BL07LSU
The University-of-Tokyo Outstation Beamline for Materials Science

1. Undulator beamline

The soft X-ray undulator beamline, BL07LSU, was constructed by the Synchrotron Radiation Research Organization [1], the University of Tokyo, at the long-straight section of SPring-8 and has been devoted to joint research among domestic and international researchers since 2009B. User operation was closed in 2022A. Advanced spectroscopy and imaging techniques, developed at the beamline, were transferred to the next stage of usage. In this article, we report selected achievements by users at the experimental stations in 2022.

2. Experimental stations

In 2022, there were five different end-stations at the beamline: 1) time-resolved soft X-ray (TR-SX) spectroscopy, 2) ambient-pressure X-ray photoelectron spectroscopy (AP-XPS), 3）3D nano-ESCA, 4）ultrahigh-resolution soft X-ray emission spectroscopy (HORNET), and 5) free port. All the stations were opened to users. Innovative developments of novel soft X-ray experiments, such as imaging and nanofocused spectroscopy, were conducted at the free-port station.

3. Selected Achievements

3-1. Free-port station: Surface reaction of MoS_2 studied by ambient-pressure XPS [2]

Molybdenum disulfide (MoS_2) has been used in a variety of function materials, ranging from electronics to catalysts. Such materials are used in industry, for example, the hydrodesulfurization (HDS) catalyst, which removes sulfur impurities from crude oils. In these chemical events, sulfur vacancies serve as active sites, but the details remained unknown, especially those of the catalytic reaction.

To unveil the surface chemistry, the Yoshinobu group conducted *operando* experiments with ambient-pressure X-ray photoelectron spectroscopy (AP-XPS). Figure 1 shows a set of the AP-XPS data for characterizing the surface of the MoS_2 basal plane in H_2 gas (~1.5 mbar) at elevated temperatures (302–750K).

Above 600 K, the spectral peaks change

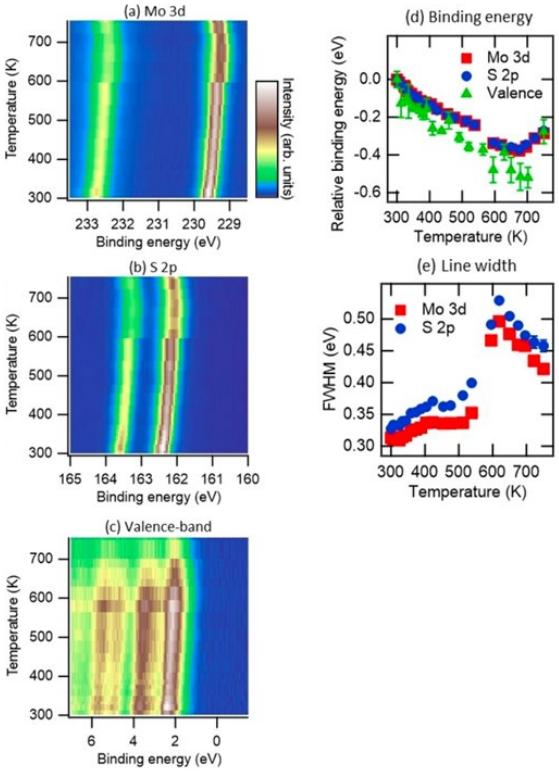

Fig. 1. A collection of AP-XPS spectra of the MoS_2 basal plane in H_2 gas of ~1.5 mbar, measured at various temperatures: (a) Mo 3d, (b) S 2p, (c) valence band, (d) relative binding energy shifts, and (e) full width at half-maximum (FWHM). [2]

discontinuously, followed by a moderate dependence on temperature, as shown in Figs. 1(a)–1(c). Focusing on the Mo 3d and S 2p core levels, a drastic energy shift and large broadening of the peak width (FWHM) were observed at 600 K [Figs. 1(d) and 1(e)]. The temperature matches with that at the occurrence of the HDS reaction. The spectral change corresponds to the appearance of a new component, which may be related to the sulfur vacancy. The theoretical simulation of the electron energy unveiled the corresponding atomic structure. The material information obtained in the present research provides fundamental knowledge on the HDS reaction and will lead to the precise control of electronic and chemical states of the MoS_2 basal plane via the sulfur vacancies.

3-2. Free-port station: Development and application of soft X-ray ptychography system CARROT (coherent achromatic rotational reflective optics for ptychography) [3]

Soft X-rays, with wavelengths of a few nanometers or less, interact largely with matter and are suitable for the high-resolution imaging of biological samples such as cells, which are mainly composed of light elements.

The soft X-ray region also has absorption edges and fluorescence X-ray energies of light elements, such as carbon, nitrogen, and oxygen, which form cells. Therefore, the combination of soft X-ray imaging and spectroscopic techniques makes it possible to study the intracellular microstructure, including elemental and chemical states, with unprecedented resolution.

We took advantage of these features of soft X-ray microscopy to visualize the intracellular stress response to drug administration [4]. For soft X-ray microscopy, we used CARROT, a soft X-ray ptychography system that we developed.

Figure 2 shows the results of observation of the control [Fig. 2(a)] and anti-HIV drug-treated [Fig. 2(b)] cells. HepG2 cell lines were used for the cells. Upon the administration of anti-HIV drugs, it was observed that the round structures (solid arrows) of a few microns in size became larger, and the gaps (dotted arrows) around the nucleus became thicker on the nanometer scale.

We also mapped the intracellular distribution of light elements using the soft X-ray fluorescence system in CARROT and found it to be consistent with the results of ptychography. These results strongly suggest that the application of soft X-ray microscopy to drug evaluation systems is useful.

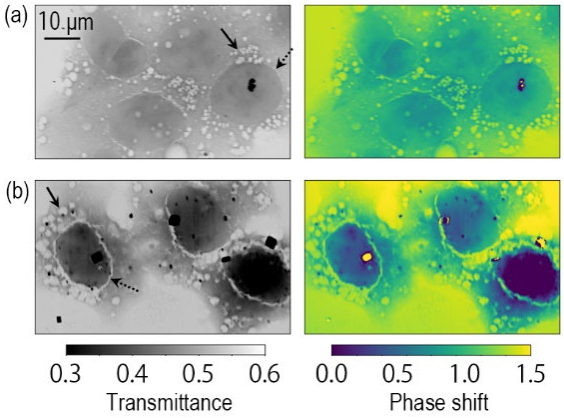

Fig. 2. Soft X-ray ptychography images of HepG2 cells with and without GPL-142 treatment. (a) Reconstructed images of cells without anti-HIV drug. (b) Reconstructed images of cells treated with anti-HIV drug. [3]

3-3. 3D nano-ESCA station: Facet-dependent electrochemical performance and electronic structure of $LiCoO_2$ polyhedral particles [5]

The morphology of active material particles has a significant impact on the charge–discharge cycle performances of lithium-ion batteries because each

crystal surface constructed of different elemental arrangements indicates a different surface energy. In this study, we applied 3D nano-ESCA with a spatial resolution of 100 nm to reveal the electronic structure of each facet of prototypical layered $LiCoO_2$ cathode particles, where the characteristic facets are (001), (104), and (012). We detected a difference in an electronic structure near the valence-band maximum (around 1–3 eV) on different $LiCoO_2$ facets. As shown in Fig. 3(e), the dominant Co 3d bands at the valence band of the (001), (104), and (012) facets showed binding energies of 2.48, 2.25, and 2.02 eV, respectively. The closer the Co 3d band of the (012) facet to the Fermi level, the easier it is to lose electrons than other facets, suggesting its more reactive property than the other facets. As demonstrated, the electronic structure of each crystal facet can be determined by 3D nano-ESCA, which is an important technique for improving the electrochemical performance of active materials for LIBs and designing active materials with excellent charge–discharge cycle performance.

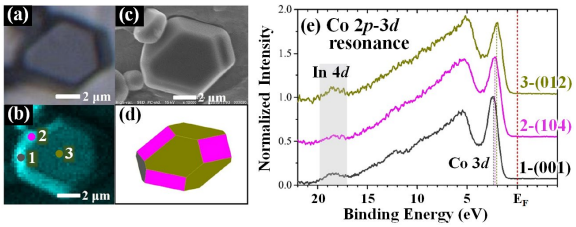

Fig. 3. (a) 2D optical microscopy image, (b) O 1s photoelectron intensity mapping image, and (c) SEM image of a $LiCoO_2$ particle. (d) SHAPE simulation of the $LiCoO_2$ particle with indicative facets. (e) Facet-dependent resonant XPS of the $LiCoO_2$ particle with a photon energy of 780.6 eV.

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