Tomographic X-ray Absorption Spectroscopy

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Introduction

Hard x-ray absorption spectroscopy is combined with scanning microtomography to reconstruct the full near-edge spectra of an elemental species at each point on an arbitrary virtual section through a sample. These spectra reveal the local concentration of different chemical compounds of the absorbing element inside the sample and provide insight into the oxidation state and local projected free density of states. The method is implemented by combining a quick scanning monochromator and data acquisition system with a scanning microprobe setup based on refractive x-ray lenses. The full x-ray absorption near-edge structure (XANES) spectra reconstructed at each point of the tomographic slice allow the detection of slight variations in the concentrations of the chemical compounds, such as Cu and $Cu(I)_2O$.

X-ray absorption spectra reveal the local chemical environment of an element of interest. Its near-edge spectra (XANES) can be used as a fingerprint for different chemical compounds, allowing one to determine their concentrations in a mixture. Inhomogeneous samples are encountered in many fields of science, such as physical chemistry (catalysts), materials science, biology, geology, and environmental science. In these samples, the composition of different chemical compounds can vary greatly as a function of position.

A spatially averaged analysis often fails to reveal the information needed to understand the local chemical processes. XANES microanalysis allows one to locally analyze inhomogeneous samples, provided the sample is thin enough to avoid averaging along the microbeam. This often requires sample preparation, which is difficult and, in addition, prone to change the chemical composition. One of the main strengths of hard x-rays is their large penetration depth in matter, which allows one to probe the volume of a specimen.

Methods and Materials

In this project, we have combined near-edge spectroscopy with scanning microtomography to obtain full spectral information for an arbitrary virtual slice through an inhomogeneous bulk sample. The method is illustrated for a specimen from catalysis. Except for possible radiation damage, the method is nondestructive. A detailed description of the method is given in Ref. 1. The experimental setup for this technique is shown in Fig. 1 and combines a fast scanning monochromator and data acquisition system developed at the University of Wuppertal [2-4] with a scanning microprobe setup based on beryllium parabolic refractive x-ray lenses [5, 6].

The hard x-rays from a synchrotron radiation source are monochromatized by a channel-cut Si (111) double-crystal monochromator and focused onto the sample position by using a beryllium parabolic refractive lens. The resulting pencil beam has a lateral dimension in the micrometer range. As shown in Fig. 1(a), three ionization chambers measure the flux incident on the sample (I_0), transmitted by the sample (I_1), and transmitted by a reference foil (I_2), respectively. Simultaneously, a positive intrinsic negative (PIN)-diode measures the fluorescence radiation emitted by the sample (I_3) [denoted I_F in Fig. 1(b)].
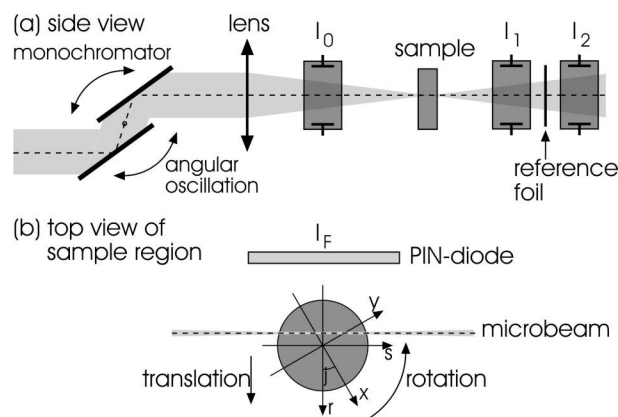

FIG. 1. (a) Side view of the setup for absorption spectroscopy tomography. (b) Top view of the sample region. The sample fixed coordinates (x, y) are rotated with respect to (r, s) by the angle φ. Both coordinate systems are translated with the sample. The parameter r denotes the position of the microbeam. The z coordinate perpendicular to the slice is the same in both coordinate systems. Reprinted with permission from Ref. 1, copyright 2003, American Institute of Physics.

An absorption spectroscopy tomogram was recorded by scanning the sample through the microbeam in a 2-D scan in r and ϕ, as shown in Fig. 1(b). The translational scan in r corresponds to a single tomographic projection. After each projection was recorded, the sample was rotated in ϕ by an integer fraction of 360, and the next projection was recorded. This procedure was repeated until the sample had completed a full rotation. At each position of the scan, a full absorption spectrum was recorded. In order to record the full tomogram in a reasonable time, the time to record an absorption spectrum at a single position in the scan must be on the order of 1 second or shorter. This is possible with a quick extended x-ray absorption fine structure (QEXAFS) monochromator and a fast data acquisition system [2-4]. In this experiment, the system recorded 10 full absorption spectra per second with 10^4 data points each, measuring simultaneously the signals I_0 through I_3 described above.

The main advantage of this scanning technique is that it yields full absorption spectra at each point (r, ϕ) in the sinogram, both in absorption and fluorescence (for example, Fig. 2). In addition, all spectra are calibrated in energy. The method was first tested at bending magnet beamline BM5 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Although the feasibility of the method could be demonstrated at this beamline, recording larger tomograms requires the brilliance of a third-generation light source, such as the APS. The experiment reported on here was conducted at APS undulator beamline 1-1D. The sample was composed of a 30% CuO/ZnO catalyst that was twice reduced and reoxidized by 4% H_2/He and 2% O_2/He at 200–300°C. After a final reduction, the thus grown Cu particles on ZnO were reoxidized at room temperature. The aim of the experiment was to analyze their structure and oxidation state in the volume. XANES tomograms were recorded both at the copper and zinc K edge. At the copper K edge, 101 projections with 90 translational steps of 10-μm each were recorded over 360°.

Results and Discussion

The spectra recorded during the acquisition time of 1 second at a given position are calibrated in energy by using the spectra of the reference foil and summed up into a single spectrum. This is done for both the transmission and fluorescence channel. The negative logarithm of the transmission data yields the integral of the attenuation coefficient along the microbeam for each energy E. Figure 2 (inset) shows the transmission data at fixed energy for a full set of r and ϕ. This set constitutes the input data for transmission tomography. At each position (r, ϕ), a full XANES spectrum is available, an example of which is shown in Fig. 2.
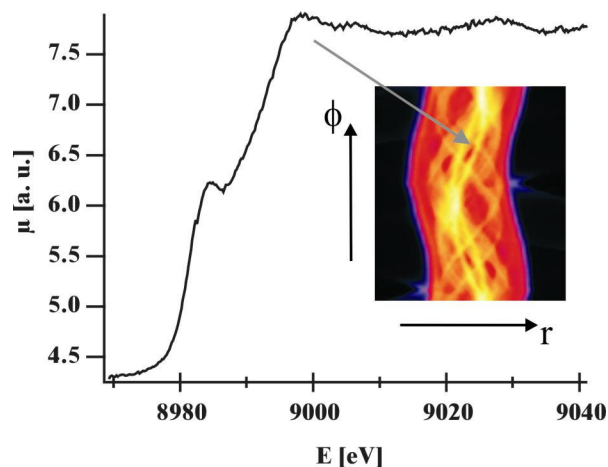

FIG. 2. XANES spectrum (color inset) obtained at a single position (r, ϕ) in the tomographic scan. The position corresponds to the coordinates (r, ϕ) pointed to by the arrow in the inset that shows the absorption coefficient μ (at fixed energy E = 9000 eV) as a function of r and ϕ, the so-called sinogram.

Tomographic reconstruction yields the attenuation coefficient μ at each location (x, y) on the virtual slice. The attenuation coefficients below and above the K edge of copper are depicted in Fig. 3(a) and 3(b), respectively. Fig. 3(c) shows the reconstructed spectra at the locations marked in Fig. 3(b), together with the reference spectra for metallic Cu, $Cu(I)_2O$, and $Cu(II)O$. At each location on the slice, the reconstructed spectra can be fitted by these reference spectra (plus a constant). Two exemplary fits are shown as the red dashed curves in Fig. 3(c). This way, the distribution of different copper compounds and of other elements (constant spectrum) can be obtained. The resulting distributions are shown in Fig. 3 of Ref. 1. The quality of the fits to the spectra excludes significant concentrations of other compounds that have not *a priori* been taken into account. Copper is mainly present in the prepared sample in a metallic or monovalent state.

Slight variations in the relative concentrations of these two compounds lead to small changes in the near-edge spectra. Faithful reconstruction of the relative concentrations requires full spectra, analyzing the residuals of the fits. For a detailed discussion, see Ref. 1.

For more dilute samples, such as biological specimens, the fluorescence signal can be reconstructed. For fluorescence data, the tomographic model is more complicated, as self-attenuation effects need to be taken into account [7]. In the general case, absorption spectra of neighboring elements may overlap to produce a more complicated spectrum. This is the case for some of the spectra in the XANES tomogram recorded for the same sample at the zinc K edge. Here, the Zn near-edge spectra lie on top of the extended absorption fine structure of
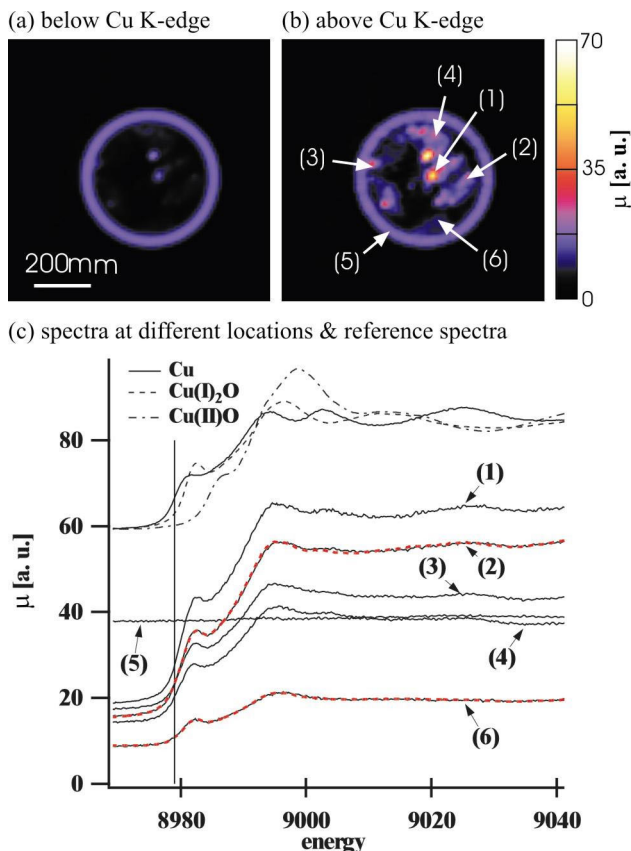
(a) below Cu K-edge (b) above Cu K-edge

200mm

(4) (1) (3) (2) (5) (6)

70
35
0
μ [a. u.]

(c) spectra at different locations & reference spectra

— Cu
--- Cu(I)₂O
-·-· Cu(II)O

μ [a. u.]

(1) (3) (2) (5) (4) (6)

8980   9000   9020   9040
energy

FIG. 3. Reconstructed tomogram (color) of a capillary filled with a CuO/ZnO catalyst (a) below (E = 8970 eV) the Cu K edge and (b) above (E = 8995eV) it. (c) Reconstructed XANES spectra at different locations marked in (b) and (offset) reference spectra of metallic Cu, Cu(I)₂O, and Cu(II)O. The dashed red curves in (c) represent two fits using the reference spectra. Reprinted with permission from Ref. 1, copyright 2003, American Institute of Physics.

copper. Figure 4 shows two spectra at locations marked by (1) and (2) in the reconstructed slice (lower right corner of Fig. 4). Spectrum (1), which is reconstructed at a location with a high Cu concentration, shows a slowly varying oscillation of Cu EXAFS being superimposed on the Zn XANES spectrum. Special care needs to be taken to separate these spectra from each other. Spectrum (2), on the other hand, comes from a pixel in the sample that does not contain an excessive amount of Cu. For this pixel, a contribution of the Cu EXAFS to the spectrum is negligible. The spatial resolution of the method is ultimately limited by the smallest spot size obtainable with hard x-ray optics [8]. The QEXAFS monochromator can be adjusted to cover the full EXAFS energy range. In combination with achromatic x-ray optics, such as a Kirkpatrick-Baez total reflection mirror system, the

(1)

(2)

below edge   above edge

(1)

(2)

140
70
0
μ [a. u.]

9659eV energy

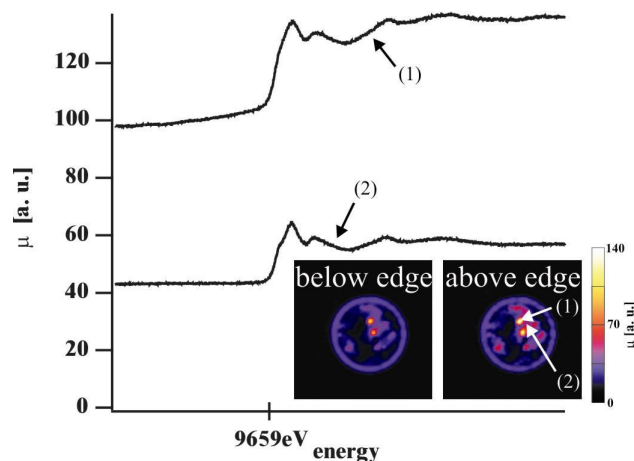μ [a. u.]
120
100
80
60
40
20
0

FIG. 4. XANES spectra (Zn K edge) reconstructed at the locations marked by (1) and (2) in the tomographic slice shown in the inset (color). The tomographic reconstructions in the lower right corner show the absorption coefficient below and above the K edge of Zn. The total attenuation in both spectra has contributions from Cu and lighter elements as well as from Zn.

method can be extended to reconstruct full EXAFS spectra at each location on the reconstructed slice.

Acknowledgments

References

[1] C.G. Schroer, M. Kuhlmann, T.F. Guenzler, B. Lengeler, and M. Richwin et al., Appl. Phys. Lett. **82**, 3360 (2003).
[2] D. Luetzenkirchen-Hecht, S. Grundmann, and R. Frahm, J. Synchrotron Radiat. **8**, 6 (2001).
[3] M. Richwin, R. Zaeper, D. Luetzenkirchen-Hecht, and R. Frahm, J. Synchrotron Radiat. **8**, 354 (2001).
[4] J.-D. Grunwaldt, D. Luetzenkirchen-Hecht, M. Richwin, S. Grundmann, and B.S. Clausen et al., J. Phys. Chem. B **105**, 5161 (2001).
[5] B. Lengeler, C.G. Schroer, B. Benner, A. Gerhardus, and T.F. Guenzler et al., J. Synchrotron Radiat. **9**, 119 (2002).
[6] C.G. Schroer, M. Kuhlmann, B. Lengeler, T.F. Guenzler, and O. Kurapova et al., Proc. SPIE-Int. Soc. Opt. Eng. **4783**, 10-18, edited by D.C. Mancini (2002).
[7] C.G. Schroer, Appl. Phys. Lett. **79**, 1912 (2001).
[8] C.G. Schroer, M. Kuhlmann, U.T. Hunger, T.F. Guenzler, and O. Kurapova et al., Appl. Phys. Lett. **82**, 1485 (2003).