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

BL07LSU is a soft X-ray undulator beamline at the long-straight section of SPring-8 constructed by the Synchrotron Radiation Research Organization [1] and The University of Tokyo. Since 2009B, it has been devoted to joint research with domestic and international researchers. In this article, we report the status of the beamline and introduce selected achievements at the experimental stations.

1. Undulator beamline

The high-brilliant soft X-ray undulator beamline generates a synchrotron radiation beam with (1) E: 250–2000 eV, (2) E/ΔE: > 10,000, (3) spot-size: < 10 μm (zone-plate: 70 nm), (4) flux: ~ 10^{12} photons/s, and (5) variable light polarization. The beamline offers continuous polarization switching at a frequency of 13 Hz for user experiments at the end-stations.

2. Experimental stations

There are currently four different end-stations at the beamline: 1) time-resolved soft X-ray (TR-SX) spectroscopy, 2) three-dimensional nano-ESCA, 3) ultra-high-resolution soft X-ray emission spectroscopy (HORNET), and 4) free-port. All the stations are open to users. Here, two achievements are introduced [1, 2].

2-1. Free-port station: Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS)

The station is open to researchers, who can bring their machines and perform experiments using the high-brilliant soft X-ray beam. The groups of Profs. Jun Yoshinobu and Iwao Matsuda recently constructed the AP-XPS system to study catalytic reactions with an emphasis on activation and hydrogenation reactions of CO_2 molecules. In catalysts, graphene is important as a support due to its high surface area and unique electronic properties. In this study, we investigate the adsorbed states of CO_2 on graphene under a gas atmosphere using AP-XPS (Fig. 1(a)) [2].

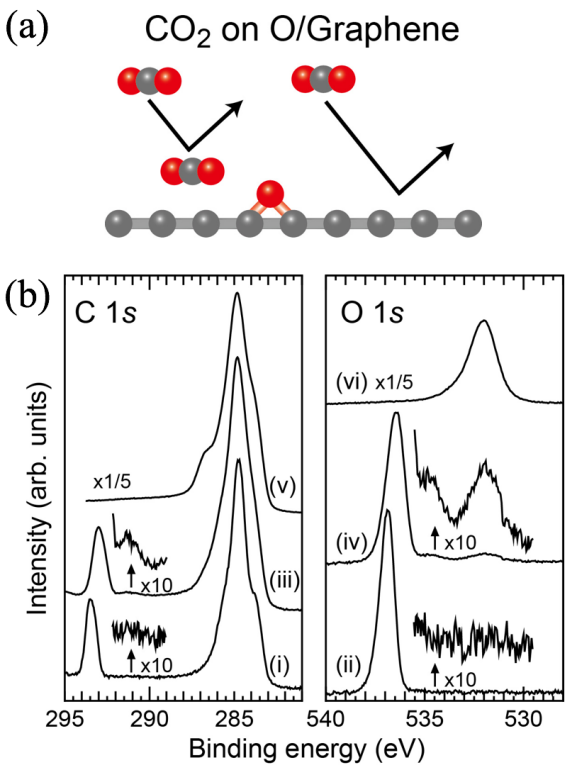

Fig. 1. (a) Schematic drawing of (oxidized) graphene in CO_2 gas. (b) C 1s and O 1s AP-XPS spectra taken in a CO_2 atmosphere (1.6 mbar): (i,ii) on graphene, (iii,iv) on oxidized graphene, and (v,vi) after the evacuation.

Figure 1(b) shows C 1s and O 1s XPS spectra of the graphene surface measured under 1.6 mbar CO_2 at 175 K. The peaks at 293.4 eV and 536.9 eV are assigned to the gas-phase CO_2, and the peak at ~285 eV is ascribed to the substrate (graphene and SiC). When the graphene surface is oxidized [Fig. 1(b) (iii, iv)], new spectral features appear at 286.7 eV and 532.0 eV due to the epoxy (C–O–C) species. In 1.6 mbar CO_2, adsorbed CO_2 molecules are observed only on oxidized graphene, as evidenced by the small peaks at 291.2 eV and 534.7 eV. After gas evacuation [Fig. 1(b) (v, vi)], both the adsorbed CO_2 and gas-phase CO_2 disappear. Therefore, *operando* observations using AP-XPS are essential to study the adsorbed states of CO_2 on graphene at realistic temperatures in catalysts. The present result shows that the surface oxidation of graphene enhances the adsorption of CO_2, which is the necessary elementary step in the activation and reaction of CO_2. This insight may assist in developing guidelines to design novel graphene-based catalysts.

2-2. Ultrahigh-resolution soft X-ray emission spectroscopy (HORNET)

A perovskite-type crystal of $LaCoO_3$ is a strongly correlated material. The Co ions assume various electronic states (spins) by competing electron–electron and electron–phonon interactions. However, the actual states of the material were unknown due to an inadequate experimental probe for direct observations. Recently, epitaxial growth of the $LaCoO_3$ film was reported. Novel spin states are expected by the tensile-strain effect induced by the substrate.

Resonant inelastic scattering of soft X-rays is associated with variations of electron configurations and spin states in a material. Thus, the measurement should probe the electronic states in $LaCoO_3$ crystals. We devised an experiment and systematically investigated the spectra by comparing the theoretical calculations based on the impurity Anderson model. As shown in Fig. 2, the spectra between bulk and film crystals differ, especially at an energy loss of ~ 1 eV. The theoretical calculation indicates that the losses around 0.3, 1.0, and 1.3 eV are assigned to high-spin, distorted high-spin, and low-spin states, respectively. A comparison between the experiment and calculation reveals that a ratio of the spin-states

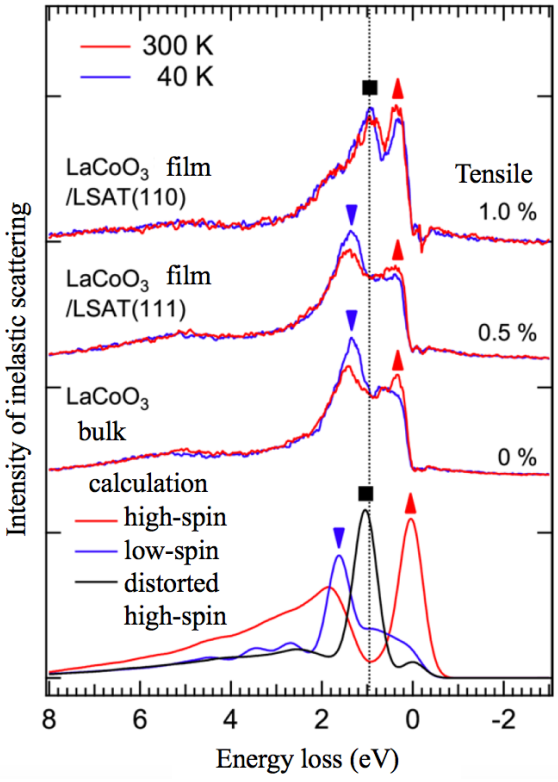

Fig. 2. Crystals of bulk and film of $LaCoO_3$, measured with L-edge resonant inelastic scattering of soft X-ray (experimental and theoretical spectra). LSAT is an abbreviation of the substrate, $(LaAlO_3)_{0.3}$-$(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$.

also differs between the crystals. This research demonstrates resonant inelastic scattering of soft X-rays can detect variations of the electronic states in strongly correlated materials with a high precision [3].

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References:

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[2] S. Yamamoto et al., *Physical Chemistry Chemical Physics* **20**, 19532 (2018).
[3] Y. Yokoyama et al., *Phys. Rev. Lett.* **120**, 206402 (2018).