BL46XU
HAXPES II

1. Introduction

BL46XU is an undulator beamline at SPring-8 that has been reorganized into a beamline dedicated to hard X-ray photoelectron spectroscopy (HAXPES) in response to the growing demand for diverse HAXPES-based studies [1]. The beamline has two specialized instruments: 1) a high-throughput HAXPES system optimized for automated measurements in experimental hutch (EH) 1 and 2) an ambient-pressure (AP) HAXPES system designed for experiments under controlled gas atmospheres in EH2. These instruments provide high capabilities for investigating bulk-sensitive electronic structures and chemical states across a wide range of research fields. To further expand the beamline's performance, several X-ray optical components have been implemented. Two types of double channel-cut monochromator, Si(220) and Si(311), are stationed in the optics hutch, enabling users to balance energy resolution and photon flux over a broad energy range (4.9–21.8 keV) while maintaining a fixed-exit condition. In addition, each HAXPES system is equipped with a focusing mirror to provide a high-flux microbeam for advanced measurements.

The following instrumental improvements and developments were carried out in FY2024: 1) a high-throughput HAXPES system with versatile sample holders, 2) the dip-and-pull method for AP-HAXPES, and 3) the light irradiation mechanism for operando photoreaction measurements.

2. High-throughput HAXPES system with versatile sample holders

For EH1, we developed a high-throughput HAXPES system equipped with automated measurement functions and a sample exchanger to address the increasing demand for efficient measurements of multiple samples in recent years. An overview of the system is shown in Figs. 1(a) and 1(b). It consists of (1) an analysis chamber, (2) a lower load lock, and (3) a high-precision 6-axis manipulator. The analysis chamber (base pressure ~5 × 10^{-6} Pa) is equipped with a hemispherical photoelectron analyzer in horizontal geometry. The lower load lock (~1 × 10^{-5} Pa) serves as an auxiliary chamber, allowing the rapid exchange of sample holder stockers or versatile sample holders as shown in Fig. 2(a) and evacuation from ambient to UHV without disturbing the vacuum of the analysis chamber. Each stocker can accommodate up to four sample holders that are compatible not only with the EH2 AP-HAXPES system but also with the two HAXPES systems at BL09XU [2]. The load-lock chamber itself can hold up to four stockers, and a turntable mechanism selects the desired one. The end-effector of the 6-axis manipulator, equipped with a locking mechanism, secures the three pins on top of the stocker, enabling the transfer of the sample holder between chambers without breaking the vacuum. This system allows multiple samples to be introduced and evacuated simultaneously, ensuring efficient sample handling and measurement.

Moreover, a hexagonal prism-shaped sample holder was designed and fabricated to accommodate a significantly large number of samples, typically in the range of 50–80, as shown in Fig. 2(b). This design reduces the need for frequent stocker exchanges and enables continuous automated measurements lasting from several to tens of hours, thereby achieving highly efficient experiments. In addition, we fabricated a large-sample holder that can accommodate bulky specimens, such as those with dimensions of approximately 1 cm × 1 cm × 1 cm, as shown in Fig. 2(c).

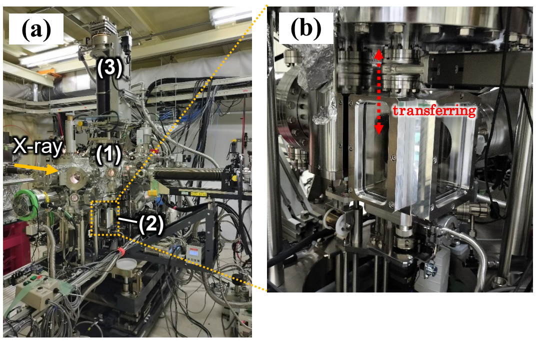

Fig. 1. (a) Photograph of high-throughput HAXPES system comprising (1) analysis chamber, (2) lower load lock, and (3) 6-axis manipulator. (b) Enlarged photograph of load-lock chamber.

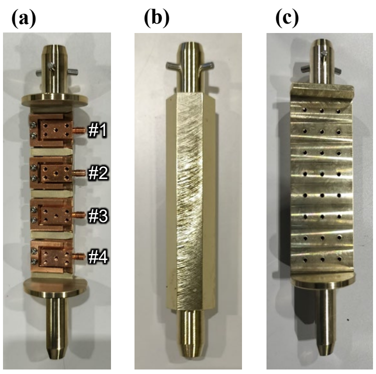

Fig. 2. (a) Sample holder stocker. (b) Hexagonal prism–shaped sample holder. (c) Large-sample holder.

3. Development of dip-and-pull method for AP-HAXPES

AP-HAXPES is a spectroscopic tool that allows us to examine the solid–liquid interface during water-splitting reactions by passing a thin liquid layer over the catalysts. XPS can directly determine the oxidation states of metals, oxygen species, and by-products. When combined with an electrochemistry system, the AP-HAXPES setup enables us to directly investigate the interface, bonding formation, and catalytic pathways. Figure 3(a) illustrates the experimental process of the dip-and-pull method using AP-HAXPES. To characterize the liquid reactions within the chamber, we designed a manipulator that connects three electrodes to a potentiostat. It features x, y, and z stages to optimize the positioning of the samples and the X-ray beam. During the dip process, catalysts are immersed in electrolytes and react with them. After the catalysts react with the electrolytes, they are pulled from the electrolytes and transferred to the electron analyzer to observe the XPS, which is called the pull process.

Figure 3(c) shows the Pt 4f spectra of the Pt foil measured in H_2SO_4 electrolyte before and after the dip-and-pull process. At -0.25 V, where the hydrogen evolution reaction (HER) occurs, there was no significant change in the oxidation state of the Pt foil. This is because the HER involves the reduction of Pt catalysts, resulting in a consistent catalytic reaction and oxidation state of the catalysts. The dip-and-pull system is now available to the public for, e.g., water splitting research.

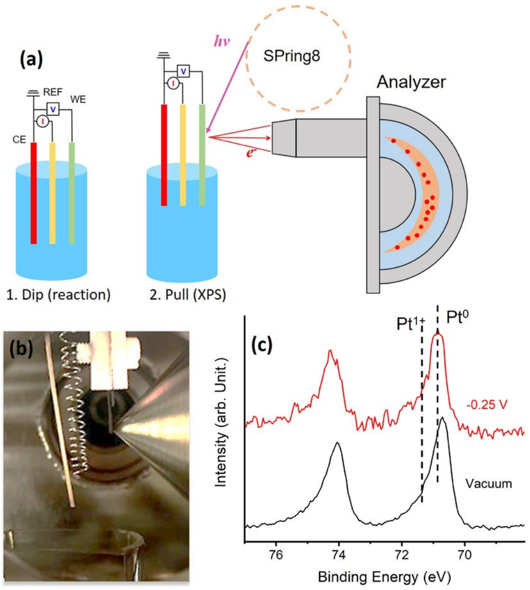

Fig. 3. (a) Illustration of dip-and-pull method. (b) Photograph of dip-and-pull system in reaction chamber. (c) Pt 4f spectra of Pt foil measured in H_2SO_4 electrolyte before and after hydrogen evolution reaction.

4. Light irradiation mechanism for operando photoreaction measurements

The AP-HAXPES instrument at EH2 is designed to operate without the need for a high vacuum, which simplifies the integration of accessories. For operando photoreaction measurements, a light irradiation mechanism has been developed. Figure 4(a) shows a schematic diagram of the light irradiation mechanism. Unlike conventional XPS instruments that irradiate light through a quartz viewport in a high vacuum, this instrument utilizes a φ6.5 mm quartz rod to directly guide light to the sample, allowing for efficient irradiation. A Xe lamp (MAX-303, Asahi Spectra Co., Ltd.) is used as the light source, and monochromatic light can be irradiated through a filter.

Using this system, HAXPES spectra were measured when a SiC substrate was irradiated with ultraviolet light. Both n-type ($1.0\times10^{16}/cm^3$) and p-type ($6.0\times10^{17}/cm^3$) 4H SiC substrates were used. The wavelength of irradiation light was 350 nm, and the C1s peak was measured when the light was ON/OFF. The incident X-ray energy used was 7.94 keV. The results are shown in Fig. 4(b). The C1s peak energies differ between n-type and p-type substrates, with the n-type being at a higher binding energy. This reflects the shift of the Fermi level due to doping. UV light irradiation demonstrated distinct responses in n-type and p-type substrates. The p-type substrate exhibited a shift to a higher binding energy following irradiation, whereas the n-type substrate showed no such shift. These findings indicate that the photoreaction varies depending on the substrate's state.

The AP-HAXPES instrument allows for HAXPES measurements under a gas atmosphere. This capability enables operando measurements of photocatalytic and photosynthetic reactions through the introduction of reactive gases or water under light irradiation. To elucidate the details of the reaction, it is necessary to accurately analyze the electronic state during the reaction and of the operando measurements of photoreactions using this instrument.

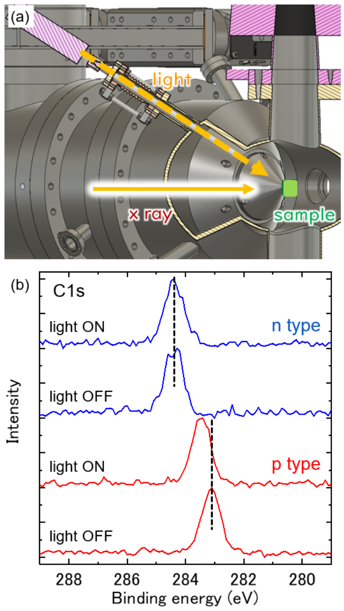

Fig. 4. (a) Schematic of setup for photo-irradiated HAXPES measurement. (b) C1s HAXPES spectra with and without UV light irradiation on SiC substrate.

YASUNO Satoshi, TAKAGI Yasumasa and SEO Okkyun

Spectroscopy and Imaging Division, JASRI

References:

[1] Yasuno, S. et al. (2024). *SPring-8 ・SACLA Annual Report FY2023*, 88-91.

[2] Yasui, A. et al. (2023). *J. Synchrotron Rad.* **30**, 1013–1022.