Selective XAFS Studies of Functional Materials by Resonant Inelastic X-Ray Scattering

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Abstract. Lifetime-broadening-suppressed (LBS), state-selective XAFS spectra can be deduced by analyzing resonant inelastic x-ray scattering (RIXS) spectra in terms of a formula derived from the Kramers-Heisenberg equation. By a combination of a third-generation synchrotron source and a spectrometer equipped with large acceptance as well as high-resolution crystals, high quality RIXS data to warrant to extract LBS-XAFS can be collected. LBS-XAFS spectra of CuO nano-particles on ZnO with various Cu concentrations up to as low as 1 mol % are presented and concentration dependence is discussed.

Keywords: Lifetime-broadening-suppressed, selective XAFS; Resonant inelastic x-ray scattering; Nano particles; Multi-crystal x-ray spectrometer

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INTRODUCTION

X-ray absorption fine structure (XAFS) provides one of the most useful tools for studying local electronic states and atomic environments around selected elements. XAFS features are, however, often smeared out because of the natural width that originates from the finite lifetimes of the core holes. The energy width increases as the atomic number (Z) increases, and for K shell it ranges from 1 eV (V, Z=22) up to 40 eV (W, Z=74) [1]. Hence, no matter how experimental techniques improve, it is impossible to unambiguously detect a chemical shift or splitting that is less than the natural lifetime width.

It is possible to circumvent this intrinsic shortcoming of XAFS spectroscopy to obtain ‘lifetime-broadening-suppressed (LBS) XAFS spectra [2-4]’ by making use of resonant inelastic x-ray scattering (RIXS) [5-7]. Here we loosely define RIXS as x-ray emissions excited with x-ray energies near absorption edge [3,4,8,9].

Wide application of RIXS has been so far hindered by its low intensity. However, the intensity problem in RIXS spectroscopy is now being solved by developing highly-sensitive emission spectrometers with high-resolution, optimized for the use at third-generation synchrotron sources [9-12]. Recently, we have demonstrated that LBS-XAFS can be deduced from analyses of high-resolution RIXS spectra about CuO [6], CuCl2 [6], Dy(NO3)3 [7], and Ho2O3 [13]. We have also proved that what corresponds to polarized absorption spectra can be obtained by using single crystal Nd2-xCexCuO4 [14] and La2-xSrxCuO4 [15].

In this paper, presented is an extension of the LBS-XAFS spectroscopy to a dilute system; CuO nano-particles on ZnO (a precursor of methanol synthesis Cu/ZnO catalyst) with Cu concentrations of 1, 5, and 30 mol%. We have deduced Cu LBS-XAFS spectra from RIXS and found that pre-edge structures significantly depend on Cu concentration.

THEORETICAL

In what follows we pick out 1s2p RIXS as an example, but essentially the same formula can be applied to other resonant processes. If the excitation x-ray energy is near a K edge, the whole process must be dealt with as a one step inelastic scattering. In this case, the scattering amplitude is described by the well-known Kramers-Heisenberg equation. In terms of the notation in Fig. 1a, the principal part of the equation is reduced to eq. 1 [5,6,16].

\[
\frac{d\sigma(\alpha)}{d\Omega} \propto \frac{\int (d\sigma/d\omega) (\omega+d\omega)}{\left[(\Omega+\omega+\omega_a)^2+\Gamma_\alpha^2/4\right]^{1/2} \left[(\Omega+\omega+\omega-a)^2+\Gamma_a^2/4\right]^{1/2}}
\]

(1)
FIGURE 1. (a) A diagram of the 1s2p resonant inelastic X-ray scattering (RIXS) process and (b) a schematic representation of lifetime-broadening-suppressed measurements by 1s2p RIXS.

The integrand of eq. 1 is the product of three functions having the energy of the excited electron $\omega$ as a common variable: two Lorentzians $f_1$ centered at $\omega_1 - \Omega_{1s}$ with the width of 1s ($\Gamma_{1s}$) and $f_2$ centered at $\omega_2 - \Omega_{2p}$ with the width of 2p ($\Gamma_{2p}$), and the oscillator strength distribution for K absorption ($dg_{1s}/d\omega$), which corresponds to K LBS-XAFS [5,6]. These three functions are schematically depicted in Fig. 1b. In RIXS measurements, incident x-ray energy $\omega_1$ is fixed and the scattering intensity $d\sigma/d\omega_2$ is monitored as a function of emitted x-ray energy $\omega_2$, which is equivalent to sliding sharp $f_2$ along the $\omega$ axis while keeping $f_1$ and $dg_{1s}/d\omega$ fixed in Fig. 1b [5,6]. The RIXS intensity is governed by the overlap of these three functions. The form of $dg_{1s}/d\omega$ can be deduced by numerical calculations as the one which best reproduces the observed RIXS spectra by the use of eq. 1. The flow chart of the analysis procedure is illustrated in Fig. 2.

Experimental

1s2p RIXS experiments were carried out at the beamline BL39XU at SPring-8. This hard x-ray undulator beamline consists of a two-crystal dispersive Si(111) monochromator, a platinum-coated cylindrically-bent mirror to focus the beam horizontally, and an x-ray phase retarder. The photon flux at the sample position is estimated to be about $1 \times 10^{13}$ photons/sec, and the typical spot size is 0.6 mm (height) $\times$ 0.4 mm (width). The spectral width measured was about 0.9 eV at 8 keV.

The x-ray emission spectrometer employed was newly constructed. It is designed to accommodate up to 7 independent pairs of a spherically-bent crystal and a photon-counting detector. Each crystal is aligned in a Johann geometry consisting of the sample position as the common source, the analyzer, and the detector on a Rowland circle. The diameter of the Rowland circle is 820 mm. RIXS spectra were measured by moving the analyzers and the detectors synchronously. In the present experiment, 5 pairs of a crystal and a detector have been employed.

![Flow chart of RIXS analysis](image-url)
As the analyzers, adopted were spherically-bent Si (444) crystals of 75 mm in diameter, which were fabricated by gluing flat polished 0.3 mm-thick wafers onto spherical glass holders. The analyzers capture a solid angle of 0.033 sr at the scattering angle of 135° in the present experiments. Under the above conditions, the overall energy resolution estimated from FWHM of elastic lines was about 1 eV at 8 keV.

The multi-crystal spectrometer was mounted on a computer-controlled X-Z stage for alignment. The beam path has 50 µm-thick Kapton windows and was evacuated by a scroll pump to avoid the absorption and scattering by air. A photograph of the spectrometer is shown in Fig. 3.

Highly-dispersive CuO nano-particles on ZnO with several Cu concentrations (1, 5, and 30 mol %) were prepared by the co-precipitation method. From the angles and widths of x-ray diffraction lines, an existence of CuO particles with the size of 25 nm is expected in the 30 mol % sample. No observation of diffraction peaks of the samples with lower concentrations suggests that the particle sizes are less than a few nm.

**Results and Discussion**

Fig. 4 shows conventional Cu K-XAFS spectra of the nano-particles by total fluorescence yield method. The spectra have characteristic features observed in Cu K XAFS of cuprates. The observed XAFS of the 30 mol % sample is essentially identical to that of bulk CuO, which is consistent with the results of x-ray diffraction. Hence the final states (and final 3d orbital configurations) associated with the features in Fig. 4 can be assigned from the literature as follows [17]: A (3d^{10} L 4pν), B (3d^{4} 4pπ), and C (3d^{10} L 4pσ). Here L denotes a hole in the ligand O 2p states. A feature P at around 8980 eV, which has been observed [5,6,18] and assigned to 3d^{9} → 1s^{1}3d^{10} quadrupole transition [17], is barely discernible in Fig. 4, but it will be demonstrated in the LBS-XAFS spectra that it does exist as an isolated band.

Fig. 5 compares the 1s2p RIXS spectra of the 30 mol % with those of the 1 mol % sample at several excitation energies indicated by arrows in Fig. 4. Here the intensities are normalized by the peak height of the most intense band in each spectrum. It should be stressed that, thanks to the high-sensitivity in the present spectrometer, even at Cu 1 mol % and off-resonant (8973 eV) excitation, the statistics of the RIXS spectra collected as short as 40 min. is enough to deduce LBS-XAFS. As is evident from Fig. 5, RIXS spectra obtained here show significant dependences on Cu concentration. Let us first pay an attention to the highest energy RIXS peaks whose energy shifts from the exciting line are about 932 eV. The energy of the peaks of the 1 mol % sample is always lower than that of 30 mol % one by 0.5-1.0 eV. In addition, the second highest energy bands having energy loss of around 938 eV in the 30 mol % sample do not have their counterparts in the 1 mol % sample.

The RIXS profiles of the 30 mol % sample are almost the same as those of CuO [6] at every excitation energy. It has been known that the intensity of the highest energy band of RIXS comes from the transition to 1s^{-1}3d^{10} and the second to 3d^{10} L 4pπ [6]. Hence it can be expected qualitatively from the RIXS profiles that 3d energy shifts to the lower energy side with decreasing particle size, and that 3d^{10} L 4pπ state is either missing or broadened in very small nanoparticles.

![FIGURE 4. Conventional Cu-K XAFS for CuO nanoparticles on ZnO. Arrows indicate excitation energies used to obtain RIXS spectra shown in Fig. 5.](image)

Quantitative analyses of the RIXS spectra in terms of eq. 1 were made and the resultant LBS-XAFS spectra are presented in Fig. 6. Naturally, when
compared with Fig. 4, every feature becomes more distinct. The most significant differences lie in the region P, which is shown in expanded scales in the inset. The pre-edge feature, too weak to allow detailed studies in conventional XAFS spectra, appears as a sharp, distinct peak and reveals undoubted concentration dependence in the LBS-XAFS spectra. As anticipated, the peak P lies at 8980.2 eV in the Cu 30 mol% sample, while it shifts to 8979.3 eV in the 1 mol% one. In addition, band A that is distinct in the 30 mol% sample gets obscured with decreasing concentration, and in the 1 mol% sample no separate feature is observed but for gradual slope. These observations clearly suggest that the local structure around Cu in small nano-particles is fairly different from that in the 25 nm size particles which are almost the same as that of bulk CuO. Some distortion from CuO₄ plane or decrease in the coordination number in surface exposed species would be responsible for the difference.

In order to unequivocally prove that LBS-XAFS spectra presented in Fig. 6 is genuine, calculated RIXS spectra from them by the use of eq.1 are shown in Fig.5 by solid lines. As is evident from the figure, the calculated RIXS spectra almost completely overlap with the observed ones, demonstrating that RIXS spectra and \( d\sigma(\omega)/d\omega_2 \) are uniquely connected through eq.1 and that the former can be deduced from the latter and vice versa. It should be emphasized that a single \( d\sigma(\omega)/d\omega_2 \) yields almost perfect agreement between the calculated and the observed RIXS spectra at every excitation energy.

Particle-size dependence has been observed also in Ti K pre-edge structure of TiO₂ nano-particles [19] in conventional XAFS, where the features are rather sharp because of small lifetime-broadening width of Ti (=0.94 eV [1]). Interestingly, low-energy shift of the 1s-3d peak is also found for particles with diameters less than 5 nm. The size-dependence was related to distortion from the octahedral unit with increase in the amount of Ti atoms exposed on the surface [19]. Our LBS-XAFS results may suggest that similar distortions take place also in CuO particles with sizes of a few nm.

**FIGURE 5.** Excitation energy dependence of 1s2p RIXS spectra of the Cu 30 mol% and the 1 mol% sample. The excitation energies indicated in the figure are marked by arrows in Fig. 4. Solid lines are calculated RIXS spectra by the use of eq. 1 and LBS-XAFS shown in Fig. 6. Note that a single LBS-XAFS spectrum for each sample has been employed to calculate RIXS spectra at all the excitation energies.

**FIGURE 6.** Cu-K LBS-XAFS spectra (\( d\sigma(\omega)/d\omega_2 \)) for CuO nano-particles on ZnO deduced from RIXS spectra.

In summary, an efficient multi-crystal spectrometer is described and employed to collect weak Cu RIXS spectra from dilute Cu/ZnO catalyst precursors. The data were quantitatively analyzed to deduce LBS-XAFS, revealing otherwise obscured structures.

By properly selecting x-ray emissions from outer-shells which are sensitive to chemical environments, not only LBS-XAFS but also various kinds of LBS ‘state-selective’ XAFS are possible [3,4,9]. For example, LBS spin-selective XAFS spectra have already been obtained from Mn 1s3p RIXS on MnO, which resolved a contradiction with Hund’s rule in a previous study [20]. Local spin-ordering in antiferromagnetic as well as paramagnetic phase has been revealed by polarized spin-selective absorption spectra deduced from Mn 1s3p RIXS on single crystal

\[ \text{CuO/ZnO} \]
\[ \circ 30\text{mol}\% \]
\[ \triangle 1\text{mol}\% \]

\[ 8979 \]
\[ 8977 \]
\[ 8975 \]
\[ 8973 \]

**Excitation energy [eV]**

\[ \text{CuO/ZnO} \]
\[ \circ \text{Cu 30 mol\%} \]
\[ \triangle \text{Cu 1 mol\%} \]

\[ 8970 \quad 8975 \quad 8980 \quad 8985 \quad 8990 \quad 9000 \]

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LaMnO$_3$ [21]. LBS valence-selective XAFS spectra have been collected on GaCl$_2$ by using Ga 1s-valence RIXS [22].

LBS selective XAFS spectra have been mostly obtained for standard substances thus far but we have demonstrated in this paper that dilute materials can also be studied by a combination of a third-generation synchrotron source and the multi-crystal spectrometer. A new field of XAFS is being developed by RIXS spectroscopy.

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