DATA PREPROCESSING METHOD OF HIGH-FREQUENCY SAMPLING XAFS SPECTRA COLLECTED IN A NOVEL COMBINED SAXS/XRD/XAFS TECHNIQUE*

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Abstract

High-frequency (HF) sampling X-ray absorption fine structure (XAFS) spectra with a time-resolution of ~8 s were collected in our newly developed synchrotron radiation small-angle X-ray scattering (SAXS)/X-ray diffraction (XRD)/XAFS combined technique. Restoring the HF XAFS spectrum which contains hundreds of thousands to millions of data points to a normal XAFS spectrum consisting of hundreds of data points is a critical step for the subsequent neighbor structure analysis. Herein, the data preprocessing method and procedure of HF XAFS spectra were proposed according to the absorption edge of the standard sample and the rotation angular velocity of the monochromator. This work is expected to facilitate the potential applications of HF XAFS spectra in a time-resolved SAXS/XRD/XAFS experiment.

INTRODUCTION

To achieve the goals of controllable synthesis and performance optimization [1, 2], the knowledge of the structural evolution of materials in the processes of synthesis or service is a prerequisite. During the material synthesis and some dynamic changes, the synthesized material structures often be hierarchical. Tracking the entire material synthesis process and capturing useful information on all possible metastable precursors and intermediates will facilitate the controllable synthesis of materials. However, it is difficult for a single technique to meet all the detection requirements of hierarchical structure. It is very necessary to develop in-situ combined techniques to obtain simultaneously time-resolved hierarchical structural information on a dynamic reaction process.

Recently, we developed a novel SAXS/XRD/XAFS combined setup [3], where an area detector, a curved detector, and a point detector are, respectively, used for the detections of SAXS, XRD, and XAFS signals. This kind of combining technique can be used to track the changes [4] ranging from the molecular (local coordination state) to nanoscale (primary units) to microscale (crystallite formation) dimension during the crystallization process of samples. It should be noted here that, an ion chamber (IC) is often used detector to collect XAFS signals due to its good linear response to the X-ray intensity. However, for this compact combined setup, it is a failure to collect the XAFS spectra using IC as a result of its large volume. Intelligently, silicon PIN photodiodes [5] (SPPD) and diamond detectors[6] (DD) were used to substitute for IC due to their small size and good performance. Furthermore, to meet the time-resolved dynamic detection requirements, a high frequency (HF) sampling transmission scheme based on the high-speed counting cards (HSCC) was adopted to collect quick XAFS (QXAFS). However, the HF sampling XAFS data are very different from the conventional XAFS data in terms of abscissa and data points. Thus, the abscissa conversion and data reduction must be properly performed for the raw HF sampling scheme XAFS data.

Herein, the data preprocessing method of HF XAFS spectra will be proposed in detail according to the absorption edge of the standard sample and the rotation angular velocity of the monochromator. The data batch preprocessing program based on MATLAB code will also be introduced.

COLLECTION AND PREPROCESSING OF HF SAMPLING XAFS DATA

Data Collection

All the data was collected at beamline 1W2B of Beijing Synchrotron Radiation Facility (BSRF). The X-ray photon flux is about 1.0×10^{12} photons/s at Cu K-edge (8979 eV) with an X-ray spot size of about 0.8 (H) × 0.5 (V) mm^2 at the sample position. In HF sampling XAFS transmission mode, DD is used to monitor the X-ray intensity (I_0) in front of the sample, and DD or SPPD is used to monitor the X-ray intensity (I) behind the sample. For a sample with a thickness of d, the absorption coefficient (μ) can be written as:

$$\mu(\mathrm{E}) = \ln(I_0/I)/d \tag{1}$$

The high-speed counting module [5] (NI 9223) instead of the 974 counter was used for the Cu K-edge XAFS measurements of Cu foil at a sampling frequency of 10 kHz. Here, the sampling frequency represents the number of times that an experimental signal (here it is the X-ray intensity) was repeatedly read out in one second. A higher sampling rate can greatly improve data quality by raising statistics. Figure 1 clearly shows the raw data of an HF sampling XAFS spectrum for standard Cu foil at the sampling frequency of 10 kHz. Figures 1a and 1b clearly show the dependences of I_0, I, and μ on counting (0~80,000). Based on the data acquisition frequency, the abscissa can also be expressed in terms of time t:

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$$t = N/F \quad (2)$$

Here, N is the total number of data, and F is the data acquisition frequency. There are large amplitude fluctuations in raw spectra before 872 numbers and after 70,231 numbers (Figs. 1c and 1d), which corresponds to the position of 200 eV before the absorption edge and 800 eV after the absorption edge, respectively. This is due to the uneven speed of the monochromator during the start and stop phases. Anyway, the HF sampling XAFS is very different than that of the conventional XAFS in appearance. It is very necessary to make a data preprocessing so that one can determine the data qualities and features from the raw HF sampling XAFS data.

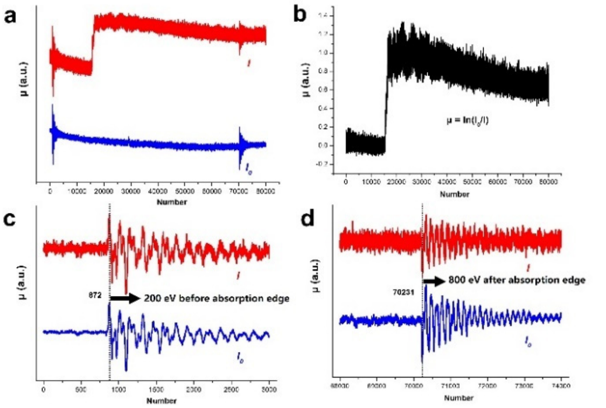

Figure 1: Raw HF sampling XAFS spectra of Cu-foil at 10 kHz. (a) I_0, I; (b) absorption coefficient μ; and the enlarged images of before (c) and after (d) absorption edge.

Abscissa Conversion

Firstly, the XAFS data should be converted from time-domain into energy-space. To do this, the absorption-edge position was first determined and marked as E_0, which corresponds to the first derivative maximum of the XAFS spectrum. For a typical double-crystal monochromator, its rotation in the Bragg-angle (θ) space is usually uniform. It means that the Bragg angle of Si (111) monochromator was linearly changed and followed the formula:

$$\theta - \theta_0 = \omega\,(t - t_0) \quad (3)$$

Here, θ_0 is the Bragg angle corresponding to the absorption edge of the element to be measured, t_0 is the required time for the monochromator to rotate to the absorption edge of the element, and ω is the rotation angular velocity of the monochromator. Based on the linear relation between the Bragg angle (θ) and the rotation time (t), the data-point distribution of HF sampling XAFS spectrum is also uniform in the Bragg-angle space. As an example, Fig. 2 clearly shows the abscissa conversion process from t-space to angular-space. After conversion, each of these data points (80,000 points) has its angle value. Meanwhile, the abscissa of the HF sampling XAFS spectra can be further converted from the Bragg angle (θ) to the incident X-ray energy (E) by the following formula:

$$E(eV) = hc/2d_{(111)}\,sin\,\theta = 1977/sin\,\theta \quad (4)$$

Here, h is the Planck constant (6.626×10^{-34} J·s); c is the velocity of light (2.998×10^{8} m·s^{-1}); $d_{(111)}$ is the interplanar spacing of Si(111) crystal plane (3.1357 Å). For the Cu-foil sample, the absorption-edge energy of Cu K-edge (E_0) is 8979 eV. Finally, the 80,000-absorption coefficient (μ) and energy (E) data points can be obtained.

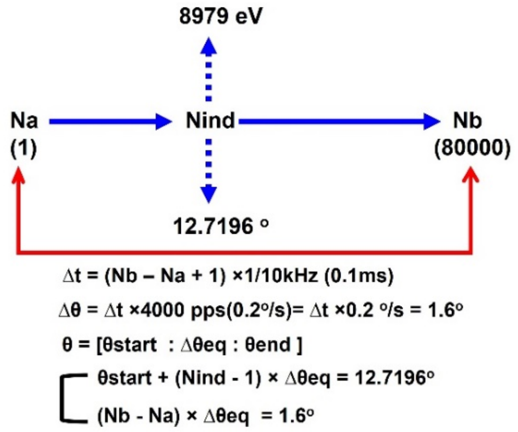

Figure 2: Abscissa conversion process from t-space to angular-space.

Data Reduction

The second step is data reduction. The simple and convenient way to reduce the number of data points is to divide the XAFS spectrum of high-frequency sampling into hundreds of segments. Each segment consists of hundreds of data points, being required to have an energy span equal to or better than the energy resolution of the monochromator. By averaging statistically all data points in each segment into one data point, the energy span between two adjacent data points was enlarged. Finally, the high-frequency sampling XAFS spectrum is restored to a normal XAFS spectrum consisting of hundreds of data points (reduced from 80,000 points to 800 points). The raw (black) and reduced (red) HF XAFS spectra are shown in Fig. 3.

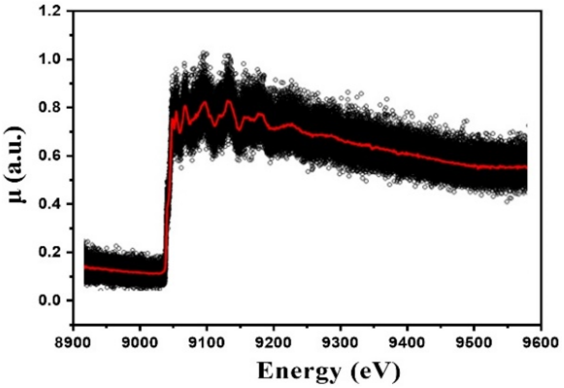

Figure 3: Raw and preprocessing (abscissa conversion and data reduction) HF sampling XAFS spectra of the standard Cu foil at 10 kHz.

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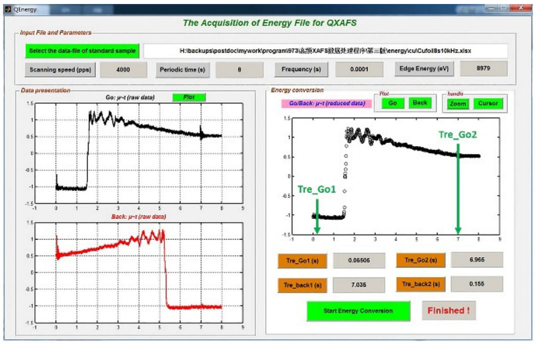
Data Batch Processing Program

Even on the first-generation synchrotron source (BSRF), the repeated acquisition of HF sampling XAFS spectra can achieve a time resolution of the order of seconds [3]. It is clear that, when conducting in situ time resolution experiments in the reaction process of materials, a huge amount of data will be obtained. Therefore, developing a data batch processing program is very necessary. According to the above theory and procedure, a data batch processing program based on MATLAB code was written by Y. Liu.

It should be mentioned that, except for the data preprocessing of HF sampling XAFS data, the obtained SAXS and XRD data also need to be energy-normalized when the follow-up analysis. Therefore, the first thing is to obtain an energy file (two columns including time and energy, and the two correspond one-to-one). Figure 4 shows the MATLAB program interface of energy file acquisition for a standard sample. The parameter values of scanning speed, periodic time, acquisition frequency, and absorption edge energy are needed to be input. To shorten the repetition interval of XAFS, we adopt a novel bidirectional (two-way) energy scanning strategy. Meanwhile, to exactly obtain the energy coordinates, the deadtime (eliminate the return difference) should also be calculated in the forward and backward scanning. The energy coordinates of these data points are considered to be the same since the monochromator has no mechanical motion.



Select the data-file of standard sample: H:\backups\postdoc\mywork\program\973\高频XAFS数据处理程序\第三版\energy\cu\Cufoil8s10kHz.xlsx

Scanning speed (pps): 4000
Periodic time (s): 8
Frequency (s): 0.0001
Edge Energy (eV): 8979

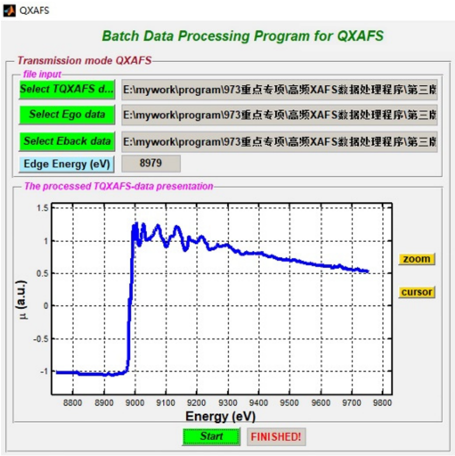
Tre_Go1 (s): 0.06506
Tre_Go2 (s): 6.966
Tre_back1 (s): 7.035
Tre_back2 (s): 0.155

Finished !

Figure 4: The MATLAB program interface of energy file acquisition for a standard sample Cu-foil.

Since the data acquisition adopts the two-way energy-scanning strategy, two conversion files (here, that is called Ego data and Eback data) from the acquisition time (*t*) to the diffraction angle (θ) of the monochromator or the incident X-ray energy (*E*) should be prepared in advance, which are used for the forward scanning process with the incident X-ray energy changing from low to high and for the backward scanning process with the X-ray energy changing from high to low, respectively. As an example, the energy calibration process using the XAFS spectra of Cu foil acquired by the two-way energy scanning strategy is shown in Fig. 4.

In the subsequent batch processing of HF sampling XAFS collected by the two-way energy-scanning strategy for the real sample, one only needs the two energy files (Ego data and Eback) of the standard sample obtained from the MATLAB program shown in Fig. 4. The batch data processing program for the HF sampling XAFS and the preprocessing result are shown in Fig. 5, which makes it easy for users to process data in batches.



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Select Ego data: E:\mywork\program\973重点专项\高频XAFS数据处理程序\第三版
Select Eback data: E:\mywork\program\973重点专项\高频XAFS数据处理程序\第三版
Edge Energy (eV): 8979

FINISHED!

Figure 5: The batch data processing MATLAB program interface for HF sampling XAFS data.

CONCLUSION

This paper presented a simple and practical data preprocessing method for the novel HF sampling XAFS data, which facilitates the potential applications of HF XAFS spectra in a time-resolved SAXS/XRD/XAFS experiment.

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