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Simultaneous Soft X-ray Absorption Measurements of Bulk Water and Interfacial Water on Gold Surfaces

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1 Introduction

Interfacial water molecules on surfaces play important roles in various catalytic, electrochemical, and biological reactions. Soft X-ray absorption spectroscopy (XAS) is effective for investigating the electronic structures of liquid water. As shown in Fig. 1(a), the O K-edge XAS spectra of bulk H_2O can be measured using the transmission method, where the thickness of a liquid layer in the liquid cell is controllable from 20 nm to 40 μm for the transmission of soft X-rays [1]. Although the XAS spectra acquired in transmission mode are mainly derived from bulk H_2O, several groups have measured the XAS spectra of the H_2O/Au interfaces using the electron-yield method [2, 3]. The electron-yield XAS spectra of the H_2O/Au interfaces were obtained by measuring drain currents from the Au/Cr/Si_3N_4 membrane to compensate electrons for H_2O^+ cations, which are formed by emitting Auger electrons after soft X-ray absorption. Most of the electron-yield XAS spectra are derived from the H_2O/Au interfaces because the effective attenuation length of electrons in liquid H_2O is 6 nm at the O K-edge [4]. This study developed simultaneous XAS measurements of bulk H_2O using the transmission method and the H_2O/Au interfaces using the electron-yield method [5].

2 Experiment

The experiments were performed at the soft X-ray beamline BL-13A. The transmission-type liquid cell was composed of polyether ether ketone resin to provide electrical insulation of the entire system. The liquid layer in the liquid cell consisted of two 100 nm-thick Si_3N_4 membranes, where one of the membranes was coated with an Au (20 nm)/Cr (5 nm) layer. The XAS spectra in transmission mode were performed by detecting the transmitted soft X-rays using a photodiode detector. The XAS spectra in the electron yield were obtained by measuring the drain currents of the Au/Cr/Si_3N_4 membrane after soft X-ray absorption.

3 Results and Discussion

Figure 1(b) shows the O K-edge XAS spectra of liquid H_2O on the Au/Cr/Si_3N_4 membrane. The XAS spectra of bulk H_2O were obtained using the transmission method, and those of the H_2O/Au interfaces were simultaneously obtained using the electron-yield method. The side of the Au/Cr/Si_3N_4 membrane in the liquid cell was irradiated with soft X-rays.

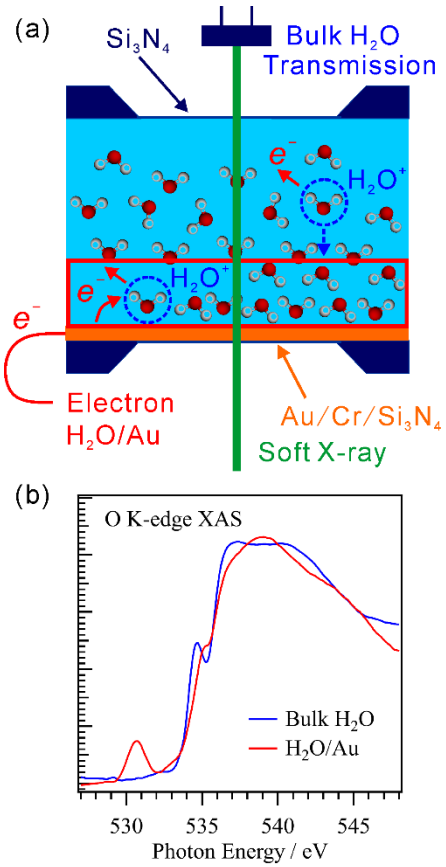

Fig. 1: (a) Schematic of simultaneous XAS measurements for bulk H_2O and H_2O/Au interfaces. (b) O K-edge XAS spectra of bulk H_2O and H_2O/Au interfaces.

The XAS spectrum of bulk H_2O is consistent with those of previous studies [6-8], where the pre-edge, main-edge, and post-edge peaks appear around 534.7, 537, and 540 eV, respectively. In the XAS spectrum of the H_2O/Au interface, the pre-edge peak merges with the shoulder of the main-edge peak owing to the higher energy shift of the pre-edge peak compared with that of bulk H_2O. These spectral shapes are consistent with the previous electron-yield measurements [2, 3]. The pre-edge peak of the H_2O/Au interface reflects the electronic structures of interfacial water molecules interacting with the Au surface. The oxide

layers of the Au/Cr/Si_3N_4 membrane give rise to a sharp peak around 530.7 eV.

The present study developed the simultaneous XAS measurement method for the H_2O/Au interfaces and bulk H_2O. This method will be applicable for investigating the mechanisms of various catalytic, electrochemical, and biological reactions involving interfacial molecules on surfaces.

References

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