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Photo-excited carrier transfer from Nb:$SrTiO_3$-photoelectrode to Co-oxide-cocatalyst for oxygen evolution studied by in situ XAFS

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Introduction

Photoelectrochemical water splitting is a promising technology for the sustainable production of hydrogen gas as an energy carrier [1]. The utilization of metal-oxide particle cocatalysts to semiconductor photocatalysts greatly enhances the overall photelectrochemical efficiency. Recently, Co-species are reported to work as an efficient catalyst for oxygen evolution reaction [2, 3]. However, the interfacial electron transfer processes are not fully understood. In this study, the electronic structure of Co-oxide cocatalyst on the Nb:$SrTiO_3$ photoelectrode under UV irradiation was investigated by the in situ electrochemical X-ray absorption fine structure (XAFS) method.

Experimental

The in-situ electrochemical XAFS measurements were performed at BL-12C in Photon Factory and BL01B1 in SPring-8. Carbon substrate electrodes or n-type Nb:$SrTiO_3$ substrate photoelectrodes were used after deposition of Co-oxide nanoparticle cocatalyst. The Teflon-made electrochemical cell was used with a Pt wire counter electrode and a Ag/AgCl (saturated KCl) reference electrode in an 0.1 M Na_2SO_4 aqueous solution with N_2 bubbling. A Xenon lamp was used for photoelectrochemical reaction under UV irradiation.

Results and Discussion

Figure 1 shows the Co K-edge XAFS spectra of Co-oxide cocatalyst on the carbon substrate at various potentials. At the potential between -0.5 V and -1.3 V vs. Ag/AgCl, peaks of Co species were observed. The edge positions at 7733 eV corresponded with that of the Co_3O_4 reference sample, indicating that the electronic structure of Co-oxide particle is likely to be the same with that of Co_3O_4. At the potential below -1.5 V, the peak was shifted to lower energy. The edge position at 7729 eV was coincident with that of CoO, implying that the Co_3O_4 nanoparticle can change to Co^{2+} species at the potential below -1.5 V.

The Co K-edge XAFS spectra of Co-oxide cocatalysts on the Nb:$SrTiO_3$ photoelectrode were observed under potential control. The XAFS spectrum taken at the potential of 0.5 V was associated with Co_3O_4. Under UV irradiation. the edge position was shifted to lower energy, suggesting that Co_3O_4 structure changed to Co^{2+} species. The lower energy shift is due to the transfer of photo-generated electrons from Nb:$SrTiO_3$ photoelectrode to Co-oxide cocatalyst, although the Co-oxide particles work as oxygen evolution cocatalyst via the photo-generated hole transfer. This result indicates that a part of Co-oxide particles was positioned at the low potential which worked as recombination sites. Thus, the cocatalyst modifier with efficient transfer of photo-generated hole appears to be an important factor for the development of better water splitting systems.

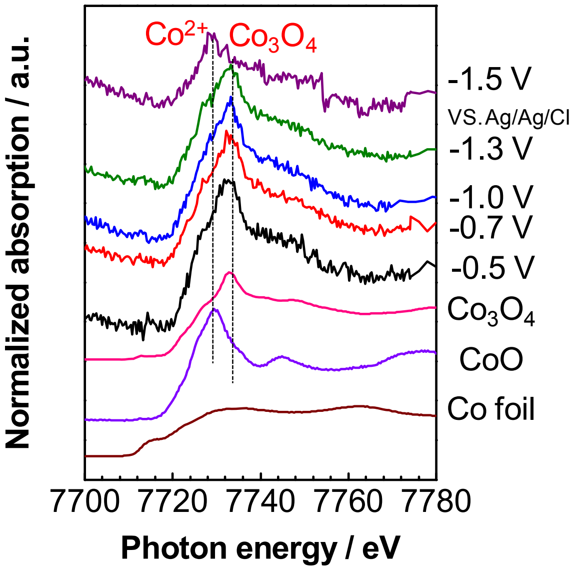

Figure 1. Potential dependent XAFS spectra of Co-oxide on carbon electrode in N_2 saturated 0.1 M Na_2SO_4 aqueous solution. The Co foil, CoO, and Co_3O_4 species were measured as reference samples.

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