Improvement in Cobalt Phosphate Electrocatalyst Activity Toward Oxygen Evolution from Water by Glycine Molecule Addition and Functional Details

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Abstract

Electrochemical water splitting using renewable energy shows promise for the development of sustainable hydrogen production methods. The process requires a highly active electrocatalyst for oxygen evolution to improve overall water splitting efficiency. The present study showed that oxygen evolution improved dramatically upon addition of glycine to cobalt phosphate, when the glycine was added to the electrolyte solution during electrodeposition. The functionality of the organic molecules was investigated using in situ UV-vis absorption, in situ X-ray absorption fine structure, and in situ infrared (IR) absorption spectroscopy in attenuated total reflection mode. The results demonstrated that the glycine molecules assembled cobalt oxide clusters composed of CoO₆ (CoOOH) octahedrons a few nanometers in diameter upon electrodeposition of cobalt catalysts. This suggests that the cobalt-glycine catalyst can decompose water to oxygen gas efficiently, because the number of cobalt oxide clusters increased as active reaction sites upon addition of glycine molecules.

**Keywords:** Water splitting, electrocatalysts, XAFS, in-situ, IR, oxygen evolution, cobalt phosphate, UV-vis, glycine.
**Introduction**

Hydrogen production by electrochemical water splitting using renewable energy sources such as solar and wind is attractive because it can provide renewable energy and promote a sustainable society.\(^1\)\(^-\)\(^6\) Substantial efforts have been made to establish an efficient system for electrochemical hydrogen evolution. However, the present efficiency is not adequate for commercial applications because the catalytic activity for the oxygen evolution reaction (OER, \(2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-\)) is a little lower than that for the hydrogen evolution reaction (HER, \(2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\)). Therefore, the development of highly active OER electrocatalysts is needed to establish an efficient electrochemical hydrogen production system.

Nocera *et al.* reported that cobalt oxide electrodeposited from a dilute \(\text{Co}^{2+}\) solution in potassium phosphate electrolyte (Co-Pi) is an efficient OER electrocatalyst.\(^7\)\(^-\)\(^12\) The Co-Pi electrocatalyst was composed of inexpensive and Earth-abundant materials and stably decomposed water at lower overvoltage.\(^7\)\(^-\)\(^16\) X-ray absorption fine structure (XAFS) spectroscopy and pair distribution function (PDF) analysis revealed that the local structure of Co species in the Co-Pi catalyst was an assembly of nano-sized clusters (ca. 2–3 nm) with an edge-sharing \(\text{CoO}_6\) octahedral structure as \(\text{CoOOH}\).\(^8\) Meanwhile, the catalyst can work, not only at the electrode surface, but also inside the electrode, because of the porous thin film that induces proton-coupled electron hopping, causing an OER activity increase with increasing film thickness.\(^10\) The Co-Pi electrocatalyst is expected to be the key to drastically enhancing water oxidation efficiency.

A recent report indicated that the addition of some organic compounds to nickel oxide catalysts enhanced the OER activity.\(^17\)\(^-\)\(^23\) Singh *et al.* and Hoang *et al.* investigated nickel OER catalysts containing amine-group-based ligands, respectively, and indicated that the enhancement of OER activity was induced by a macro morphology change.\(^17\)\(^,\)\(^19\) In addition, Allen *et al.* reported that Ni catalysts with added amino acids have high OER activity, and
stated that the presence of primary amines and phosphate is the key to formation of the catalytically active Ni-hydroxide species.\textsuperscript{18} The use of several \textit{in situ} spectroscopic techniques indicated that amino acids integrated into nickel oxide clusters enhanced the catalytic activity.\textsuperscript{22} Thus, the enhancement of the OER activity by organic materials is well known for nickel catalysts. However, investigations on cobalt catalysts are limited. Nakaoka \textit{et al.} reported that glycine molecules assisted electrodeposition of spinel-type cobalt oxide (Co$_3$O$_4$) through the electrochemical quartz microbalance technique.\textsuperscript{24} Meanwhile, a cobalt-nickel alloy films were electrodeposited from glycine-containing electrolyte solutions by Ergeneman \textit{et al.}.\textsuperscript{25} However, few reports exist on addition of organic compounds to cobalt catalysts.

The present study examined the level of OER activity after addition of organic molecules to Co-P$_i$, and the function of the organic molecule was investigated using \textit{in situ} differential ultraviolet–visible absorption (UV-vis), \textit{in situ} XAFS, and \textit{in situ} infrared absorption spectroscopy in attenuated total reflection mode (ATR-IR). The results confirmed enhanced OER activity for the Co-P$_i$ catalyst upon addition of organic molecules. The local structure of Co species in the Co-Gly was composed of edge-sharing CoO$_6$ octahedral clusters a few nanometers in diameter, as well as Co-P$_i$. The present report also describes the detailed function of cobalt catalysts and organic molecules in the water oxidation process.

\textbf{Experimental}

\textbf{Sample preparation}

Electrodeposition and electrochemical measurements were conducted using a potentiostat (HA-151B, Hokuto Denko Co.) to control the electrode potential. Milli-Q water (resistivity > 18 M\textOmega \cdot \text{cm}) was used in all experiments. A Teflon electrochemical cell was equipped with a Pt wire counter electrode and a Ag/AgCl (saturated KCl) reference electrode for all electrochemical experiments. The electrode potentials against Ag/AgCl reference electrode were
calibrated against the reversible electrode potential (RHE) by adding 0.2 V and 0.059 V × pH for all experiments. Cobalt thin films were electrodeposited on indium tin oxide (ITO)-coated glass slides, gold-coated polypropylene (Au/PP) films (6.0-µm thick), or on Pd/Pt-coated silicon substrates by controlled potential electrolysis at 1.73 V vs. RHE in a 0.1 aq. M potassium phosphate electrolyte containing 0.4 mM Co(NO₃)₂ and 6.4 mM organic molecules such as glycine (Co-Gly), ethylamine (Co-EA), ethylenediamine (Co-EDA), or potassium acetate (Co-Ac) (None: Co-P). The surface morphology, composition element, surface chemical state, and film thickness for the prepared Co-P and Co-Gly were investigated using scanning electron microscopy (SEM; JSM-7600F, Jeol Ltd.), energy dispersive X-ray spectroscopy (EDX; Hitachi High-Technologies Co., TM3030Plus), X-ray photoelectron spectroscopy (XPS; JPS-9010TR, Jeol Ltd.), and surface profilometry (Dektak XT, Bruker), respectively. The H₂ and O₂ gases evolved during reaction were analyzed using a quadrupole mass spectrometer (M-070QA-TDF, Canon Anelva Co.). It should be noted that the electrolyte solution of pH9 was used for some spectroscopic measurements, because the measurement apparatuses were less contaminated when the solution of pH9 leaks.

In situ UV/vis

In situ differential UV/vis absorption spectra were obtained in diffuse transmission mode using a UV/vis spectrometer (V-650, Jasco) equipped with an integrating sphere, according to previous work.²²,²⁶ An ITO electrode mounted in a Teflon electrochemical cell was placed in front of the integrating sphere to collect diffused transmission light. The Co-P, or Co-Gly thin film was electrodeposited on the ITO electrode, as described above. In situ UV/vis spectra of the prepared samples were obtained during the OER at 1.73 V vs. RHE by exchanging the electrolyte solution with a potassium phosphate aqueous electrolyte not including Co(NO₃)₂ and organic molecules. To obtain the differential spectra, the spectrum before electrodeposition was
used as a reference.

**In situ XAFS**

The *in situ* Co K-edge XAFS spectra were obtained at BL-9A in the Photon Factory (PF) and at BL01B1 in the SPring-8 facility, using radiation monochromatized with a Si(111) double-crystal monochromator. The X-ray intensity was monitored by an ion chamber filled with N₂ gas placed in front of the sample to obtain I₀, and by an ion chamber filled with a mixture of N₂ (75%) and Ar (25%) placed after the sample to obtain I₁. The XAFS spectra of cobalt foil, CoO, Co(OH)₂, Co₃O₄, and CoOOH powder also were acquired as references. Photon energies were calibrated using the first peak maximum of the first derivative of the Cofoil (7709.5 eV). A Teflon electrochemical cell was equipped with a Pt wire counter electrode, Ag/AgCl reference electrode, and Au/PP film working electrode, as shown in previous work. The Co-P₇ or Co-Gly thin film was electrodeposited on the Au/PP film, as described above. The X-ray beam was applied at an incident angle of 4° through a PP window behind the Co-P₇ or Co-Gly sample. The fluorescence X-rays were acquired using a 19-element Ge detector (Ortec) equipped with an Fe filter and solar slits to eliminate scatter. The XAFS spectra of the prepared samples were obtained during the OER at 1.73 V vs. RHE by exchanging the electrolyte solution with aqueous potassium phosphate electrolyte, not including Co(NO₃)₂ and organic molecules. Analysis of the raw XAFS spectra was performed using the Athena and Artemis programs.

**In situ ATR-IR**

The ATR-IR measurements were performed as described previously. The spectra were recorded using a Fourier-transform infrared spectrometer (FT-IR 4600, Jasco) equipped with a MCT detector and a custom-built single-reflection accessory. All spectra are shown in
absorbance units. A Teflon electrochemical cell was equipped with a Pt counter electrode, Ag/AgCl reference electrode, and Pt/Pd/silicon working electrode. The ATR-IR spectra of the Co-Gly sample were obtained under electrodeposition at 1.73 V vs. RHE in an aqueous potassium phosphate solution containing Co(NO₃)₂ and glycine molecule. The reference spectrum was obtained before electrodeposition.

**Results and Discussion**

The cobalt catalysts were electrodeposited on the ITO substrates as shown in Fig. 1a. Constant potential electrolysis of water for each sample was conducted at 1.73 V vs. RHE in aq. potassium phosphate electrolyte (Fig. 1b). The OER current for Co-Gly was higher than that for Co-Pₐ, indicating that the glycine enhanced the OER activity of Co-Pₐ, although those of Co-EA, Co-Ac, and Co-EDA were lower than that of Co-Pₐ. The OER currents were nearly constant during the water electrolysis measurements, indicating that the cobalt electrocatalysts were stable during the OER. It was confirmed that the OER currents for Co-Gly and Co-Pₐ were dependent on the pH value of electrolyte solution and were largest in the solution at pH12, as shown in Figure S1. Furthermore, to investigate the dependence of catalytic activity on film thickness, the sample thickness was measured by surface profilometry and UV/vis absorption spectroscopy (see Figure S2 for details). Figure 1c shows the relation between the catalytic activity and the film thickness for the Co-Pₐ and Co-Gly catalysts, and indicates that the activity of both catalysts improved as the film thickness increased. When the film thickness of the catalyst layer reached about 200 nm, no further increase was observed. Thus, the film thickness of ca. 180 nm was used for spectroscopic measurements. In contrast, no difference in the catalytic activity per unit film thickness was found between the Co-Pₐ and Co-Gly catalysts, indicating that OER activity was dependent of the amount of cobalt catalyst, but was not affected by the presence of glycine. Meanwhile, to calculate the Faraday efficiency of the OER
for the Co-Gly catalyst, the amount of evolved H\textsubscript{2} and O\textsubscript{2} gasses was measured using a quadrupole mass spectrometer and compared with the amount calculated from the observed OER currents (Fig. 1d). The Faraday efficiency for the Co-Gly catalyst was estimated to be near 100\%, demonstrating that the observed current was used almost exclusively for the OER, and not side reactions.

The SEM results confirmed that the substrate surface was flat in the μm region covered completely with the Co-P\textsubscript{i} and Co-Gly catalyst (Figure S3), although some cracks in the films were observed likely due to the drying after electrodeposition. Elemental composition analyses were performed for both catalysts using EDX spectroscopy (Acceleration voltage of electron beam: 10 kV), as shown in Figs. 2a-2b. These results show that the Co-P\textsubscript{i} and Co-Gly films were composed of Co, P, K, and O species, consistent with previous reports concerning Co-P\textsubscript{i}\textsuperscript{7}. However, nitrogen from the glycine in the Co-Gly catalyst around 393 eV could not be definitely confirmed, suggesting that the amount of glycine inside the film was small. Next, to investigate the surface state of the Co-Gly catalyst, XPS analysis was conducted. The N 1s XPS spectra (Fig. 2c) show that the nitrogen species from glycine was present only near the surface of the Co-Gly film. Note that In, Sn, and Si derived from the ITO substrate were detected in EDX and were not in XPS, confirming that EDX in this work is bulk sensitive spectroscopy compared with XPS.

To assess the film thickness of these catalysts, in situ UV-vis absorption spectroscopy was conducted under OER working conditions. Figure 3b shows the UV-vis spectra for each cobalt catalyst at 1.73 V vs. RHE in a potassium phosphate solution after continuously exchanging the electrolyte solution, including Co(NO\textsubscript{3})\textsubscript{2} and each organic molecule, during electrodeposition of 1h. The intensity of the broad peak in the UV-vis spectrum for Co-Gly was greater than those for Co-P\textsubscript{i} and the other cobalt catalysts, demonstrating that the glycine molecules promote the electrodeposition of cobalt oxide catalyst. A similar phenomenon has
been reported for cobalt oxide (Co$_3$O$_4$)$^{24}$ and nickel oxide (NiOOH)$^{22}$ catalysts utilizing amino acids. However, this is the first report of Co-Gly enhancing Co-P$_i$ catalyst OER activity by promoting electrodeposition using glycine.

To investigate the local environment of cobalt species in Co-Gly, in situ XAFS was conducted during the OER (Fig. 4a). The X-ray absorption near-edge structure (XANES) spectrum was obtained for the Co-P$_i$ catalyst and reference powders such as CoO, Co(OH)$_2$, Co$_3$O$_4$, and CoOOH (Fig. 4b). Using valence state analysis with the half-height of the main absorption edge as described in previous report$^{16}$, the valence states of cobalt species in the Co-P$_i$ and Co-Gly catalysts were estimated to be $+3.2$, meaning that the presence of glycine molecule in Co-Gly does not change the chemical state of Co species.

The extended X-ray absorption fine structure (EXAFS) spectrum was obtained for Co-Gly, Co-P$_i$ catalyst, and CoOOH reference powder (Figs. 4c-4d). The first (Co-O) and second (Co-Co) peaks for Co-Gly and Co-P$_i$ were observed at the similar peak position as those of the CoOOH reference (Figure 4d), which showed that the local structures of Co species in the Co-Gly and Co-P$_i$ were composed of an edge-sharing CoO$_6$ octahedral (CoOOH) structure. In similar work$^8$, the Co species in the Co-P$_i$ electrocatalyst at higher potential has been reported to be a nanosized CoO$_6$ cluster, because the second peak (Co-Co) intensity for Co-P$_i$ was weaker than that for CoOOH and no peak was observed above 3 Å in the EXAFS spectra. Therefore, the results suggest that the local structure of Co species in Co-Gly was composed of edge-sharing CoO$_6$ octahedral clusters a few nanometers in diameter, as well as of Co-P$_i$ catalyst$^8$.

To investigate the glycine molecules adsorbed in Co-Gly, in situ ATR-IR spectra were obtained during the initial electrodeposition process (Fig. 5a). Two upward bands emerged around 1611 and 1372 cm$^{-1}$, as shown in Fig. 5b. The former peak position was attributed to the NH$_3^+$ asymmetric deformation mode and the COO$^-$ asymmetric stretching mode, and the latter was assigned to COO$^-$ symmetric stretching mode, based on previous studies$^{33-34}$. These peak
intensities increased with electrodeposition time, suggesting that the glycine was present in the Co-Gly catalyst during the initial process of Co-Gly electrodeposition. The glycine molecules are present only near the surface of the Co-Gly catalyst, which was determined using the surface-sensitive methods of ATR-IR and XPS and the bulk sensitive method of EDX. It should be noted that the peak of NH\textsuperscript{+} symmetric deformation mode around 1523 cm\textsuperscript{-1} was not clearly observed due to the noise peak derived from moisture in air.

On the basis of these discussion, we concluded the following. The electrode potential generates cobalt catalysts as nanosized CoO\textsubscript{6} (CoOOH) clusters with an octahedral structure using the cobalt ions in the electrolyte (XAFS). Then, glycine molecules promote the electrodeposition compared with Co-P\textsubscript{i} (UV-vis), probably because the glycine combines cobalt catalyst by binding with NH\textsubscript{2} and COOH groups (ATR-IR). Figure 6 shows a schematic model of the OER process for the Co-P\textsubscript{i} and Co-Gly electrocatalysts. The catalytic activity of Co-Gly electrocatalyst is enhanced, because increasing the number of active reaction sites in three dimensions for the OER, compared with Co-P\textsubscript{i}. The difference of the number of active reaction sites is a key to decide the catalytic activity for OER process. It may be possible to observe individual particles and deeply consider the reaction mechanism in more advanced microscopic observations.

**Conclusions**

This study investigated whether organic molecules could enhance the oxygen evolution activity of an Co-P\textsubscript{i} electrocatalyst, and examined the function of the organic molecules. The OER current for Co-Gly was higher than that for Co-P\textsubscript{i}, indicating that the glycine molecules enhance the OER activity of Co-P\textsubscript{i}. *In situ* UV-vis absorption spectroscopy suggested that the glycine molecules promote the electrodeposition of cobalt oxide catalyst. To investigate the local structure of Co species in Co-Gly, XANES and EXAFS spectra were obtained for Co-Gly,
and the results demonstrated that the valence state of Co species in the Co-Gly was 3.2+, and that the local structure was composed of edge-sharing CoO₆ octahedral clusters a few nanometers in diameter. The *in situ* ATR-IR spectra contained two upward bands attributed to the NH₃⁺ asymmetric deformation mode and COO⁻ symmetric stretching mode, suggesting that the glycine molecules were present near the surface of Co-Gly. In conclusion, the glycine molecules combined cobalt oxide clusters composed of CoO₆ octahedrons, improving OER activity due to an increase in the number of active reaction sites.

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Figure Captions

Figure 1. Photographic images for prepared Co-Gly and Co-P, samples and schematic models for molecular compounds. (b) Time courses of the OER current densities for cobalt catalysts on the ITO substrates at 1.73 V vs. RHE in potassium phosphate electrolyte of pH 12. (c) Relationship between the film thickness and the catalytic activity for Co-Gly in potassium phosphate electrolyte of pH 9. (d) Change in the amount of evolved oxygen gas estimated from the current density using a potentiostat and from mass spectrometric analysis for the Co-Gly catalyst on the ITO substrate at 1.73 V vs. RHE under steady state.

Figure 2. EDX spectra for Co-P, (a) and Co-Gly (b) and N 1s XPS spectra for both catalysts (c). Note that the In, Sn, and Si are derived from the ITO substrate and Na, Mg, and Al are impurities contained in the ITO substrate in EDX spectra.

Figure 3. Schematic illustration of optical geometry for in-situ differential UV-vis measurements in diffuse transmission mode. (b) In-situ UV/vis absorption for cobalt electrocatalysts under OER process at 1.73 V vs. RHE in potassium phosphate electrolyte of pH 9.

Figure 4. (a) Schematic illustration of optical geometry for in-situ XAFS measurements with fluorescence mode. (b) In-situ Co K-edge XAFS spectra for Co-P, and Co-Gly catalysts under OER process at 1.73 V vs. RHE in potassium phosphate electrolyte of pH 12, together with reference powders. (c) $k^3$-weighted EXAFS oscillation and (d) Fourier transforms of $k^3$-weighted EXAFS oscillation for Co-P, and Co-Gly catalysts under OER process.

Figure 5. (a) Schematic illustration of optical geometry for in-situ ATR-IR measurements. (b)
In-situ ATR-IR spectrum for the electrodeposition of Co-Gly catalyst at 1.73 V vs. RHE in potassium phosphate electrolyte of pH 9 containing Co(NO$_3$)$_2$ and glycine.

Figure 6. Proposed schematic model of the electrochemical OER process for Co-Gly catalyst, together with Co-P$_i$. 
Fig. 1 (a) Photographic images for prepared Co-Gly and Co-Pi samples and schematic models for molecular compounds. (b) Time courses of the OER current densities for cobalt catalysts on the ITO substrates at 1.73 V vs. RHE in potassium phosphate electrolyte of pH 12. (c) Relationship between the film thickness and the catalytic activity for Co-Gly in potassium phosphate electrolyte of pH 9. (d) Change in the amount of evolved oxygen gas estimated from the current density using a potentiostat and from mass spectrometric analysis for the Co-Gly catalyst on the ITO substrate at 1.73 V vs. RHE under steady state.
Fig. 2 EDX spectra for Co-Pi (a) and Co-Gly (b) and N 1a XPS spectra for both catalysts (c).

Note that the In, Sn, and Si are derived from the ITO substrate and Na, Mg, and Al are impurities contained in the ITO substrate in EDX spectra.
Fig. 3 (a) Schematic illustration of optical geometry for in-situ differential UV-vis measurements in diffuse transmission mode. (b) In-situ UV/vis absorption for cobalt electrocatalysts under OER process at 1.73 V vs. RHE in potassium phosphate electrolyte of pH 9.
Fig. 4 (a) Schematic illustration of optical geometry for in-situ XAFS measurements with fluorescence mode. (b) In-situ Co K-edge XAFS spectra for Co-P, and Co-Gly catalysts under OER process at 1.73 V vs. RHE in potassium phosphate electrolyte of pH 12, together with reference powders. (c) $k^3$-weighted EXAFS oscillation and (d) Fourier transforms of $k^3$-weighted EXAFS oscillation for Co-P, and Co-Gly catalysts under OER process.
Fig. 5  (a) Schematic illustration of optical geometry for in-situ ATR-IR measurements.  (b) In-situ ATR-IR spectrum for the electrodeposition of Co-Gly catalyst at 1.73 V vs. RHE in potassium phosphate electrolyte of pH 9 containing Co(NO$_3$)$_2$ and glycine.
Fig. 6  Proposed schematic model of the electrochemical OER process for Co-Gly catalyst, together with Co-Pi.

Co-Pi  

Co-Gly  

O₂  

H₂O  

O₂  

H₂O  

CoO₆ (CoOOH)  

Glycine
References

1. I. Dincer, and C. Acar, *Int. J. Hydrogen Energy*, **2015**, *40*, 11094.
2. K. Christopher, and R. Dimitrios, *Energy Environ. Sci.*, **2012**, *5*, 6640.
3. M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, and N. S. Lewis, *Chem. Rev.*, **2010**, *110*, 6446.
4. S. Anantharaj, S. R. Ede, K. Sakthi kumar, K. Karthick, S. Mishra, and S. Kundu, *ACS Catal.*, **2016**, *6*, 8069.
5. Y. Yan, B. Y. Xia, B. Zhao, and X. Wang, *J. Mater. Chem. A*, **2016**, *4*, 17587.
6. M. W. Kanan, and D. G. Nocera, *Science*, **2008**, *321*, 1072.
7. H. S. Ahn, and A. J. Bard, *J. Am. Chem. Soc.*, **2015**, *137*, 612.
8. D. González-Flores, I. Sánchez, I. Zaharieva, K. Klingan, J. Heidkamp, P. Chernev, P. W. Menezes, M. Driess, H. Dau, and M. L. Montero, *Angew. Chem.*, **2015**, *127*, 2502.
9. K. Meyer, L. Tong, A. Scheurer, K. Kuepper, and W. Wu, *ChemSusChem*, **2018**, *11*, 255.
10. D. K. Bediako, C. Costentin, E. C. Jones, D. G. Nocera, and J.-M. Savéant, *J. Am. Chem. Soc.*, **2013**, *135*, 10492.
11. C. L. Farrow, D. K. Bediako, Y. Surendranath, D. G. Nocera, and S. J. L. Billinge, *J. Am. Chem. Soc.*, **2013**, *135*, 6403.
12. D. K. Bediako, A. M. Ullman, and D. G. Nocera, *Top. Curr. Chem.*, **2015**, *371*, 173.
13. A. Singh, S. L. Y. Chang, R. K. Hocking, U. Bach, and L. Spiccia, *Catal. Sci. Technol.*, **2013**, *3*, 1725.
14. D. Wang, G. Ghirlanda, and J. P. Allen, *J. Am. Chem. Soc.*, **2014**, *136*, 10198.
15. K. Ogura, and A. A. Gewirth, *ACS Catal.*, **2016**, *6*, 1159.
16. D. A. Kuznetsov, D. V. Konev, N. S. Komarova, A. M. Ionov, R. N. Mozchil, and I. V. Fedyanin, *Chem. Commun.*, **2016**, *52*, 9255.
17. K. Meyer, L. Tong, A. Schauer, K. Kuepper, and W. Wu, *ChemSusChem*, **2018**, *11*, 255.
18. M. Yoshida, S. Onishi, Y. Mitsutomi, F. Yamamoto, M. Nagasaka, H. Yuzawa, N. Kosugi, and H. Kondoh, *J. Phys. Chem. C*, **2017**, *121*, 255.
19. A. Singh, S. L. Y. Chang, R. K. Hocking, U. Bach, and L. Spiccia, *Energy Environ. Sci.*, **2013**, *6*, 579.
20. K. Nakao, M. Nakayama, and K. Ogura, *J. Electrochem. Soc.*, **2002**, *149*, 1C159.
21. O. Ergeneman, K. M. Siyaraman, S. PANÉ, E. Pellicer, A. Teleki, A. M. Hirt, M. D. Baró, and B. J. Nelson, *Electrochim. Acta*, **2011**, *56*, 1399.
22. T. Takashima, K. Hashimoto, and R. Nakamura, *J. Am. Chem. Soc.*, **2012**, *134*, 18153.
Asakura, and H. Kondoh, Chem. Lett., 2016, 45, 277.
28. M. Newville, J. Synchrotron Radiat., 2001, 8, 322.
29. B. Ravel, J. Synchrotron Radiat., 2001, 8, 314.
30. B. Ravel, and M. Newville, J. Synchrotron Radiat., 2005, 12, 537.
31. M. Osawa, Bull. Chem. Soc. Jpn., 1997, 70, 2861.
32. M. Yoshida, A. Yamakata, K. Takanabe, J. Kubota, M. Osawa, and K. Domen, J. Am. Chem. Soc., 2009, 131, 13218.
33. A. Ihs, B. Liedberg, K. Uvdal, C. Törnkvist, P. Bodö, and I. Lundström, J. Colloid Interface Sci., 1990, 140, 192.
34. K. Uvdal, P. Bodö, A. Ihs, B. Liedberg, and W. R. Salaneck, J. Colloid Interface Sci., 1990, 140, 207.