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Self-Supporting np-AlFeNiO Bifunctional Electrode Material for Electrochemical Water Splitting Prepared by Electrooxidation

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Abstract: Hydrogen production through water splitting is a promising path to develop renewable green energy. Effective, stable, and low-cost catalysts are the key to water splitting. In the present work, a series of self-supporting nanoporous alloys are prepared by using a dealloying process followed by electrooxidation. Among them, the np-AlFeNiO-4s sample exhibits remarkable activity (10 mA cm⁻² at 32 mV for the HER and 278 mV for the OER) and good long-term stability (100 h) in alkaline conditions for both the HER and the OER. It only requires 1.56 V to reach 10 mA cm⁻² current density for total water splitting performance. The very short time of electrooxidation can significantly improve the HER performance. Electrooxidation makes the metal and metal oxide sites on the electrode surface effectively coupled, which greatly enhances the kinetic rate of the Volmer and Heyrovsky steps. Appropriate electrooxidation is a rapid and easy way to improve the activity of the electrocatalyst, which has a broad application prospect in electrochemical water splitting.

Keywords: self-supporting; bifunctional electrocatalyst; oxidation; hydrogen evolution reaction

1. Introduction

Nowadays, the consumption of huge amounts of traditional fossil fuels has led to the global energy shortage and serious environmental problems [1]. Hydrogen energy is considered one of the most promising energies of the future due to its cleanliness, high efficiency, and renewability [2]. Hydrogen can be achieved by steam methane reforming, gasification, and electrochemical water splitting. Among them, electrochemical water splitting has attracted much attention because of its low pollution and high efficiency in converting energy [3]. Currently, noble metals are the best catalysts for electrochemical water splitting, such as Pt/C for the hydrogen evolution reaction (HER) and RuO₂ for the oxygen revolution reaction (OER). However, the low abundance and high cost of noble metals limit their large-scale application [4]. Recently, many researchers have focused on transition metal catalysts for electrochemical water splitting. Due to their valence bonding structure of empty or semi-filled orbitals, transition metal elements are prone to exhibit electrocatalytic synergy with other elements, thus effectively improving their catalytic activity [5,6]. Many transition metallic compounds, such as oxides, sulfides, and phosphides, were developed as water-splitting catalysts. These nanoscale compounds have unique geometrical and electronic properties and further exhibit good electrochemical catalytic properties [7–9].

Among them, the transition metal Ni and its oxides exhibit outstanding HER catalytic activity [10]. Ni has a very high ability to adsorb H*, which plays a crucial role in the Volmer step by dissociating H* from water molecules attached to the surface of the catalytic electrode. NiO has a strong adsorption capacity for water, which is very beneficial for the Heyrovsky step. Hence, the combination of Ni and NiO would effectively promote the



Citation: Ma, Z.; Xu, W.; Gao, Z.; Liang, Y.; Jiang, H.; Li, Z.; Cui, Z.; Zhang, H.; Zhu, S. Self-Supporting np-AlFeNiO Bifunctional Electrode Material for Electrochemical Water Splitting Prepared by Electrooxidation. *Energies* **2024**, *17*, 1591. https:// doi.org/10.3390/en17071591

Academic Editors: Nikolaos Koukouzas and Vladislav A. Sadykov

Received: 21 February 2024 Revised: 18 March 2024 Accepted: 22 March 2024 Published: 26 March 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). chain reaction of the HER and increase the reaction rate [11–13]. Peng et al. used a process of electrooxidation on porous Ni to prepare Ni/NiO, which exhibits outstanding catalytic performance with an overpotential of 25 mV at the current density of 10 mA cm⁻². The synergic effect of NiO and Ni improves the kinetics of Volmer and Heyrovsky steps and the nanoporous structure provides more active sites and facilitates the transfer of substances and charges [14]. This effect can also be extended to other metals and their oxides [15–18].

The incorporation of Fe into Ni-based catalysts can promote intermetallic synergy. Ni-Fe-based alloys show potential as bifunctional catalysts for both the HER and the OER [19–21]. Their oxides also play a great role in improving the water-splitting process. Survanto et al. synthesized the Janus Ni-Fe nanoparticle with Ni bonded to γ -Fe₂O₃. The Ni-Fe bimetallic structure surface offers effective active sites for the OER and the HER. Ni provides metallic-type electron conduction and favors electron transport towards the active HER sites, and Fe oxide provides more M-OOH intermediates [22]. In addition, the introduction of Fe can change the surface electronic state of other metal elements and make the oxidation process more difficult, which can facilitate the kinetic steps of the OER. The presence of Fe also can reduce the interfacial charge transfer resistance and promote HER kinetics [23]. Al incorporation into transition metals also enhances the HER activity of transition metals. It can provide electrons to transition metal active sites and promote the reaction process. Meanwhile, Al doping also changes the adsorption energy on the electrode surface, which in turn changes the electrocatalytic reaction energy [24]. Zhou et al. designed a nanoporous NiO/Al₃Ni₂ catalyst [25]. The presence of Al₃Ni₂ provided good electrical conductivity for the electrode and also adsorbed more H_{ad}. Together with the good synergistic catalytic ability of Ni and NiO, the nanoporous NiO/Al₃Ni₂ catalyst exhibited excellent HER performance.

Al-Fe-Ni-based materials and their oxides show great potential for electrochemical water splitting. However, more research is still needed on how to integrate metals and their oxides more efficiently and utilize their synergistic effects to construct electrocatalysts with excellent performance. Meanwhile, most of the current catalysts for water splitting are in powder form and must be loaded on conductive support for the reaction, which could damage the catalytic activity and long-term stability and also bring additional costs for large-scale commercial applications [26,27].

Herein, we report a self-supporting nanoporous transition metal bifunctional electrode material for electrochemical water splitting. This high-performance material utilizes a very fast and simple preparation method to effectively couple transition metals and their oxides. Due to the excellent hydrogen adsorption ability of the transition metals and the water adsorption ability of their oxides, the overpotential of the electrode for the HER is greatly reduced. In addition, the transition metal oxides provide a large number of intermediates for the OER to accelerate the OER rate.

2. Materials and Methods

2.1. Material Preparation

In this work, the melt spinning method was used to prepare the precursor alloy ribbons. The synthesis process is shown in Figure 1. The pure metals Al, Ni, and Fe were mixed in the ratio of 70:15:15 under argon atmosphere and melted in a high vacuum arc-melting furnace. The alloy ingot was then remelted in a quartz tube and ejected onto the surface of a rotating copper wheel at a linear speed of 32 m s^{-1} . The thickness and width of the as-formed alloy ribbons were about 30 µm and 1.5 mm, respectively. The nanoporous ribbons were prepared by the potential-static electrochemical dealloying method using a standard three-electrode system with an Ag/AgCl electrode and a Pt mesh electrode as the reference and counter electrodes. At room temperature, the Al₇₀Fe₁₅Ni₁₅ precursor ribbons were dealloyed in 1 M KOH at a potential of -0.9 V (vs. Ag/AgCl) for 4000 s. Al can be corroded in KOH solution. After the dealloying process, the active Al metal was etched, and the material turned into a nanoporous structure. Then, the as-dealloyed ribbons were treated by electrooxidation at the applied potential of 0.77 V (vs. Ag/AgCl)

for various amounts of time. Applying a higher potential to the material makes it more susceptible to oxidation, which in turn leads to the effective coupling of the metal and the oxide. The ribbons after electrooxidation were labeled np-AlFeNiO-Xs, where X is the seconds of electrooxidation.



Figure 1. Schematic illustration of the formation of the samples.

In order to make a comparison, a commercial Pt/C electrode was prepared as a control sample. First, 4 mg of Pt/C powder was mixed with 800 μ L of deionized water, 200 μ L of ethanol, and 50 μ L of Nafion, and then the ink was sonicated for 30 min. A glassy carbon electrode with an area of 0.2826 cm⁻² was used to load 50 μ L of the ink for the subsequent tests.

2.2. Characterization

The phase composition was characterized by X-ray diffraction (XRD, Bruker D8, Billerica, MA, USA) with Cu K α as the radiation source. The morphology was determined by scanning electron microscopy (SEM, Hitachi S-4800, Tokyo, Japan) and transmission electron microscopy (TEM, JEOL 2100M, Tokyo, Japan). X-ray photoelectron spectroscopy (XPS, PHI 1600ECSA, Chigasaki, Japan) was used to identify the elemental composition and chemical state on the surface.

2.3. Electrochemical Measurements

All electrochemical tests were performed using a Gamry interface 1000 electrochemical workstation with a classical three-electrode system. The tests were carried out in 1 M KOH solution with the as-prepared catalysts, Pt mesh, and Ag/AgCl electrode as working electrode, counter electrode, and reference electrode, respectively. Linear Sweep Voltammetry (LSV) was performed with a fast sweep of 50 curves at a scan rate of 50 mV s⁻¹ followed by a test at a scan rate of 2 mV s⁻¹. The polarization curve at the 2 mV s⁻¹ scan rate was used to compare the electrocatalytic performance of the as-prepared samples. Each curve was delayed by 5 s to prevent large changes in voltage from affecting the results. The electrode material is activated by fast sweeping, but the high speed of sweeping also makes the reaction speed of the material unable to keep up with the polarization speed, which leads to the deviation of the test results. Therefore, after fast sweeping to make the material activation complete, the test results of the slow sweeping speed were selected for

comparison and analysis. All measured potentials in this work were converted to potentials versus reversible hydrogen electrode (RHE) using the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.199 + 0.059 pH$$
(1)

Electrochemical impedance spectra (EIS) measurements were performed at an overpotential of 50 mV with a frequency range of 0.1 Hz to 100 kHz. In addition, the polarization curves were iR-compensated according to the following equation:

$$E_{corr} = E_{mea} - iR_s \tag{2}$$

where E_{corr} , E_{mea} , i, and R_s are the iR-compensated potential, the measured potential, the current density, and the equivalent series resistance measured by EIS. Cyclic voltammetry (CV) measurements were performed at potentials from -0.05 to 0.05 V versus open circuit potential (OCP) at different scan rates from 10 to 200 mV s⁻¹. The electrochemical active area was determined by the double-layer capacitance (C_{dl}), which was calculated from the linear slope of $\Delta J = (J_f - J_r)/2$ at 0 V (vs OCP). The ECSA of the catalyst was calculated by the following equation:

$$ECSA = \frac{C_{dl}}{C_S}$$
(3)

where C_S is the ECSA constant, and the C_S of a typical material is 40 μ F cm⁻² [28]. The turnover frequency (TOF) value was calculated by the following equation [29]:

$$TOF = jA/F(2n) \tag{4}$$

where j is the current density at a potential of 100 mV, A is the surface area of the working electrode, F is Faraday's constant (96,485 c mol⁻¹), and n is the number of moles of active substance loaded on the electrode. Stability was tested under a static current density of 10 mA cm⁻² in 1 M KOH for 100 h.

3. Results and Discussion

Figure 2 shows the XRD patterns of the samples. The precursor alloy ribbon is composed of Al_5FeNi , Al_4Ni_3 , Fe, Al_2O_3 , and NiO phases. The oxides should be generated due to the exposure of the ribbon in air. The peak intensities of the Al_4Ni_3 phase and the Al_5FeNi phase of the as-dealloyed sample decrease, indicating that these phases would be mainly removed during the dealloying process. The intensity of oxide peak has little change in the electro-oxidized samples, indicating the formation of tiny amount of oxides. The peaks of the Al_5FeNi , Fe, and Al_4Ni_3 phases are weakened, which indicates that they are the components that mainly undergo the oxidation reaction to produce oxides during the electrooxidation process.

Figure 3 shows the SEM images of the samples. Table S1 lists the EDX results of the samples. Figure S1 shows the cross-section of the dealloyed sample. After 4000 s of etching, Al in the samples was basically removed, and the samples were completely corroded. The corroded samples were mainly composed of nanosheets with a thickness of about 20 nm. After oxidation for 4 s, there was no significant change in the sample morphology, and only a small number of tiny spheres appeared on the nanosheets. With the increase in oxidation time, the spheres further increased. When the oxidation time of the sample reached 100 s, the nanosheets were coarsened significantly, and the thickness of the nanosheets grew to about 40 nm. The TEM images of np-AlFeNiO-4s are shown in Figure S2. The sample shows a porous morphology with a pore size of about 20 nm. Figure S2b shows a lattice analysis of this part. The lattice fringes of $d_{(111)} = 0.24$ nm and $d_{(200)} = 0.22$ nm with a 54° angle match Fe_{0.942}O. There is no obvious diffraction peak of Fe_{0.942}O in the XRD, which may be due to the low level of oxidation of the sample. It is presumed that after electrooxidation, the spheres grown in the sample nanosheets indicate the oxide spheres of Fe.



Figure 2. XRD patterns of the precursor ribbon, the ribbon after dealloying, and the ribbons oxidized for 4 s and 100 s.



Figure 3. SEM images of the (**a**) precursor ribbon, (**b**) the dealloyed ribbon, and ribbons oxidized for (**c**) 4 s and (**d**) 100 s.

Figure 4 shows the XPS spectra of samples with different oxidation times. As shown in Figure 4a–c, the surface of the as-dealloyed sample mainly consists of the oxidized form of the metals, which should result from the charge transfer and oxidation during the

dealloying process [25,30]. In Figure 4a, the Al on the surface of the np-AlFeNiO-0s sample mainly exists in the Al^{3+} state. However, there is still a small amount of Al^0 located at 72.8 eV, which would be attributed to the intermetallic compounds AlFeNi and Al₄Ni₃ [31]. The Al⁰ peak disappears after electrooxidation, suggesting that the surface Al atoms in the intermetallic compounds should be oxidized. Figure 4b exhibits the 2p orbit peaks of Ni. Ni exists in the Ni²⁺ form with a small amount of Ni⁰ [25]. After electrooxidation, the peak of Ni⁰ at 852.4 eV reduces but does not completely disappear. Figure 4c shows the 2p peaks of Fe. After dealloying, Fe has two valence peaks including an Fe⁰ peak at 718.3 eV and oxidation state peaks at 710.4 eV and 724.5 eV [32]. After electrooxidation, the peak at 718.3 eV almost disappears, indicating that Fe would be oxidized. Figure 4d shows the O 1s profiles of the samples. For np-AlFeNiO-0s, O in the H₂O molecule (M-OH) located at 531.7 eV and divalent lattice O (M–O) located at 531.0 eV can be detected. The O at 531.7 eV represents the H_2O molecule attached to the surface of the sample, which would participate in the Volmer step in the electrolysis water reaction process [33–36]. The ability of the sample to adsorb H₂O molecules influences the catalytic performance of the water electrolysis reaction. After electrooxidation, the peak strength of the M–OH bond at 531.7 eV becomes stronger, indicating that the oxide on the surface could improve the adsorption ability for H₂O, which would greatly enhance the reaction rate of the Volmer step. In the alkaline electrolytic water reaction, the Volmer step is often a rate-limiting step [37]. Meanwhile, after electrooxidation, the M–OOH bond at 533.1 eV appears on the surface, which is an important intermediate in the OER [31].



Figure 4. The XPS spectra of (a) Al 2p, (b)Ni 2p, (c) Fe 2p, and (d) O 1s.

Figure 5 shows the results of the HER properties. From Figure 5a, it can be seen that with the increase in electrooxidation time, the overpotential at -10 mA cm^{-2} shows a trend of first decreasing and then increasing. The overpotential data are listed in Table S2. The np-AlFeNiO-4s sample has the smallest overpotential of 32 mV vs. the RHE at 10 mA cm⁻², which shows a significant reduction by about 100 mV compared with the unoxidized sample. Figure 5b shows the Nyquist plots. The impedance data are fitted and analyzed by an equivalent electrical circuit (inset of Figure 5b), which consists of an electrolyte solution resistance (R_s) , interfacial capacitance (C_{int}) , and charge transfer impedance (R_{ct}) . With an increase in electrooxidation time, the R_{ct} of the nanoporous samples shows a tendency of first decreasing and then increasing. A certain degree of oxidation could increase the reaction sites and promote the reaction rate. However, due to the poor conductivity of the oxides, too many oxides would reduce the charge transfer rate, further damaging the catalytic performance. Figure 5c shows the Tafel slopes of the samples with different oxidation times. The Tafel slope reflects the hindering of the polarization process, which is determined by the rate-limiting step of the catalytic reaction [38]. The Tafel slope values for the catalysts at each oxidation time are listed in Table S2. The Tafel slope of the unoxidized sample is 141 mV dec⁻¹, which is close to 120 mV dec⁻¹, indicating that its reaction ratelimiting step in the HER should be the Volmer step. It is suggested that the adsorption capacity of water on the surface of the catalyst would significantly influence the HER rate. When the Tafel slope is between 40 mV dec⁻¹ and 120 mV dec⁻¹, the HER ratelimiting step is the Heyrovsky step [39]. After oxidation, the Tafel slope decreases to below $120 \text{ mV} \text{ dec}^{-1}$. The strong adsorption ability of the oxides to water would accelerate the Volmer step, resulting in a decrease in the Tafel slope, and the rate-limiting step would turn into the Heyrovsky step. With a further increase in oxidation time, the Tafel slope starts to increase. The oxides on the surface cover the original metal sites. The metal atoms have a strong adsorption ability for H_{ad} , so the number of metal sites has a great influence on the reaction rate of the Heyrovsky step [14]. Even though the generation of oxides promotes the occurrence of the Volmer step, an excess of oxides can hinder the progress of the Heyrovsky step. Hence, the HER catalytic performance of the samples shows a tendency to increase first and then decrease with the increase in oxidation time. Figure 5d shows the CV curves of np-AlFeNiO-4s, and Figure 5e shows the double-layer capacitances (C_{dl}) , which were obtained from Figure 5d. With the increase in electrooxidation time, the double-layer capacitance C_{dl} shows a trend of increasing and then decreasing. TOF values were calculated for each sample at $\eta = 100$ mV, as shown in Table S2 [29]. With the increase in oxidation time, the TOF value shows a trend of increasing and then decreasing. These results indicate that the formation of a certain proportion of oxide spheres would increase the electrochemically active area, but too much oxide would reduce the number of active sites on the electrode surface, resulting in a decrease in the intrinsic catalytic activity. Table S3 and Figure 6 show the data of overpotentials and Tafel slopes at 10 mA cm^{-2} from the present work and some recently reported papers. np-AlFeNiO-4s has a great competitive advantage compared with most of the other catalysts.

Figure 7 shows the HER stability test results for np-AlFeNiO-4s. The stability of the sample was tested by the constant current method. It can be seen that the potential under the constant current of 10 mA cm⁻² has no significant change after the 100 h test (as shown in Figure 7a). Figure 7b shows the SEM image of the sample after 100 h of the stability test. The surface of the sample subjected to the stability test still maintains the nanosheet morphology with certain attached oxide spheres. Figure 7c–f show the comparison of XPS results of np-AlFeNiO-4s before and after the stability test. After a long period of work, both the Al and Ni contents decrease and a few oxides appear, but there is no significant change in the valence state. The above results indicate that np-AlFeNiO-4s would have outstanding long-term stability.



Figure 5. (a) LSV curves of the np-AlFeNiO catalyst and Pt/C for the HER. (b) Tafel plots derived from corresponding LSV curves. (c) Nyquist plots of the np-AlFeNiO catalysts. (d) The CV curve of np-AlFeNiO-4s. (e) Linear fitting of the capacitive currents of the plotted against the scan rates.



Figure 6. Comparison of the Tafel slope and η_{10} for the reported HER catalysts [4,9,17,19,25,35,40–45].



Figure 7. (**a**) Time-dependent potential profile of np-AlFeNiO-4s for the 100 h HER test, (**b**) the SEM image after the stability test, and (**c**–**f**) XPS results before and after the stability test.

Figure 8a shows the OER test results of the samples. Table S4 shows the overpotentials of the OER of the catalysts at 10 mA cm⁻² and 100 mA cm⁻² for each oxidation time. The amount of oxidation time does not have a significant effect on the OER catalytic performance of the electrode. Nonetheless, the catalysts still exhibit good OER performance, especially at the high current density. The overpotentials of np-AlFeNiO-4s are 279 mV at 10 mA cm⁻² and 318 mV at 100 mA cm⁻². Figure 8b shows the Tafel curves of the samples with different oxidation times, and the Tafel slopes are listed in Table S4. The Tafel slopes of all samples are around 40 mV dec⁻¹, indicating the oxidation process would have little influence on the OER performance. Figure 9 and Table S5 compare the overpotentials and Tafel slopes of some OER catalysts. Based on the fact that np-AlFeNiO-4s exhibits excellent OER performance at high currents, we also compared it with other catalysts reported in the literature at 100 mA cm⁻². The catalysts in this work exhibit highly competitive compared with the other reported high-activity alkaline OER catalysts. Figure 10 shows the results of the OER stability tests on np-AlFeNiO-4s. The stability of the samples was tested by

the constant current method. It can be seen that the potential is stable during the constant current (10 mA cm⁻²) test of 100 h, which indicates that np-AlFeNiO-4s would have good OER stability.



Figure 8. (a) LSV curves of np-AlFeNiO catalysts for the OER and (b) Tafel plots derived from the corresponding LSV curves.



Figure 9. Comparison of (**a**) the Tafel slope and η_{10} and (**b**) the Tafel slope and η_{100} for the reported OER catalysts [31,35,40,41,43,45–49].



Figure 10. Time-dependent potential profile of np-AlFeNiO-4s for the 100 h OER test.

Based on the good HER and OER performance, the overall water-splitting electrolyzer was built using nanoporous ribbons as both the anode and cathode in an alkaline aqueous solution. As shown in Figure 11a, np-AlFeNiO-4s exhibits excellent total water-splitting performance. Only 1.56 V of voltage is required to reach 10 mA cm⁻² of current density, while the unoxidized sample requires a voltage of 1.78 V. For the long-time oxidized samples, such as np-AlFeNiO-100s, although the required voltage at a small current (10 mA cm⁻²) is similar to that of np-AlFeNiO-4s, greater voltages are required to drive them at high currents because of the poorer conductivity of the oxides. The LSV curves of the np-AlFeNiO-0s, -4s, and -100s two-electrode configuration systems in 1 M KOH with iR correction are shown in Figure S3. Figure 11b shows the overall water-splitting performance stability of the np-AlFeNiO-4s catalyst. The water-splitting the excellent stability of np-AlFeNiO-4s. Figure 12 and Table S6 list the total water-splitting performance of the catalysts in this



work and other reports in the literature. It can be seen that the catalysts in this work have

excellent total water-splitting performance.

Figure 11. (a) LSV curves of the np-AlFeNiO-0s, -4s, and -100s two-electrode configuration systems in 1 M KOH without iR correction and (b) the time-dependent potential profile of np-AlFeNiO-4s serving as both the cathode and anode under a current density of 10 mA cm⁻² for 100 h in 1 M KOH solution.



Figure 12. Comparison of the overall water-splitting performance at the current density of 10 mA cm⁻² for electrocatalysts in the recently reported literature [35,40,41,43,45–50].

4. Conclusions

In the present work, electrooxidation was carried out to improve the water-splitting performance of the nanoporous AlFiNi alloy with a self-supporting structure. A very short time of electrooxidation can significantly enhance the HER activity of the nanoporous AlFeNi alloy. The np-AlFeNiO-4s electrode exhibits remarkable HER activity with the overpotential of 32 mV at 10 mA cm⁻². Electrooxidation makes the metal and metal oxide sites on the electrode surface effectively coupled, which greatly enhances the kinetic rate of the Volmer and Heyrovsky steps. The np-AlFeNiO-4s electrode also shows good OER activity with an overpotential of 279 mV at 10 mA cm⁻². Only 1.56 V of voltage is required to drive 10 mA cm⁻² of current density for the whole water electrolysis reaction. Electrooxidation improves HER performance by enhancing water adsorption abilities. The np-AlFeNiO-4s electrode exhibits outstanding long-term stability with little change after a 100 h water splitting test. Overall, np-AlFeNiO-4s has a promising application in water electrolysis reactions.

Supplementary Materials: The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/en17071591/s1, Figure S1: The SEM of a cross-section of the dealloyed sample; Figure S2: (a) TEM and (b) HRTEM images of the np-AlFeNiO-4s sample; Figure S3: The LSV curves of the np-AlFeNiO-0s, -4s, and -100s two-electrode configuration systems in 1 M KOH with iR correction; Table S1: The EDX results of the samples; Table S2: The overpotentials at 10 mA cm⁻², Tafel slope, C_{dl}, ECSA, and TOF of np-AlFeNiO for the HER; Table S3: The overpotentials at 10 mA cm⁻², Tafel slope for HER electrocatalysts in the recently reported literature; Table S4: The overpotentials at 10 mA cm⁻² and 100 mA cm⁻², the Tafel slope of np-AlFeNiO for the OER; Table S5: The overpotentials at 10 mA cm⁻² and 100 mA cm⁻², the Tafel slope for OER electrocatalysts in the recently reported literature; Table S6: Comparison of the overall water-splitting performance for electrocatalysts in the recently reported literature.

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

Funding: This research was funded by the National Natural Science Foundation of China, grant numbers 52271152 and 52371161, and the Tianjin Natural Science Foundation, grant number 22JCQNJC00670.

Data Availability Statement: The data are contained within this article.

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

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