Real-Time and *Operando* Observation of Intermediates on TiO_2 Photoelectrocatalysis by Soft X-Ray Absorption Spectroscopy

The oxygen evolution reaction (OER) on the TiO_2 surface at the solid–liquid interface was observed in real-time and *operando* using fluorescence-yield X-ray absorption spectroscopy (XAS) in the soft X-ray region. The OER was observed during a potential sweep with ultraviolet (UV) light on or off, focusing on the oxygen K-edge XAS. The spectra during the reaction were obtained every 3 s in the present experiment via wavelength-dispersive XAS technique. An increase in the X-ray absorption intensity at approximately 533.8 eV was observed during the potential sweep only with UV light on. The observed spectral change is discussed in relation to the reaction mechanism of the OER.

Hydrogen generation via electrolysis is one of the most popular research fields for achieving carbon neutrality. Among them, photoelectrocatalysis has garnered significant interest because it utilizes solar energy for water splitting. In the photoelectrocatalysis process, an anodic material for the oxygen evolution reaction (OER) in alkaline solution is considered to be a four-electron charge-transfer reaction as follows, where M is the surface catalytic active site.

$$M + OH^- \rightarrow MOH + e^- \quad (1)$$
$$MOH + OH^- \rightarrow MO + H_2O(l) + e^- \quad (2)$$
$$MO + OH^- \rightarrow MOOH + e^- \quad (3)$$
$$MOOH + OH^- \rightarrow M + O_2(g) + H_2O(l) + e^- \quad (4)$$

In the case of photocatalysts, such as n-type anatase TiO_2, electrons in the valence band are excited to the conduction band by the illumination with a light with an energy greater than its bandgap. When the electrode potential is applied to a positive direction, OER of eqs. (2)–(4) proceeds by the reaction with a hole in the valence band. It is known that the OER electrode is a performance bottleneck. Therefore, substantial efforts have been devoted to elucidating the reaction mechanism, which is important for fundamental studies and development of more effective OER catalytic materials. *Operando* evaluation focusing on the solid–liquid interface is key to elucidating the chemical states of the catalytic material surface and identifying the intermediate species at the surface.

We have recently developed a real-time observation system using wavelength-dispersive X-ray absorption spectroscopy (XAS) [1], as shown in **Fig. 1** on the right side. This system also enables the observation of chemical reactions at the solid–liquid interface during cyclic voltammetry measurements and with ultraviolet (UV) light on or off, by adopting the fluorescence yield method, with a time resolution of 3 s. Therefore, a dedicated cell for the liquid was prepared for the real-time XAS observation of photoelectrochemical OER [2, 3]. Here, we focused on anatase TiO_2 and observed time-dependent changes in the O K-edge XAS at electrode interface [3].

As illustrated in **Fig. 1** on the left side, electrochemical measurements were conducted with a three-electrode system, and 0.1 M NaOH solution was used as an electrolyte. 15-nm TiO_2 was deposited onto a 200-nm-thick Si_3N_4 window with a 10-nm Au conductive layer with 1-nm Cr, and subsequently the electrode was annealed at 400 °C for 1 h. The sample was illuminated with a 365-nm wavelength light-emitting diode light during a potential sweep.

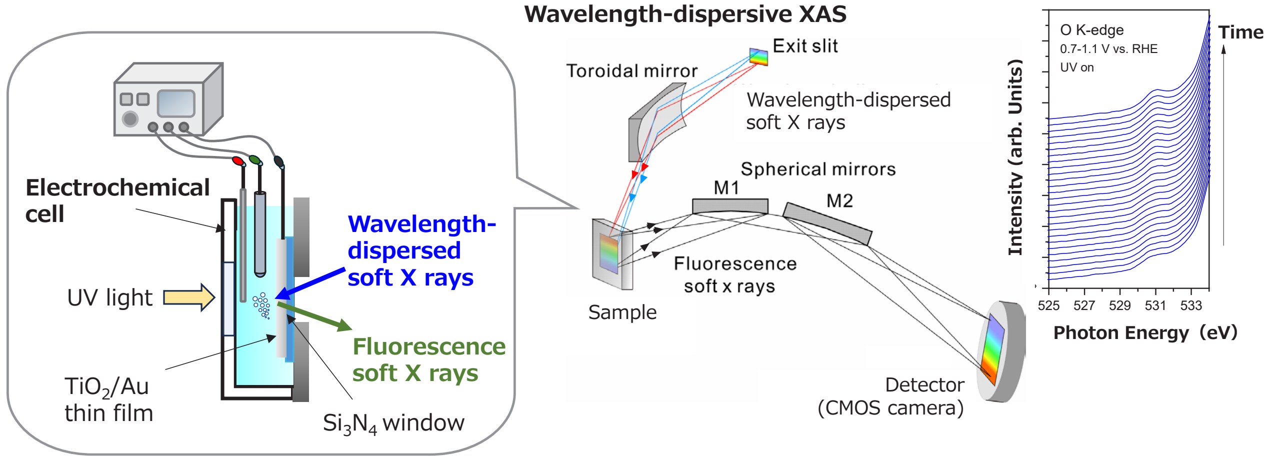

Figure 1: Schematic of wavelength-dispersive XAS apparatus and dedicated electrochemical measurement cell. XAS spectra are obtained in real-time, and the spectral changes correspond to the applied potential.

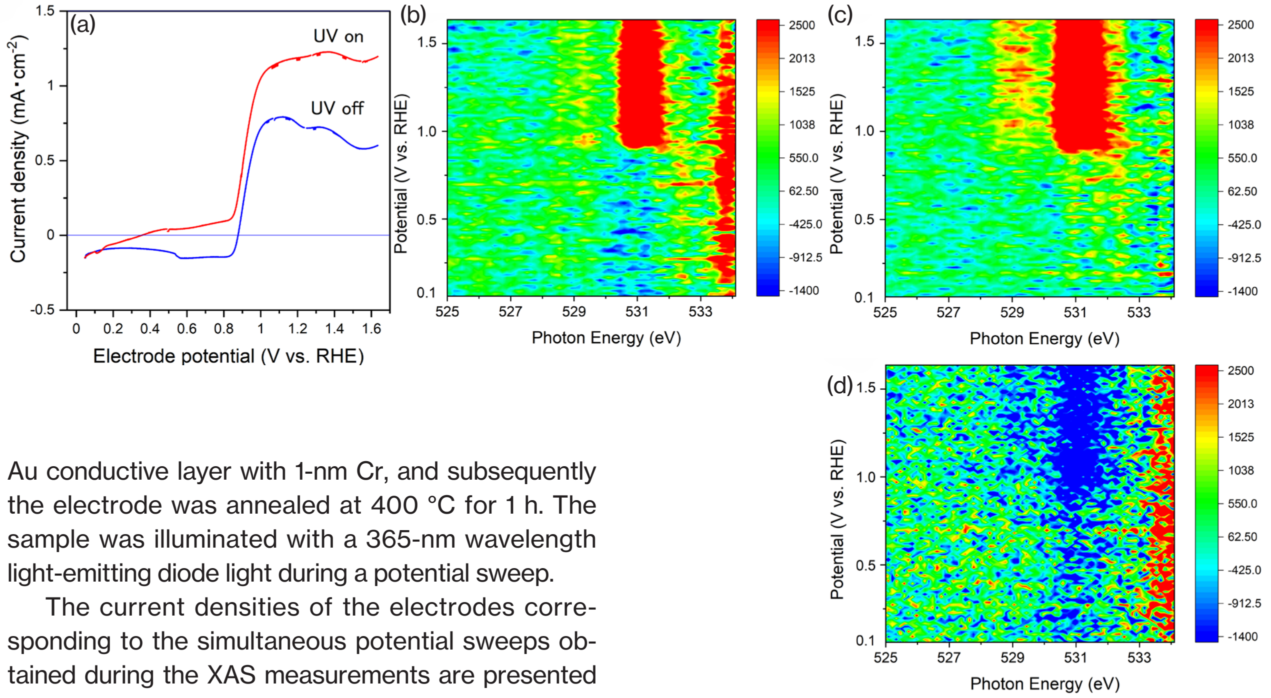

Figure 2: **(a)** The linear sweep voltammogram of the electrode obtained during the XAS measurement when the electrode potential was swept from 0.1 V vs. RHE to 1.6 V, with the UV light on and off. The difference between these currents is the photocurrent generated by the UV light. **(b-d)** Contour maps of differences in XAS spectral intensity from the initial measurement stage without UV light (the electrode potential was from 0.0 V to 0.12 V vs. RHE) for visualization of change, for **(b)** UV light on, **(c)** UV light off, and **(d)** difference of the intensity between UV on and off, based on the case of UV off.

The current densities of the electrodes corresponding to the simultaneous potential sweeps obtained during the XAS measurements are presented in **Fig. 2(a)**. The current density was higher when the measurement was performed under UV light illumination than when the UV light was turned off; therefore, the anatase-type TiO_2 electrode in this study worked as a photovoltaic material. During the electrode potential sweep, XAS spectra were obtained simultaneously at the O K-edge in real time.

The difference spectra based on the initial stage of the measurement without UV light are prepared. **Figure 2** shows a contour map of **(b)** UV light on and **(c)** UV light off during the potential sweep. Please note that the figures show the intensity difference from the initial stage of the measurement without the UV light (the electrode potential ranged from 0.0 V to 0.12 V vs. reversible hydrogen electrode (RHE)). The difference between the UV on and off cases was used to visualize the changes in the sequentially obtained XAS spectra (**Fig. 2(d)**). The results revealed that the changes in the XAS intensity corresponded to the applied potential of the electrode. The intensity at 531 eV changed drastically when the electrode potential was 0.9 V vs. RHE, however, the change in the peak intensity occurred mainly above 0.9 V vs. RHE, where the oxidation of Au and/or Cr is suggested. On the other hand, at 533.8 eV, there is a large difference between the cases of UV on and off, and the intensity for UV on was always higher than that for UV off. Therefore, it can be assumed that this peak is assigned to the intermediate for the OER stimulated by UV light illumination. At low potentials, the reaction rate for the OER is limited by the rate-determining step, and the intermediate species accumulate on the electrode surface. At higher potentials, the reaction for the rate-determining step, and consequently the entire OER, accelerates, resulting in a decrease in the intermediate species observed at 533.8 eV. We assume that the peak at 533.8 eV is assigned to the MOH species, and it can be suggested that the rate-determining step of the OER is expressed by eq. (2) when the UV light was illuminated.

As results of these, we would suggest that wavelength-dispersive XAS in the soft X-ray region is a valuable tool for studying chemical reactions at solid-liquid interfaces, and can be applied to a wide range of analyses of electrochemical reactions.

REFERENCES

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