MOF-Derived $CoSe_2$@NiFeOOH Porous Arrays for Efficient Oxygen Evolution Reaction

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Keywords: Oygen evolution reaction; NiFeOOH; Water electrolysis; Selenidation; CoSe2

Article

MOF-Derived $CoSe_2$@NiFeOOH Porous Arrays for Efficient Oxygen Evolution Reaction

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Abstract: Water electrolysis is a compelling technology for the production of environmentally-friendly hydrogen, minimizing carbon emissions. The electrolysis process of water heavily relies on the effective and steady oxygen evolution reaction (OER) taking place at the anode. Herein, we introduce a highly promising catalyst for OER called $CoSe_2$@NiFeOOH arrays, which are supported on a nickel foam. This catalyst, referred to as $CoSe_2$@NiFeOOH/NF, is fabricated through a two-step process involving the selenidation of a Co-based porous metal organic framework and subsequent electrochemical deposition on a nickel foam. The $CoSe_2$@NiFeOOH/NF catalyst demonstrates outstanding activity for the OER in an alkaline electrolyte. It exhibits a low overpotential (η) of 254 mV at 100 mA cm^{-2}, a small Tafel slope of 73 mV dec^{-1}, and excellent high stability. The high performance of $CoSe_2$@NiFeOOH/NF can be attributed to the combination of the high conductivity of the inner layer and the synergistic effect between $CoSe_2$ and NiFeOOH. This study offers an effective method for the fabrication of highly efficient catalysts for the OER.

Keywords: Oygen evolution reaction; NiFeOOH; Water electrolysis; Selenidation; $CoSe_2$

1. Introduction

The storage of renewable energy presents a significant challenge in constructing an environmentally-friendly energy system. [1–6] Water electrolysis has become a promising technology for storing electricity generated from renewable sources by converting it into clean energy carrier, H_2. It involves two distinct half-reactions: the hydrogen evolution reaction (HER) occurring at the cathode and the oxygen evolution reaction (OER) taking place at the anode. [7–10] Relative to the HER, the OER suffers from a much more sluggish kinetic, which requires highly efficient electrocatalysts. Thus far, IrO_2 and RuO_2 represent the state-of-the-art OER electrocatalysts because of their high activity and stability. [11–16] However, the high cost and scarcity of these resources limit their extensive utilization. [12,17–19] Therefore, it is crucial to develop alternative, affordable electrocatalysts that are abundant in the Earth's crust. Transition-metal chalcogenides (TMCs) with the formula M_xC_y (M = Fe, Co, Ni; C = S, Se) have gained significant interest for high performance in OER catalysis, as well as their low-cost and abundance in the Earth's crust.[20] Yang Shao-Horn and colleagues conducted a catalytic analysis of perovskite oxide, where they elucidated a correlation between OER activity and the occupancy of 3d electrons with eg symmetry in transition metal cations on the surface. Their findings revealed that an optimized OER electrocatalyst possesses an eg occupancy of approximate one. [21] Liu et al. applied this principle to explain the high OER activity of $CoSe_2$ which exhibits $t_{2g}6e_g1$ electronic configuration, approaching the optimal eg filling. [22,23] However, they overlooked the surface reconstruction or oxidation of $CoSe_2$ under the OER catalysis. The surface oxidation of $CoSe_2$ would theoretically lead to the generation of Co oxides or hydroxides on the $CeSe_2$ surface. This indicates that the actual catalytic phase is the Co oxides/hydroxides rather than the $CoSe_2$. Therefore, the inner $CoSe_2$ serves as an electron-transfer conductor, and is also probably influence the electronic structure of the surface Co oxides/hydroxides.

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Based on the above analysis, we incline to believe that the high OER catalytic performance of $CoSe_2$ may results from the synergistic effect of the surface oxides and the inner $CoSe_2$. Since NiFeOOH species have been recognized as very efficient OER electrocatalysts both from the theoretical calculations and experimental investigations, [24,25] we proposed to fabricate thin NiFeOOH onto $CoSe_2$ surface, aiming to achieve an optimized OER performance through the synergistic effect of NiFeOOH and $CoSe_2$. To increase the accessibility of $CoSe_2$, we prepared it by selenidation of a Co-based metal-organic framework (MOF) array grown on Ni foam. [23,26] The deposition of NiFeOOH onto $CoSe_2$ was achieved through electrochemical deposition. The $CoSe_2$@NiFeOOH/NF composite exhibited high performance in alkaline electrolytes for the OER, demonstrating an overpotential of 254 mV at a current density of 100 mA cm^{-2} and a Tafel slope of 73 mV dec^{-1}. Furthermore, it showed excellent stability with negligible current density decay after 100 hours of operation. The high OER activity can be attributed to the increased exposure of active sites, and the synergistic effect of NiFeOOH out layer and $CoSe_2$ inner layer.

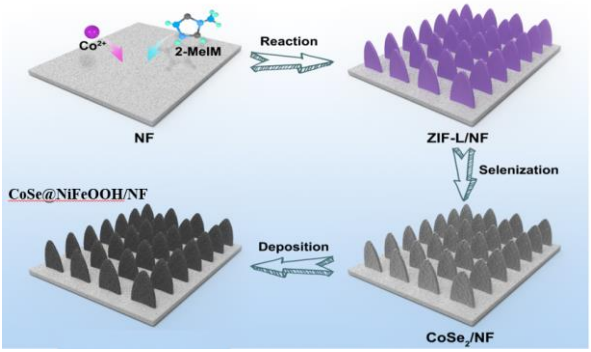

Figure 1. Schematic illustration of the routes to $CoSe_2$@NiFeOOH/NF.

2. Experimental Section

2.1. Materials

$Co(NO_3)_2{\cdot}6H_2O$, 2-methylimidazole (2-MeIM, 99%), $Ni(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, sodium borohydride ($NaBH_4$), selenium powder (Se) and absolute ethanol were purchased from Aladdin. The Ni Form was obtained from J&K Chemical Technology and subsequently subjected to sonication with acetone, ethanol, and deionized water for 30 minutes each prior to use.

2.2. Preparation of cobalt-based ZIF-L/NF

Initially, a solution of 2×10^{-3} mol Co $(NO_3)_2$ and another solution of 1.6×10^{-2} mol 2-MeIM were prepared by dissolving them individually in 40 mL of deionized water in a beaker. Then, the two solutions were combined by stirring. Subsequently, a nickel foam (NF) measuring 2×3 cm was immersed in the mixture and left at room temperature for 4 hours to generate ZIF-L/NF. To prepare it for future use, ZIF-L/NF was subjected to three rounds of rinsing with both ethanol and deionized water. Subsequently, it was dried overnight in an oven at 60 ºC.

2.3. Synthesis of $CoSe_2$/NF

The ZIF-L/NF selenidation process was carried out using a hydrothermal method. Initially, 60 mg of $NaBH_4$ was completely dissolved in 25 mL of deionized water. Subsequently, 20 mg of selenium powder was added to the solution. The mixture was continuously stirred for 40 minutes until a light-yellow solution was formed. The solution was then transferred into a Teflon-lined stainless-steel autoclave, and a ZIF-L/NF sample with dimensions of 1 cm × 1.5 cm was immersed in the solution. The autoclave was kept at a temperature of 180°C for a duration of 8 hours. Afterward, the resulting $CoSe_2$/NF product was rinsed with ethanol and water, and finally dried in an oven at a temperature of 60°C for 12 hours.

2.4. Synthesis of $CoSe_2$@NiFeOOH/NF

The $CoSe_2$@NiFeOOH/NF composite was synthesized by electrochemically deposition with $CoSe_2$/NF as the working electrode in a solution containing $Ni(NO_3)_2$ and $Fe(NO_3)_3$ (molar ratio of Ni^{2+}/Fe^{3+}= 4:1). The electrochemical deposition was conducted at a constant potential of -1.4 V vs. RHE for 8 seconds.

2.5. Characterization

X-ray power diffraction (XRD) data were recorded on Bruker D8 ADVANCE DAVINCI. The morphologies and nanostructures were probed by field-emission scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, Tecnai F20, JEM-ARM200F). The surface chemical valences of the samples were analyzed by X-ray photoelectron spectroscopy (XPS) (Axis SUPRA Kratos).

2.6. Electrocatalytic measurement

The electrochemical measurements were conducted on a CHI760E electrochemical workstation. The as-prepared samples served as the working electrode (geometric area: 1.0 cm^2). The counter electrode was a Pt mesh with dimensions of 1 cm × 1 cm, and an Ag/AgCl electrode was used as the reference electrode. A 1.0 M KOH electrolyte was utilized. To convert the measured potentials to the reversible hydrogen electrode (RHE) scale, the following equation was used: $E_{RHE} = E_{Ag/AgCl} + 0.059$ pH+ 0.197 V. Linear sweep voltammetry (LSV) curves were measured at a scan rate of 5 mV s^{-1}, while cyclic voltammetry (CV) curves were recorded at scan rates ranging from 10 to 50 mV s^{-1}. Electrochemical impedance spectra (EIS) were measured at 1.52 V vs.RHE. All polarization curves were IR-corrected. The double-layer capacitances were determined by analyzing the CV curves obtained at different scan rates, ranging from 10 to 50 mV s^{-1}. The stability of the electrocatalyst was evaluated through chrono-amperometry performed at a constant potential. Faraday efficiency (FE) was determined using the bubbling method, following the formula: $FE = 4 \times F \times V/(1000 \times V_m \times It)$, where V is the rising volume (mL) of the soap bubble over time t, I is the current density (It representing the total number of charges transferred under constant current), Vm is the molar volume (24.5 L mol^{-1} at 25 °C), and F is the Faraday constant (96485 C mol^{-1}).

3. Results and Discussion

ZIF-L was deposited onto NF prepared by facilely immersing NF into a solution of cobalt nitrate and 2-methylimidazole at room temperature. The morphology of the ZIF-L/NF sample was analyzed bySEM, which allows for detailed imaging of the sample surface at high magnification. The crystal structure of the synthesized catalyst was determined using powder XRD. Figure 2a, d, and g illustrate the triangular ZIF-L plates with smooth surfaces vertically aligned on the NF. The sharp diffraction peaks at 44.5°, 51.9°, and 76.2° are attributed to the Ni substrate, and the peak at 29.4° belongs to ZIF-L. This confirms the successful fabrication of ZIF-L on NF. After selenization, ZIF-L transformed into $CoSe_2$ phase while maintaining its morphology, except that the surface became rougher (Figure 2b, e, and h). Subsequently, NiFeOOH was electrochemically deposited onto $CoSe_2$, resulting in a morphological change where $CoSe_2$ formed an array with increased surface roughness and additional folds. XRD analysis of the $CoSe_2$@NiFeOOH/NF sample showed no visible peaks except those of the Ni substrate, suggesting the amorphous structure in the NiFeOOH layer. [27] The absence of XRD signals for $CoSe_2$ demonstrates that a relatively compact NiFeOOH layer is formed on the $CoSe_2$ surface. The three-dimensional $CoSe_2$@NiFeOOH can aid in the transportation of electrolytes and the diffusion of reactive gases, thereby accelerating the reaction process. [27]

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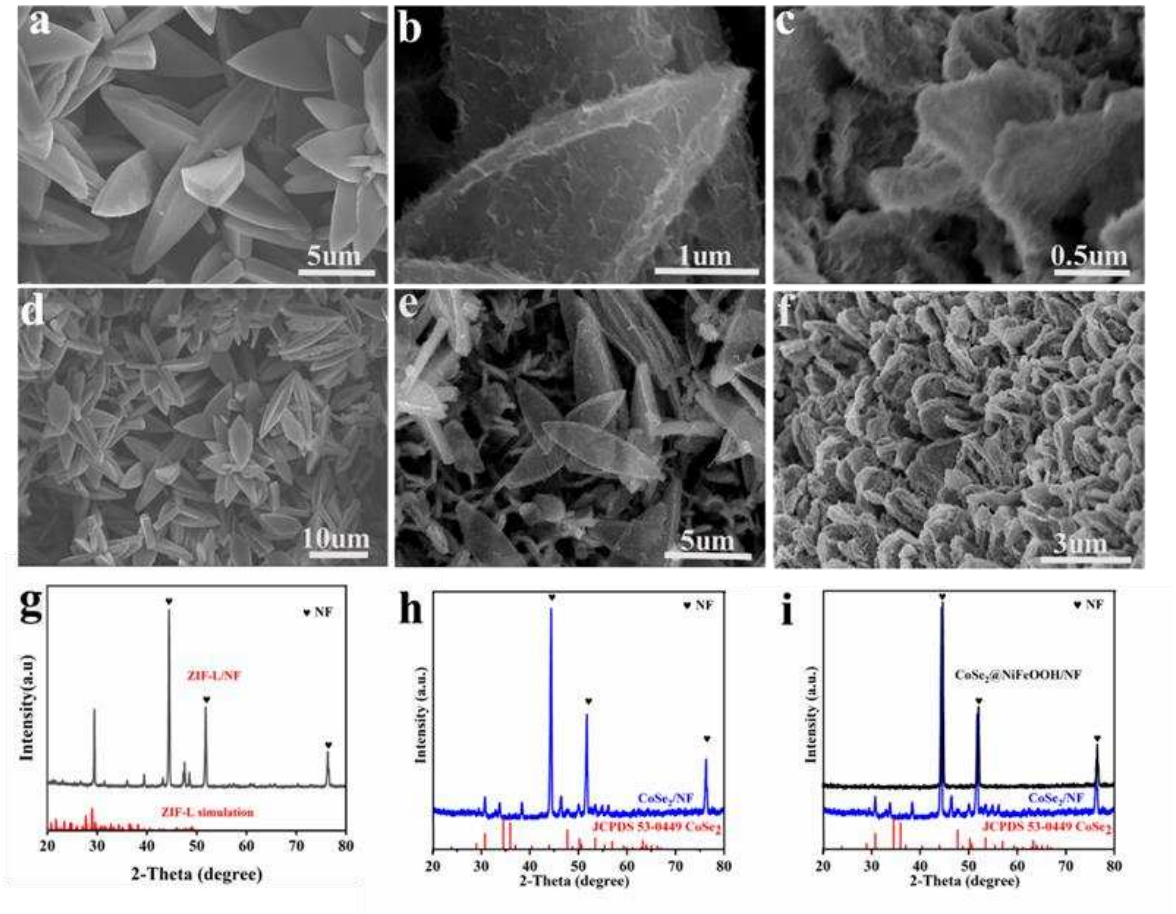

Figure 2. SEM images of (a, d) ZIF-L, (b, e) $CoSe_2$ and (c, f) $CoSe_2$@NiFeOOH/NF. XRD pattern of (g) ZIF-L/NF, (h) $CoSe_2$/NF, (i) $CoSe_2$@NiFeOOH/NF.

The detailed morphology of $CoSe_2$@NiFeOOH was further characterized by TEM. Figure 1a shows that $CoSe_2$@NiFeOOH possesses a thin-leaf like morphology. The weak polycrystalline rings in the selected area electron diffraction (SAED) pattern (Figure 2c) indicate the poor crystallization of these thin-leaf structures in the single derived $CoSe_2$@NiFeOOH. (Figure 2c). The structure of $CoSe_2$@NiFeOOH/NF was precisely characterized using high-resolution TEM (HRTEM). At the top surface of $CoSe_2$@NiFeOOH, two fringes with lattice spacings of 0.259 and 0.223 nm are observed, corresponding to the (111) and (210) planes of $CoSe_2$, respectively. Elemental mapping images demonstrate the homogeneous dispersion of Ni, Fe, Co, Se, and O elements throughout the entire $CoSe_2$@NiFeOOH/NF.

X-ray photoelectron spectroscopy (XPS) measurements were performed to analyze the elemental composition and chemical valence states of the as-prepared $CoSe_2$@NiFeOOH/NF. As shown in Figure 3a, two peaks centered at 855.7 and 873.5 eV were identified as the main peaks corresponding to oxidized Ni $2p_{3/2}$ and Ni $2p_{1/2}$, respectively. Another two peaks at 861.2 and 879.3 eV were attributed to the shakeup satellite peak. [28] Figure 3b displays the Co $2p_{1/2}$ and Co $2p_{3/2}$ peaks, which can be further divided into four peaks located at 796.8/780.8 eV (Co^{2+}) and 783.8/802.2 eV (Co^{3+}). This suggests that the Co atom in $CoSe_2$@NiFeOOH/NF is predominantly in the valence states of +2 and +3. [28] In the XPS spectra of Fe 2p (Figure 3c), two characteristic peaks at 712.9 and 726.1 eV correspond to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively, indicating the presence of Fe^{3+}. [29] The findings collectively indicate that Ni and Fe exist as Ni and Fe oxidation states in $CoSe_2$@NiFeOOH/NF. Furthermore, the analysis of the Se 3d peak reveals that the peak at 54.5 eV corresponds to Se 3d in $CoSe_2$@NiFeOOH/NF, and the presence of a peak at 59.2 eV indicates bonding between Se and O, confirming the surface oxidation of Se species. [30–33]

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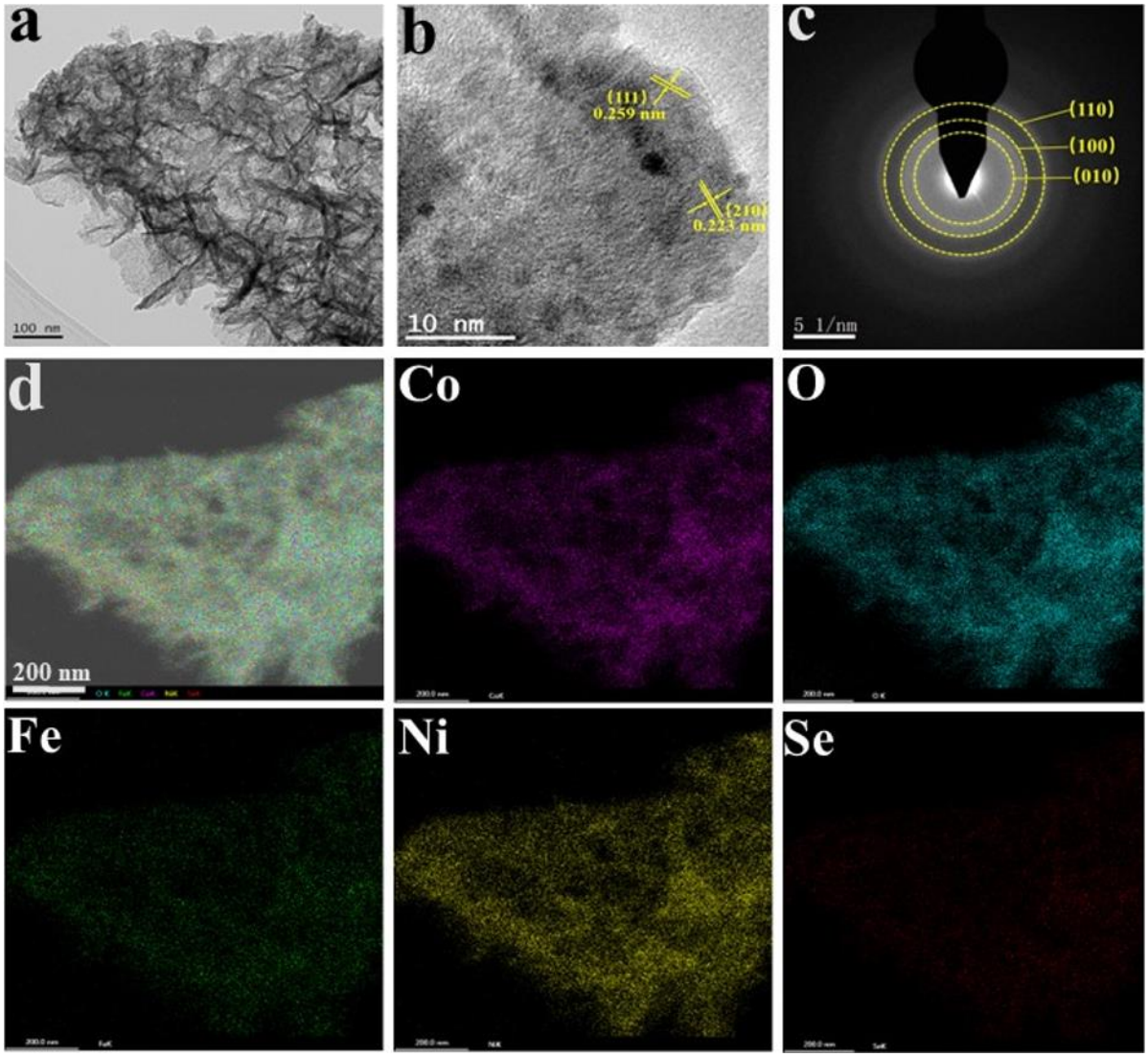

Figure 3. (a) TEM, (b) HRTEM, (c) SAED pattern, and (d) STEM images and the corresponding elemental mapping images of Co, O, Fe, Ni and Se of $CoSe_2$@NiFeOOH/NF.

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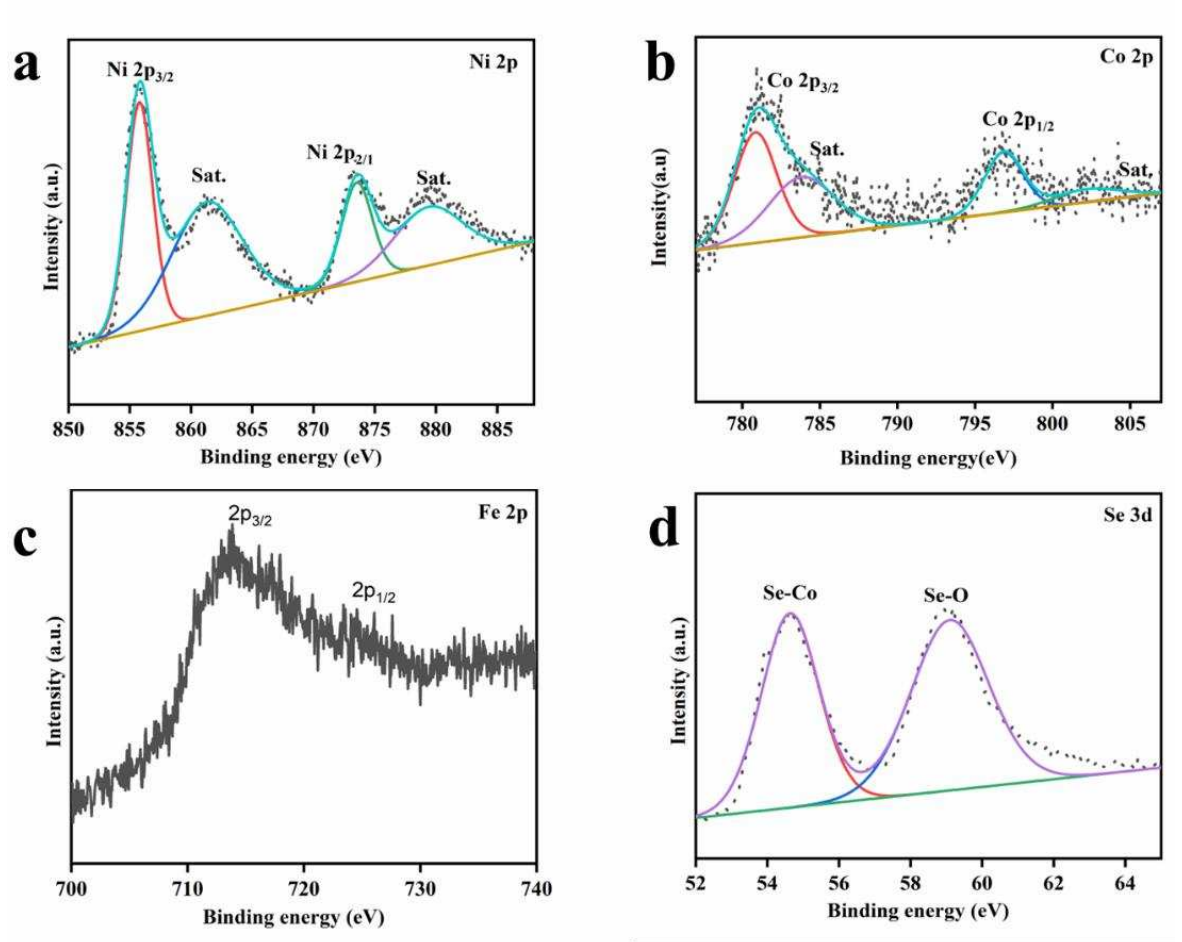

Figure 4. High-resolution XPS spectra of $CoSe_2$@NiFeOOH/NF.

The catalysts' OER performance was assessed using an electrochemical three-electrode system in a 1 M KOH alkaline solution. As shown in Figure 5a, $CoSe_2$@NiFeOOH/NF exhibits an overpotential of 254 mV at 100 mA cm^{-2}, which is significantly lower than that of $CoSe_2$/NF, NiFe-LDH/NF, NF/Selenization, $CoSe_2$@NiOOH/NF, and $CoSe_2$@FeOOH/NF. The OER activity of $CoSe_2$@NiFeOOH/NF is also among the best OER electrocatalysts reported. (Table S1). The Tafel slopes of the four samples, namely $CoSe_2$@FeOOH/NF, $CoSe_2$@NiOOH/NF, $CoSe_2$/NF, and $CoSe_2$@NiFeOOH/NF, were calculated to analyze their kinetics. As shown in Figure 5c, $CoSe_2$@NiFeOOH possesses the smallest Tafel slope of 73 mV dec^{-1}, much smaller than those of $CoSe_2$@FeOOH/NF (102 mV dec^{-1}), $CoSe_2$/NF (119 mV dec^{-1}) and $CoSe_2$@NiOOH/NF (126 mV dec^{-1}), suggesting a faster OER kinetics. To gain further insight into the kinetics of electron transfer, EIS measurements were performed. Figure 5b displays the Nyquist plots of all the samples. Notably, the $CoSe_2$@NiFeOOH/NF sample exhibits the smallest diameter of the semicircle in the high frequency region, which unequivocally confirms the presence of charge-transfer resistance (R_{ct}). This resistance facilitates smooth charge transfer, ultimately resulting in excellent oxygen evolution reaction (OER) activity. Additionally, to understand the intrinsic catalytic activity of $CoSe_2$@NiFeOOH/NF for OER, the electrochemical surface area (ECSA) was estimated by measuring the double-layer capacitance (C_{dl}) in the potential range of 1.07-1.17 V at scan rates ranging from 10 to 50 mV s^{-1} (Figure S1). Interestingly, $CoSe_2$@NiFeOOH/NF exhibits the highest Cdl value of 29.0 mF cm^{-2} among all the samples, surpassing those of $CoSe_2$@NiOOH/NF (23.1 mF cm^{-2}) and $CoSe_2$@FeOOH/NF (20.5 mF cm^{-2}). Furthermore, the electrocatalytic stability of $CoSe_2$@NiFeOOH/NF was evaluated. As depicted in Figure 5h, the current variation is negligible after a 100-hour continuous test at 1.54 V. The overpotential increase for every 50 mA cm^{-2} of current density is illustrated in Figure 5f. It is evident

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from the Figure 5a that $CoSe_2$@NiFeOOH/NF has a significantly lower overpotential than $CoSe_2$@FeOOH/NF and $CoSe_2$@NiOOH/NF, signifying higher catalytic activity of $CoSe_2$@NiFeOOH. Figure 5e illustrates the chrono-potentiometric curve of $CoSe_2$@NiFeOOH, showing multiple steps with the current density incrementing from 10 to 100 mA cm^{-2} in ten steps. In the initial step, the potential rapidly stabilizes at 1.44 V and remains nearly constant for a duration of 320 s. Similar phenomena are observed in the subsequent steps, indicating the exceptional mass transport and electronic conductivity characteristics of $CoSe_2$@NiFeOOH/NF. The faradaic efficiency for OER on the $CoSe_2$@NiFeOOH/NF electrodes was evaluated by measuring the O_2 produced during a constant current test experiment. According to Figure 4g, the measured amount of O_2 is in close agreement with the theoretical yield, resulting in a remarkable faradaic efficiency of 97.8% for the $CoSe_2$@NiFeOOH/NF electrode.

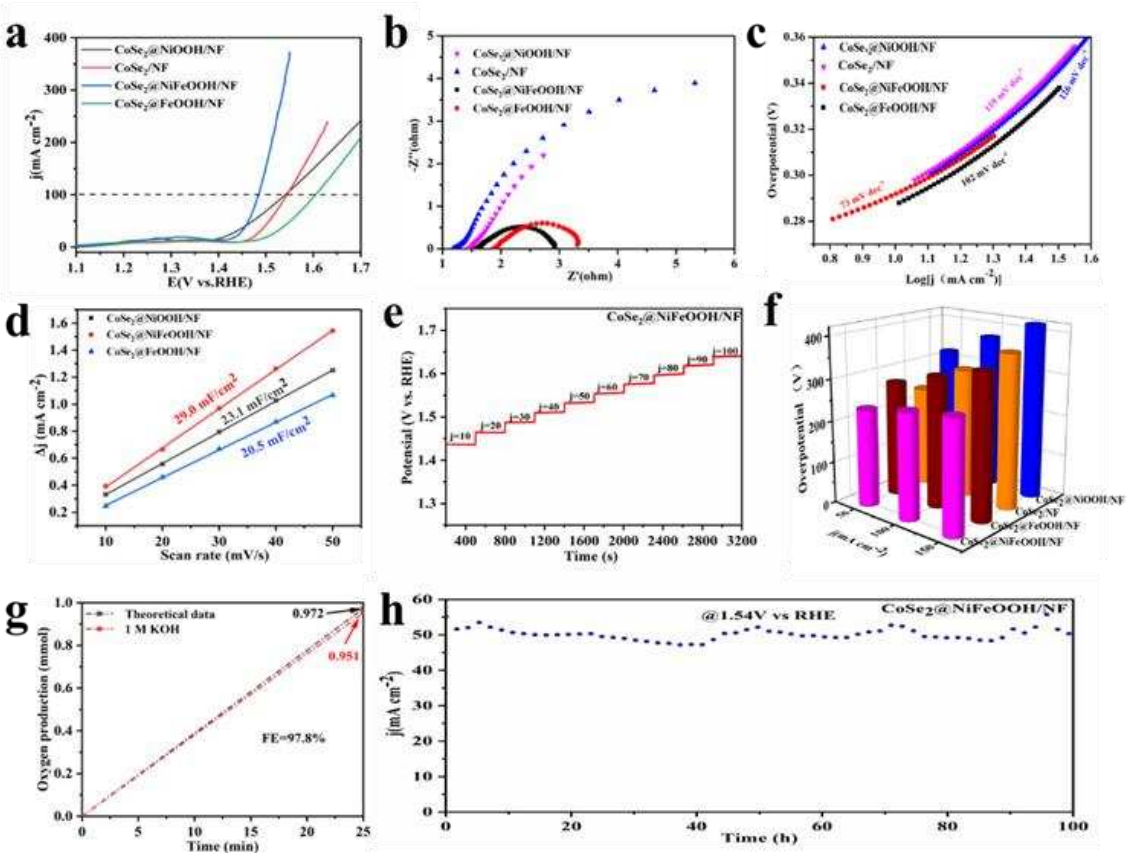

Figure 5. (a) LSV curves for $CoSe_2$/NF, $CoSe_2$@FeOOH/NF, $CoSe_2$@NiOOH/NF, NiFe-LDH/NF, NF/Selenization and $CoSe_2$@NiFeOOH/NF. (b) EIS curves, (c) Tafel plots, (d) C_{dl} plots. (e) Rate capability evaluation of $CoSe_2$@NiFeOOH/NF. (f) Catalyst overpotentials at dif-ferent current densities. (g) Faraday efficiency. (h) i–t curve for $CoSe_2$@NiFeOOH at the η=0.31 V for 100 h.

4. Conclusions

In summary, a three-dimensional $CoSe_2$@NiFeOOH supported on nickel foam for efficient OER catalysis was fabricated. The excellent conductivity of $CoSe_2$ and the synergistic effect between $CoSe_2$ and NiFeOOH facilitate the OER catalysis on $CoSe_2$@NiFeOOH/NF. The $CoSe_2$@NiFeOOH/NF catalyst demonstrated excellent performance in the alkaline electrolyte achieving an overpotential of 254 mV at 100 mA cm^{-2} and a Tafel slope of 73 mV dec^{-1}. Furthermore, the catalyst demonstrated remarkable stability with minimal decay in current density, even after 100 hours. The findings of this study represent a prototype of a synergistic strategy for creating highly efficient electrocatalysts.

Supplementary Materials: The following supporting information can be downloaded atthe website of this paper posted on Preprints.org. Figure S1. CV curves of a) CoSe2@FeOOH/NF. b) CoSe2@NiFeOOH/NF and c) CoSe2@NiOOH/NF. Table S1. Comparison of the OER activity of CoSe2@NiFeOOH/NF with other non-noble metal electrocatalysts in alkaline solution.

Author Contributions: Conceptualization, Y.L., Y.W. and K.T.; methodology, Y.L., Y.T., Z.L. and J.L.; formal analysis, J.L., Y.T., Y.W. and Y.L.; investigation, Y.T. and J.L.; data curation, Y.T. and J.L.; writing—original draft preparation Y.T. and J.L.; writing—review and editing, Y.L. and Y.W.; supervision, Y.L., and K.T.; project administration, Y.L. Y.T. and J.L.; funding acquisition, Y.L. and Y.W. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: We would like to share our data upon request from the authors.

Conflicts of Interest: The authors declare no conflict of interest.

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