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Advanced XAFS analysis for local structure of functional materials

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Summary

X-ray absorption fine structure (XAFS) provides bond distance, a type of atom, and coordination number around the X-ray absorbing atom. Therefore, XAFS is the most suitable technique to identify. However, there are several drawbacks in XAFS making it difficult to obtain the desired local structural information for the particular system. In this study, I demonstrate how to overcome the drawbacks by applying several techniques in the investigation of the local structure of various systems which show unique properties, but it is difficult to obtain its structure from EXAFS.

- Conventional XAFS provides one-dimensional local structural information. Nevertheless, three-dimensional local structural information is preferred for the dispersed metal species on metal oxide surface in order to elucidate the complete local structure around the metal species. Such information was obtained by the technique so-called PTRF-XAFS which was demonstrated in Chapter 3.
- The number of independent points is limited in EXAFS. Thus it is difficult to analyze the complex system which contains many atoms (scattering shells), so the number of parameters uses in the curve fitting. Moreover, care must be taken for the system potentially having scattering shell that slightly contributes to the overall EXAFS oscillation. It was overcome by employing the Hamilton test or F-test which was demonstrated in Chapter 4.
- It is quite difficult to observe the XAFS of the low-Z element under the reaction conditions. I demonstrated the evidence which might lead to the development of a new kind of spectroscopy, which has coined the name as Multi-Atom Resonant X-ray Raman (MARX-Raman). It will be a new way to perform an *in situ* XAFS measurement for low Z-element with bond-specific capability.

The thesis is composed of 6 chapters to describe my contributions to new development in XAFS techniques.

The first system is about determining the three-dimensional structure of supported metal catalysts. Supported metal catalysts have drawn much attention for

their wide applications such as catalysts, sensors, electronic and magnetic devices. It is very important to control the structure and electronic state of the supported metal, including the metal cluster size. Metal oxides are widely used as substrates for preparing highly dispersed metal clusters with their size less than a few nm. To investigate the metal-metal oxide interaction, a well-defined single crystal metal oxide is needed as a model substrate. In addition, an analysis method capable of providing three-dimensional structural information of the surface species is essential. Polarization-dependent Total-Reflection Fluorescence X-ray absorption fine structure (PTRF-XAFS) analysis can uniquely provide such information around highly dispersed metal species on the single crystal surface. In this study, Ni and Pt were deposited on $TiO_2(110)$ surfaces premodified with ortho-mercaptobenzoic acid (o-MBA). The three-dimensional structure of the Ni species was determined using the PTRF-EXAFS technique. A S-Ni-O motif, which is similar to the local metal structure found in previous studies with Cu and Au, was formed on the modified $TiO_2(110)$ surface. In contrast, Pt was not atomically dispersed but instead aggregated to form clusters on the o-MBA/$TiO_2(110)$ due to the low affinity of Pt atoms for S atoms compared with that for other Pt atoms. These results demonstrate that Polarization-dependent X-ray absorption fine structure (PTRF-XAFS) analysis can uniquely provide three-dimensional structural information around highly dispersed metal species on the single crystal surface which conventional XAFS cannot. In addition, A new indicator, R_{X-M-O} (X=S or O), has been proposed for the single metal dispersion on the $TiO_2(110)$ surface. This indicator would help the scientific community predict whether metal could be used to obtain the highly dispersed on the $TiO_2(110)$ surface.

The second system is about XAFS applications to the unique compound (the gold (I) complex, $[(C_6F_5Au)_2(\mu\text{-}1,4\text{-diisocyanobenzene})]$ (**1**)) (JACS, 2008 130 100044). The compound exhibits the unique properties called reversible mechanochromism. The luminescence color was changed, from blue to yellow, when applying the mechanical force such as grinding with a spatula. The polycrystalline state is changed to the amorphous state as expected when applying the mechanical force. According to the author, it was found that grinding does not destroy the molecular structure. Recrystallization of the complex yields the single crystal suitable for the single crystal X-ray diffraction analysis. Single crystal X-ray diffraction (XRD) reveals the structure of blue luminescence polymorph having Single crystal X-ray diffraction (XRD) reveals the structure of blue luminescence polymorph having shortest Au-Au distance around 5.19 Å. The amorphous state that exhibits yellow luminescence, however, remains unknown. I applied the Extended X-ray Absorption Fine Structure (EXAFS) to get the local structure of Au. EXAFS results show that the shortest Au-Au distance is reduced to 2.87 Å. As a result, the ground crystal has the new kind of interaction called Aurophilic interaction which is not found in the blue polymorph. The Aurophilic interaction might be the origin for the mechanochromism. In addition, I will also demonstrate how Hamilton test or F-test plays an important role in curve fitting analysis of the complicated system in which slightly contribution to the overall oscillation of the atomic species could be identified. This test will be a big help for us working on a complicated system which has a lot of element. Applying the Hamilton test during the analysis process helps us determining relevancy in EXAFS and get rid of data errors especially when the system being studied has the shell that slightly contribution to the overall EXAFS oscillation, as described previously.

Next, the evidence that might lead to the brand-new kind of spectroscopy is reported. XAFS that has been used in the aforementioned provides invaluable local structural information. Since the X-ray has a large penetration ability, it is possible to carry out an *in situ* measurement of catalysts and electrodes under reaction conditions. However, when applied to low Z elements, which have an X-ray absorption edge in the soft X-ray regime, it is quite difficult to observe the XAFS under the reaction conditions. On the other hand, X-ray Raman scattering (XRS) can provide *in situ* XAFS measurements on low Z elements because the XRS uses hard X-rays. However, the X-ray Raman intensity is quite low. Resonant XRS is observed and enhances the Raman sensitivity. In this resonant XRS, the X-ray is tuned to the absorption edge and the Raman signal of the same X-ray absorbing atom is detected. Therefore, the X-ray absorption and Raman emission occur at a single atom. If one uses an absorption edge of the central metal in a metal complex to which low Z atoms are directly coordinated and if the excitation energy transfer occurs from the X-ray absorbing atom to the coordinating low Z atoms, one can obtain the X-ray Raman spectrum of the directly bonded low Z atoms, which is enhanced through the X-ray absorption of the central atom. In this study, the interatomic resonant Raman signals were measured by tuning the X-ray to the excitations of Ta L_3-edge and Er L_1-edge with the detection of Raman emission of N K-edge and C K-edge, respectively, in order to see such an enhancement occurs or not, qualitatively.

TaN is excited at before (9865 eV) and just after (9886 eV) Ta L_3-edge and N K-edge loss spectrum are measured. Figure 1 shows the 2-dimensional mapping of emitted x-ray of 10 wt% TaN/SiO_2. Figure 2 shows the Raman spectra TaN excited at 9865 eV (smaller than Ta L_3-edge) and 9886 eV (a little larger than Ta L_3-edge), respectively. Enhancement of emission spectrum is found when the excitation X-ray energy was tuned to the Ta L_3-edge and inelastic scattering spectra were recorded around 400 eV loss corresponding to the N K-edge Raman region. The enhancement at N K-edge Raman region was not observed when the excitation X-ray energy was below Ta L_3-edge. In addition, the same enhancement was not observed in Ta foil even though the excitation X-ray energy was tuned to the Ta L_3-edge. The same measurement was also applied to $Er(C_5H_5)_3$ with have different absorbing metal and neighboring atom. Figure 4 shows the C K-edge Raman spectra tuned at 9752 eV just above the Er L_1-edge of $Er(C_5H_5)_3$. We observed the change at -286 eV loss energy position (corresponding to C K-edge Raman region), but we did not observe a clear change at C K-edge energy in the emission spectrum of Er_2O_3. Therefore, both spectra indicate the most probable assumption is Multi-Atom Resonance X-ray Raman process. These experimental results indicated the possibility of MARX-Raman phenomenon which may lead to a new *in situ* and bond-specific XAFS spectroscopy for low Z elements. In this Raman spectroscopy, we can use hard X-rays to obtain the N X-ray absorption spectra. Thus, it will be a new way to perform an *in situ* measurement for low Z-element. In addition, it is a bond-specific method. The Only N which has a bond to Ta is enhanced even if the other N is present. This is important when the method is applied to the real system. For example, Raman spectra of C or O adsorbed on Pt surfaces of nanoparticles can selectively be measured even if the Pt is present on graphite(C) in the water (H_2O) atmosphere like fuel cell electrodes. Since the incident X-ray energy can be fixed to a certain energy, X-ray free electron laser (XFEL) may be a good X-ray source. It will provide a high time resolution technique using the pump-probe measurement and the Von Hamos type energy analyzer. The new X-ray Raman spectroscopy is coined as Multi-Atom Resonant X-ray Raman (MARX-Raman) though we need many further studies such as improvement of the S/N ratio of the spectrum and the applicability to other elements as well as theoretical justifications.