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# 整体多毛细管 X 光透镜在扩展 X 射线吸收精细结构分析技术中的应用

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**摘要:**为了将整体多毛细管 X 光透镜应用到扩展 X 射线吸收精细结构分析技术中,对整体多毛细管 X 光透镜的功率密度增益、光斑稳定性、高能滤波性质等进行了系统表征。通过实验可知,利用基于整体多毛细管 X 光透镜的扩展 X 射线吸收精细结构分析设备可对样品进行微区分析,其空间分辨为 25  $\mu\text{m}$  左右;利用整体多毛细管 X 光透镜会聚激光等离子体发出的 X 射线进行超快时间分辨扩展 X 射线吸收精细结构分析时,透镜的功率密度增益约为 3 000。实验结果证明,整体多毛细管 X 光透镜可以改善扩展 X 射线吸收精细结构分析设备的性能。

**关键词:**毛细管 X 射线光学器件;扩展 X 射线吸收精细结构;微区扩展 X 射线吸收精细结构;超快时间分辨扩展 X 射线吸收精细结构

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## Application of a monolithic polycapillary X-ray lens in EXAFS experiments

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**Abstract:** The performance of the Monolithic Polycapillary X-ray Lens (MPXRL) for application in the Extended X-ray Absorption Fine Structure (EXAFS) technique is reported, especially, the main

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characters of the MPXRL such as gain in flux density, stabilizing effect, and high energy filtering. Experimental results show that the spatial resolution of the EXAFS facility based on the MPXRL is about  $25\ \mu\text{m}$ , and the gain in flux density of the Monolithic Polycapillary Focusing X-ray Lens (MPFXRL) is about 3 000 when the MPFXRL is used to focus the laser plasma pulsed X-ray for ultrafast time-resolved EXAFS experiments. These indicate that the MPXRL is helpful in the improvement of the EXAFS facilities.

**Key words:** capillary X-ray optics; EXAFS; micro-EXAFS; ultrafast time-resolved EXAFS

## 1 Introduction

There is a range of focusing X-ray optics which can be used to focus X-rays into a microbeam with high flux density, such as multi-layer optics, refractive X-ray lens, Kirkpatrick-Baez mirrors, capillary optics, *etc.*<sup>[1-5]</sup> The fabrication of capillary optics is straightforward, and they can be used expediently in many fields.

A MPFXRL can focus a divergent X-ray beam into a micro focal spot, and a Monolithic Polycapillary Half-focusing X-ray Lens (MPHFXRL) can focus a quasi-parallel X-ray beam into a micro focal spot. The order of magnitudes of these focal spot sizes and the gain in power flux density in these focal spots is  $10\ \mu\text{m}$  and  $10^3$ , respectively. A Monolithic Polycapillary Parallel X-ray Lens (MPPXRL) can focus a divergent X-ray beam into a quasi-parallel beam with a divergence of several mrad. Thus the MPFXRL, MPHFXRL and MPPXRL are widely used in micro X-ray analysis.

There has been some studies on the application of the capillary X-ray optics in the EXAFS experiments, since capillary optics is used in X-ray analysis. In the early years, most of these studies were on a single capillary or an assembling polycapillary X-ray lens, and recently on the MPXRL. Research on the application of the MPXRL in in-laboratory EXAFS equipment began 8 years ago<sup>[6]</sup>, and this research is still in progress. There are two kinds of in-laboratory EXAFS equipment based on a MPXRL. One is based on a MPPXRL and the other is based on a

MPFXRL. The MPHFXRL is often used to focus synchrotron radiation to develop the micro-EXAFS technique. In this paper, studies on the application of the MPXRL in EXAFS experiments are presented.

## 2 EXAFS equipment based on MPPXRL

### 2.1 Experimental apparatus

A schematic of the EXAFS equipment based on a MPPXRL is shown in Fig. 1. The divergent X-ray beam, emerging from a Mo rotating anode X-ray generator (RIGAKU RU-200, 60 kV-200 mA), is collimated with a MPPXRL to form a quasi-parallel X-ray beam. This quasi-parallel beam is diffracted by a flat crystal monochromator. This diffracted X-rays are measured with a NaI scintillation counter. The sample (Cu film) is placed in front of the collimating device before the scintillation counter.

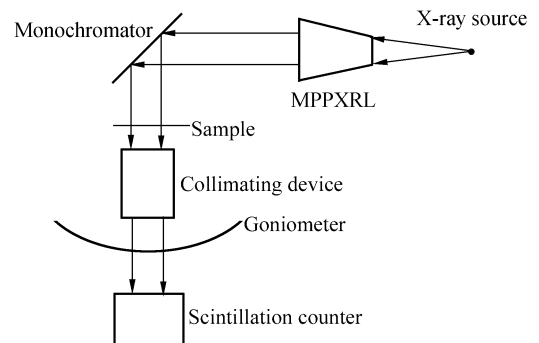


Fig. 1 Schematic experimental set-up for measuring EXAFS spectra

## 2.2 Results and discussion

Fig. 2 shows the measured transmission efficiency as a function of X-ray energy for the MPPXRL used here. As shown in Fig. 2, the MPPXRL chosen for measuring the EXAFS spectra of metal Cu thin film has high transmission efficiency near the Cu K-edge. The transmission efficiency decreases from 33.2% to 7.6% in the energy range 8~17 keV. This indicates that the MPPXRL can be used as a filter for high energies, which is helpful in avoiding higher harmonics. Consequently, intense X-rays are available over a wide energy range by applying a high accelerating voltage to the X-ray tube.

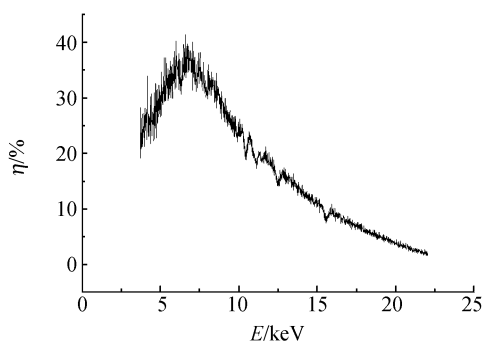


Fig. 2 Transmission efficiency of MPPXRL

The energy resolution of the spectrometer based on a MPPXRL is estimated by measuring the energy width of the  $WL_{\beta 1}$  line. When a Si (444) flat crystal in combination with a point X-ray source (0.3 mm×0.3 mm) is used, the energy resolution is 15.4 eV, while  $3.12 \times 10^4$  cps (25 kV-100 mA, @ 9.92 keV) is obtained.

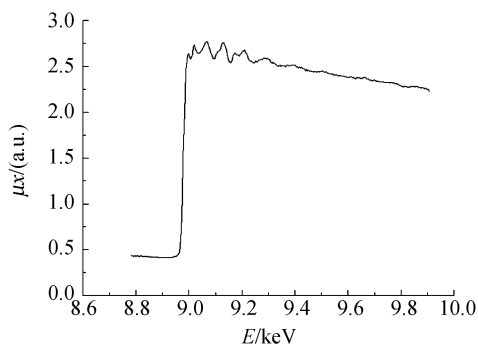


Fig. 3 EXAFS spectra of metal Cu thin film

Fig. 3 shows the copper EXAFS spectra measured with the spectrometer based on a MP-PXRL<sup>[7]</sup>.

## 3 Micro-EXAFS equipment based on MPFXRL

### 3.1 Experimental apparatus

Fig. 4 shows the schematic experimental set-up based on a MPFXRL for measuring EXAFS spectra. As shown in Fig. 4, the divergent X-ray beam is focused by a MPFXRL, and the sample is placed at the focal spot of the MPFXRL. The diffracted X-ray beam from the flat crystal is detected with a Position-sensitive Proportional Counter (PSPC).

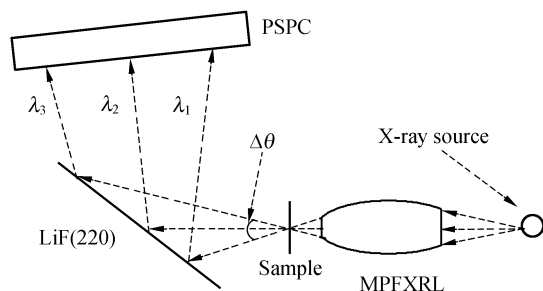


Fig. 4 Schematic experimental set-up based on MPFXRL for measuring EXAFS spectra

### 3.2 Results and discussion

At 9.0 keV, the focal spot size of the MPFXRL and divergence (as shown in Fig. 4) of the beam after focal spot of the MPFXRL are 28  $\mu\text{m}$  and 4.5°, respectively. This makes the equipment based on a MPFXRL very well suited for application in micro-EXAFS experiments with dispersive spectrometers. The transmission efficiency of the MPFXRL decreases from about 11.3% to about 0.53% in the energy range of 7~20 keV, and accordingly a MPFXRL can also be used as a filter for high energies just as a MP-PXRL. The spatial resolution of the PSPC was measured as 72  $\mu\text{m}$  by using a pair of narrow

slits. The energy resolution of the spectrometer based on the MPFXRL is 10.4 eV for the  $WL_{a1}$  line when the LiF(220) is used. When the working voltage and current of a Mo rotating anode X-ray generator are 25 keV and 100 mA, respectively, it takes 6 h to obtain the EXAFS spectrum of the Cu film with a 12  $\mu\text{m}$  thickness at room temperature by using LiF(220). Fig. 5 shows the Fourier transform of the EXAFS spectra of this Cu film<sup>[8]</sup>.

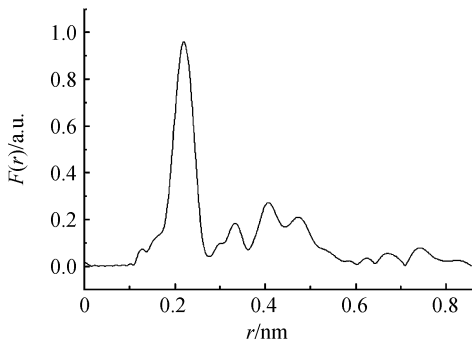


Fig. 5 Fourier transform EXAFS spectra of the Cu film

Comparing with the EXAFS equipment based on a MPPXRL, the EXAFS equipment based on a MPFXRL needs no goniometer and the entire EXAFS spectrum of interest is recorded simultaneously. This avoids the influence of fluctuations in the incident X-ray beam intensity on the quality of the EXAFS spectrum. In addition, the EXAFS equipment based on a MPFXRL can perform the micro-EXAFS experiments.

## 4 Micro-EXAFS equipment based on MPHFXRL

### 4.1 Experimental apparatus

The experiments were carried out at the X-ray absorption fine structure (XAFS) station in the National Synchrotron Radiation Laboratory

(NSRL) of China<sup>[9]</sup>. Fig. 6 shows a sketch of the micro-EXAFS facility based on a MPHFXRL and the synchrotron radiation. As shown in Fig. 6, the synchrotron radiation from the double-crystal monochromator is focused by a MPHFXRL into a microbeam. Because the size of the synchrotron radiation from a double crystal monochromator is larger than the entrance size of the MPHFXRL, a cross-slit is placed in front of the ionization chamber to shut off the synchrotron radiation beyond the entrance of the MPHFXRL.

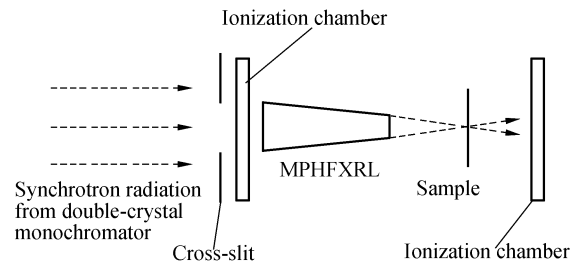


Fig. 6 Sketch of micro-EXAFS facility based on MPHFXRL and synchrotron radiation

### 4.2 Results and discussion

The monochromator causes the unfocused monochromatic beam impinging on the entrance of the MPHFXRL to translate vertically by about 80  $\mu\text{m}$  when the X-ray energy is changed from 5.5 to 11.5 keV. In the same energy range, the total translation of the vertical position of the focused beam by the MPHFXRL is only 3  $\mu\text{m}$ . The reason for this is that the MPHFXRL is not an imaging optics, and accordingly the position of the focal spot does not rely on the source position. This demonstrates that a MPHFXRL has a stabilizing effect on the vertical position of the centre of its focal spot when the X-ray energy is changed. The output focal distance of a MPHFXRL changes slightly with the change in the X-ray energy, which results from the decrease of the critical angle of total reflection at higher energies. However, the change of output focal distance may be ignored at an ener-

gy range of 1 keV, i. e. , a MPHFXRL has a stabilizing effect on the horizontal position of the center of its focal spot at 1 keV range which is the scan range when an EXAFS spectrum is obtained. The order of magnitude of the focal spot size and gain in flux density in the focal spot of the synchrotron radiation microbeam focused by a MPHFXRL are  $10\ \mu\text{m}$  and  $10^3$ , respectively. It is well known that a MPHFXRL is a nonlinear optic. The channels near the axis of the MPHFXRL have smaller bending than the channels far away from the axis, and therefore, they have higher transmission. In order to further increase the gain of the synchrotron radiation microbeam, a larger synchrotron radiation beam can be first focused efficiently into a smaller beam by a toroidal mirror, and then the smaller beam is focused efficiently into a micro focal spot by using the central part of a MPHFXRL. This was proved by our experiments performed at beam-line 1W1B-XAFS of the Beijing Synchrotron Radiation Facility of China<sup>[10]</sup>. When a toroidal mirror is used in front of the MPHFXRL, the order of the magnitude of the gain in flux density in the focal spot of the MPHFXRL is  $10^4$ .

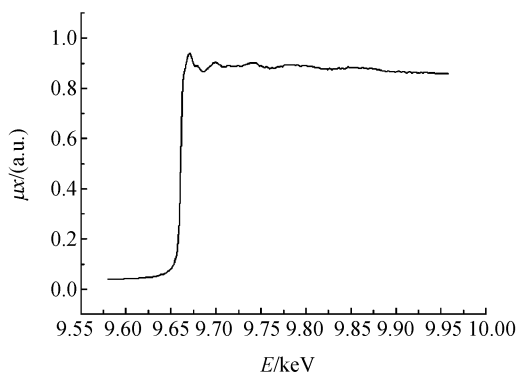


Fig. 7 Fluorescent EXAFS spectrum of Zn in the hyperaccumulative plant.

Because of the high gain of the synchrotron radiation microbeam focused by a MPHFXRL, this micro-EXAFS facility can be used to measure the EXAFS spectra of a sample with relative-

ly low content. Fig. 7 shows the fluorescent EXAFS spectrum of Zn in the hyperaccumulative plant in which the content of the Zn is about  $1 \times 10^{-3}$ . The thickness of the hyperaccumulative plant sample is about  $40\ \mu\text{m}$ . The measured time is 10 min.

## 5 Ultrafast time-resolved EXAFS equipment based on MPHFXRL

### 5.1 Experimental apparatus

Fig. 8 shows a sketch of the ultrafast time-resolved EXAFS equipment based on MPHFXRL<sup>[11]</sup>. As shown in Fig. 8, the laser pulse is split into two beams. One beam is used for sample excitation, and the other is used to produce a plasma-pulsed X-ray source for time-resolved EXAFS experiments. The diffracted X-rays are detected by using an X-ray charge coupled devices (CCD).

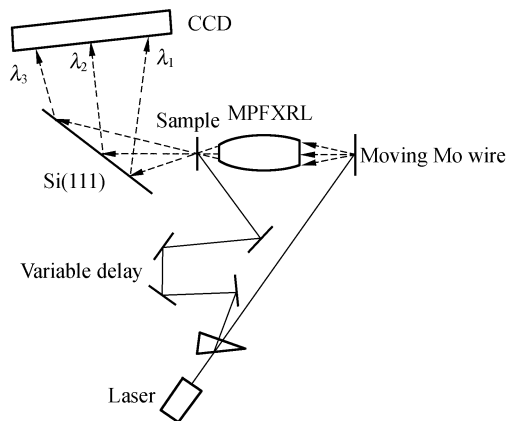


Fig. 8 Sketch of ultrafast time-resolved EXAFS equipment based on MPHFXRL

### 5.2 Results and Discussion

The pulse broadening in time introduced by the MPHFXRL is less than 1 ps. The divergence of the beam after the focal spot of the MPHFXRL is several degrees. This makes the EXAFS equipment based on MPHFXRL very well suited for

applications in time-resolved EXAFS experiments in conjunction with dispersive spectrometers. The gain in flux density in the focal spot of the MPFXRL is about 3 000. This high gain of the MPFXRL allows us to perform time-resolved EXAFS experiments in liquids where the cross-section is small and the need for high X-ray flux is necessary<sup>[12]</sup>.

The structure of the intermediates evolved during the course of the  $\text{Fe(III)}(\text{C}_2\text{O}_4)_3^{3-}$  redox photochemical reaction was studied. The Fourier transform of the EXAFS spectra of ferrioxalate sample  $-20$  ps before excitation and  $+25$  ps af-

ter excitation are shown in Fig. 9. This implies that the ferrioxalate photo redox reaction involves a fast dissociation process before the electron transfer takes place<sup>[13]</sup>.

## 6 Conclusions

The MPXRL can be applied in EXAFS experiments. The MPXRL has a high gain in flux density in its focal spot and can stabilize the position of its focal spot. This enables micro-EXAFS experiments to be performed. The MPXRL can be used as a filter for high energies. This is helpful in improving the energy resolution of the EXAFS equipment. The MPFXRL can be used to focus the X-rays from the plasma pulsed X-ray source for time-resolved EXAFS experiments.

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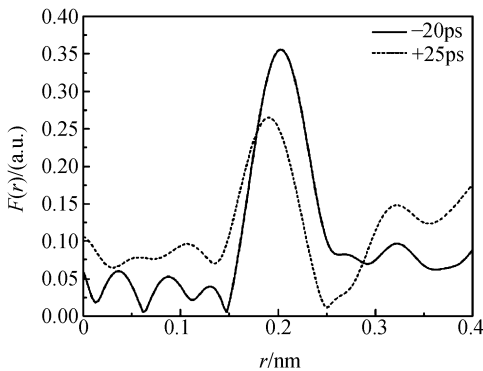


Fig. 9 Fourier transform of the EXAFS spectra of ferrioxalate sample  $-20$  ps before excitation and  $+25$  ps after excitation

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