$  surface was determined by polarization-dependent total reflection fluorescence XAFS (PTRF-XAFS). PTRF-XAFS can determine definite three-dimensional surface

structures of the overlayer metals interacting with the substrate surface at sub-Ångstrom resolutions[9, 21-24]. The present PTRF-XAFS results indicate that the adsorbed TCA on the TiO<sub>2</sub> (110) surface can strongly trap Cu atoms through the formation of S-Cu bonds.

## 2. Experimental

All procedures were conducted in a PTRF-XAFS UHV chamber equipped with standard sample preparation and surface analysis techniques, with a base pressure less than  $3 \times 10^{-8}$  Pa[25]. Optically polished rutile TiO<sub>2</sub>(110) single crystal samples (20 x 20 x 1 mm<sup>3</sup>, Furuuchi Co., Japan) were cleaned using cycles of Ar<sup>+</sup> sputtering (1 keV) at room temperature (RT) and annealing at 873 K. These procedures gave a sharp (1 x 1) LEED pattern and no C 1s XPS peak. Copper was evaporated by resistively heating a tungsten filament wrapped with a copper wire (99.999 % purity, The Nilaco Co., Japan). Cu coverages were estimated by the XPS peak area ratios of Cu 2p<sub>3/2</sub> to Ti 2p<sub>3/2</sub>. 1 ML (monolayer) was defined as  $5.2 \times 10^{14}$ /cm<sup>2</sup> corresponding to the TiO<sub>2</sub>(110) (1 x 1) unit cell. 3-Thiophenecarboxylic acid (TCA) (99 % purity, Wako Co., Japan) was purified by several freeze-pump-thaw cycles and its purity was checked by a quadrupole mass spectrometer (QMS 200, Balzers, Germany). A

cleaned  $\text{TiO}_2(110)$  surface was covered with a saturated amount of TCA at 300 K and then Cu was deposited on the TCA-premodified  $\text{TiO}_2(110)$  surface. No significant decreases in XPS peaks of C 1s attributed to  $\text{COO}^-$  groups or S 2p were observed after the Cu evaporation. The sample thus obtained is designated as Cu/TCA/ $\text{TiO}_2(110)$  hereafter. For comparison we also deposited Cu on a clean  $\text{TiO}_2(110)$  surface, denoted as Cu/ $\text{TiO}_2(110)$  hereafter.

PTRF-XAFS measurements were performed at BL9A of the Photon Factory in the Institute of Material Structure Science (KEK-IMSS-PF, Tsukuba, Japan) [12]. The storage ring energy and the ring current were 2.5 GeV and 400 mA, respectively.

Considering the anisotropic surface structure of  $\text{TiO}_2(110)$ , PTRF-XAFS measurements were carried out in three orientations against the electric vector ( $\vec{E}$ ) of incident X-rays, *i.e.*, two orientations parallel to the surface;  $\vec{E} // [001]$ ,  $[1\bar{1}0]$  and an orientation perpendicular to the surface;  $\vec{E} // [110]$  as reported elsewhere [9, 22, 24].

The Cu  $K_\alpha$  fluorescence was detected by a 19-element Ge solid state detector (SSDGL0110S, Canberra, USA). PTRF-XAFS analysis was carried out by REX 2000 (Rigaku Co., Japan) and FEFF8.02 code [26].

### 3. Results and Discussion

Figure 1 shows the polarization dependent XANES spectra of 0.18 ML Cu/TiO<sub>2</sub>(110) and 0.35 ML Cu/TCA/TiO<sub>2</sub>(110) in three orientations with reference compounds. All spectra were normalized to the edge jump. The XANES spectrum of Cu foil has characteristic features denoted as A, B, and C as shown in Figure 1 (c). Peaks A, B and C were found in the XANES spectra of Cu/TiO<sub>2</sub>(110) for all orientations, indicating the presence of a metallic Cu-Cu bond. Peak B in the spectra for Cu/TiO<sub>2</sub>(110) was less strong than that of Cu foil. Greaves et al. have claimed that peak B is reproduced only when multiple scattering calculations are included in the third or higher shells around a Cu atom [27]. A similar feature for peak B was also observed in a small Cu cluster [9, 28, 29]. Thus the Cu species on a bare TiO<sub>2</sub> (110) was in the form of small clusters. Peak A exhibited polarization dependence. This was strongest in the [110] direction (normal to the surface), indicating asymmetry in the Cu cluster structure.

The XANES spectra of Cu/TCA/TiO<sub>2</sub>(110) showed completely different features from those of Cu/TiO<sub>2</sub>(110) and Cu foil, though the amount of Cu deposition was twice as large as for Cu/TiO<sub>2</sub>(110). The mid-edge features at around 8982 eV in all orientations could be assigned to the 1s → 4pπ\* transition from previous XANES experiments and *ab initio* calculations [30, 31]. The

inflection points of the edge appeared around 8980 eV in all orientations. Considering that the inflection points of Cu foil, Cu<sub>2</sub>O, CuO, CuS and Cu(mnt)<sub>2</sub> (maleonitriledithiolato copper) appeared at 8979.5, 8980.3, 8983.3, 8981.4 and 8981.2 eV, respectively, the oxidation state of Cu species formed on the TCA-covered TiO<sub>2</sub>(110) surface was monovalent.

Figure 2 (a) shows the polarization dependent EXAFS spectra of 0.18 ML Cu/TiO<sub>2</sub>(110) and 0.35 ML Cu/TCA/TiO<sub>2</sub>(110) in three orientations with reference compounds. The EXAFS spectra of Cu/TiO<sub>2</sub>(110) obtained from the three orientations showed similar oscillations. Curve fitting analysis showed the presence of Cu-Cu interaction for all orientations at 0.244 nm, indicating the presence of Cu clusters. The EXAFS spectra for the Cu/TCA/TiO<sub>2</sub>(110) (Figure 2 (b)) showed drastically different features from those of Cu/TiO<sub>2</sub>(110). The envelopes of the PTRF-EXAFS oscillations damped quickly compared to those of Cu/TiO<sub>2</sub>(110). This means that the nearest neighbor atom of Cu is not Cu, but a lighter atom like sulfur or oxygen. We also found a polarization dependence in the [110] direction. In the range of 30 ~ 50 nm<sup>-1</sup> the amplitude of EXAFS oscillation in the [110] was slightly stronger than for the other two parallel directions. This may originate from the Cu-substrate interaction because the [110] orientation corresponds to the

electric vector pointing to the  $\text{TiO}_2$  substrate direction. A preliminary single shell curve fitting analysis indicated the main contribution was a Cu-S interaction and Cu-Ti or Cu-Cu interactions were less likely. We could not get physically meaningful fitting parameters when Cu-O was only assumed. The bond distances of Cu-S determined in this preliminary curve fitting analysis were estimated at about 0.214 ~ 0.216 nm in all orientations. Note that these are shorter than the Cu-S bond lengths found in CuS and  $\text{Cu}(\text{mnt})_2$  [32]. We supposed that the shorter Cu-S bond length plays an important role in preventing the diffusion of Cu species. We found that there was no significant difference in the ratio of the effective coordination numbers, indicating that the Cu-S bond was directed to the magic angle ( $54.7^\circ$ ) with respect to three directions,  $[110]$ ,  $[1\bar{1}0]$  and  $[001]$ .

To derive a detailed structure, an iteration method using a FEFF code and a real-space model structure was employed [9, 22-24]. Figure 3 shows the proposed model structure and polarization dependent FEFF simulation. The calculated EXAFS oscillations originating from the proposed model showed a good agreement with the observed spectra. The bond distance of Cu-S interactions was estimated to be 0.215 nm while that of the Cu-O interaction was 0.184 nm. The bond angles of the Cu-S and Cu-O bonds to the surface normal were  $\theta = 50^\circ$  and  $\beta = 43^\circ$ ,

respectively. The bond angle S- Cu-O was estimated as  $165^\circ$ , which is close to  $180^\circ$ . Many Cu(I) compounds have a linear structure accompanied by two ligands. Thus Cu may be monovalent, in agreement with the XANES result. Note that one Ti-carbonate bond is cleaved to have a monodentate adsorption structure in order to maintain the TCA molecular structure, which will be confirmed by the vibrational studies.

EXAFS results indicate that our new approach (a premodified surface method) can provide monoatomic metal species without elaborate chemical syntheses of organometallic compounds. Our previous PTRF-EXAFS studies have shown that the atomically dispersed Ni interacts strongly with the dangling bond of oxygen atoms on oxide surfaces [23, 24]. The  $\text{TiO}_2$  (110) surface has an oxygen dangling bond at the bridging oxygen. Accordingly, the stable adsorption site for Cu atoms on the clean  $\text{TiO}_2$  (110) surface should be the atop site of the bridging oxygen. The Cu deposited on the bare  $\text{TiO}_2$  (110) surface, however, showed aggregation to clusters [2, 5-8, 10]. This indicates that the single Cu-bridging oxygen bond is not sufficient for fixing the Cu atom, which can easily migrate to other atop sites of the bridging oxygen atoms, consequently leading to the aggregation to Cu metal clusters. On the other hand, we found atomically

dispersed Cu species on the TCA-premodified  $\text{TiO}_2(110)$ . Compared to Cu behavior on the bare  $\text{TiO}_2(110)$  surface, the S ligand can firmly attach Cu to the surface in cooperation with the bridging oxygen. In our previous work, atomically dispersed Ni atoms were found on the  $[1\bar{1}n]$  step where Ni atoms were fixed to the surface with two oxygen atoms[23, 24]. Two coordination sites may be required for Cu atoms to be fixed. Recently, M.C.Valero et al. pointed out the blocking of OH group on  $\gamma\text{-Al}_2\text{O}_3$  is important for the metal migration on the surface[33]. TCA in this work prevents the migration of Cu not due to the blocking effect but due to the thermodynamical stabilization through making a chemical bond with Cu.

#### 4. Conclusion

Atomically dispersed Cu species on a  $\text{TiO}_2(110)$  surface were successfully obtained by employing a surface premodified with 3-thiophenecarboxylic acid. The premodified surface method can be a novel method for obtaining a highly dispersed metal species on a single crystal metal oxide surface and the new method is also of interest with respect to understanding the metal-support interaction. We are now extending our work to prepare a well-defined Cu array on the  $\text{TiO}_2(110)$  surface.

## Acknowledgements

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## Figure Captions

Figure 1. Cu *K*-edge XANES spectra in three different orientations. (a) 0.18 ML Cu deposited on clean TiO<sub>2</sub>(110); (b) 0.35 ML Cu deposited on the TCA-premodified TiO<sub>2</sub>(110) surface; (c) reference compounds. \*Cu(mnt)<sub>2</sub>: maleonitriledithiolato copper.

Figure 2. Cu *K*-edge EXAFS spectra. (a) 0.18 ML Cu deposited on clean TiO<sub>2</sub>(110); (b) 0.35 ML Cu deposited on the TCA-premodified TiO<sub>2</sub>(110) surface in three different orientations; (c) reference compounds. \*Cu(mnt)<sub>2</sub>: maleonitriledithiolato copper.

Figure 3. Left panel: A proposed model structure of 0.35 ML Cu deposited on the TCA-premodified TiO<sub>2</sub>(110) surface. Right panel: Cu *K*-edge XAFS spectra. Thin and thick lines are EXAFS oscillations observed and calculated based FEFF, respectively.

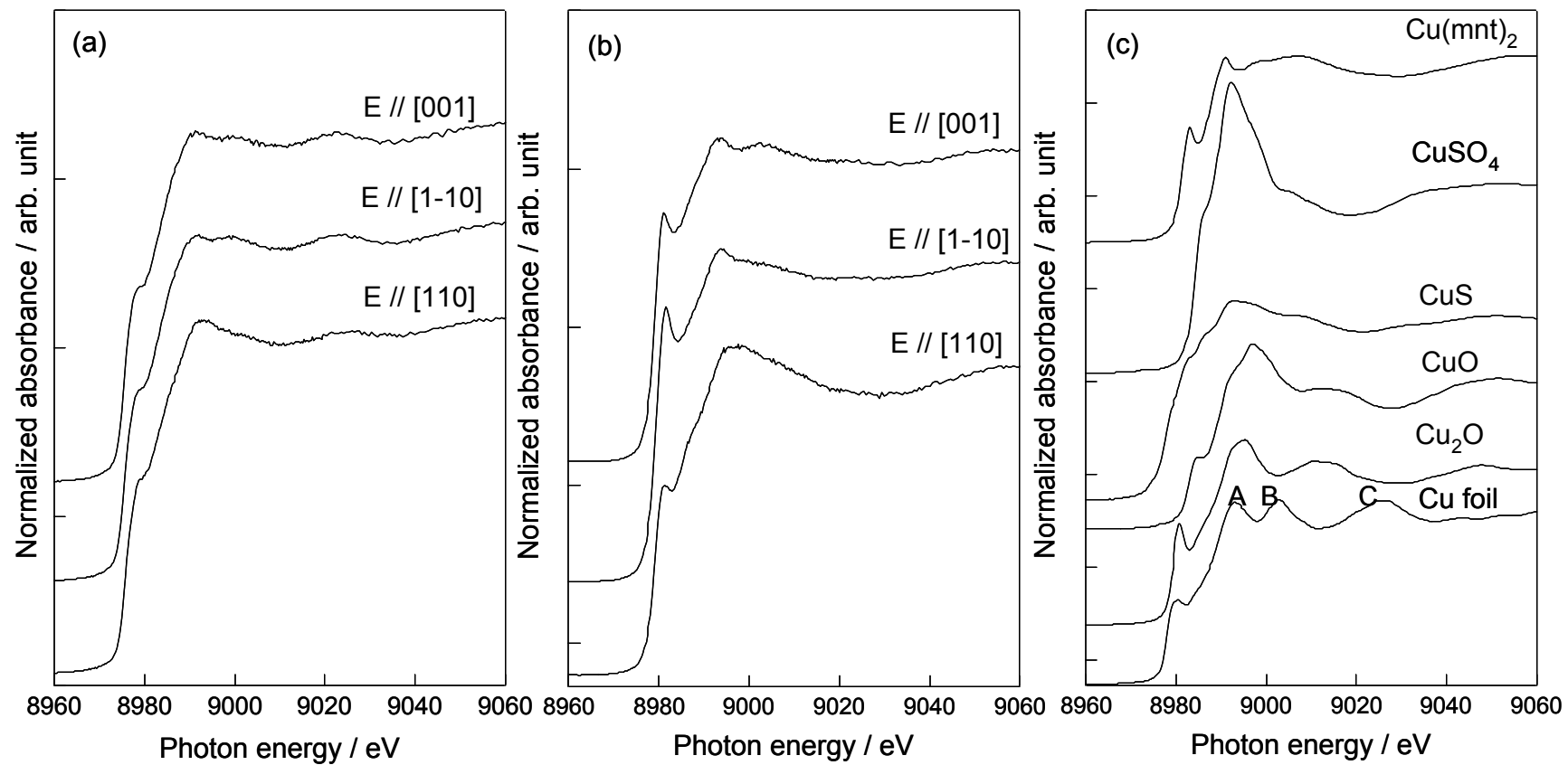


Figure 1 W.J.Chun et al.

Figure

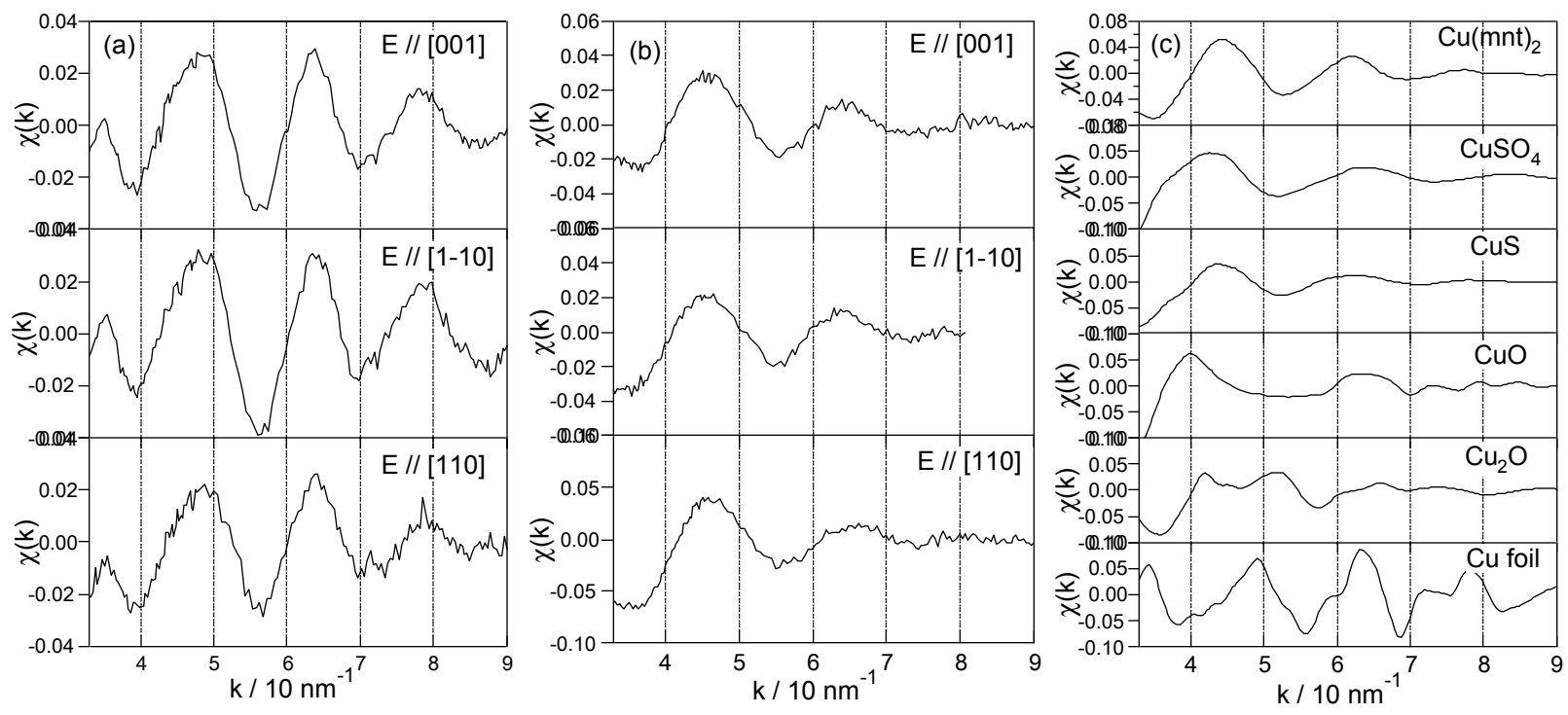


Figure 2 W.J.Chun

Figure

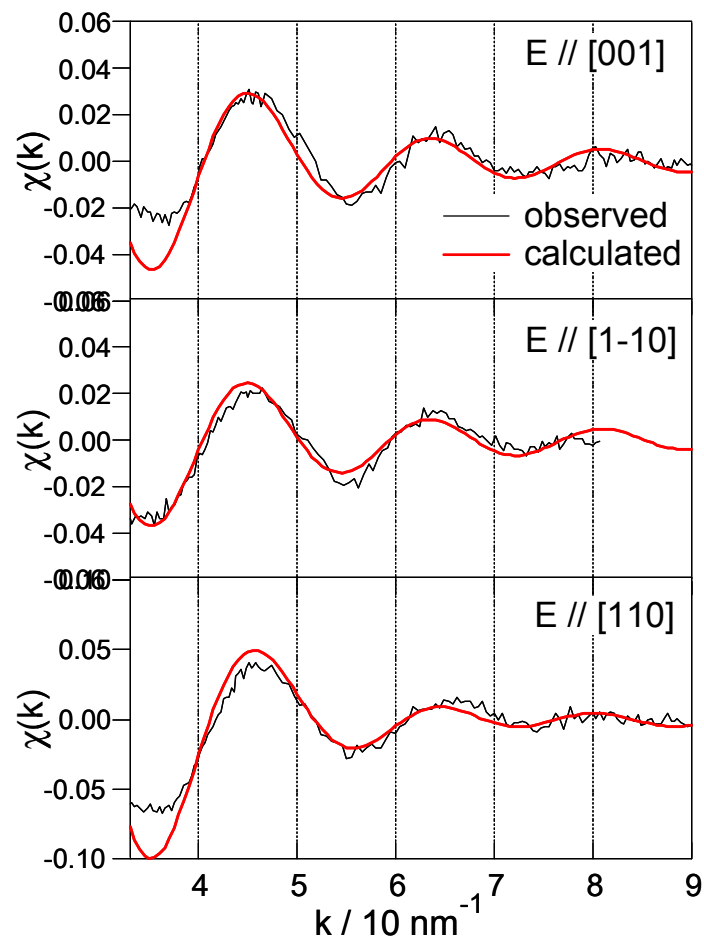
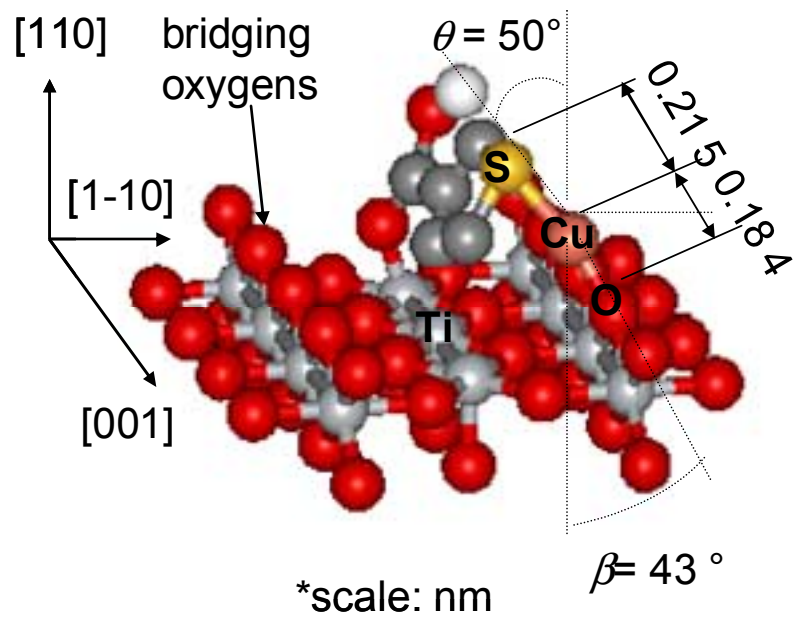


Figure 3 W.J.Chun



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Dear Prof. H. -J. Freund,  
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We have studied the Cu structure on the thiophene-modified TiO<sub>2</sub> (110) surface. The metal nanoparticles are important as catalysts, sensors and nanodevices. The physical and chemical properties are dependent on the size and structure of nanoparticles and it is critical to obtain clusters with less than 1 nm for the catalytic applications. Well defined crystal oxide surfaces are used to reveal the behavior of metal nanoparticle on oxide precisely using surface science techniques. TiO<sub>2</sub> (110) is the most extensively studied surface. When Cu is deposited on the TiO<sub>2</sub> (110) by vacuum evaporation, the Cu on the TiO<sub>2</sub> (110) surface aggregates readily to form Cu particles and it is difficult to obtain Cu species with its size less than 1 nm on TiO<sub>2</sub> (110). It is due to the weak interaction between TiO<sub>2</sub> (110) and Cu species. The only way to obtain the highly dispersed Cu species on the TiO<sub>2</sub> (110) surface is to use an organometallic compound. But usually organometallic compounds are expensive and air sensitive. We tried to prepare a small Cu species by premodifying the TiO<sub>2</sub> (110) surface with 3-thiophenecarboxylic species that has a S atom coordinating to Cu. This premodified surface method is easier and less expensive. We have studied the Cu species structure using the polarization dependent total reflection fluorescence X-ray absorption fine structure (PTRF-XAFS). The PTRF-XAFS provides us information about the three dimensional structure of Cu species even if it has no long range order. We successfully stabilized the monoatomically dispersed Cu species with the Cu-S bonding. In this paper we would like to present the three dimensional structure of the Cu species and describe the new approach of premodified surface method to create highly dispersed Cu species. This new method will open a new preparation of nanoparticles in an easy and controllable manner. I hope the paper is accepted in Chemical Physics Letters and the method will prevail widely.

Best regards

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