Iron Oxyhydroxide Hierarchical Micro/Nanostructured Film as Catalyst for Electrochemical Oxygen Evolution Reaction

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Abstract

A key requirement in developing oxygen evolution reaction (OER) electrocatalysts is increasing their surface area. Herein, we report the design of a hierarchical micro/nanostructured catalyst. Based on polystyrene colloidal template electrodeposition, an ordered microcup array surrounded by nanoflakes was fabricated. The effect of the deposition time on the formation of the catalyst and the corresponding OER performance of the catalyst were investigated using scanning electron microscopy, in-situ X-ray absorption fine structure (XAFS) spectroscopy, and electrochemical analysis. The in-situ XAFS measurements indicate that the structure of the hierarchical structured catalyst is similar to that of $\gamma$-FeOOH. The electrochemical analysis indicates that the hierarchical catalyst has large surface area and low charge transfer resistance, which lead to its excellent catalytic performance for the OER. Our study provides new insights in designing high-performance OER catalysts. Moreover, the synthesized hierarchical micro/nanostructured catalyst could be used as a platform for further studies on low-cost iron-based electrocatalysts.

Keywords: Iron oxide, Oxygen evolution reaction electrocatalyst, Colloidal crystal templated synthesis, Electrodeposition, X-ray absorption fine structure.
Introduction

Generating electricity from renewable resources, such as sunlight and wind, is essential for developing a sustainable society. The problem with such renewable resources is that they are often not reliable due to weather or environment. Hydrogen produced from water splitting by an electrochemical process offers a viable solution for storing intermittent energy associated with renewable resources\(^1\). Currently, oxygen evolution reaction (OER) represents a major bottleneck in the efficient electrolysis of water during hydrogen production\(^2,3\). The inefficiency of OER arises from the sluggish four-proton-coupled electron transfer and rigid oxygen–oxygen bonding (\(2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ +4\text{e}^-\)). To overcome this challenge, a technique that can facilitate the OER must be developed.

To date, a great many 3d metal-based materials have been demonstrated to be efficient catalysts for the OER, including metal oxides\(^3,4\), sulfides\(^5,6\), nitrides\(^7\), phosphates\(^8,9\), borides\(^10\), and perovskites\(^11\). However, the performance of these catalysts are inferior to those of noble metal-based catalysts (Pt, RuO\(_2\), and IrO\(_2\)) owing to their sparse catalytic edge sites and poor electrical conductivity\(^12\). Substantial improvements in the design and fabrication of OER electrocatalysts that comprise only inexpensive and earth-abundant materials are still needed and have been considered a great challenge.

Generally, there are three routes to improve the performance of OER catalysts: (i) increasing the number of active sites exposed to electrolytes, (ii) increasing the intrinsic activity of each active site, and (iii) enhancing the conductivity of electrocatalysts\(^13,14\). Recent studies have indicated that hierarchically structured films could increase the surface area and porosity of catalysts, which would greatly improve their performance\(^15\). Colloidal crystal templated synthesis has been used to fabricate ordered hierarchical arrays because of its facile process and low equipment cost\(^16-19\). Monodispersed colloidal spheres can be self-assembled into highly ordered templates on substrate using various self-assembly strategies, such as spin coating\(^20\), evaporation\(^21\), and electrophoretic deposition\(^22\). The structures and morphologies of the arrays could be tuned by adjusting the packing density and size of the colloidal spheres in the template and by controlling the synthesis parameters\(^23-25\). Among various synthesis techniques, electrodeposition has been demonstrated to be a viable method to consistently produce nanostructured metals or metal oxides on conductive substrates\(^26\). Moreover, the structures and
morphologies of the electrodeposition products could be tuned by controlling the surface chemistry or geometry of the substrate\textsuperscript{27}.

These features of colloidal crystal templates and electrodeposition process provided some ideas in fabricating novel OER catalysts. Thus, we report here the design of a hierarchical micro/nanostructured iron oxide (FeO\textsubscript{x}) OER catalyst using colloidal crystal templated electrodeposition. We analyzed the morphologies and structures of the FeO\textsubscript{x} films and examined the corresponding OER catalytic performance of the FeO\textsubscript{x} films using scanning electron microscopy (SEM), in-situ X-ray absorption fine structure (XAFS) spectroscopy, and electrochemical analysis. XAFS spectroscopy is a powerful tool for investigating the local electronic states for OER catalysts\textsuperscript{28}. In particular, we focused on the in-situ O K-edge XAFS technique, which has been demonstrated to be useful for observing the O species in transition-metal oxides directly, because it is sensitive to the unoccupied p-weighted density of states\textsuperscript{29}. Overall, our study provides new insight into the development of OER catalysts using colloidal templated electrodeposition.

**Experimental**

*Synthesis of Polystyrene Spheres*

Polystyrene (PS) spheres were synthesized via suspension polymerization. Prior to use, styrene (Kanto Chemical) was distilled under reduced pressure to remove inhibitors. Distilled water (180 mL) was poured into a two-necked flask and was purged with N\textsubscript{2} for 10 min to remove O\textsubscript{2} from the flask. Styrene (12.2 g) was added to the flask and the contents of the flask were stirred at 200 rpm. The flask was then heated with an oil bath until the temperature reached 70 °C. Subsequently, potassium peroxodisulfate (0.08 g) (>98%, Kanto Chemical), the polymerization initiator, was dissolved in distilled water (1 mL) and was added to the flask. Lastly, the mixture was heated at 75 °C and was stirred under reflux for 24 h.

*Fabrication of PS Colloidal Templates*

An 80 \textmu L of the PS sphere suspension was pipetted onto the center of a glass substrate and was spun by a spin-coater (K-359S1, Kyowa Riken) for 30 s at 3000 rpm to form a monolayer of PS spheres. To
obtain a highly ordered PS colloidal monolayer, the monolayer was re-organized at the air/water interface using the following steps. Distilled water was poured into a Teflon trough, followed by setting a size of 2.5 × 1 cm² indium tin oxide (ITO) coated glass slide (surface resistivity of 30 Ω/sq) at the bottom of the trough. Prior to use, the ITO glass slide was rinsed ultrasonically with acetone (>99%, Kanto Chemical), ethanol (>99.5%, Kanto Chemical), and distilled water. The slide was then dried by N₂ gas. The PS monolayer floated to the water surface after the glass substrate covered with the PS colloidal monolayer was dipped into water. Subsequently, the monolayer was compressed by two Teflon barriers to obtain a highly ordered PS monolayer, which was transferred onto the ITO glass by aspirating the water using a syringe. After it was dried in air, the ITO glass slide covered with the PS colloidal monolayer was heated at 110 °C for 3 min in an oven (S-70, KDF) to bond the monolayer to the substrate.

**Electrochemical Synthesis of FeOₓ Array**

Electrodeposition was conducted at 60 °C in a three-electrode cell with a platinum counter electrode and a silver chloride reference electrode (Ag/AgCl, soaked in saturated KCl). An ITO slide or the ITO glass slide covered with the PS colloidal monolayer served as working electrodes. FeOₓ was deposited by applying a constant potential of 1.2 V (vs. Ag/AgCl) in 1 mM iron(II) chloride hexahydrate (99%, Kanto Chemical) aqueous solution at pH 5.6. After the removal of the PS colloidal template by tetrahydrofuran (THF, 99.5%, Kanto Chemical) etching for 2 h, the films were rinsed several times with distilled water and were dried in air for 30 min.

**Characterization of FeOₓ films**

The morphology of the FeOₓ films was examined using a SEM instrument (HITACHI S-4800). X-ray diffraction (XRD) patterns were recorded on an Ultima IV (Rigaku) diffractometer that operated at 40 mA and 40 kV using monochromatic Cu Kα₁ radiation. The Raman spectra of the FeOₓ films deposited on the platinum sheet were recorded with a confocal Raman microscope (NRS-3200, JASCO) at the excitation wavelength of 532 nm provided by a 1-2 mW laser. The amount of FeOₓ films electrodeposited on the substrate was determined using an inductively coupled plasma optical emission spectroscopy device (ICP-OES, SPECTRO ARCOS, Hitachi). The electrodeposited films were dissolved in 2 mL mixture of nitric acid (HNO₃, 65%, Kanto Chemical) and hydrochloric acid (HCl,
35%, Kanto Chemical). The volume ratio of HNO$_3$/HCl was 3:1. The mixture was collected and diluted with distilled water to 20 mL for the ICP-OES measurements. Calibration solutions were prepared from iron standard solutions (iron nitride, Fe:1000 mg/L, Kanto Chemical) with concentrations of 10, 50, and 100 ppm.

Electrochemical measurements were performed in a conventional three-electrode system, which was composed of the FeO$_x$ sample, Ag/AgCl, and a Pt sheet as the working, reference, and counter electrodes, respectively, using a CHI660A (CHI Instruments) or HA-151B (Hokuto Denko) potentiostat. All potentials were reported with respect to the Ag/AgCl reference. The measured currents were converted to current densities by normalization in respect with the geometric area of each sample. The OER catalytic performance of the FeO$_x$ films was measured in 0.1 M potassium hydroxide (KOH, 86.0 %, Kanto Chemical) solution. The Redox properties of the FeO$_x$ films was carried out in 0.1 M sodium sulfate (Na$_2$SO$_4$, 99.0%, Kanto Chemical) containing 5 mM potassium ferricyanide (K$_3$[Fe(CN)$_6$], 99.0%, Fujifilm Wako). Electrochemical impedance spectra (EIS) were measured at the superimposed 10 mV sinusoidal voltage in the frequency range of 10 kHz to 0.1Hz. The measurements were performed in 0.1 M Na$_2$SO$_4$ solution containing 5 mM K$_3$[Fe(CN)$_6$].

In-situ Fe K-edge XAFS

In-situ Fe K-edge XAFS spectra were collected at the BL01B1 beamline of SPring-8 and at the BL9A beamline of the Photon Factory under fluorescence mode using a 19 element Ge detector (Ortec) equipped with a manganese filter and solar slits to eliminate scatter. The radiation was monochromatized by a Si(111) double-crystal monochromator. The intensity of incident X-rays was monitored by N$_2$-filled ion chambers (I$_0$) in front of the sample (17 cm in length) and N$_2$ (75%) and Ar (25%) gas mixture-filled ion chambers (I$_1$) at the back of the sample (31 cm long). The photon energy was calibrated from the first peak maximum of the first derivative of Fe foil (7112 eV)$^{34}$. The electrochemical XAFS Teflon cell contained an Ag/AgCl reference electrode, a platinum wire counter electrode, and a platinum-and-palladium-coated polyester film (Pt-Pd/PET, 6.0 μm thick) as the working electrode. The XAFS spectra of the FeO$_x$ films in 0.1 M lithium chloride (LiCl, 99.0 %, Kanto Chemical) solution were recorded at 0.2 V intervals in the potential range of 1.2 to -1.2 V. The XAFS spectra of the reference compounds:
ferrous oxide (FeO, 99.5%, Fujifilm Wako), magnetite (Fe₃O₄, 95.0%, Fujifilm Wako), hematite (α-Fe₂O₃, 99.9%, Fujifilm Wako), maghemite (γ-Fe₂O₃, 99.9%, Fujifilm Wako), goethite (α-FeOOH, 95.0%, Kanto Chemical), and lepidocrocite (γ-FeOOH, 99%, Fujifilm Wako) were acquired in transmission mode. The X-ray beam was applied at an incident angle of 4° through a PET window behind the sample. Data reduction of the XAFS spectra was performed with the Athena and Artemis program. The pre- and post-edge backgrounds were subtracted from the XAFS spectra and the results were normalized with respect to the edge height.

*In-situ O K-edge XAFS*

In-situ O K-edge XAFS spectra were collected at the BL16A beamline of the Photon Factory (PF) under fluorescence yield mode. The radiation was monochromatized with variable-included-angle varied-line-spacing plane-grating monochromators. A handmade vacuum chamber (ca. 10⁻² Torr) was connected to the beamline under ultra-high vacuum condition (<10⁻⁸ Torr) by separating both spaces using an X-ray window made of silicon nitride thin film (500 nm).

An electrochemical Teflon cell that contained an Ag/AgCl reference electrode, a platinum wire counter electrode, and a gold-coated silicon nitride film (Au/Si₃N₄, Au:20 nm, Si₃N₄:150 nm) as the working electrode was set in the center of vacuum chamber. The Teflon cell was positioned at an angle to allow the incident X-ray beam to pass through the Si₃N₄ window behind the Au electrode. The intensity of the fluorescence X-ray from the Au/Si₃N₄ electrode (I₁) was detected using a silicon drift detector (XR-100SDD, Amptek Inc.) and then it was normalized to the mirror current of incident X-ray (I₀). After the FeOₓ films were electrodeposited on the Au/Si₃N₄ electrode, the XAFS spectra were recorded at 1.2 V in 0.1 M lithium hydroxide (LiOH, 99.0 %, Kanto Chemical) aqueous solution. The photon energies of the O K-edge XAFS spectra were calibrated according to the first peaks of O₂ gas at 530.80 eV.

**Results and Discussion**

**Morphological Evolution of FeOₓ Array**

The morphological evolution of FeOₓ on the ITO glass with PS colloidal template (termed as PS-ITO)
during electrochemical growth was investigated by SEM. Prior to the SEM analysis, the FeO<sub>x</sub> films were immersed in THF solution to remove the PS template and were subsequently dried by N<sub>2</sub> gas.

Figure 1(A) shows the SEM image of the FeO<sub>x</sub> film electrodeposited for 25 min. The image reveals an ordered array of hemispherical microcups. The diameter of the microcups matched that of the used PS spheres. The average diameter of the PS spheres was measured using SEM to be approximately 520 nm (the results have not been included here). This suggests that the shape of the FeO<sub>x</sub> microcups remained hemispherical even after THF etching. The high-magnification SEM image in the inset of Fig. 1(A) shows that the microcups consisted of closely stacked round particles, which were deposited along the surface of the PS sphere, as reported in the literature<sup>36,37</sup>. In addition, the interstitial spaces of the microcups were filled with crumpled flakes. After 30 min of deposition, the FeO<sub>x</sub> continuously deposited along the top half of the PS sphere, forming spherical shells (Fig. 1(B)). The spherical shells consisted of mostly round particles and a small fraction of crumpled flakes, which were randomly distributed over the shell. When the deposition time was increased to 40 min, the size and amount of crumpled flakes markedly increased (Fig. 1(C)). The crumpled flakes consisted of agglomerated particles and grew vertically on the spherical shells. Further increasing the deposition time to 50 min led to increase in the amount of crumpled flakes on top of the microsphere array (Fig. 1(D)). The average length and width of the crumpled flakes ranged from 90 to 125 nm and from 25 to 55 nm, respectively. The crumpled flakes closely resemble those deposited on ITO glass without PS spheres (Fig. S1, Supporting Information). These results suggest that the formation of round particles was favored when FeO<sub>x</sub> was electrodeposited on the PS colloidal template.

**Structural Characterization of FeO<sub>x</sub> Array**

The structure of the as-deposited FeO<sub>x</sub> film was investigated using XRD, and the results are depicted in Fig. S2. The XRD pattern did not show the typical series of peaks associated with crystalline FeO<sub>x</sub>, which indicates the FeO<sub>x</sub> film was amorphous. The as-deposited FeO<sub>x</sub> film was also investigated using Raman spectroscopy (Fig. S3). The sharp peaks at 250, 377, and 527 cm<sup>-1</sup> and the broad peak at approximately 655 cm<sup>-1</sup> in the Raman spectrum of the FeO<sub>x</sub> film were assigned to γ-FeOOH<sup>38</sup>. To
identify the local structure of the amorphous FeOx film, the in-situ Fe K-edge XAFS spectra for the FeOx film electrodeposited on Au/PET substrates poised at 1.2 V in 0.1 M LiCl solution were obtained. The peak positions and shape of the spectral line of the 3d metal K-edge XAFS spectrum depend on the local electronic structure of the metal ions. Consequently, XAFS could be used to identify different inorganic Fe phases in unknown samples. Figure 2(A) shows the X-ray absorption near-edge structure (XANES) spectrum for the FeOx film poised at 1.2 V. The spectra of reference compounds: FeO, Fe2O4, α-Fe2O3, γ-Fe2O3, α-FeOOH, and γ-FeOOH are also included in Fig. 2(A). The XANES spectrum showed a small pre-edge peak, which was assigned to the 1s → 3d transitions, and a main peak, which corresponded to the 1s → unfilled 4p states transitions. The spectrum of the FeOx film (black line) resembled that of γ-FeOOH (red line), although its edge position was lower than that of γ-FeOOH. Here the edge position of each sample is defined at the point of the half maximum of the normalized-edge. Figures 2(B) and (C) compare the k^3-weighted extended X-ray absorption fine structure (EXAFS) spectra and the corresponding Fourier transform extended X-ray absorption fine structure (FT EXAFS) spectra for the FeOx film poised at 1.2 V with those of the reference compounds, α-FeOOH and γ-FeOOH. The oscillations observed in the k^3-weighted EXAFS spectra were nearly in phase for the FeOx film and γ-FeOOH. The FT EXAFS spectra show two dominant peaks. The peaks between 1 and 2 Å corresponded to the Fe-O interactions, and the peaks between 2 and 3 Å corresponded to the Fe-Fe interactions. Unlike the spectra of the FeOx film and γ-FeOOH, the spectrum of α-FeOOH shows a large second peak that featured a shoulder peak. These results indicate that the local structure of the FeOx film (black line) was more similar to that of γ-FeOOH (red line) than to that of α-FeOOH (blue line).

In situ O K-edge XAFS spectra were also obtained for the FeOx film poised at 1.2 V. Fig. 3 shows the O K-edge XAFS spectra of the FeOx films and those of the FeO, Fe2O4, α-Fe2O3, γ-Fe2O3, α-FeOOH, and γ-FeOOH reference compounds. Similar to the spectrum of γ-FeOOH, that of the FeOx film shows two prominent peaks at approximately 532.0 and 533.6 eV. These peaks were attributed to the transition of an O 1s electron to the O 2p σ* states that were hybridized with empty Fe 3d orbitals. Peak splitting (the split peaks were labeled as a and b) was due to the t_{2g}→e_g splitting of the 3d orbitals. The O K-edge
XAFS results combined with the previously reported Fe K-edge XAFS results indicate that γ-FeOOH could be an appropriate model compound for the structure of the FeOₓ film poised at 1.2 V.

To evaluate the effect of electrode potential on the structure of the FeOₓ film, the in-situ Fe K-edge XAFS spectra for the FeOₓ film were recorded at 0.2 V intervals in the potential range of 1.2 to -1.2 V. Figure 4(A) shows the XANES spectra for the FeOₓ film, which was acquired as a function of the applied potential. As the potential decreased from 1.2 to -0.2V, the spectra of the FeOₓ film show marginal differences in their edge shape and position. This suggests that the resultant film still consisted of mostly γ-FeOOH. At the potential of -0.4 V, the slight shift in the edge position toward lower energy levels indicates that the FeOₓ film was partially reduced. For a more qualitative comparison, the iron valences of the FeOₓ film poised at various potentials were fitted and the results are presented in Fig. 4(B). Changing the potential from 1.2 to -0.4 V resulted in the Fe valence of the FeOₓ film changing from 2.9 to 2.7. At the potential of -0.8 V, the spectrum showed a large shift compared to that observed at -0.4 V, and also a simultaneous change in the edge shape which corresponded to the presence of FeO. These results demonstrate that the FeOₓ film was gradually reduced from γ-FeOOH to FeO in the potential range of -0.4 to -1.2 V (Fig. 4(C)). This phenomenon was in agreement with the reduction peak observed in the cyclic voltammogram (CV) (Fig. S4), which indicates that electrochemical reduction occurred at potentials ≤ -0.4 V.

**Electrochemical Performance of FeOₓ Film**

To investigate the morphological effect of the FeOₓ films on their catalytic performance for the OER, FeOₓ films were electrodeposited on PS-ITO substrates for 25 and 30 min (which generated microcup and microsphere film, respectively). The OER catalytic performance of the microcup and microsphere films was investigated in 0.1 M KOH solution using a standard three-electrode setup. For comparison, the FeOₓ film electrodeposited without using a PS colloidal template (flat film) was subjected to the same test. Figure 5(A) shows the linear sweep voltammograms for all samples. Both the microcup and microsphere films exhibited significantly higher anodic current densities and lower onset potentials than the flat film. For the microcup and microsphere films, a pronounced catalytic wave appeared, and
its onset was observed at approximately 0.67 V. Conversely, the onset potential of the flat film was approximately 0.78 V. The time evolution of the OER current densities for all sample is shown in Fig. 5(B). The microcup and microsphere films exhibited higher OER current densities than the flat film. In particular, the OER current density for the microcup film was the highest, which was about 3.4 times higher than the flat film. These results indicate that the OER performance of the hierarchically structured film was greatly improved. Although the 30 min deposition process (microsphere) generated a film that contained a higher amount of FeO₄, the corresponding current density was still low. To analyze this phenomenon, the OER current densities for all samples were normalized by the mass of deposited FeO₄ (i.e., specific current). The mass of FeO₄ deposited on the substrate was quantified using ICP-OES. The detailed procedure is provided in the experimental section. Figures 5(C) and (D) indicate that the specific current ratio between the microcup and microsphere films was higher than the current density one. This result may be derived from that the electrolyte cannot penetrate to the deepest layer of the microsphere film to carry out the OER process.

To further explore the interplay between the morphology and surface area exposed to the electrolyte for each sample, we evaluated the redox properties of the microcup, microsphere, and flat films by the direct determination of the [Fe(CN)₆]³⁻/⁴⁻ redox probe in 0.1 M Na₂SO₄ solution using CV. Fig. 6(A) shows the CVs of 5 mM K₃[Fe(CN)₆] in 0.1 M Na₂SO₄ solution for these films at the scan rate of 20 mV/s. During the negative sweep, the reduction peak gradually appeared as [Fe(CN)₆]³⁻ was converted to [Fe(CN)₆]⁴⁻. The oxidation peak appeared during the positive sweep when the conversion was reversed. For the flat film, the CVs have no observable redox peaks. This may be explained by considering the slow electron transfer between the [Fe(CN)₆]³⁻/⁴⁻ probe and the flat film. The microcup and microsphere films showed quasireversible responses to the [Fe(CN)₆]³⁻/⁴⁻ probe, which is in agreement with the literature. The separation of peak potentials for the microcup and microsphere films were 280 mV and 300mV, respectively. The peak current density for the microcup film was the highest of all analyzed samples. The smaller separation of peak potential and higher peak current density for the microcup film could be attributed to its larger surface area, which benefits the electron transfer between the [Fe(CN)₆]³⁻/⁴⁻ probe and the microcup film. The changes in peak current density
with the scan rate for the microcup and microsphere films are shown in Fig. S5. The peak current density was proportional to the square root of the scan rate, which suggests that the $[\text{Fe(CN)}_6]^{3-/4-}$ redox processes for the microcup and microsphere films were diffusion-controlled processes.

To investigate the electron-transfer kinetics of the microcup, microsphere, and flat films, EIS measurements were performed in 0.1 M Na$_2$SO$_4$ solution containing 5mM K$_3[\text{Fe(CN)}_6]$. Figure 6(B) shows the Nyquist plots for all samples. The diameter of the semicircle corresponds to the charge transfer resistance ($R_{CT}$) at the electrode surface$^{43}$. The results show that the diameter of the semicircle for the microcup film was much smaller than that of the microsphere film, which indicates that the $R_{CT}$ of the microcup film was lower than that of the microsphere film. In particular, the $R_{CT}$ of the flat film was the highest of all analyzed samples. This provide evidence for the slow electron transfer between the $[\text{Fe(CN)}_6]^{3-/4-}$ probe and the flat film. Therefore, we conclude that the microcup film presented the highest OER catalytic activity of all films, which could be attributed to its large surface area and low $R_{CT}$ value.

**Conclusion**

We have obtained and analyzed a novel hierarchical micro/nanostructured catalyst that was fabricated using PS colloidal templated electrodeposition. The SEM analysis results shows that this hierarchical micro/nanostructured catalyst was an ordered microstructure array surrounded by nanoflakes. The formation of these two structures depends on the surface chemistry and/or geometry. The microstructure was tuned from cup-like to sphere-like by varying the deposition time. The in-situ Fe K-edge and O K-edge XAFS measurements indicate that the catalyst mainly comprised $\gamma$-FeOOH, and the chemical structure of the catalyst was dependent on the electric potential. As the potential decreased from 1.2 to -1.2 V, the chemical structure of the FeO$_x$ film was gradually converted from $\gamma$-FeOOH to FeO. Electrochemical analysis indicates that the OER current density of the microcup film was much higher than those of the other films. This could be attributed to its large surface area and low $R_{CT}$ value. This study provides a good foundation for the preparation of OER catalysts via colloidal crystal templated electrodeposition, where the compositions and morphology of catalysts could be further developed.
Supporting Information

Four figures on SEM image of the FeOₓ flat film, supplementary XRD pattern, additional CV result.

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Notes

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Acknowledgements

Synchrotron facilities were provided by the Photon Factory (2016G647, 2017G529, 2018G589, 2019G674) and SPring-8 (2017B1082, 2019A1386). The authors are indebted to Yung-Chen Wang (University of Washington) for many helpful discussions and Misato Onizuka (Tokyo University of Science) for experimental support. One of the authors (M. Y.) was supported by Grant-in-Aid for Scientific Research (C) (17K05843) from JSPS and the Electric Technology Research Foundation of Chugoku.

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**FIGURE CAPTIONS**

**Fig. 1** SEM images of the FeOₓ films deposited on the PS-ITO substrate for: (A) 25, (B) 30, (C) 40, and (D) 50 min. The insets in panels A-D show zoomed-in images of the films.

**Fig. 2** (A) XANES spectra of the FeOₓ film poised at 1.2 V (black line) in 0.1 M LiCl electrolyte, and those of α-FeOOH (blue line), γ-FeOOH (red line), α-Fe₂O₃ (yellow dashed line), γ-Fe₂O₃ (green line), Fe₂O₄ (grey line), and FeO (purple line) reference compounds. (B) k³-weighted and (C) FT EXAFS spectra of α-FeOOH (blue line), γ-FeOOH (red line), and FeOₓ (black line) poised at 1.2 V.
Fig. 3 O K-edge XAFS spectra of the FeO$_x$ films poised at 1.2 V (black line) and those of $\alpha$-FeOOH (blue line), $\gamma$-FeOOH (red line), $\alpha$-Fe$_2$O$_3$ (yellow line), $\gamma$-Fe$_2$O$_3$ (green line), Fe$_3$O$_4$ (grey line), and FeO (purple line) reference compounds.

Fig. 4 (A) Structural evolution of the FeO$_x$ film as a function of the applied potential. (B) Relationship between Fe valence and half edge energy of reference compounds and the FeO$_x$ film poised in the potential region of 1.2 to -1.2 V. (C) Potential-dependent structural evolution of the FeO$_x$ film in the potential region of 1.2 to -1.2 V.

Fig. 5 (A) Linear sweep voltammograms and (B) time evolution of the OER current densities for the microcup, microsphere, and flat films of FeO$_x$ in 0.1 M KOH solution. Linear sweep voltammograms were recorded at a scan rate of 20 mV/s. (C) and (D) plot the OER current densities normalized to the mass of FeO$_x$ electrodeposited on substrate for the microcup, microsphere, and flat film.

Fig. 6 (A) Cyclic voltammograms of 5 mM K$_3$[Fe(CN)$_6$] in 0.1 M Na$_2$SO$_4$ solution for the microcup, microsphere, and flat films at a scan rate of 20 mV/s. The inset shows a zoomed-in view of the redox peaks for the flat film. (B) Electrochemical impedance spectra recorded at 0.3 V in 0.1 M Na$_2$SO$_4$ solution containing 5 mM K$_3$[Fe(CN)$_6$] for the microcup, microsphere, and flat films represented in the Nyquist format.
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Graphical Index

Current density/mA cm² μg⁻¹

Potential/V (vs. Ag/AgCl)