Cobalt-Doped Goethite-Type Iron Oxyhydroxide (α-FeOOH) for Highly Efficient Oxygen Evolution Catalysis

Daijiro Inohara,† Heishi Maruyama,‡ Yasuo Kakihara,‡ Haruki Kurokawa,‡ and Masaharu Nakayama*†‡

1Department of Applied Chemistry, Graduate School of Sciences and Technology for Innovation, Yamaguchi University, 2-16-1 Tokiwadai, Ube 755-8611, Japan
2Research and Development Division, Todakogyo Corporation, 1-4 Meiji-Shingai, Otake 739-0652, Japan

ABSTRACT: It is an urgent challenge to develop low-cost and high-performance catalysts for the oxygen evolution reaction (OER). We synthesized nanoparticulate electrocatalysts consisting of cobalt-doped goethite-type iron oxyhydroxide (α-FeOOH) with controlled Co/Fe ratios [CoFe1−xOx(OH) (x ≤ 0.20)] based on our own wet process. A Co0.20Fe0.80OOH-coated glassy carbon electrode generated a current density (j) of 10 mA cm−2 at an overpotential (η) as small as 383 mV (1.61 V vs the reversible hydrogen electrode) in an alkaline electrolyte, with a small Tafel slope of 40 mV dec−1 and excellent durability, whereas pure α-FeOOH required η = 580 mV to reach the same current density. This can be ascribed to the effect of Co doping, which resulted in an increase in electrochemically active surface area and a decrease in charge-transfer resistance. The content of cobalt, a scarce resource, in the catalyst is much smaller than those in most of the other Fe-based catalysts reported so far. Thus, this study will provide a new strategy of designing cost-effective and high-performance catalysts for the OER in alkaline solution.

INTRODUCTION

Conversion of renewable energy sources such as sunlight, wind, and geothermal heat to clean and sustainable fuels has attracted much attention because of the rapid depletion of fossil fuels and growing environmental concerns. Hydrogen has a great potential as an energy carrier because it does not exhaust carbon dioxide as a combustion product. Hydrogen production via electrochemical water splitting by means of renewable energy is a promising approach. However, the slow kinetics of oxygen evolution reaction (OER, 2H2O → 4H+ + O2 + 4e−) taking place at the counter electrode reduces the total efficiency of the water electrolysis system and therefore needs a high overpotential to generate adequate current. So far, most of the high-performance electrocatalysts for the OER have been made of precious metals, that is, Mo, Ru and Ir. However, their scarcity and toxicity limit their widespread use. Accordingly, it is of prime importance to create cost-effective and highly efficient catalysts composed of much more earth-abundant elements. Over the past decades, tremendous efforts have been made to solve this problem by the use of transition metals (e.g., Co, Ni, Fe, and Mn) to substitute precious metal-based catalysts. Among transition metals, iron, one of the most abundant metals in the earth, has gained limited attention as a catalyst for the OER. Because iron oxyhydroxide (FeOOH) has an open structure and is abundant in the environment and inexpensive, it has been applied to not only catalysts but also supercapacitors and rechargeable batteries. However, the intrinsically poor electrical conductivity of FeOOH (∼10−5 S cm−1) remains the main obstacle to good performance in its electrochemical applications. Pure FeOOH is highly unstable in alkaline electrolyte at high anodic potentials because of its oxidation to a soluble species, FeO. Doping is a commonly used strategy to tune the electrical properties of transition-metal oxides and (oxy)hydroxides, yielding hybrid materials with desired properties in various applications. As a result, binary-metal oxyhydroxides have exhibited an enhancement of the OER activity compared to their parent single-metal species. For example, Swierk et al. reported that iron-doped nickel oxyhydroxide [Fe1−xNix(OH) (x = 0.35)] afforded a current density of 10 mA cm−2 at a small overpotential of 320 mV with a Tafel slope of 48 mV dec−1, although both values changed for the worse with time. Zhang et al. synthesized CoFe1−xOx(OH) (x = 0.54) nanoparticles with an akaganeite structure (β-FeOOH) showing an overpotential of 390 mV to achieve a 10 mA cm−2 current with a Tafel slope of 47 mV dec−1. In both cases, the contents of Ni and Co are larger than that of Fe in the binary-metal oxyhydroxide. Considering that Ni and Co are also classified as scarce metals, their use should be minimized in the design of catalysts. Here, we aim to develop an outstanding OER catalyst consisting of Co-doped iron oxyhydroxide whose Co content is lower than those of any other Fe-based catalysts with comparable catalytic activity.

* Supporting Information

© 2018 American Chemical Society

DOI: 10.1021/acsomega.8b01206
ACS Omega 2018, 3, 7840−7845

Received: June 8, 2018
Accepted: July 2, 2018
Published: July 13, 2018
RESULTS AND DISCUSSION

A series of catalysts were synthesized with different CoSO₄ to FeSO₄ molar ratios in solution. The same molar ratios were confirmed in the resulting products by inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurements. X-ray diffraction (XRD) patterns of the products are depicted in Figure 1. A sample that was synthesized without CoSO₄ exhibited the pattern assignable to goethite-type iron oxyhydroxide (α-FeOOH) (JCPDS no. 29-0173). The same pattern was observed for the samples made with different CoSO₄ concentrations, where no peak shift was accompanied. With an increase in the content of Co, all diffraction peaks were broadened due probably to a decrease in crystalline size. No feature associated with Co oxides/hydroxides was detected. This indicates that Co ions were successfully doped into the lattice of goethite (α-FeOOH) without forming any other phases. Hereafter, the obtained Co-doped products will be denoted as Coₓ(Fe₁−ₓOOH) (x = 0.09, 0.17, and 0.20).

Morphology of the synthesized Coₓ(Fe₁−ₓOOH) powders was investigated by transmission electron microscopy (TEM), and the obtained images are displayed in Figure 2. Spindlelike particles, which are characteristic of α-FeOOH, are seen in Figure 2a, which are ∼1 μm in length and ∼200 nm in width. A similar shape appears in Figure 2b, the size of which decreases with the doping of Co. The images in Figure 2c,d consist of the aggregates of finer particles. This observation agrees well with the broadening of the diffraction peaks in Figure 1.

Figure 1. XRD patterns of the materials synthesized with different CoSO₄/FeSO₄ molar ratios where the FeSO₄ concentration was fixed at 0.8 M: (a) 0, (b) 0.09:0.91, (c) 0.17:0.83, and (d) 0.20:0.80.

Figure 2. TEM images of α-type (a) FeOOH and (b-d) CoₓFe₁−ₓOOH, x = (b) 0.09, (c) 0.17, and (d) 0.20.

Figure 3a shows the linear sweep voltammetry (LSV) curves of the CoₓFe₁−ₓOOH samples coated on a glassy carbon (GC) rotating disk electrode (RDE) (rotation rate: 1600 rpm), which were recorded in an O₂-saturated 1.0 M KOH solution. Here, a slow scan rate of 1 mV s⁻¹ was applied to minimize the capacitive current, while the iR drop between the working and reference electrodes was corrected. For comparison, the commercial RuO₂ powder was subjected to the same test. The contribution from the carbon additives was negligibly small. For OER performance evaluation, the operating potential necessary to reach a current density (j) of 10 mA cm⁻² is often compared. Pure α-FeOOH needed an overpotential of 580 mV to achieve 10 mA cm⁻², corresponding to low activity. Contrary to this, when cobalt was introduced into the catalyst, the overpotential decreased depending on its content, that is, 580 mV (α-FeOOH) > 451 mV (Co₀.₀₉Fe₀.₉₁OOH) > 404 mV (Co₀.₁₇Fe₀.₈₃OOH) > 383 mV (Co₀.₂₀Fe₀.₈₀OOH). Clearly, the doping of Co into α-FeOOH enhanced its catalytic activity toward the OER. It is noteworthy that the Co-doped catalysts showed a monotonous increase in the OER current at more positive potentials, which was not true in the nondoped FeOOH and commercial RuO₂ catalysts. As expected, from the TEM images in Figure 2, the Co doping also led to smaller crystalline sizes and poor crystallinity, which would result in a structure favorable for the diffusion of reactants and products during the OER.

Figure 3. (a) LSV curves of CoₓFe₁−ₓOOH taken in an O₂-saturated 1.0 M KOH solution at a scan rate of 1 mV s⁻¹ and (b) the corresponding Tafel plots.
As indicated in Figure 3b, the linear portion of the Tafel plot was fitted to the Tafel equation ($\eta = b \log j + a$, where $\eta$ is the overpotential and $j$ is the current density) to determine the slope. The OER onset potential was determined from the beginning of linear portion in the Tafel plot, and the values are summarized in Table 1, together with $\eta$ at 10 mA cm$^{-2}$ and Tafel slopes. The Co doping shifted the onset overpotential to less positive values as the Co content increased. The smallest Tafel slope was measured to be 40 mV dec$^{-1}$ for Co$_{0.20}$Fe$_{0.80}$OOH, which is much smaller than those of pure $\alpha$-FeOOH (77 mV dec$^{-1}$), commercial Ru$_{0.3}$O$_{2}$ (66 mV dec$^{-1}$), and other Co-doped FeOOH samples (42–46 mV dec$^{-1}$). Clearly, the Co doping into the goethite lattice can kinetically facilitate the OER process. A further increase in the Co content of the catalyst did not cause a significant improvement in the OER activity. Considering the cost effectiveness, Co$_{0.20}$Fe$_{0.80}$OOH can be regarded as the best catalyst. Table S1 (Supporting Information) summarizes the OER performance of the electrocatalysts composed of pure and mixed oxides and (oxy)hydroxides based on Fe, Co, and Ni, including our catalysts. All data were acquired on the usual GC rod electrode. As seen from this table, the present catalyst (Co$_{0.20}$Fe$_{0.80}$OOH) contains a larger amount of Fe than the others with comparable performance.

To further investigate the OER performance of the catalysts, turnover frequency (TOF) was estimated for pure and Co-doped FeOOH samples. TOF is generally defined as the number of produced molecules per mole of the catalyst per unit time, which can be derived from the following equation:

$$\text{TOF} = \frac{jS}{4nF\eta}$$

(1)

where $j$ is the measured current density (mA cm$^{-2}$) at $\eta = 380$ mV, which is the overpotential required for Co$_{0.20}$Fe$_{0.80}$OOH to achieve a current density of 10 mA cm$^{-2}$, as described above. $S$ is the geometric surface area (0.196 cm$^2$) of the working electrode, $F$ is the Faraday constant (96 485 C mol$^{-1}$), and $n$ is the total molar number of Co and Fe in the catalyst loaded on the GC surface, which was determined based on ICP-AES measurements. The faradaic efficiency for the OER is assumed to be 100%. From the figure, the TOF value at $\eta = 380$ mV was enhanced with increasing the Co content (Table 1), that is, FeOOH (0.00011 s$^{-1}$) < Co$_{0.09}$Fe$_{0.91}$OOH (0.0013 s$^{-1}$) < Co$_{0.17}$Fe$_{0.83}$OOH (0.0055 s$^{-1}$) < Co$_{0.20}$Fe$_{0.80}$OOH (0.0103 s$^{-1}$). The TOF value of 0.0103 s$^{-1}$ observed for Co$_{0.20}$Fe$_{0.80}$OOH is the same order of those obtained for Co$_{0.09}$Fe$_{0.46}$OOH (0.0225 s$^{-1}$ at $\eta = 390$ mV) and Co$_{0.09}$Fe$_{0.33}$OOH (0.0142 s$^{-1}$ at $\eta = 300$ mV) reported in very recent papers. It is generally accepted that when the crystalline size becomes smaller, the electrochemically active surface area (ECSA) increases, and as a result, the OER performance is improved. Thus, we estimated the ECSA of pure and Co-doped FeOOH samples based on the electrochemical double-layer capacitance ($C_{dl}$) taken by using a simple cyclic voltammetry (CV) method because the $C_{dl}$ is proportional to the ESCA. Figure S1 shows the CV curves recorded in the potential region where no faradaic current was observed. The $C_{dl}$ was estimated for each catalyst by plotting the $\Delta j$ ($=j_a- j_c$) where $j_a$ and $j_c$ are the anodic and cathodic current densities at the mid potential, respectively) as a function of the scan rate, as shown in Figure 4. The slope of the straight line is equivalent to twice the double-layer capacitance. The ECSA can be determined from the $C_{dl}$ of the catalyst surface according to eq 2.

$$\text{ECSA} = \frac{C_{dl}}{C_a}$$

(2)

where we used a typical $C_a$ value of 0.040 mF cm$^{-2}$, which was reported for an atomically smooth metal electrode in an aqueous KOH solution. The estimated $C_{dl}$ and ECSA values of all catalysts are included in Table 1, along with their Brunauer–Emmett–Teller (BET) surface areas. As seen from Table 1, Co$_{0.20}$Fe$_{0.80}$OOH coated on a GC substrate provided $C_{dl}$ of 0.80 mF cm$^{-2}$, which is 4.7-fold larger than that (0.17 mF cm$^{-2}$) of pure $\alpha$-FeOOH. However, Co$_{0.20}$Fe$_{0.80}$OOH yielded 91-fold larger current (10 mA cm$^{-2}$) at 383 mV, whereas pure $\alpha$-FeOOH delivered a 0.11 mA cm$^{-2}$ current density. Therefore, the enhancement of the OER performance that we observed cannot simply be associated with the increased ECSA but also another factor as described below. The former can facilitate the access of reactants (OH$^-$) to the electrolyte to the active sites as well as the fast diffusion of reaction products (O$_2$).

To investigate the electron-transfer kinetics of the catalysts, electrochemical impedance spectroscopy (EIS) was carried out. Figure 5 displays the Nyquist plots of the indicated catalysts on a GC electrode obtained at $\eta = 300$ mV [+1.53 V vs reversible hydrogen electrode (RHE)] in KOH solution, where the reaction is governed by the electron transfer. An equivalent circuit model composed of electrolyte resistance ($R_e$), charge-transfer resistance ($R_{ct}$), and constant-phase element was employed for each catalyst. The kinetics of the electrocatalysis taking place on an electrode can be

| Sample         | $\eta$@10 mA cm$^{-2}$ (mV) | $\eta$@onset (mV) | Tafel slope (mV dec$^{-1}$) | TOF (10$^{-3}$ s$^{-1}$) | BET S.A. (m$^2$ g$^{-1}$) | $C_{dl}$ (mF cm$^{-2}$) | ECSA (m$^2$ g$^{-1}$) | $R_e$ (\(\Omega\)) | $R_{ct}$ (\(\Omega\)) |
|----------------|-----------------------------|-------------------|-----------------------------|--------------------------|--------------------------|------------------------|----------------------|----------------------|----------------------|
| $\alpha$-FeOOH | 580                         | 379               | 77                          | 0.01                     | 59.5                     | 0.17                   | 2.35                 | 8.66                 | 33 717               |
| Co$_{0.09}$Fe$_{0.91}$OOH | 451                   | 312               | 46                          | 0.13                     | 109.3                    | 0.51                   | 6.38                 | 9.76                 | 22 503               |
| Co$_{0.17}$Fe$_{0.83}$OOH | 404                   | 315               | 42                          | 0.55                     | 183.3                    | 0.61                   | 7.65                 | 8.22                 | 1187                |
| Co$_{0.20}$Fe$_{0.80}$OOH | 383                   | 304               | 40                          | 1.03                     | 231.6                    | 0.80                   | 9.95                 | 8.19                 | 701                |
reflected in the charge-transfer resistance ($R_{ct}$), and a lower $R_{ct}$ value corresponds to a faster reaction rate. The EIS parameters obtained by fitting the Nyquist plots are summarized in Table 1. The semicircles in the plots of Co-doped catalysts were much smaller than those of the nondoped one, which indicates a much lower charge-transfer resistance, and it decreased in size with an increase in Co content. This is highly accordant with the result of the Tafel slope, indicating that a fast electron transfer can be realized by the doping of Co into the goethite lattice.

Durability is another crucial factor to assess an electrocatalyst. The long-term stability of Co$_x$Fe$_{1-x}$OOH was tested by chronopotentiometry at a constant current density of 10 mA cm$^{-2}$, in comparison with pure $\alpha$-FeOOH, as shown in Figure 6. During the measurements, the electrode was rotated at a speed of 1600 rpm. In $\alpha$-FeOOH, the potential started to increase abruptly after about 1 h, and the catalyst film was peeled off from the substrate. This can be associated with the oxidative dissolution of FeO$_4^{2-}$ at the positive potential. On the other hand, Co$_{0.20}$Fe$_{0.80}$OOH exhibited a nearly unchanged potential over at least 12 h. FeO$_4^{2-}$ could not be formed at such a low overpotential. Figure 6b shows the consecutive CV curves of the Co$_{0.20}$Fe$_{0.80}$OOH electrode obtained at a scan rate of 20 mV s$^{-1}$. All four curves overlapped almost exactly, corresponding to the excellent stability of the catalyst.

CONCLUSIONS

We synthesized nanoparticulate electrocatalysts composed of cobalt-doped goethite-type iron oxyhydroxide ($\alpha$-FeOOH) with the controlled Co to Fe ratio by the simple procedure. The GC-coated Co$_{0.25}$Fe$_{0.75}$OOH catalyst yielded a current density of 10 mA cm$^{-2}$ at a small overpotential of 383 mV in KOH solution, with a small Tafel slope of 40 mV dec$^{-1}$. The OER catalytic performance achieved in this study is comparable to those of the FeOOH composites, which contain much more amount of scarce metals. This can be attributed to the effect of Co doping into the goethite lattice, which causes an increase in the ECSA and a faster electron-transfer kinetics. The catalyst also exhibited excellent durability, essential for practical use.

EXPERIMENTAL SECTION

Materials. All materials were used as received without further purification. A Nafion solution (Nafion 117, ~5% in a mixture of lower aliphatic alcohols and water) and acetylene carbon black (99.99%) were purchased from Sigma-Aldrich and Strem Chemicals, respectively. All other chemicals were obtained from Wako Pure Chemicals. All solutions were prepared with doubly distilled water.

Synthesis of Catalysts. All catalysts were synthesized according to the procedure reported by Kurokawa et al. with minor modification. In brief, a mixed aqueous solution consisting of ferrous sulfate (0.8 M) and sodium carbonate (1.6 M) was prepared, to which cobalt sulfate was added so that the Co/Fe atomic ratio in the solution was from 0 to 0.25. The resulting slurry was aged for 4 h at 47 °C. Nitrogen bubbling was carried out at a constant flow rate of 50 dm$^3$ min$^{-1}$. The slurry was further warmed to 53 °C and aerated at a constant flow rate, 90 dm$^3$ min$^{-1}$, for the purpose of oxidation. The precipitate was filtered out, washed thoroughly with water, and then dried at 120 °C for 3.5 h.

Structural Characterization. XRD patterns were recorded on a Rigaku Ultima IV diffractometer, using Cu Kα radiation ($\lambda = 0.154051$ nm). The data were collected over the 2θ range from 10 to 70° at a scan rate of 1° min$^{-1}$, applying a beam voltage of 40 kV and a beam current of 40 mA. TEM was performed using a JEOL JEM 100S microscope operated at 80 kV. The amounts of Fe and Co were determined based on ICP-AES using an ICAP6500 Duo (Thermo Fisher Scientific). All samples were dissolved with a concentrated HCl/HNO$_3$ mixture in a 3:1 volume ratio to make an aqueous solution. The surface areas of the powder samples were estimated by BET gas adsorption of the catalyst particles, where a Quanta Chrome Multisorb 16 was used.

Electrochemical Measurements. All electrochemical measurements except for electrochemical impedance spectrometry (EIS) were conducted on an HZ-5000 potentiostat.
(Hokuto Denko) in a standard three-electrode configuration. The working electrode was a RDE made of GC (5 mm in diameter) embedded in a Teflon sheath. A Ag/AgCl (saturated KCl) and a platinum mesh were used as the reference and counter electrodes, respectively. Catalyst powder (5.0 mg) and 5.0 mg of carbon were dispersed in a mixture of 95 μL of Nafion solution (5 wt %) and 700 μL of water/ethanol (1:1 in volume) and sonicated for 60 min to form a homogeneous ink. The homogeneous ink (7.8 μL, containing 20 μg of catalyst) was drop-casted onto the RDE with a geometric area of 0.196 cm² (mass loading ~0.20 mg cm⁻²) using a micropipetter, followed by drying in atmospheric conditions for 30 min. To examine the catalytic performance for the OER, LSV measurements were made from the open-circuit potential to +1.0 V versus Ag/AgCl at a slow scan rate of 1 mV s⁻¹ in an aqueous solution of 1.0 M KOH. The electrolyte solution was bubbled with O₂ for at least 30 min. Here, the RDE was rotated at a constant rate of 1600 rpm to minimize mass transport effects. All LSV polarization curves were corrected with iR compensation. The measured potentials versus Ag/AgCl were calibrated to the RHE scale via the Nernst equation:

\[ E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 0.059pH + 0.199 \]  

(3)

Chronopotentiometry and CV were utilized to further evaluate the catalysts in terms of TOF and long-term durability. EIS was conducted in the same three-electrode configuration connected to an SP-150 potentiostat/galvanostat (Biologic Science Instruments). Here, a static GC disk electrode (3 mm in diameter) was used as the working electrode. The homogeneous catalyst ink (2.8 μL) was drop-casted on the GC surface for the same mass loading of 0.20 mg cm⁻². All measurements were carried out at an overpotential of 300 mV (1.53 V vs RHE) with an ac amplitude of 5 mV in a frequency range from 100 mHz to 100 kHz.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01206.

CV curves of pure and Co-doped FeOOH in a 1.0 M KOH solution (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: nkymm@yamaguchi-u.ac.jp* (M.N.)

**ORCID**

Masaharu Nakayama: 0000-0002-5308-0126

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The present work is under the support by the following organizations: Japan Society for the Promotion of Science (grant no. 16KO5938), Electric Technology Research Foundation of Chugoku, and Sasakura Enviro-Science Foundation. The authors gratefully acknowledge all of these supports.

**REFERENCES**

(1) Cook, T. R.; Dogutan, D. K.; Reece, S. Y.; Surendranath, Y.; Teets, T. S.; Nocera, D. G. Solar Energy Supply and Storage for the Legacy and Nonlegacy Worlds. *Chem. Rev.* 2010, 110, 6474–6502.

(2) Dau, H.; Limberg, C.; Reier, T.; Risch, M.; Roggan, S.; Strasser, P. The Mechanism of Water Oxidation: From Electrolysis via Homogeneous to Biological Catalysis. *ChemCatChem* 2010, 2, 724–761.

(3) Trasatti, S. Electrocatalysis in the Anodic Evolution of Oxygen and Chlorine. *Electrochim. Acta* 1984, 29, 1503–1512.

(4) Frame, F. A.; Townsend, T. K.; Chamoussis, R. L.; Sabio, E. M.; Dittrich, T.; Browning, N. D.; Osterloh, F. E. Photocatalytic Water Oxidation with Nonsensitized IrO₂ Nanocrystals under Visible and UV Light. *J. Am. Chem. Soc.* 2011, 133, 7264–7267.

(5) Louie, M. W.; Bell, A. T. An Investigation of Thin-Film Ni-Ir Oxide Catalysts for the Electrochemical Evolution of Oxygen. *J. Am. Chem. Soc.* 2013, 135, 12329–12337.

(6) Trotochaud, L.; Ranney, J. K.; Williams, K. N.; Boettcher, S. W. Solution-Cast Metal Oxide Thin Film Electrocatystes for Oxygen Evolution. *J. Am. Chem. Soc.* 2012, 134, 17253–17261.

(7) Subbaraman, R.; Tripkovic, D.; Chang, K.-C.; Strmcnik, D.; Paulikas, A. P.; Hirnsut, P.; Chan, M.; Gere, J.; Stamenkovic, V.; Markovic, N. M. Trends in Activity for the Water Electrolyser Reaction on 3D M(Ni,Co,Fe,Mn) Hydroxide Catalysts. *Nat. Mater.* 2012, 11, 550–557.

(8) Burke, M. S.; Kast, M. G.; Trotochaud, L.; Smith, A. M.; Boettcher, S. W. Cobalt-Iron (Oxy)hydroxide Oxygen Evolution Electrocatalysts: The Role of Structure and Composition on Activity, Stability, and Mechanism. *J. Am. Chem. Soc.* 2015, 137, 3638–3648.

(9) Chemelewski, W. D.; Lee, H.-C.; Lin, J.-F.; Bard, A. J.; Mullins, C. B. Amorphous FeOOH Oxygen Evolution Reaction Catalyst for Photoelectrochemical Water Splitting. *J. Am. Chem. Soc.* 2014, 136, 2843–2850.

(10) Friebl, D.; Louie, M. W.; Bajdich, M.; Sanwald, K. E.; Cai, Y.; Wise, A. M.; Cheng, M.-J.; Sokaras, D.; Weng, T.-C.; Alonso-Mori, R.; Davis, R. C.; Bargar, J. R.; Nørskov, J. K.; Nilsson, A.; Bell, A. T. Identification of Highly Active Fe Sites in (Ni,Fe)OOH for Electrocatalytic Water Splitting. *J. Am. Chem. Soc.* 2015, 137, 1305–1313.

(11) Jin, W.-H.; Cao, G.-T.; Sun, J.-Y. Hybrid supercapacitor based on MnO₂ and columned FeOOH using Li₂SO₄ electrolyte solution. *J. Power Sources* 2008, 175, 686–691.

(12) Sassin, M. B.; Mansour, A. N.; Pettigrew, K. A.; Rolison, D. R.; Long, J. W. Electroless Deposition of Conformal Nanoscale Iron Oxide on Carbon Nanarchitectures for Electrochemical Charge Storage. *ACS Nano* 2010, 4, 4505–4514.

(13) Xiong, Y.; Xie, Y.; Chen, S.; Li, Z. Fabrication of Self-Supported Patterns of Aligned β-FeOOH, a new positive electrode material for lithium secondary batteries. *J. Power Sources* 1999, 81–82, 221–223.

(14) Feng, X.; Sayle, D. C.; Wang, Z. L.; Parais, M. S.; Santora, B.; Sutorik, A. C.; Sayle, T. X. T.; Yang, Y.; Ding, Y.; Wang, X.; Her, Y.-S. Effective Converting Ceria Polyhedral Nanoparticles into Single-Crystal Nanospheres. *Science* 2006, 312, 1504–1508.

(15) Wang, F.; Han, Y.; Lim, C. S.; Lu, Y.; Wang, J.; Xu, J.; Chen, H.; Zhang, C.; Hong, M.; Liu, X. Simultaneous Phase and Size Control of Upconversion Nanocrystals through Lanthanide Doping. *Nature* 2010, 463, 1061–1065.

(16) Swier, J. R.; Klaas, S.; Trotochaud, L.; Bell, A. T.; Tilley, T. D. Electrochemical Study of the Energetics of the Oxygen Evolution Reaction at Nickel Iron (Oxy)Hydroxide Catalysts. *J. Phys. Chem. C* 2015, 119, 19022–19029.

(17) Zhang, X.; An, L.; Yin, J.; Ji, P.; Zheng, Z.; Du, Y. Effective Construction of High-quality Iron Oxy-hydroxides and Co-doped Iron Oxy-hydroxides Nanostructures: Towards the Promising Oxygen Evolution Reaction Application. *Sci. Rep.* 2017, 7, 43590.

(18) Liu, T.; Liang, Y.; Liu, Q.; Sun, X.; He, Y.; Asiri, A. M. Electrodeposition of Cobalt-sulfide Nanosheets Film as an Efficient Electrocatalyst for Oxygen Evolution Reaction. *Electrochem. Commun.* 2015, 60, 92–96.
(20) Jung, S.; McCrory, C. C. L.; Ferrer, I. M.; Peters, J. C.; Jaramillo, T. F. Benchmarking Nanoparticulate Metal Oxide Electrocatalysts for the Alkaline Water Oxidation Reaction. *J. Mater. Chem. A* 2016, 4, 3068−3076.

(21) Huang, J.; Chen, J.; Yao, T.; He, J.; Jiang, S.; Sun, Z.; Liu, Q.; Cheng, W.; Hu, F.; Jiang, Y.; et al. CoOOH Nanosheets with High Mass Activity for Water Oxidation. *Angew. Chem., Int. Ed.* 2015, 54, 8722−8727.

(22) Abellán, G.; Carrasco, J. A.; Coronado, E.; Romero, J.; Varela, M. Alkoxide-intercalated CoFe-Layered Double Hydroxides as Precursors of Colloidal Nanosheet Suspensions: Structural, Magnetic and Electrochemical Properties. *J. Mater. Chem. C* 2014, 2, 3723−3731.

(23) Han, S.; Liu, S.; Yin, S.; Chen, L.; He, Z. Electrodeposited Co-Doped Fe3O4 Thin Films as Efficient Catalysts for the Oxygen Evolution Reaction. *Electrochim. Acta* 2016, 210, 942−949.

(24) Gao, M.-R.; Cao, X.; Gao, Q.; Xu, Y.-F.; Zheng, Y.-R.; Jiang, J.; Yu, S.-H. Nitrogen-Doped Graphene Supported CoSe2 Nanobelt Composite Catalyst for Efficient Water Oxidation. *ACS Nano* 2014, 8, 3970−3978.

(25) Ye, S.-H.; Shi, Z.-X.; Feng, J.-X.; Tong, Y.-X.; Li, G.-R. Activating CoOOH Porous Nanosheet Arrays by Partial Iron Substitution for Efficient Oxygen Evolution Reaction. *Angew. Chem., Int. Ed.* 2018, 57, 2672−2676.

(26) McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F. Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. *J. Am. Chem. Soc.* 2013, 135, 16977−16987.

(27) He, Z.; Mansfeld, F. Exploring the Use of Electrochemical Impedance Spectroscopy (EIS) in Microbial Fuel Cell Studies. *Energy Environ. Sci.* 2009, 2, 215−219.

(28) Kurokawa, H.; Senna, M. Morphology Control of Goethite Acicular Particles during Aging by Nitrogen Bubbling and Subsequent Reactive Aeration. *J. Mater. Sci.* 2008, 43, 4737−4741.