Electrodeposition of Unary Oxide on a Bimetallic Hydroxide as a Highly Active and Stable Catalyst for Water Oxidation

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S Supporting Information

ABSTRACT: For industrial-scale water electrolysis, development of a highly stable and active oxygen evolution reaction (OER) electrocatalyst is highly demanded. In this study, we report an efficient OER electrocatalyst of CeO_x (unary oxide) and NiFe-OH (bimetallic hydroxide) electrochemically deposited on a macroporous nickel foam substrate. The synthesized electrocatalyst exhibits remarkably improved OER performance by reaching a current density of 100 mA cm⁻² at a low overpotential of 280 mV, which is quite superior to that of most of the previously reported non-noble-metal-based OER electrocatalysts. Furthermore, the developed catalyst demonstrated a minor Tafel slope of 43.2 mV dec⁻¹ with good stability under a large current at a continuous operation of 80 000 s in a strong alkaline electrolyte. Experimental observations revealed that the combination of CeO_x and NiFe-OH accelerates the electroadsorption energies between the electrocatalyst surface and oxygen intermediates, considerably contributing to the OER enhancement. These results undoubtedly represent an important milestone toward the development of efficient OER electrocatalysts for applications as industrial water electrolyzers.

KEYWORDS: electrodeposition, heterogeneous catalysis, oxygen evolution, water electrolysis

INTRODUCTION

Electrochemical water splitting is considered to be one of the best methods to produce hydrogen (H₂), and it is proposed to be a sustainable route to convert water into hydrogen (H₂) and oxygen (O₂).^{1–6} The water splitting reaction typically involves the combination of two half-cell reactions: oxygen evolution reaction (active oxygen evolution reaction (OER): 4OH⁻ → O₂ + 2H₂O + 4e⁻, V_{OER} = -0.40 V vs reversible hydrogen electrode (RHE)) and hydrogen evolution reaction (HER: 2H₂O + 2e⁻ → H₂ + 2OH⁻, V_{HER} = -0.83 V vs RHE).^{7–10} From the kinetic viewpoint, OER, also referred to as water oxidation, is a diverse process because it is a multiproton-coupled four-electron-transfer reaction and restricts the overall efficiency of water splitting.^{11–14} Hence, the development of efficient OER catalysts has become an important frontier for overall water splitting as well as for overcoming the sluggish OER kinetics. Recently, catalysts based on cerium (Ce) and its oxide (CeO₂) have attracted considerable attention as economic alternatives to ruthenium (Ru)- and iridium (Ir)-based catalysts for OER.^{15–23} Moreover, from the results of previous studies, it is promising that CeO₂-based catalysts, such as CeO₂/Ni(OH)₂, Ni_xCe_y@CP, NiFeCeO_x, FeOOH/CeO₂, and CeO₂/NiO, play a crucial role in the OER activity. All of these catalysts demonstrate an analogous phenomenon:

When CeO₂ is alloyed with transition metals, it exhibits higher catalytic activity, corresponding to the higher storage capability of oxygen and generation of strong electronic interactions between different components.^{17–19,23–25} Currently, CeO₂-doped transition metal oxide OER catalysts are predominantly prepared by solution-based methods, including sol-gel synthesis, colloidal synthesis, zeolitic imidazolate frameworks, and solvo- (or) hydrothermal methods.^{19–24} However, solution-based methods pose some serious issues related to the catalyst efficacy. Disadvantages of solution-based systems include (i) lack of control of the nanomaterial size, (ii) non-uniformity of the loading and distribution of the catalyst on a conductive substrate (such as carbon cloth and nickel foam, nickel foam (NF)), (iii) no monitoring of the crystal growth during the synthesis. In addition, this solution-based system is not recommended for industrial applications due to the complicated synthesis procedures.

To overcome these issues, the electrodeposition technique for the synthesis of OER catalysts comes into play. This technique permits the control of the degree of irreversibility of

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the growth process and exploits interatomic interactions of the growth process by controlling the potential. Furthermore, it is a simple process, and it can be significantly promoted for industrial applications.²⁶ Thus far, researchers have employed electrodeposition, and studies have reported an electrodeposited CeO₂ electrocatalyst with a composition of a unary oxide/hydroxide/oxyhydroxide such as NiCeO_x, FeOOH/CeO₂, and CeO₂/Ni(OH)₂.^{15,17,18} Nevertheless, it requires a further enhancement in its performance. For instance, Jia et al. have prepared gold (Au)-supported cerium-doped NiO_x as a water oxidation catalyst and reported the clear improvement in the OER performance via the enhancement of the dopant, i.e., cerium active species; however, NiCeO_x is deposited on an expensive material such as the Au substrate, which is also a flat substrate. Previous studies have reported that a flat substrate comprises restricted available active sites and only scarce farthest layers of the substrate are in contact with the electrolytes.²⁶ Besides, the effervescence generated due to O₂ evolution especially under high current densities be apt to gather on flat substrates, thereby restricting the mass transport.^{26,27} To overcome these obstacles, a nonplanar substrate with porous morphology will be highly desirable to provide a higher surface area. Based on structural engineering, the OER activity of transition metal oxides can be further improved by using multimetallic oxides, which are advantageous due to synergistic metal–metal interactions.^{15,26} In this regard, recently, Obata et al. have depicted this metal–metal interaction by depositing a CeO_x layer on NiFeO_x.²⁵ Nevertheless, scarce enhancement of the OER activity is observed for large-area-coated layers, which restricts the contact between the electrolyte solution and active site centers; thus, it is crucial to focus on boosting the catalytic performance. In summary, a versatile, efficient method to synthesize CeO₂-based catalysts for use in industrial applications is still lacking.

In this work, we developed a composite type of catalyst CeO_x/NiFe-OH on a three-dimensional (3D) macroporous nickel foam (NF) substrate, which combines the features of CeO_x and NiFe-OH, such as outstanding mass-transfer properties, enhanced active sites, energetics for the OER, and mechanical robustness. CeO_x/NiFe-OH was synthesized by a two-step strategy starting with the preparation of NiFe-OH by facial electrodeposition, followed by anodic electrolysis to introduce the CeO_x species into the NiFe-OH coated film. The resulting composite catalyst CeO_x/NiFe-OH exhibited excellent OER activity with a current density of 100 mA cm^{−2} at an overpotential of 280 mV and the lowest Tafel slope of 43.2 mV dec^{−1}. Notably, this composite catalyst exhibited outstanding electrochemical performance without any compromise in the magnitudes of the overpotential as well as the Tafel slope, outperforming previously reported catalysts. In addition, this composite catalyst did not exhibit any noticeable deactivation up to 80 000 s of continuous electrolysis, demonstrating outstanding operational stability.

RESULTS AND DISCUSSION

The OER electrocatalysts of amorphous CeO_x/NiFe-OH films on NF substrates were prepared by a facile, two-step electrodeposition technique. In the current experiment, NF was selected as the substrate primarily because it promotes rapid interfacial electron charge transfer between the water oxidation catalyst and aqueous electrolyte.^{23,28} Furthermore, it exhibited an extremely high specific surface area and integrity

compared with those of conventional free-standing substrates.²⁶ Typically, a NiFe-OH-based film was initially deposited on the NF electrode by the cathodic electrolysis of 3 mM nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and a 3 mM iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O) deposition solution at a fixed cathodic voltage of −1.0 V vs Ag/AgCl for 300 s. Then, CeO_x was incorporated into the NiFe-OH/NF electrode by the application of a fixed anodic potential of +0.5 V vs Ag/AgCl in an aqueous solution comprising 0.1 M cerium nitrate (Ce(NO₃)₃) and 0.1 M ammonium acetate at a pH of ~6.3. Notably, prior to CeO_x deposition, the ammonium acetate solution was bubbled with argon (Ar) for 1 h to eliminate the dissolved oxygen, and at that point, 0.1 M Ce(NO₃)₃ was added. The above process not only eliminated the dissolved oxygen in solution but also prevented the formation of a colloidal suspension of ceria powder during deposition.²⁹ The complete sketch of the electrodeposition process and the film evaluation is schematically illustrated in Figure 1a and expressed as follows (eqs 1–3).^{26,29–31}

Step-1: Electrodeposition of NiFe-OH films on NF

Step-2: Electrodeposition of CeO_x on NiFe-OH films

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Figure 1) were recorded to observe the morphologies of the prepared electrocatalysts. Figure 1b,c shows the SEM images of CeO_x/NiFe-OH/NF under different magnifications: An extremely even morphology through the intact area was observed at lower magnification, whereas “ripple marks” were observed for the nanofilms at higher magnification (Figure 1c). This morphology will probably lead to an effortless mass transport (reactants and oxygen bubbles) during OER. In addition, such nanofilm catalysts can afford more accessible active sites and a considerably rougher surface, significantly decreasing the interaction between gas bubbles and the adhesion of the electrode surface; this decreased interaction and adhesion lead to the increased evolution of the adhered gas products; hence, it is advantageous for electrocatalytic gas evolution.^{18,26,32} The morphology of CeO_x/NiFe-OH deposited on NF catalysts was significantly different from that of NiFe-OH/NF and CeO_x/NF catalysts (Figure S1a,b). Figure 1d shows the high-resolution TEM image of the as-synthesized CeO_x/NiFe-OH film and its corresponding selected-area electron diffraction (SAED) pattern. The as-synthesized CeO_x/NiFe-OH film comprised a highly disordered structure, and typical lattice fringes were not detected, indicative of the amorphous phase of the as-prepared catalysts (Figure 1d). The inset of Figure 1d revealed a diffused halo SAED pattern, indicative of the absence of the nanocrystalline phase; this result confirmed the amorphous phase of the prepared electrocatalyst.²⁶ To confirm

Figure 1. Fabrication and morphological studies of the $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$ catalyst. (a) Schematic of $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$ catalyst preparation using the electrodeposition method, including cathodic electrolysis (step-I) followed by anodic electrolysis (step-II). Reference electrode: Ag/AgCl, counter electrode: Pt. (b, c) Scanning electron microscopy (SEM) images under different magnifications. (d) Transmission electron microscopy (TEM) image of a typical $\text{CeO}_x/\text{NiFe-OH}$ catalyst (the inset shows the corresponding selected-area electron diffraction (SAED) pattern). The TEM sample of the $\text{CeO}_x/\text{NiFe-OH}$ catalyst was scratched off from $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$. (e) Elemental energy-dispersive X-ray spectroscopy (EDX) mapping for Ni, Fe, Ce, and O recorded for the $\text{CeO}_x/\text{NiFe-OH}$ catalyst. Scale bar: 100 μm . (f) The corresponding EDX spectrum. (g) Magnified EDX spectrum of the highlighted region in (f). (h) Elemental atomic percentage estimated from the EDX spectrum.

the presence of Ni, Fe, Ce, and O and to identify the elemental distribution in $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$, energy-dispersive X-ray spectroscopy (EDX) and elemental mapping analyses were carried out. Figure 1e–h shows the resultant images with the composition. Figure S2a–c shows the TEM and elemental mapping images of the bare NiFe-OH catalyst. Pristine NiFe-OH comprised an amorphous phase with the presence of Ni, Fe, and O, further confirming the uniform distribution of NiFe-OH on NF.

To validate the amorphicity of the prepared electrocatalyst, X-ray diffraction (XRD) patterns were recorded in the 2θ range from 20 to 80° (Figure 2a). As reported elsewhere, pristine NF is well known to exhibit broad Bragg's crystallographic peaks at $2\theta = 45.2, 52.4,$ and 76.9° .^{23,26,28,33} From the XRD pattern shown in Figure 2a, new crystalline peaks were not observed, reaffirming the fact that an amorphous phase is present; this result was in accordance with those obtained from TEM and SAED analyses. Previous studies have revealed that

the amorphous nature of $\text{CeO}_x/\text{NiFe-OH}$ on NF can afford a larger surface area and better electrical conductivity, thereby possibly enhancing its catalytic activity.^{10,26,28} To further examine the strong electronic-state interactions between CeO_x and NiFe-OH, X-ray photoelectron spectroscopy (XPS) profiles of $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$, NiFe-OH/NF, and CeO_x/NF were recorded. Figure 2b–f shows the resultant electronic states of Ce 3d, Fe 2p, Ni 2p, and O 1s. The survey spectra clearly confirmed the presence of Ni, Fe, Ce, and O, suggesting the formation of $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$, NiFe-OH/NF, and CeO_x/NF films. The Ni 2p XPS spectra of NiFe-OH and $\text{CeO}_x/\text{NiFe-OH}$ (Figure 2c) were deconvoluted into four peaks, and higher-intensity peaks corresponded to Ni^{2+} and Ni^{3+} .⁶ Notably, the Ni^{2+} and Ni^{3+} peaks corresponding to the $\text{CeO}_x/\text{NiFe-OH}$ catalyst were shifted to lower binding energies due to the incorporation of CeO_x on NiFe-OH, as compared to the NiFe-OH catalyst, which is indicative of the strong electronic interactions between CeO_x and NiFe-OH. Furthermore, Ni^{3+} is typically believed to exhibit favorable catalytic active sites for water oxidation reactions. It was predominant in the electrocatalyst prepared herein.^{18,24} In this scenario, the ratio $\text{Ni}^{2+}/\text{Ni}^{3+}$ in $\text{CeO}_x/\text{NiFe-OH}$ (0.81) was slightly changed in comparison with that in bare NiFe-OH (0.89), which was denoted as the highest concentration of Ni^{3+} in $\text{CeO}_x/\text{NiFe-OH}$ catalysts.²⁴ In the Fe 2p XPS spectra (Figure 2d), peaks were observed at ~ 724.6 eV ($2p_{3/2}$) and ~ 711.7 eV ($2p_{1/2}$), without dramatic changes in the line shape and peak position, confirming the presence of the Fe species as Fe^{3+} in both catalysts.^{17,34} Figure 2e shows the deconvoluted XPS spectra of Ce 3d. The Ce $3d_{3/2}$ component was obtained at the binding energy peaks of 922–913 and 903–893 eV, whereas it is obtained at 877–866 eV in the case of Ce $3d_{5/2}$ components of $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$ and CeO_x/NF films.^{18,19,23,24} These two strong signals confirmed the presence of Ce^{3+} and Ce^{4+} in both samples. Furthermore, the magnified view of the peak positions indicated that Ce^{4+} of $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$ is significantly increased in comparison to Ce^{4+} of CeO_x/NF . The results strongly confirmed the significant electronic rearrangement between CeO_x and NiFe-OH. The O 1s signals corresponding to $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$, NiFe-OH/NF, and CeO_x/NF were observed at 529.2, 530.8, and 532.4 eV, related to Ce–O, Ni–O–Fe, and the adsorbed oxygen species (i.e., hydroxides and water molecules), respectively (Figure 2f).^{14,16,17,35,36} Its relevant deconvoluted spectra indicated that the O 1s signal of $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$ shifts to higher binding energies than those of NiFe-OH/NF and CeO_x/NF . The large positive shift of O 1s in the catalyst samples was indicative of a possible in-depth electronic interaction between CeO_x and NiFe-OH, and this supposition was in agreement with previously reported results.¹⁷

The OER performance was examined in an O_2 -saturated 1 M KOH (pH ~ 13.8) solution at a scan rate of 5 mV s^{-1} . For comparison, bare NF and RuO_2 on glassy carbon (GC) were also examined under the same conditions. $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$ exhibited the best OER performance (Figure 3a). $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$ only required an overpotential (η_{OER}) of 249 mV to reach 20 mA cm^{-2} ; this value is considerably less than those of NiFe-OH/NF (270 mV), CeO_x/NF (351 mV), bare NF (410 mV), and RuO_2/GC (449 mV). Furthermore, to attain a current density of 100 mA cm^{-2} , the $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$ film required a comparatively low overpotential of 280 mV, whereas the NiFe-OH/NF and CeO_x/NF electrodes required overpotentials of 310 and 392 mV, respectively (Figure 3b).

Figure 2. Physical and chemical characterization of $\text{CeO}_x/\text{NiFe-OH/NF}$. (a) XRD patterns of the as-prepared catalysts. The pentagram symbol represents the diffraction peaks of nickel foam. (b) XPS survey spectra. High-resolution XPS spectra of Ni 2p (c), Fe 2p (d), Ce 3d (e), and O 1s (f). Dashed gray lines denote the peak shift in the Ni 2p and O 1s spectra, while no peak shift was observed in the Fe 2p and Ce 3d spectra.

Figure 3. Electrochemical characterization of the prepared catalysts. (a) Polarization curves after iR correction show the OER performance of $\text{CeO}_x/\text{NiFe-OH/NF}$ compared to that of NiFe-OH/NF , CeO_x/NF , bare NF, and commercial RuO_2/GC in an alkaline solution of 1 M KOH (pH ~ 13.8). (b) Overpotential (η) required for $J = 20$ and 100 mA cm^{-2} . (c) Cyclic voltammetry curves (CV) of $\text{CeO}_x/\text{NiFe-OH}$ and NiFe-OH catalysts. (d) Differences in the charging current density ($J_a - J_c$) plotted against scan rates. The linear fitting slope, approximating twice the double-layer capacitance (C_{dl}), was used to represent the electrochemical active surface area. (e) Tafel plots of $\text{CeO}_x/\text{NiFe-OH/NF}$, NiFe-OH/NF , and CeO_x/NF recorded in (a). (f) Nyquist plots of different electrocatalysts recorded at 1.45 V vs RHE.

The decrease in the overpotential apparently corresponded to the introduction of the CeO_x species, which enhanced the overall activity of $\text{CeO}_x/\text{NiFe-OH/NF}$. In addition, the obtained potential of $\text{CeO}_x/\text{NiFe-OH/NF}$ at 100 mA cm^{-2} was even less than those of the state-of-the-art catalysts of IrO_2 and RuO_2 , and it was even considerably less than those of the most reported CeO_2 - and NiFe-OH -based catalysts (Figure S3, Table S1). To investigate the origin of the high catalytic activity of the $\text{CeO}_x/\text{NiFe-OH/NF}$ film, cyclic voltammetry (CV) curves were recorded (Figure 3c). Both catalysts (i.e., $\text{CeO}_x/\text{NiFe-OH/NF}$ and NiFe-OH/NF) exhibited proton-coupled electron-transfer reactions of the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ redox. Oxidation reactions possibly occurred as follows.^{34,37–39}

Step-1: Surface oxidation

Step-2: Hydroxide adsorption

Step-3: Charge transfer

Figure 4. Stability and postcatalytic characterization. (a) Long-term stability measurements of CeO_x/NiFe-OH/NF for 80 000 s at constant potentials of 249 and 270 mV for current densities of 20 and 50 mA cm⁻², respectively. The chemical state in CeO_x/NiFe-OH/NF (after stability) was examined by XPS analysis. (b) Ni 2p, (c) Fe 2p, (d) Ce 3d, and (e) O 1s spectra. O^I, O^{II}, and O^{III} correspond to the oxide ions (CeO_x), hydroxide ions (OH⁻), and lattice oxygen (O²⁻) on the CeO_x/NiFe-OH/NF electrocatalyst surface.

After the incorporation of CeO_x, a positive shift toward the anodic direction was observed, favoring the increment of the Ni²⁺/Ni³⁺ transformation, and an extremely large amount of highly oxidative cation species was formed in the CeO_x/NiFe-OH film (Figure 3c).^{40,41} Moreover, we have also investigated the extent of the Ni²⁺/Ni³⁺ transformation by integrated oxidation peak areas of CeO_x/NiFe-OH and NiFe-OH film.¹⁸ As shown in Figure S4, CeO_x/NiFe-OH was found to have more oxidative cation species as compared to NiFe-OH and eventually yield better electrocatalytic activity in OER. In addition, the embedded CeO_x boosted surface-oxygen ion exchange and electron interactions between neighboring atoms caused by the multivalence state of CeO_x, while Fe³⁺ enhanced the hydroxide adsorption and generated surface defects for coordination species.^{17,41} The above-mentioned aspects can lead to the enhancement of the OER catalytic activity. The electrochemical double-layer capacitance (C_{dl}) values for the CeO_x/NiFe-OH, NiFe-OH, and CeO_x films on NF electrodes were estimated to be 9.1, 7.8, and 2.3 mF cm⁻², respectively (Figures 3d and S5). This result indicated that the

incorporation of CeO_x into NiFe-OH leads to the formation of more active sites than in the control samples, and this larger surface coverage of active sites is one of the reasons for the better OER activity of the CeO_x/NiFe-OH film. By the incorporation of the CeO_x species, the aggregation of interfacial oxygen defects is expected to be enhanced in oxide-based electrocatalysts.²³ To further understand the catalytic kinetics of the as-prepared catalyst, Tafel slopes determined from the polarization plots of Figure 3a are shown in Figure 3e. CeO_x/NiFe-OH/NF films also exhibited the lowest Tafel slope (43.2 mV dec⁻¹), while NiFe-OH/NF and CeO_x/NF exhibited Tafel slopes of 44.1 and 55.7 mV dec⁻¹, respectively, confirming more rapid OER kinetics for the CeO_x/NiFe-OH/NF films. This conclusion can be further examined by electrochemical impedance spectroscopy (EIS). The charge-transfer resistance (R_{ct}) of CeO_x/NiFe-OH was less than those of NiFe-OH and CeO_x films, indicating that CeO_x/NiFe-OH exhibits a considerably higher electron transport ability for OER (Figure 3f). Furthermore, to examine the stability of the CeO_x/NiFe-OH catalyst, chronoamperometric measurements were carried out for 80 000 s at constant applied potentials of 249 mV (20 mA cm⁻²) and 270 mV (50 mA cm⁻²). The CeO_x/NiFe-OH films exhibit negligible degradation during continuous operation over 80 000 s, confirming their excellent stability as can be seen in Figure

4a. Also, we performed 5000 continuous cyclic voltammograms (CVs) for the $\text{CeO}_x/\text{NiFe-OH}$ catalyst between 1.2 to 1.7 V vs RHE. The linear sweep voltammetry (LSV) curves of $\text{CeO}_x/\text{NiFe-OH}$ before and after 5000 CVs were identical with each other, which further confirm their excellent durability. (Figure S6). The surface morphology of $\text{CeO}_x/\text{NiFe-OH}$ (Figure S7a,b) still maintained a homogenous distribution of $\text{CeO}_x/\text{NiFe-OH}$ on NF after the stability test of 80 000 s at an overpotential of 249 mV. XPS results (Figures 4b–e and S8) revealed no obvious change in the electronic interactions between CeO_x and NiFe-OH , confirming the high structural stability of the $\text{CeO}_x/\text{NiFe-OH}$ catalyst.

Furthermore, the amount of O_2 released on the $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$ electrode as a function of time was examined at a constant current density of 4 mA cm^{-2} using a Hoffman electrolysis apparatus²² and compared with the volumes calculated by theory (see the Supporting Information for the theoretical calculation). Experimental data were in good agreement with the theoretically calculated volumes of O_2 , indicative of a Faradaic efficiency of nearly greater than 95% (Figure 5a). In addition, the inherent OER catalytic activities

Figure 5. (a) Evolution of O_2 gas on the $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$ electrode over 120 min recorded at 4 mA cm^{-2} . (b) TOF of the as-deposited $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$ electrocatalyst. (c) TOFs of $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$ compared with those of the recently reported transition-metal-based catalysts such as $\text{NiCeO}_x\text{-Au}$ (ref 4a), $\text{NiCeO}_x\text{-GC}$ (ref 4a), $\alpha\text{-Ni(OH)}_2$ (ref 17), $\gamma\text{-CoOOH}$ (ref 18), Pt/C (ref 17), $\text{Fe-Co}_3\text{O}_4/\text{Fe-Co-Bi/CC}$ (ref 19), Ru^0/CeO_2 (ref 4h), and RuO_2 (ref 17). (d) OER process of the $\text{CeO}_x/\text{NiFe-OH}$ catalysts.

of $\text{CeO}_x/\text{NiFe-OH}$ were investigated by the calculation of the turnover frequency (TOF), supposing that almost all of the metal sites participated in the electrochemical reaction. The TOF of $\text{CeO}_x/\text{NiFe-OH}$ was 0.0684 s^{-1} at an overpotential (η) of 280 mV (Figure 5b); this value is reasonably low and comparable to those reported previously (Figure 5c) for transition-metal-oxide-based catalysts, i.e., $\text{NiCeO}_x\text{-Au}$ (0.0795 s^{-1} at $\eta = 280 \text{ mV}$),¹⁵ $\text{NiCeO}_x\text{-GC}$ (0.0052 s^{-1} at $\eta = 280 \text{ mV}$),¹⁵ $\alpha\text{-Ni(OH)}_2$ (0.0361 s^{-1} at $\eta = 350 \text{ mV}$),⁴² $\gamma\text{-CoOOH}$ (0.09 s^{-1} at $\eta = 300 \text{ mV}$),⁴³ Pt/C (0.0053 s^{-1} at $\eta = 350 \text{ mV}$),⁴² $\text{Fe-Co}_3\text{O}_4/\text{Fe-Co-Bi/CC}$ (0.14 s^{-1} at $\eta = 400 \text{ mV}$),⁴⁴ Ru^0/CeO_2 (0.004 s^{-1} at $\eta = 350 \text{ mV}$),²² and RuO_2 (0.0104 s^{-1} at $\eta = 350 \text{ mV}$).⁴² From this collective data, $\text{CeO}_x/$

NiFe-OH is confirmed to be an efficient electrocatalyst toward water oxidation.

To understand the reason for the enhanced catalytic activity of $\text{CeO}_x/\text{NiFe-OH}$ films, it is crucial to understand the OER mechanism. The most common OER mechanism under alkaline conditions is given below^{12,45}

Here, S denotes the active site on the catalyst surface. Notably, the OER activity mainly depended on the electroadsorption energies between the electrocatalyst surface and oxygen intermediates (such as peroxides and superoxides).

Similar to that reported previously, in this study, highly oxidative cations ($\text{Ni}^{3+}/\text{Fe}^{3+}$) are also thought to be the main active sites.^{40,41} According to earlier studies based on density functional theory calculations and experimental results, the presence of Fe sites in a conductive host matrix leads to a more disordered local structure as well as an ideal binding energy with oxygen intermediates ($-\text{OH}$ and $-\text{OOH}$).^{41,46} The enhanced OER activity of the $\text{CeO}_x/\text{NiFe-OH}$ catalyst was probably related to the activation of the more conductive Ni(III)OOH phase (compared to the nonconductive Ni(II)-OH phase) and to the charge-transfer effects from the CeO_x species (Figure 5d). Doping with CeO_x also shortened the bond distance of the host lattice (NiFe-OH) due to the higher oxidation state, thereby yielding the optimized bond strength of S-OH/S-OOH and leading to the optimal OER performance.

CONCLUSIONS

In summary, a 3D porous network of a $\text{CeO}_x/\text{NiFe-OH}$ electrode on NF was successfully fabricated by two-step simple electrodeposition. The electrochemical OER performance of the as-synthesized electrode revealed high catalytic activity by achieving a high current density of 100 mA cm^{-2} at an overpotential of 280 mV, with a low Tafel slope of 43.2 mV dec^{-1} . The high catalytic activity corresponded to the embedding of CeO_x into NiFe-OH , leading to the modulation of the electronic structures of catalytic active sites. Besides the good catalytic activity, the electrode also exhibited excellent stability in an alkaline medium. Working with CeO_x -based catalysts, advantages such as a large amount of surface-active sites, reduced size of catalyst, and lower regulation of Ce-O and Ce-Ce to promote the activation of adsorbed water can be exploited. Therefore, developing catalysts with CeO_x is expected to be beneficial for industrial-level water splitting.

EXPERIMENTAL SECTION

Materials. Precursors such as iron(III) nitrate nonahydrate ($\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$), nickel(II) nitrate hexahydrate ($\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cerium(III) nitrate hexahydrate ($\text{Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O}$), ammonium acetate ($\text{CH}_3\text{COONH}_4$), and potassium hydroxide (KOH) pellets obtained from Sigma-Aldrich were used as received. Nickel foam (>99.99%, $80 \mu\text{m}$) was acquired from MTI Korea. The entire experiment was performed using Milli Q water with a conductivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$.

Electrodeposition of the $\text{CeO}_x/\text{NiFe-OH}/\text{NF}$ Film. The $\text{CeO}_x/\text{NiFe-OH}$ film on nickel foam (NF) was prepared by electrodeposition according to a method described elsewhere.^{26,29} In a

typical procedure, NF ($2 \times 4 \text{ cm}^2$) was initially subjected to ultrasonication in a 3 M HCl solution for 20 min to eliminate unwanted surface-oxide layers. The acid-treated NF was eroded with water and ethanol and subsequently dried in air. A three-electrode cell assembly was used for deposition in which NF, Pt gauze, and saturated Ag/AgCl were used as the working, counter, and reference electrodes, respectively. An aqueous solution of 3 mM $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 3 mM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used as the electrolyte solution. The deposition potential was maintained at -1.0 V (vs Ag/AgCl) for 300 s at ambient temperature. After deposition, the substrate NF was carefully removed from the electrolyte, washed with water, and immersed in a freshly prepared aqueous solution of $\text{Ce}(\text{NO}_3)_3$ (0.1 M) and ammonium acetate (0.1 M) under argon. Prior to the deposition of CeO_x , the electrolyte bath was prepared using a 0.1 M ammonium acetate solution, and after complete dissolution, the aqueous solution was bubbled with Ar for 60 min to remove the dissolved oxygen in the solution. Then, the 0.1 M $\text{Ce}(\text{NO}_3)_3$ solution was included under constant magnetic stirring for 15 min to ensure homogeneity. The above-mentioned anodic electrolysis was carried out at a constant potential of $+0.5 \text{ V}$ vs Ag/AgCl for 600 s. The film thus formed was referred to as $\text{CeO}_x/\text{NiFe-OH}$. Finally, the resultant electrodeposited NF was appropriately removed from the deposition bath, rinsed with water and ethanol, and dried under hot air conditions. The loaded catalyst was weighed using a high-precision microbalance (CAS analytical balance, CAX200). The starting and final weights of NF were calculated before and after the deposition of the $\text{CeO}_x/\text{NiFe-OH}$ catalysts. The loading of the measured $\text{CeO}_x/\text{NiFe-OH}$ catalyst was $\sim 1.92 \text{ mg cm}^{-2}$. For comparison, NiFe-OH/NF and CeO_x/NF films were also prepared under the same procedure in the absence of the respective deposition bath.

For comparison, the OER performance of noble-metal catalyst RuO_2 on a glassy carbon (GC) electrode was studied using a procedure (drop-casting method) similar to that reported in our previous work.¹⁰ Briefly, 12 mg of the RuO_2 powders was dispersed in a 2 mL mixture solution (120 μL of 5% Nafion solution, 800 μL of deionized water, and 1.08 mL of ethanol) and then the mixture was continually sonicated for 30 min to form a stable suspension. Eventually, 6 μL of obtained ink was dropped on the GC electrode and dried in ambient air. The amount of RuO_2 onto the GC electrode was 2 mg cm^{-2} .

Material Characterization. XRD patterns were recorded on a Rigaku X-ray diffractometer with a Cu $K\alpha$ emission wavelength λ of $1.514 \text{ \AA}$. XPS profiles were recorded on a Thermo VG scientific X-ray photoelectron spectrophotometer. The morphology, elemental distribution, and composition were examined by field-emission scanning electron microscopy (HITACHI S-4800 microscope) and HR-TEM (JEOL JEM-2100F microscope) analyses.

Electrochemical Characterization. OER analyses were conducted in a 1 M KOH (O_2 saturated) solution using a Gamry Reference 3000 electrochemical workstation at room temperature. In a standard three-electrode cell, a graphite rod, Hg/HgO (in 1 M NaOH), and electrodeposited $\text{CeO}_x/\text{NiFe-OH}$, NiFe-OH , and CeO_x on NF were used as the counter, reference, and working electrodes, respectively. The reference electrode was calibrated against a reversible hydrogen electrode (RHE), and the applied potential values were converted to the RHE scale using the following equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.931 \text{ V}$. All voltages were iR (where R and i represent the electrolyte resistance and current, respectively) amended by EIS ($E_{\text{corrected}} = E_{\text{raw}} - iR$), and the LSV curve was recorded at potentials ranging from 1.0 to 1.8 V vs RHE at a slow and steady scan rate of 5 mV s^{-1} . EIS for electrocatalysts was carried out under 1.45 V vs RHE (frequency range: 1–100 kHz, AC signal amplitude: 25 mV). Chronoamperometry was carried out under the same experimental setup without iR drop compensation. The electrochemical surface area was determined using the capacitive current associated with the double-layer charging from the voltamogram scan rate. C_{dl} values were employed by plotting the negative and positive current density differences ($\Delta j = j_a - j_c$) as a function of the CV scan rates ($10\text{--}50 \text{ mV s}^{-1}$) within the electrochemical potential

window between 1.10 and 1.20 V vs RHE. The linear slope is twice of the double-layer capacitance is equal to one half of the linear slope.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acssuschemeng.9b03496](https://doi.org/10.1021/acssuschemeng.9b03496).

SEM and TEM images; XPS data; cyclic voltammograms; turnover frequency and theoretical volume of oxygen calculation (PDF)

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Notes

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