Polarization Dependent Fluorescence X-ray Absorption Fine structure Studies on the Metal species at the interface of Organic Molecule.

− Its Possibility to the Application of Biointerface

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X-ray absorption fine structure is a powerful technique to investigate the local structure around X-ray absorbing atom. However, when it is applied to a biointerface created on a substrate surface, it will be difficult due to the small concentration of the X-ray absorbing atoms. We have developed a new technique to determine the three-dimensional structures of the surface metal species dispersed on the flat substrate with low concentration(1×10^{13} atoms / cm^2).[1] The technique is called as polarization dependent total reflection fluorescence XAFS(PTRF-XAFS). In this paper we describe some examples about metal species dispersed on the TiO_2 (110) single crystal and organic compounds modified TiO_2(110) surfaces. We will discuss the possibilities of its application to biointerface problems.

Cu and Au on TiO_2(110)

TiO_2 is one of the typical support materials for catalysts on which metal is dispersed as a nanocluster but its structure, interaction with surface and formation mechanism are not yet clear. TiO_2 (110) surface has an anisotropic structure with both exposed Ti and oxygen running along the [001] direction shown in Fig. 1 When the Cu and Au were deposited on the surface, they aggregate to give 3 dimensional nanoclusters. This indicates the weak interaction between Cu (Au) and the TiO_2(110) surface and it was quite difficult to obtain atomically dispersed Cu (Au) species on this surface.[2]

Cu and Au on the modified TiO_2(110) surface

A strategy to have an atomically dispersed Cu(Au) is to increase the interaction of TiO_2(110) surface with Cu(Au). S atom has a larger interaction with Cu and Au. A carboxylic acid is adsorbed strongly on the TiO_2(110) surface. Thus we use a molecule with two moieties S and COOH. We put thiophene carboxylic acid(TCA) on top of the TiO_2(110) surface and obtained atomically dispersed Cu species [3] and flat 2 layer Au clusters. The different structures were due

to the different interaction of S with Cu and Au. The o-mercaptobenzoic acid(o-MBA) was adsorbed on the surface, we could make the Au atomically dispersed.[4]

Application of PTRF-XAFS to biointerface.

One demerit of PTRF-XAFS is the presence of liquid phase which created strong scattering and deteriorated the S/B ratio. We are constructing a new highly sensitive method to which enables us to carry out the lower concentration with the presence of solution. We will discuss the possibility of the bioapplications of the PTRF-XAFS.

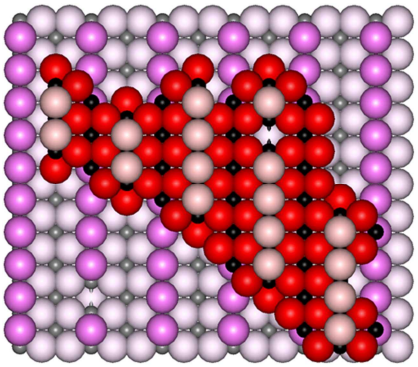

Fig.1 The TiO_2(110) surface. Large ball and small ball indicates the oxygen and Ti

References

1. K. Asakura, Catalysis, 2012, Vol. 24, 281-322. Catalysis Spivey, J. J., Gupta, M., Eds.; RSC publishing: Cambridge.
2. W. J. Chun, Y. Koike, K. Ijima, K. Fujikawa, H. Ashima, M. Nomura, Y. Iwasawa, K. Asakura, Chem.Phys.Lett 2007, 433, 345-349.
3. S. Takakusagi et al. in preparation.
4. K. Asakura, S. Takakusagi, H. Ariga, W.-J. Chun, S. Suzuki, Y. Koike, H. Uehara, K. Miyazaki,Y. Iwasawa, Faraday Discussion 2013, submitted,

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