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Electronic Supplementary Information for

A newly designed compact CEY-XAFS cell in the soft X-ray region and its application to surface XAFS measurements under ambient-pressure conditions without photoinduced side effects

Hiroshi Shimizu[a], Ryo Toyoshima[a], Kazuhisa Isegawa[a],
Kazuhiko Mase[b,c], Junji Nakamura[d] and Hiroshi Kondoh[a,b]

[a] *Department of Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan*

[b] *Institute of Materials Structure Science, High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan*

[c] *SOKENDAI (The Graduate University for Advanced Studies), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan*

[d] *Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan.*

Contents

X-ray photoelectron spectra of surface oxides at stainless steel surface

X-ray photoelectron spectroscopy (XPS) experiments were performed with a lab-XPS system (JPS9010TR; JEOL Ltd., Japan) using a Mg-Ka X-ray source. A stainless steel (SUS 304; Nilaco, Japan) substrate was polished with a polishing cloth (MicroCloth PSA; Buehler, U.S.A) and a suspension of polycrystalline diamond (MetaDi Supreme; Buehler, U.S.A), and then ultrasonicated in methanol for 10 minutes before measurements. To investigate the depth profile of the sample, XP spectra were measured at different emission angles from the surface normal (0°, 45°, 70°). Each spectrum is curve-fitted by a convolution of Doniach−Šunjić and Gaussian functions and Shirley-type background. The binding energy scale is calibrated with respect to the main C 1s XPS peak (284.6 eV).

Fig. S1 shows Fe $2p_{3/2}$ XP spectra obtained from a SUS substrate. The component at ~706.8 eV (light-blue) corresponds to metallic iron (Fe^0), while the components at ~709.2 eV (dark-blue) and ~710.4 eV (green) are associated with Fe^{2+} and Fe^{3+}, respectively, of iron oxides.[1] The component with a higher binding energy (orange) is attributed to a high valence state of iron. The relative intensity of the Fe^0 component clearly decreases when the emission angle is changed from 0° to 70°, indicating that the metallic iron is distributed in the bulk region. On the other hand, the relative intensities of the oxide species (Fe^{2+}, Fe^{3+}, high valence state) with respect to the Fe^0 component becomes larger with increasing the emission angle, which indicates that the surface of polished SUS is covered with the thin iron oxide layers while the metallic iron exists in the bulk region.

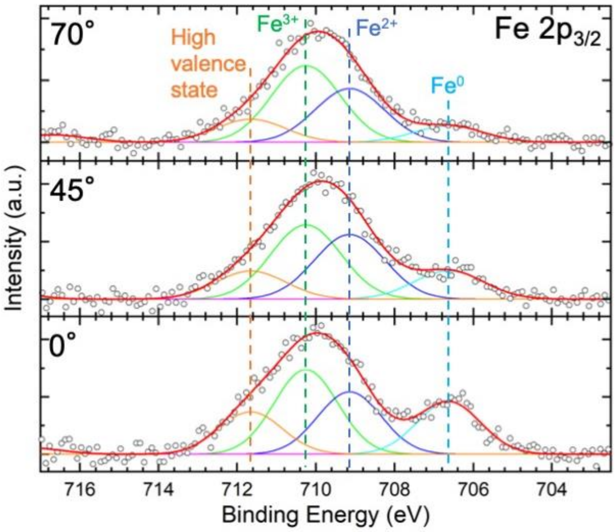

Fig. S1 Fe $2p_{3/2}$ XP spectra of the polished SUS substrate measured at different angles of analyzer.

Time dependence of Fe-$L_{2,3}$ edge XAFS spectra measured with the TEY method

Fig. S2 shows time dependence of Fe-$L_{2,3}$ edge XAFS spectra measured for the SUS substrate with the TEY method under a vacuum condition (about 1.5×10^{-6} mbar). All the spectra were normalized to the intensity of Fe^{3+} component. As shown in the inset, the relative intensity of Fe^{2+} component slightly increases in 1225 s and remains unchanged in the following spectra even after the X-ray irradiation for 1642 s, indicating that the photoinduced autoreduction of iron oxides is very limited at least under the vacuum condition.

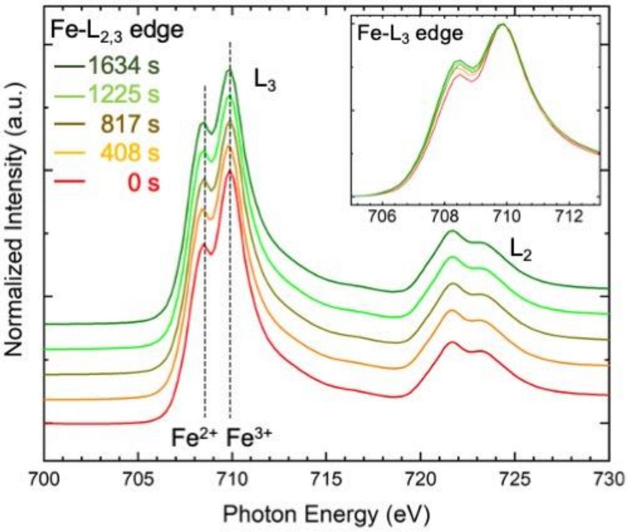

Fig. S2 Time dependence of Fe-$L_{2,3}$ edge XAFS spectra measured for the SUS substrate with the TEY method under a vacuum condition (about 1.5×10^{-6} mbar).

Fe-L_3 edge XAFS spectra measured with the CEY method after gas purification

To eliminate gaseous impurities in the carrier gas, we conducted an additional experiment where a liquid N_2 cold trap was used at the gas tubing located before the flowmeter. Fe-L edge CEY XAFS spectra were measured with the same experimental condition as Fig. 6(b) in the main text (bias voltage at +7.5 V, in 1 bar He) after flowing purified He into the gas line at the flowrate of 50 mL/min for about 40 minutes. The results are shown in Fig. S3. Each spectrum is normalized to the intensity of Fe^{3+} component. The relative intensity of Fe^{2+} component increases with time (red to dark green), i.e. the surface iron is also reduced even when the He gas is purified before introduced into the cell. It is the same tendency as the Figure 6(b) in the main text. According to this result, it is assumed that the change of the sample is not due to effects of gaseous impurities.

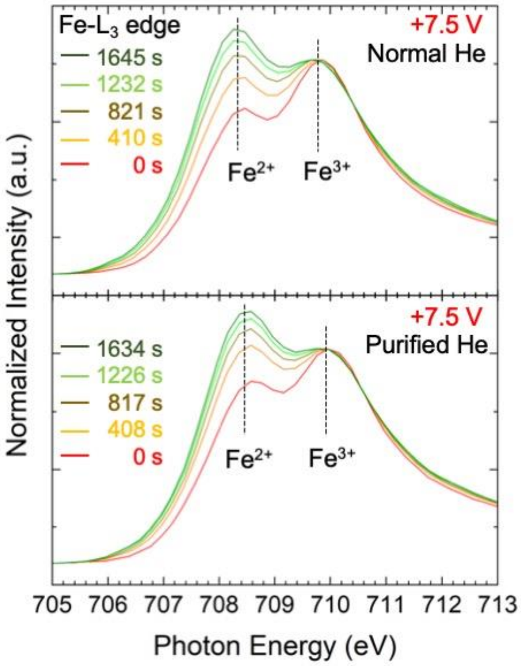

Fig. S3 Time evolution of Fe-L_3 edge XAFS spectra measured for the SUS substrate with the CEY method at a bias voltage of +7.5 V in 1 bar He (a) without and (b) with the gas purification.

Linear combination fitting of the Fe-L_3 edge XAFS spectra

To elucidate the ratio of consisting chemical components of the SUS substrate surface, the spectral shapes of the Fe-L_3 edge XAFS spectra measured with the CEY method are analyzed by the linear combination fitting by using standard spectra. Fig. S4 shows the reproduced curves and deconvoluted components: Black open circles in Fig. S4 indicate the experimental data which were taken (a) at 1654 s under a bias voltage of +7.5 V (dark-green curve in Fig. 6(a)) and (b) immediately after changing the bias voltage from +7.5 V to –7.5 V (light-blue curve in Fig. 6(a)). The green-colored component corresponds to the metallic iron (Fe^0), which is referred from the previous report by Giménez-Marqués *et al.*[2] The dark-blue-colored and orange-colored components are associated with Fe^{2+} and Fe^{3+}, respectively, which are measured for the completely reduced / oxidized SUS substrate surface obtained by the CEY XAFS measurements with a highly biased collector electrode (±117 V). The red lines indicate results of linear combination fitting. As shown in Fig. S4(a), the Fe-L_3 edge spectrum measured at a bias voltage of +7.5 V consists of mainly Fe^{2+} and Fe^{3+} components, while the contribution of the Fe^0 component is negligibly small. When the polarity of bias voltage is switched from positive to negative, the intensity ratios of all the components changed. The relative intensity of Fe^{2+} component decreases while that of Fe^{3+} and Fe^0 components increase, indicating that Fe^{2+} component was transformed into Fe^{3+} and Fe^0 species. The post-edge region of the spectra at –7.5 V shown in Fig. S4(b) cannot be well reproduced by the curve fitting, probably because high valence states are generated in the near-surface region and/or the background exhibits somewhat deviation between the experimental and the standard spectra.

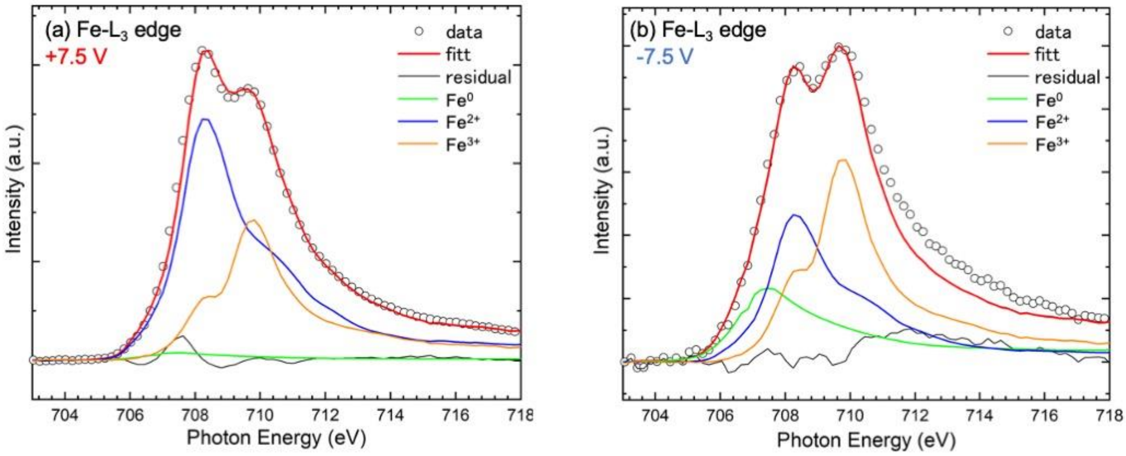

Fig. S4 Deconvolution of the Fe-L_3 edge XAFS spectra measured for the SUS substrate with the CEY method at a bias voltage of (a) +7.5 V and (b) –7.5 V.

References

1 C. S. Doyle, C. K. Seal and B. J. James, *Appl. Surf. Sci.*, 2011, **257**, 10005–10017.

2 M. Giménez-Marqués, E. Bellido, T. Berthelot, T. Simón-Yarza, T. Hidalgo, R. Simón-Vázquez, Á. González-Fernández, J. Avila, M. C. Asensio, R. Gref, P. Couvreur, C. Serre and P. Horcajada, *Small*, 2018, **14**, 1–11.