Exploitation of Novel Spectroscopic Methods for Material and Surface Science

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For the developments of novel functional materials, it is quite important to exploit simultaneously new analytical methods based on advanced technology. Novel materials and devices often require spatial and/or time resolved analysis to optimize their qualities. In our group, we have been exploiting spectroscopic methods for material and surface science using mainly synchrotron radiation (SR) and partly lasers.

The first subject in our group is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism (UV MCD) photoelectron emission microscopy (PEEM), which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed *in situ* x-ray magnetic circular dichroism (XMCD) system using an ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The XMCD measurement system contains ultrahigh vacuum sample preparations chamber, with which one can clean substrates (substrate single crystals *etc.*), deposit materials (metallic and molecular magnets *etc.*) and characterize the samples using low energy electron diffraction, reflection high energy electron diffraction and Auger electron spectroscopy. The apparatus is extensively open for public usage and many domestic and foreign researchers visit us every year.

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (HAXPES) for polymer electrolyte fuel cells (PEFC) under working conditions. Although usually photoelectron spectroscopic measurement is done under ultrahigh vacuum, recent material science requires ambient pressure measurements under working conditions. In 2014, we successfully exploited near ambient pressure (up to ~5000 Pa) HAXPES apparatus in Beamline 36XU of SPring-8, and in 2017 eventually we have succeeded in real ambient pressure (100,000 Pa) HAXPES measurements. This work is supported by the NEDO Fuel Cell project.

The third subject is the pico- and femtosecond pump-and-probe time resolved x-ray absorption fine structure (XAFS) spectroscopy. XAFS is a quite powerful technique for investigating quantitative local structures of very low concentrated non-crystalline element by using the energy-resolved x-ray fluorescence detection technique. Fast time resolved XAFS measurement is difficult since the repetition frequencies of probe SR and pumping lasers are usually far different, requiring pulse picking of the SR probe and resultantly time resolved detection of only energy-integrated x-ray fluorescence. To detect energy- resolved x-ray fluorescence, a picosecond laser with high repetition rate (up to 1 MHz) was installed in Photon Factory Advanced Ring with single bunch operation (794 kHz). This allows us to investigate XAFS of low concentration elements using a slow but energy-resolved x-ray fluorescence detector.

Selected Publications

- T. Nakagawa *et al.*, *Phys. Rev. Lett.* **96**, 237402 (2006).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **110**, 075901 (2013).
- M. Dabrowski *et al.*, *Phys. Rev. Lett.* **113**, 067203 (2014).
- Y. Takagi *et al.*, *Appl. Phys. Lett.* **105**, 131602 (2014).
- Y. Takagi *et al.*, *Appl. Phys. Express* **10**, 076603 (2017).
- Y. Wakisaka *et al.*, *Phys. Rev. B* **92**, 184408 (2015).
- Y. Uemura *et al.*, *Chem. Commun.* **53**, 7314 (2017).

1. X-Ray Photoelectron Spectroscopy under Real Ambient Pressure Conditions[1)]

We have successfully developed a real ambient pressure (10^5 Pa) hard X-ray photoelectron spectroscopic system equipped with a differential pumping system at beamline BL36XU of SPring-8 for the first time in the world. Photoelectron spectra from gold single crystal were recorded using excitation light of 8 keV focused to 20×20 μm^2 and adopting an aperture diameter of 30 μm at the entrance of the electron lens (see Figures. 1(a)–(c)) and a working distance of 60 μm (see Figure 1(d)). The Au 4f and $3d_{5/2}$ spectra were successfully measured by increasing the ambient pressure from 1 Pa to atmospheric pressure as shown in Figure 2 and demonstrated that the instrument is capable of measuring the photoelectron spectrum under atmospheric pressure.

The kit shown in Figure 1 allows us to keep the high vacuum pressure in the electron energy analyzer and the ambient pressure at the sample surface. Figure 2 clearly exemplifies successful observation of the photoelectron spectra at 10^5 Pa. The present system is widely applicable to various kinds of investigations as fuel cells under real working conditions, solid/liquid/gas interfaces, ambient pressure chemical reactions *etc*.

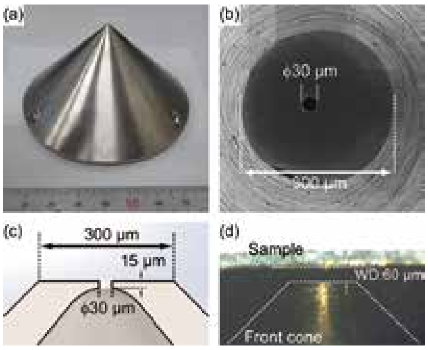

Figure 1. (a) Front cone of the electron energy analyzer. (b) Scanning electron microscope image of the aperture shaped at the top of the front cone. (c) Schematic diagram of the cross section of the aperture. (d) CCD microscopic image of the sample and the front cone at a WD of 60 μm.

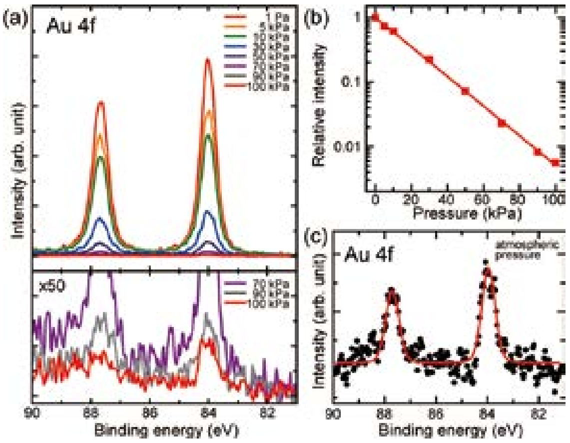

Figure 2. (a) Au 4f spectra recorded using 7.94 keV X-rays at pressures of 1 to 10^5 Pa. (b) Relative intensity of Au $4f_{7/2}$ as a function of pressure. (c) Background subtracted Au 4f recorded at 10^5 Pa.

2. Capturing Local Structure Modulations of Photoexcited $BiVO_4$ by Ultrafast Transient XAFS[2)]

$BiVO_4$ is a promising material for fabricating practically useful photocatalysts and photoelectrodes, exhibiting a bandgap of ~2.5 eV and having the potential to excite electrons from the valence band to the conduction band and to form valence band holes by absorbing visible sunlight. In this work, ultrafast excitation of photocatalytically active $BiVO_4$ was characterized by femto- and picosecond transient X-ray absorption fine structure (XAFS) spectroscopy.

Figure 3 shows the transient Bi L_3-edge XAFS and their time dependence. An initial photoexcited state changed to a metastable state (<<500 fs) accompanied by a structural change with a time constant of ~14 ps. The structural change might stabilize holes on oxygen atoms since the interaction between Bi and O increases. A proposed diagram of the photoexcitation process of $BiVO_4$ is shown in Figure 4.

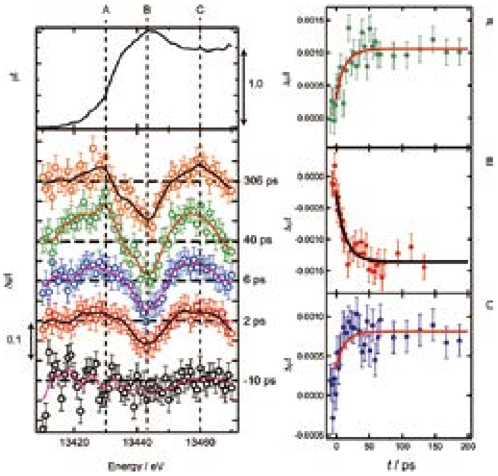

Figure 3. (Left) Bi L_3-edge XAFS spectra of the ground state (top) and the difference spectra of the excited states after the given delay times. (Right) Changes in X-ray absorption intensities at points A, B, and C.

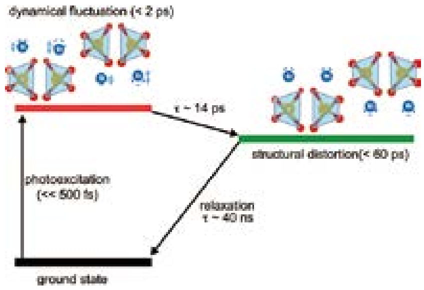

Figure 4. A proposed diagram of the photoexcitation process of $BiVO_4$.

References

1) Y. Takagi, T. Nakamura, L. Yu, S. Chaveanghong, O. Sekizawa, T. Sakata, T. Uruga, M. Tada, Y. Iwasawa and T. Yokoyama, *Appl. Phys. Express* **10**, 076603 (2017).

2) Y. Uemura, D. Kido, A. Koide, Y. Wakisaka, Y. Niwa, S. Nozawa, K. Ichiyanagi, R. Fukaya, S. Adachi, T. Katayama, T. Togashi, S. Owada, M. Yabashi, K. Hatada, A. Iwase, A. Kudo, S. Takakusagi, T. Yokoyama and K. Asakura, *Chem. Commun.* **53**, 7314–7317 (2017).