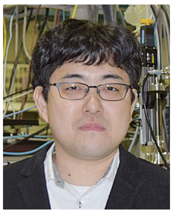
Soft X-Ray Absorption Spectroscopy for Observing Chemical Processes in Solution

Department of Photo-Molecular Science
Division of Photo-Molecular Science III



NAGASAKA, Masanari
Assistant Professor

Soft X-ray absorption spectroscopy (XAS) observes local structures of liquids with different light elements. We have developed liquid cells and devices with precise absorbance control and observed several chemical processes in solution by using *operando* XAS.[1,2] In this year, we have developed time-resolved XAS of photochemical reactions by synchronizing soft X-ray probe pulses with the laser pump pulses.[3]

1. Time-Resolved XAS of Photochemical Reactions in Solutions

The time-resolved XAS system has been developed at the soft X-ray beamline BL-13A of the Photon Factory, KEK.[3] The laser pump pulses (515 nm, 290 fs) were almost coaxially introduced to the liquid cell with the soft X-ray probe pulses. A trigger clock system and a frequency synchronization module were used for the synchronization of the laser pulses with soft X-ray pulses.

By using this measurement system, we have measured the time-resolved N K-edge XAS spectra of iron phenanthroline $[Fe(phen)_3]^{2+}$ aqueous solutions during the photoexcitation process with the time resolution of 45 ps. The C=N π* peaks of the ligands in the photoexcited (high spin) state of $[Fe(phen)_3]^{2+}$ are shifted to the lower photon energy compared to those in the ground (low spin) state. The temporal evolution of the peak intensity difference as a function of the delay time of the soft X-ray pulses with the laser pulses has determined that the time constant of the relaxation process from the high spin state to the low spin state is 550 ± 12 ps.

References

1) M. Nagasaka and N. Kosugi, *Chem. Lett.* **50**, 956–964 (2021).
2) M. Nagasaka, H. Yuzawa and N. Kosugi, *Anal. Sci.* **36**, 95–105 (2020).
3) F. Kumaki, M. Nagasaka, R. Fukaya, Y. Okano, S. Yamashita, S. Nozawa, S. Adachi and J. Adachi, *J. Chem. Phys.* **158**, 104201 (7 pages) (2023).

Mesoscopic Structural Analysis of Polymer Materials

UVSOR Synchrotron Facility
Division of Advanced Photochemistry

IWAYAMA, Hiroshi
Assistant Professor

Polymer composites, made by mixing multiple materials, have become increasingly important in developing polymer materials with higher functionality. Structural analysis is required for each constituent material (chemical species). However, with conventional small-angle X-ray and neutron scattering methods (SAXS/SANS), it is not easy to analyze the structure of each constituent material because the overall structural information is obtained simultaneously.

1. Resonant Soft X-Ray Scattering for Polymer Materials

Recently, we have developed resonant soft X-ray scattering (RSoXS) method. RSoXS has element, molecule and molecular orientation selectivity, making it possible to observe specific mesoscopic structures that cannot be observed with conventional SAXS. In particular, soft X-rays have the advantage of being able to selectively observe light elements such as carbon, nitrogen, and oxygen. Last year, we succeeded in analyzing the twisted structure of self-assembled liquid-crystal helical nanofilaments without electron density modulation.[1]

This year, we started researching polymers. In order to understand the performance of epoxy resins, it is necessary to analyze the crosslinked structure, which is usually composed of light elements and cannot be observed by conventional SAXS. Therefore, by using our resonant soft X-ray scattering method, we focused on the elements peculiar to crosslinked molecules and started to analyze the crosslinked structures of polymers by utilizing the resonance scattering of these elements.

Reference

1) Y. Takanishi, F. Araoka and H. Iwayama, *RSC Adv.* **12**, 29346 (2022).