

Photo-excited carrier transfer from Nb:SrTiO₃-photoelectrode to Mn-oxide-cocatalyst studied by in-situ electrochemical XAFS

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1 Introduction

Photoelectrochemical water splitting is an attractive candidate for the sustainable production of hydrogen gas by solar energy [1]. The surface modification of Mn-oxide particles to semiconductor photoelectrodes greatly enhances the overall efficiency for water splitting, because Mn-oxide species work as an efficient cocatalyst for oxygen evolution reaction. However, the immigration processes of photo-excited carriers from photoelectrode to cocatalyst have not yet been enough realized. In this study, the electronic structure of Mn-oxide cocatalyst on the Nb:SrTiO₃ photoelectrode under UV irradiation was investigated by the in-situ electrochemical X-ray absorption fine structure (XAFS) spectroscopy.

2 Experiment

The in-situ electrochemical XAFS measurements were performed at BL-12C of Photon Factory and BL01B1 of SPring-8. An n-type Nb:SrTiO₃ substrate was used as a photoelectrode after deposition of Mn-oxide particle 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 Na₂SO₄ aqueous solution with Ar bubbling. A Xenon lamp was used for photoelectrochemical reaction under UV irradiation.

3 Results and Discussion

Fig. 1 shows the Mn K-edge XAFS spectra taken for Mn-oxide cocatalysts on the Nb:SrTiO₃ photoelectrode were observed under potential control between -1.0 V and 1.0 V vs. Ag/AgCl. At the potential of -1.0 V, the peak of Mn species was observed at 6551 eV. The edge position corresponded with that of the MnO reference sample, indicating that the electronic structure of Mn-oxide particles is likely to be the same with that of Mn²⁺. With changing the potential from -1.0 V to 1.0 V, the higher energy peak was gradually observed at 6557 eV. The edge position was coincident with that of the Mn₂O₃ reference sample, implying that the structure of Mn-oxide particles can change between Mn²⁺ and Mn³⁺ species. The Mn-K edge XAFS spectra were taken at the potential of 1.0 V under UV irradiation. The edge position at 6557 eV was gradually shifted to lower energy at 6551 eV under

irradiation, suggesting that some Mn³⁺ species changed to Mn²⁺ due to the immigration of photo-excited electrons, although the Mn-oxide particles apparently work as oxygen evolution cocatalyst via the photo-excited hole transfer. This result indicates that a part of Mn-oxide particles was positioned at the lower potential by the photo-excited electron transfer and does not function as oxygen evolution sites. Thus, the efficient transfer of photo-excited carriers to cocatalyst particles is likely to be an essential key for improvement of water splitting capability.

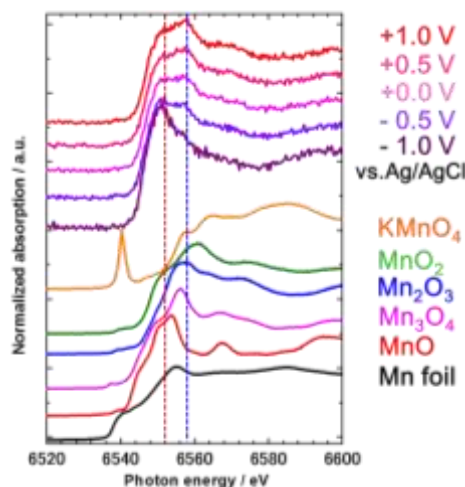


Fig. 1: Mn K-edge XAFS spectra taken for the Mn-oxide on Nb:SrTiO₃ electrode at various applied potentials in Ar saturated 0.1 M Na₂SO₄ aqueous solution.

Acknowledgement

The present work has been performed at Photon Factory (2010G677) and SPring-8 (2011A1976 (Priority Program for Disaster-Affected Quantum Beam Facilities), 2011B1080, 2012A1623). This work was supported by MEXT/JSPS KAKENHI (22850015, 24750134).

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