Feasibility Study on Anomalous Small-Angle X-ray Scattering near Sulphur $K$-edge

Masashi Handa$^1$, Yuya Shinohara$^1$, Hiroyuki Kishimoto$^2$, Yusuke Tamenori$^3$, and Yoshiyuki Amemiya$^1$

$^1$Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba, Japan
$^2$Sumitomo Rubber Industries Co. Ltd., Kobe, Hyogo 651-0071, Japan
$^3$JASRI/SPring-8, 1-1-1 Kouto, Sayo 679-5198, Japan

E-mail: yuya@k.u-tokyo.ac.jp

Abstract. Anomalous small-angle X-ray scattering (ASAXS) is expected to be a powerful and vital tool for the structural study of soft matter. We investigated feasibility of ASAXS near sulphur $K$ absorption edge at SPring-8. Scattering pattern was successfully obtained and the dependence of scattering intensity on the energy of X-ray well agreed with the calculated one. This study can be the basis of structural study of soft matter using ASAXS, especially non-crystalline/amorphous materials.

1. Introduction

Small-angle Scattering (SAS) is a powerful tool to investigate the structure of soft matter, especially for non-crystalline and inhomogeneous structures (for example [1]). By using SAS, one can obtain the structural information of such non-crystalline/inhomogeneous structure. In the case of SAXS (Small-Angle X-ray Scattering) in which an X-ray is used as a probe, the scattering is caused by inhomogeneities of the electron scattering length density which depends on the density distribution of the atomic form factors inside the sample. The scattering contrast can be varied near the absorption edge of a specific element due to its anomalous dispersion. The dispersion of the atomic form factor $f$ is described as

$$f(E) = f_0 + f'(E) + if''(E),$$

where $f'$, and $f''$ represent the real and imaginary parts of the dispersion corrections, respectively. By using this dispersion, one can perform not only the scattering measurement with a higher contrast but also element-specific structural studies. SAXS using this anomalous dispersion is called as anomalous SAXS (ASAXS) [2, 3]. Though ASAXS has been used in the fields of ceramics [4], catalysts [5], quasicrystals [6] alloys [7, 8, 9], ionomers[10], polyelectrolytes[11], nanoparticles [12], and nanocomposites containing high-Z elements [13, 14, 15], the application of ASAXS to soft matter has been restricted.

Soft matter is usually made of low-Z elements, such as carbon, nitrogen, oxygen, phosphorus, and sulphur. The difference of electron density between these elements is relatively small. This sometimes leads to the lack of contrast between elements which results in insufficient SAXS intensity for structural analysis. Thus it is effective to enhance the contrast of electron density...
by using ASAXS in the structural analysis of soft matter. ASAXS of soft matter, however, includes some technical challenges at the same time. First, SAXS has to be performed at lower X-ray energy than that used with conventional SAXS. Soft matter has its absorption edges at lower energy region: the $K$-absorption edge of low-$Z$ elements such as sulphur ($Z = 16$) and phosphorus ($Z = 15$) is below 2.5 keV. This energy is much lower than the energy range of conventional SAXS, 8 - 15 keV, which is available at “hard X-ray” beamline where samples can be placed in ambient atmosphere due to beryllium windows. Though ASAXS study has been performed in many fields as is described above, there are few ASAXS studies performed near the $K$-edges of sulphur and phosphorus [16]. Thus we have to develop SAXS technique at the energy region, $E < 2.5$ keV, which is available at “soft X-ray” beamline where samples have to be kept in vacuum. Some attempts of sulphur ASAXS have been performed at hard X-ray beamlines by using the tail of anomalous dispersion. It is, however, obvious that ASAXS at the absorption edge is preferable from the viewpoint of signal-to-noise ratio than that at the tail of absorption edge. Thus ASAXS at soft X-ray beamlines should be developed.

In addition to the requirements to use soft X-rays, ASAXS of soft matter needs to be performed with an extremely high precision. In macromolecular crystallography, the importance of X-ray diffraction measurement at this energy region has been recognized for a long time and the diffraction studies using X-ray near the $K$-edge of sulphur and phosphorus were performed [17, 18]. Most of soft matter such as non-crystalline and inhomogeneous materials, however, does not show distinctive intensity profiles like Bragg peaks, which generally requires measurements with a higher precision than in macromolecular crystallography.

The goal of our research is to apply sulphur ASAXS to non-crystalline/amorphous materials. In the present study, we aimed at the measurement of accurate SAXS images near sulphur $K$-edge. As a first step, we used a model sample that consisted of silica particles and polymer matrix containing a large amount of sulphur. This is because only the scattering intensity, which is determined by the electron density contrast between particles and matrix, does depend on the energy of X-rays while the shape of scattering pattern does not. Because no soft X-ray beamline is designed for SAXS measurement, we have developed SAXS measurement at a soft X-ray beamline, BL27SU, SPring-8. In this report, SAXS experiment near the $K$-edge of sulphur is first described and then the change in X-ray scattering intensity near the sulphur $K$-edge is favorably compared with the calculated one.

2. Experimental Section

2.1. Beamline layout

ASAXS experiments was performed at BL27SU, SPring-8 (Hyogo, Japan). This beamline was originally designed for photochemical processes in inner-shell excitation. The experimental setup of our ASAXS measurement is described in Fig. 1. In this layout figure-8 undulator firstly generates X-rays in the range from 0.1 to 5.0 keV [19]. Then, two pre-mirrors (M0 and M1) focus the X-ray beam vertically on the entrance slit and horizontally on the sample, respectively. These two mirrors also play an important role in diverting the X-ray beam into this experimental arrangement. The X-rays with a specific energy is selected with a varied-line-spacing plane grating monochromator (VLS-PGM, [20, 21]), where M2 focuses the X-ray beam vertically on the exit slit. An upper available energy of X-ray is limited to 2.8 keV using the VLS-PGM. This monochromator has an energy resolution of $E/\Delta E \approx 2000$ in 2.0 - 2.5 keV. Post-mirror (M3) focuses the monochromatized beam vertically on the sample. These mirrors hardly reflect higher harmonics.

A Remarkable feature of this beamline is the use of a differential pumping system [22] which allows windowless experiments under normal atmospheric conditions in soft X-ray region. This system is composed of three sections, which are separated with walls having a hole to let the X-ray beam go through. These three sections are evacuated with respective vacuum pumps, and
Figure 1. Schematic view of the experimental setup. X-ray beam is monochromatized with the combination of grating, mirrors, and slits. We adopt a differential pumping system which enables us to perform experiments without any vacuum window.

Figure 2. Photon flux at BL27SU, which is normalized to a ring current of 100 mA and $E/\Delta E = 3000$. This spectrum was measured with the photodiode placed in the 3rd section of the differential pumping system. It is clear that the flux sharply decreases in 2.00 – 2.25 keV. This decrease is caused by the absorption by gold that is coated on the mirrors and grating, and the low reflectivity of M2.

the degrees of vacuum are $10^{-5}$, $10^{-1}$, and $10^{1}$ Pa in the 1st, 2nd, and 3rd section, respectively.

We set a 4-way slit and a pinhole at the upstream of the differential pumping system, and another pinhole in the 3rd section in order to eliminate the parasitic scattering. These pinholes have the same diameter of 50 $\mu$m. A sample and a detector were also arranged in the 3rd section and the distance between them was about 50 cm. SAXS measurement was performed in a transmission mode. We put a removable photodiode (AXUVPSV, International Radiation Detectors Inc.) between the sample and the detector so that we can monitor the incident beam intensity during scattering measurement. Just downstream of the photodiode, a crossed-wire made of 200 $\mu$m tantalum was placed and used as a beamstop.

Although a high flux is achieved in this beamline below 2.0 keV, it steeply decreases above 2.0 keV [23], as is shown in Fig. 2. The decrease of the flux above 2.0 keV is due to the X-ray absorption by all of the mirrors (M0, M1, M2 and M3) and grating, which are coated with gold having its $M$-edges at 2.21 and 2.29 keV. As a result, the flux decreases to
Table 1. Principal characteristics of the CCD detector

| Description                        | Value               |
|------------------------------------|---------------------|
| Format                             | 1024 × 1024         |
| Pixel Size                         | 13 µm × 13 µm       |
| Effective Area                     | 13.3 mm × 13.3 mm   |
| Frame Rate (slow scan)             | 0.28 frame/s        |
| Readout Noise (catalogue)          | 6 electrons (r.m.s.)|
| Cooling Temperature                | -60 °C              |
| Full Well                           | 80,000 electrons    |

$10^9$ photons/s/100mA/0.03 %B.W. above 2.0 keV. Angles of incidence at these mirrors (M0, M1, M2 and M3) are 89.4, 89.4, 88.0 and 89.0 degrees, respectively. It should be noted that the critical angle is 2.3 – 1.8 degrees for 2.0 – 2.5 keV, which means that regarding M2, the angle of incidence does not meet the requirement for the total reflection in the higher region of 2.0 – 2.5 keV. This fact also cause the decrease of the photon flux.

2.2. Detector

We adopted an indirectly-illuminated X-ray area detector. This detector consists of a phosphor screen, an optical relay lens, and a CCD detector. In this system, an X-ray image was first converted to a visible light image by the phosphor screen, then it was focused onto the CCD detector by the optical relay lens. The CCD can be easily exchanged by the adoption of mechanical attachment that is called a Phillips mount. In the present study a full-frame back-illuminated CCD detector (C4742-98-KAG, Hamamatsu Photonics Co. Ltd.) was used, the characteristics of which being shown in Tab. 1.

Two types of phosphor screen available were tested: one was a thin plate of LSO (Lu$_2$SiO$_5$:Ce) single crystal and the other was P-43 (Gd$_2$O$_2$S:Tb) powders. By using the LSO screen, measurement with a higher-spatial resolution was available. When we used the LSO screen, however, stray light from upper-stream transmitted the screen and was incident onto CCD. This severely limited the signal-to-noise ratio of SAXS measurement. Furthermore the quantum detective efficiency with P-43 was much higher than that with LSO due to the high emission efficiency of P-43. Therefore the P-43 screen was used in the present study. The thickness of P-43 screen was 10 µm, which was thin enough to perform measurements with a high spatial resolution. In this whole system, one incident X-ray photon upon the P-43 screen produces about one electron in the CCD, considering the luminous efficiency of P-43, the transmission efficiency of the lens and the quantum efficiency of the CCD detector.

2.3. Materials

As a model sample, we used nanocomposite which contains a large amount of sulphur in its matrix part. The matrix is thiol (LP-2, Toray Fine Chemicals Co. Ltd.), the chemical formula of which is -C$_2$H$_4$-O-CH$_2$-O-C$_2$H$_4$-S-. Monodispersive spherical silica particles (Seahoster, Nippon Shokubai Co. Ltd.) were added to thiolol. The volume fraction of particles was 20 %. After the particles were added to thiolol, it was carefully stirred and then kept at 120 °C for 48 hours so that it stiffens. Then the sample was sliced into a piece in a thickness of 30 µm by using a microtome.
3. Results and Discussion

Before measuring SAXS images, we measured the absorption spectrum of thiokol and the result is shown in Fig. 3 (left), which is calculated by

\[ \mu t = -\ln \frac{I}{I_0}, \]

where \( \mu \), \( t \), \( I \), and \( I_0 \) represent the linear absorption coefficient, the thickness of sample, the intensity of transmitted X-ray, and that of incident X-ray, respectively. \( I \) and \( I_0 \) were measured with and without the sample, using the photodiode placed in the 3rd section. Fig. 3 (left) shows that the \( K \)-edge of sulphur in thiokol is hardly shifted from the edge of isolated sulphur atom, 2472 eV. We selected six energies, 2100, 2300, 2400, 2446, 2461 and 2466 eV to perform SAXS experiment.

An image taken at 2100 eV is shown in Fig. 3 (right). The exposure time was 300 sec. We processed the data in each quadrant to avoid the cross-shaped shadow due to the beamstop. From the obtained images we calculated scattering profiles by circularly averaging the intensities of corresponding pixels and normalized them with the effect of absorption by the sample and with the intensity of incident X-ray. The errors in the normalization process is estimated about 0.2%. It should be noted that the energy dependence of the detector is ignored because we did not find any significant effect of energy on the sensitivity in the present study. When a measurement with an even higher precision is required, this factor needs to be carefully corrected.

The obtained profiles are shown in Fig. 4 (left). The scattering intensity profiles show a characteristic scattering pattern of isotropic monodisperse polymer particles. The average diameter of contained silica particles is found to be 130 ± 11 nm, which is consistent with the SAXS measurement with a higher X-ray energy, 8 keV. It is clear that the scattered X-ray intensity increases as the energy approaches to the edge. This can be explained as follows: near the absorption edge, the atomic scattering factor of sulphur greatly depends on the energy of incident X-rays and is described as Eq. (1). In this expression, the real part of dispersion correction, \( f'(E) \), sharply decreases as the energy approaches to the edge, and the imaginary part \( f''(E) \) is nearly zero at the energy below the absorption edge. In SAXS experiments of nanocomposites, the intensity of scattered X-ray is determined by the difference of electron density between filled materials and matrix. This difference can be calculated by using an atomic scattering factor.
mentioned above. In the present case, the intensity is proportional to

\[ |\Delta \rho(E)|^2 = |\rho_{\text{SiO}_2} - \rho_{\text{thio}}(E)|^2, \]  

(3)

where \( \rho_{\text{SiO}_2} \) and \( \rho_{\text{thio}} \) are the electron densities of silica particle and thiokol, respectively. It should be noted that the energy dependence of the X-ray intensity originates from only thiokol. In this equation, a decrease of real part of \( f(E) \) enlarges the difference of electron density between silica and thiokol, which results in the increase of X-ray scattering intensity near the sulphur K-edge. The detailed value of \( f(E) \) appears in some articles [24, 25], and we calculated \( |\Delta \rho(E)|^2 \) as shown in Fig. 4 (right, blue). Here we took it into consideration that the scattering intensity profiles at different energies needed to be convolved due to the finite resolution of the monochromator.

To compare the experimental results and the calculation, we used the invariant Q. It is defined in Eq. (4) and can be calculated for a two-phase system with Eq. (5):

\[
\text{Invariant Q} = \int_0^{\infty} I(q)q^2 dq
\]

where \( \phi \) is the volume fraction of one of the two phases. The experimental and expected invariants are compared in Fig. 4 (right side). The experimental values have been calculated with Eq. (4) and are shown as red dots. The expected energy dependence has been calculated with Eq. (5) and is shown as a blue line. The mean RMS deviation of the experimental values from the expected values is 7.5%. This is a fairly good value in consideration of the low flux of incident X-rays at the sample position in this energy region as shown in Fig. 2.

We used the sample which contains sulphur as much as 32 wt. %. Most non-crystalline/amorphous materials, however, contain less sulphur. For example, rubbery materials contain sulphur of only 1 – 2 wt. % which gives intensity variation of about 1 % near sulphur K-edge, assuming a similar two-phase system. In such ASAXS experiments the relative errors of less than 1 % are required. In order to reduce the relative errors, we need to improve the detector and the optical system in BL27SU.
4. Summary and Outlook

SAXS experiments near sulphur K-edge were performed and we obtained scattering intensity profiles of nanocomposites containing sulphur with a high accuracy. By changing the energy of incident X-rays near sulphur K-edge, we successfully measured the change of scattering intensity due to the sulphur component in the sample. The change of scattering intensity was well described by the energy dependence of anomalous dispersion of sulphur. This study can be the basis of the structural study of non-crystalline/amorphous materials by using ASAXS near the sulphur K-edge.

To apply ASAXS to non-crystalline/amorphous materials of interest, slight changes in the shape of scattering intensity profiles needs to be analyzed. To accomplish the analyses, the accuracy of measurement needs to be improved. We consider that the decrease of the photon flux above 2.0 keV and the low energy resolution near sulphur K-edge deteriorate the data quality, being limited by the use of the present optical system. Therefore we are planning to build a new experimental station on BL27SU, where we will install a silicon double-crystal monochromator to achieve an increased flux above 2.0 keV with an improved energy resolution. In addition, a new detector with higher quantum efficiency is being developed, which will be dedicated to SAXS experiments in soft X-ray region.

Acknowledgments

The authors acknowledge Drs. N. Ohta, Y. Suzuki, K. Uesugi, and N. Yagi (JASRI) for their kind support on the experiment. Dr. T. Itou and Y. Kajiura (Kao ltd.) supported us to perform ASAXS experiment. The ASAXS measurement was performed under the approval of JASRI program committee (Proposal No. 2008B1151 and 2009A1897).

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