

1. Status of Beamline BL07LSU at SPring-8

The University-of-Tokyo high-brilliance synchrotron soft X-ray outstation beamline BL07LSU at SPring-8 has been maintained by the permanent staff members with adjuncts for user operations. The scientific aim of the beamline is to promote advanced spectroscopy for solid state and soft (including bio-) materials. There are four regular endstations for time-resolved soft X-ray spectroscopy (TR-SX spectroscopy), ambient pressure X-ray photoelectron spectroscopy, 3D-scanning photoelectron microscope (3D nano-ESCA) and high-resolution soft X-ray emission spectroscopy (HORNET) that are open for users. There is also a free port station for users who bring their own experimental apparatus.

The beamline BL07LSU is equipped with a segmented cross-type undulator. By using phase shifter among the undulator segments, a polarization control of soft X-ray was started since 2016. Circularly and linearly polarized soft X-rays at full energy range (250 – 2000 eV) have been available by tuning the permanent magnet type phase shifter.

At the endstations, various scientific researches were carried out by both the laboratory staffs and general users (G-type and S-type applications). In addition, from this fiscal year, we started to accept priority issues (P type problem) for the purposes of utilizing the advanced synchrotron radiation light source technology, especially high-speed polarization switching, at BL07LSU and of promoting developments of the beamline and endstation technologies for the next generation synchrotron light source.

Recent activities at each station is briefly introduced below.

(1) Time-Resolved soft X-ray spectroscopy station (TR-SX spectroscopy)

The station is to perform time-resolved photoemission spectroscopy experiments by synchronizing the high-brilliant soft X-ray and the ultra-short laser pulses. A two-dimensional angle-resolved time-of-flight (ARTOF) analyzer has been equipped for the efficient time-resolved measurements and the measurement temperature can be controlled from 15 K to 1150K. The station adopts two different optical laser systems synchronized with synchrotron soft X-ray; low repetition rate and high pulse energy (1 kHz, mJ) and high repetition rate and low pulse energy (208 kHz, μ J).

In 2019, Hayashi group succeeded in observing the temporal variation of the Si $2p$ photoelectron diffraction pattern of a silicene layer after the laser pulse irradiation. The time-resolved pattern agreed with the simulation results and revealed the lattice dynamics. The research paper is submitted as the world's first time-resolved photoelectron diffraction data. The system of time-resolved photoelectron spectroscopy will be transferred to Kashiwa Campus in 2020 for experiments with the vacuum ultraviolet/soft

X-ray lasers. The time-resolved photoemission measurement will be continued users with the AP-XPS system, see the following section, that has been updated for this purpose recently.

(2) Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS)

AP-XPS station allows *Operando* observation of catalysts under reaction conditions. The AP-XPS station was constructed in 2014 by an external funding (JST ACT-C project), and was opened to external users since 2018. The AP-XPS system is equipped with a differentially pumped electron analyzer (SPECS, PHOIBOS 150 NAP) and an ambient-pressure gas cell. XPS measurements can be performed both under ultrahigh vacuum and in near-ambient gas pressure up to 20 mbar. Catalytic activity is monitored by mass spectrometer, and simultaneous evaluation of adsorbate and catalyst electronic states is performed. In addition to the experiments using synchrotron soft X-ray, off-line experiments using a twin-anode X-ray source can be performed.

In 2019, a variety of research projects have been conducted using the AP-XPS station: (i) Methanol synthesis on Cu-Zn catalysts, (ii) Sabatier reaction on Ni catalysts, (iii) H₂ adsorption/absorption in Pd nanoparticles and Pd alloys (PdAg and PdCu), (iv) CH₄ partial oxidation on Pd catalysts, (v) CO₂ adsorption on graphene support, (vi) band alignment at a semiconductor photoelectrode and electrolyte interface, and (vii) development of time-resolved AP-XPS. Koitaya *et al.* published a research paper on CO₂ hydrogenation on a Zn modified Cu surface in ACS Catalysis (IF 11.384). Tang *et al* reported *articles* on H₂ adsorption and storage on a PdCu alloy surface in Appl. Surf. Sci.

(3) 3D-scanning photoelectron microscope (3D nano-ESCA)

3D-nano-ESCA can be used for sub-100 nm range microscopic 2D mapping and depth profile of the chemical structure of functional materials and devices.

In 2019, elucidation of facet-wise Li de-insertion characteristics of LTO in all-solid-state LIB was carried out as a joint research by Asakura and Hosono group at AIST. By changing the solid electrolyte from LLZ and dry polymer to sulfide solid electrolyte, the degas rate was reduced, and a clearer image was obtained. Also conducted was photoelectron spectromicroscopy of SnS as a joint research by Nagamura at NIMS and Prof. Nagashio group at UTokyo. The reason behind the monolayer growth of SnS by the simple PVD remains unclear. A single SnS film was not grown from high-purity SnS powder. By nano-ESCA observation, it is confirmed that the lateral growth of monolayer SnS is facilitated due to the enhanced surface diffusion of SnS precursor molecules by Sn₂S₃ contaminants in low-purity powder. Lastly, super-resolution imaging and depth profiling analysis of hetero-junction transistor fine structures using III-V compound

semiconductors were performed as a joint research by Fukidome group at Tohoku Univ. In the viewpoint of measurement informatics, sparse modeling approach is applied to overcome the limits of spatial resolution and make it possible to observe objects in the size of several nms.

(4) Ultra high-resolution soft X-ray emission spectroscopy (HORNET)

The station is dedicated for soft X-ray emission (or resonant inelastic X-ray scattering: RIXS) spectroscopy measurements with high-resolution ($E/\Delta E > 10,000$) and under various environmental conditions (gas, liquid, and solid).

In 2019 the station accepted 19 joint researches. Studies on solid state physics include i) O K-edge RIXS of holes doped in $\text{Pr}_{1.4-x}\text{La}_{0.6}\text{Ce}_x\text{CuO}_4$, ii) Observation of magnon-induced state of spintronics material $\text{Y}_3\text{Fe}_5\text{O}_{12}$ by operando RIXS by application of high-frequency electromagnetic wave, iii) XAS and RIXS studies of the electric-field-induced metal insulator transition of $\text{Ca}_3(\text{Ru}_{1-x}\text{Ti}_x)_2\text{O}_7$, iv) Fe L-edge RIXS of diluted magnetic semiconductors (Ga, Fe)Sb and (In, Fe)As. For the battery and catalyst materials, the valence state of Li-ion battery electrode materials $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ and $\text{Li}(\text{Li}_{2/3}, \text{Mn}_{4/3})\text{O}_4$ during charge and discharge as well as water decomposition catalyst $\text{Co}_x\text{Fe}_y\text{O}_4$ were observed by operando RIXS. For the studies on the behavior of interfacial water, water hydrating thermo-responsive polymer PNIPAM, polyvinyl alcohol aqueous solution, water confined in a subnanopore of liquid crystalline membrane, interfacial water in the polymer-brush form of PBuA and PMEA were observed. All the measurements were successful in the determination of specific hydrogen bond structure of water responsible for materials functions such as phase transition, folding, ice nucleation process, water filtration, and biocompatibility.