Small Angle X-ray Scattering at Siam Photon Laboratory

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A Small Angle X-ray Scattering (SAXS) beamline has been constructed at the Siam Photon Laboratory (SPL) of the Synchrotron Light Research Institute (SLRI). The SAXS beamline is dedicated for nano structural characterization of materials. The synchrotron light originated from a bending magnet is monochromatized using a Double Multilayer Monochromater (DMM) to provide x-ray in the energy range of 6–9 keV. A toroidal mirror is used to focus x-ray to the sample position. The experimental station is equipped with a CCD detector, in which the sample-detector distance can be extended to up to 4 m. The beamline has been commissioned and opened for users in March 2011. The commissioning result of the beamline, including SAXS measurement of nano particles, is presented.

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I. INTRODUCTION

SAXS is an important non-destructive tool for structural characterization of materials that has electron density fluctuation on the length scale of approximately 1–100 nm [1, 2]. It provides information about size and shape of the sample nano-structure. Since variety of materials such as powder, solid, liquid or fibers can be used as a sample for SAXS measurements, this technique is proven to be useful in many fields of research, such as polymer sciences, nano-physics and structural biology. In order to facilitate the growing community of nano-scale research, a SAXS beamline was constructed at SLRI. The beamline BL2.2: SAXS is the first dedicated SAXS station in Thailand. The construction of the beamline was completed and opened for users in March 2011.

II. PHOTON SOURCE AND BEAMLINE OPTICS

II-1. Photon source

The Siam Photon Source (SPS) is a 1.2 GeV synchrotron light source of Thailand [3]. It is operated at the maximum beam current of 150 mA. The SAXS beamline utilizes the synchrotron radiation from a bending magnet of the SPS. At the photon energy between 6–9 keV, the calculated photon flux density of above 10¹¹ photons/sec/0.1% BW/mrad²/mm² is obtained [4]. Fig. 1 illustrates the schematic diagram of the SAXS beamline. The positions

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of each device are provided in cm along the bottom of the figure.


II-2. Monochromator
A double multilayer monochromator (DMM) is employed at the SAXS beamline. It consists of 150 periodic layers of W/B₄C, having d-spacing of 2.5 nm, coated on a Si substrate (the mirrors are fabricated by Rigaku Innovative Technology Inc.). Calibration of the DMM has been carried out by measuring K-absorption edge of Ni, Co and Fe metal foils. The photon energy was varied by rotating the DMM angle while an ionization chamber with the foil attached in the front was used to monitor the beam intensity. The results are shown in Fig. 2 where the absorption edges appearing as the abrupt change in intensity from the three metal foils can be clearly observed. From the tabulated K-edge data [5], the corresponding Bragg’s angle can be computed using the modified Bragg’s equation with the correction term for multilayer [6]. The actual DMM angle for any value of photon energy can then be obtained from the linear relation between the measured and calculated DMM angles.

FIG. 2: K-edge absorption spectra of the Ni, Co and Fe foils.
In order to measure the DMM energy bandwidth, a Si-111 crystal was employed as an energy analyzer. The crystal has the $d$-spacing of 0.3136 nm and energy resolution of 0.01%. It was installed after the DMM while an ionization chamber used for monitoring the beam intensity is placed behind the crystal. The grazing angle of the incident beam, with regard to the crystal plane, were scanned by rotating the crystal. The beam intensity as a function of photon energy was then measured. The resultant energy bandwidth measurement for different nominal photon energies of 6, 7, 8 and 9 keV are shown in Fig. 3. They appear to be distorted Gaussian shapes with apparent systematic distortion as a function of monochromatized x-ray energy. The nature of such distortion is not yet clear. To obtain the DMM energy bandwidth the measured spectrum at each energy was fitted by a combined double Gaussian curve, matched at the peak intensity. The energy bandwidth of the DMM was calculated from the standard deviation of the fitted double Gaussian curves. The measured energy bandwidth for the photon energy of 6, 7, 8 and 9 keV were found to be 0.92%, 1.01%, 0.93% and 0.95%, respectively. The DMM therefore provides the monochromatic x-ray with the energy resolution of approximately 1% in the energy range between 6–9 keV. Although the poorer resolution is obtained in comparison with that of 0.01% from a double crystal monochromator [6], effects of this large energy bandwidth is negligible for SAXS measurements [7]. The advantage of using DMM is that the higher photon flux is achieved.

![DMM bandwidth measurement](image)

**FIG. 3:** DMM bandwidth measurement at the photon energies (a) 6 keV, (b) 7 keV, (c) 8 keV and (d) 9 keV.

**II-3. Focusing mirror**

In order to increase photon flux at the sample position, a toroidal mirror is used to focus the beam in both horizontal and vertical direction. The mirror was made from ultra...
low expansion glass substrate coated with Rh and Pt (fabricated by SESO). It has the tangential and the sagittal radii of curvature of 213.334 cm and 5.33 cm, respectively. In order to optimize the beam acceptance the mirror is designed to operate at 5 mrad grazing angle. Ray tracing has been carried out using the program Shadowvui [8] and the focusing effect is shown in Fig. 4. The beam size at the sample position obtained by calculating the FWHM of the Gaussian function fitted into the histogram was found to be $1 \times 0.2 \text{ mm}^2$.

![FIG. 4: Simulated beam cross section at (a) 1 m before focusing position, (b) at the focusing position and (c) 1 m after the focusing position.](image)

II-4. Detector

A CCD detector (Mar CCD) with a diameter of 165 mm is used for capturing the scattering pattern. An ionization chamber installed in front of the sample holder and a photo diode attached in front of a beam stop are used to monitor the beam intensity before and after the sample, respectively. The sample-detector distance between 0.5–4 meter can be varied by removing or adding the vacuum tubes between the sample and the detector.

III. DATA PROCESSING SOFTWARE

A SAXS data processing software SAXSIT (Small Angle X-ray Scattering Image Tool) has been developed under Matlab. It is compiled into executable modules such that it can be run without Matlab installed. The basic SAXS data processing such as pattern alignment, calibration of sample-detector distance, background subtraction, circular averaging as well as radial integration of the profile can be performed. The numerical output of the software is provided in Microsoft Excel spreadsheet format for the ease of further data processing. The module for profile analysis using Guinier and Porod fit is also available.
IV. EXPERIMENTAL RESULTS

Silver behenate with $d = 3.838$ nm is a commonly used periodic calibrant for SAXS measurement. Figure 5(a) shows a SAXS pattern of silver behenate measured at the sample-detector distance $z = 2.5$ m. Their randomly oriented periodic structure results in peaks which appeared as circular rings. By comparing the position of these peaks with that predicted from the Bragg’s law, the sample-detector distance can be calibrated. The center of the primary beam can also be determined from the center of this circular peak. For a longer sample-detector distance, the position of the first order peak from the silver behenate may exceed the detector area. Thus, other periodic calibrants with larger $d$ spacing must be employed. Fig. 5(b) shows the SAXS pattern of rat tail tendon measured at $z = 3$ m. Their periodic structure with $d = 66.7$ nm is useful for calibration of a longer sample-detector distance.

![Figure 5: SAXS pattern of (a) AgBH recorded at $z = 2.5$ m and (b) rat tail tendon recorded at $z = 3$ m.](image)

Performance of the beamline has been tested by measuring SAXS pattern of poly(methyl metacrylate) (PMMA) spherical nano particle dispersed in water. In this measurement, the sample-detector distance was set to 2.5 meter. In order to subtract background properly, the measurements of the empty cell, the cell filled with water and the cell filled with PMMA were performed. Here, mica is used as the window material of the sample cell. The thickness of the liquid inside the sample cell is 1.5 mm.

In order to compare the SAXS profile of PMMA with that of the spherical nano particle, a form factor of sphere is simulated from [2]

$$I(q) \propto \left[ \frac{3 \sin(qR) - (qR) \cos(qR)}{(qR)^3} \right]^2,$$

(1)

where $R$ is the sphere radius, $q$ is the scattering vector defined as $q = (4\pi/\lambda) \sin(\theta)$, where $2\theta$ is the scattering angle. The finite wavelength, slit length and slit width result in a
smearing of the $I(q)$ which can be mathematically expressed by [2]
\[
\tilde{I}(m) = 2\int_{-\infty}^{\infty} \int_{0}^{\infty} Q(x) \cdot P(t) \cdot W(\lambda') \cdot I\left(\frac{\sqrt{(m-x)^2 + t^2}}{\lambda'}\right) d\lambda' dt dx,
\]
where $m$ is the distance between the scattered beam and the primary beam measured in the plane of registration. The function $Q(x)$ and $P(t)$ are the intensity distribution functions of the primary beam at detector position corresponding to the slit length and slit width, respectively. $W(\lambda')$ is the wavelength distribution where $\lambda' = \lambda/\lambda_0$ and $\lambda_0$ is the mean wavelength. Finally, the smearing from the effect of size distribution is taken into account [9]
\[
I_{\text{exp}}(q) = \int f(R) \tilde{I}(q, R).
\]
Here, $f(R)$ represents the size distribution function. By using Eq.(1) – Eq.(3), the SAXS intensity profile of spherical particles was simulated as shown using solid line in Fig. 6, while the circular averaged profile of the SAXS pattern of PMMA is plotted using the dot symbols. In this calculation, by measuring the primary beam at the detector position, the slit length and slit width were approximated by the Gaussian function with the FWHM of 2 and 0.5 mm, respectively. As for the wavelength smearing, the Gaussian function with the FWHM of 1% was employed. The sphere radius $R = 40.5$ nm and the Gaussian size distribution with FWHM = 7.5 nm were used.

FIG. 6: SAXS profile of PMMA and the simulated smeared profile of spherical nano particle.

V. CONCLUSION

The construction of SAXS beamline at the SPL has been completed and opened for users. The DMM is used for monochromatizing the synchrotron light from the bending
magnet. Calibration of the DMM has been done via K-edge measurement of the metal foils. By using Si-111 as the energy analyzer the energy bandwidth measurement of the DMM was carried out and found to be approximately 1% for the photon energy range of 6–9 keV. The photon flux density is increased by focusing the x-ray to the sample position using a toroidal mirror. The SAXSIT software for SAXS data processing has been developed. The SAXS measurement result of the PMMA spherical nano particle shows a good agreement with the simulation.

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References