ACS APPLIED MATERIALS

Porous Nickel—Iron Selenide Nanosheets as Highly Efficient Electrocatalysts for Oxygen Evolution Reaction

Zhaoyang Wang, Jiantao Li, Xiaocong Tian, Xuanpeng Wang, Yang Yu, Kwadwo Asare Owusu, Liang He,* and Liqiang Mai*

State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, Hubei, People's Republic of China

Supporting Information

ABSTRACT: Exploring non-noble and high-efficiency electrocatalysts is critical to large-scale industrial applications of electrochemical water splitting. Currently, nickel-based selenide materials are promising candidates for oxygen evolution reaction due to their low cost and excellent performance. In this work, we report the porous nickel–iron bimetallic selenide nanosheets $((Ni_{0.75}Fe_{0.25})Se_2)$ on carbon fiber cloth (CFC) by selenization of the ultrathin NiFe-based nanosheet precursor. The as-prepared three-dimensional oxygen evolution electrode exhibits a small overpotential of 255 mV at 35 mA cm⁻² and a low Tafel slope of 47.2 mV dec⁻¹ and keeps high stability during a 28 h measurement in alkaline solution. The outstanding catalytic performance and strong durability, in comparison to the advanced non-noble metal catalysts, are derived from the porous nanostructure fabrication, Fe incorporation, and selenization, which result in fast charge transportation and large electrochemically active surface area and enhance the release of oxygen bubbles from the electrode surface.



KEYWORDS: nickel-iron bimetallic selenide, porous nanosheets, carbon fiber cloth (CFC), electrochemical catalyst, oxygen evolution

INTRODUCTION

With excessive consumption of fossil fuels, great effort has been made to develop renewable energy sources.¹ The clean and unlimited hydrogen for fuel cells and other energy-related storage devices can be produced through electrochemical water splitting $(2H_2O \rightarrow 2H_2 + O_2)^{2,3}$ Oxygen evolution reaction (OER; $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ in base and $2H_2O \rightarrow O_2 +$ $4H^+ + 4e^-$ in acid) is a significant half-reaction during water splitting. However, OER is a kinetically sluggish process with high overpotential both in acidic and basic media, because it includes multistep proton-coupled electron transfer and the formation of O-O bond.^{4,5} Thus, highly efficient catalysts for accelerating the reaction are in great demand. As we know, precious metal-based catalysts, such as Pt, Ru, Ir, RuO₂, and IrO₂, have been widely studied and lots of impressive achievements have been realized, whereas the low abundance, high cost, and poor long-term stability largely prevent their widespread applications.^{6,7} Therefore, it is still a tremendous challenge to find catalysts with desirable characteristics such as high electrocatalytic activity, excellent durability, and earth abundance.

Electrocatalyts based on first-row transition metals (Mn, Fe, Co, and Ni, *etc.*) have been widely studied, and most of them are considered as promising candidates for OER.^{8–10} Among them, Ni-based catalysts are extensively investigated due to their considerable electrocatalytic performance. However, their catalytic performance is limited by their poor electronic

conductivity and instability.¹¹⁻¹³ In order to obtain highly efficient catalysts for OER, there are several general rules which need to be followed. One common strategy involves the rational morphology control to improve the electrochemical reaction interface. For instance, the construction of nanowires,^{14–17} nanotubes,^{18,19} nanosheets,^{20,21} and porous nanostructures²² can increase the electrochemically active surface area (ECSA) and promote mass diffusion during electrocatalytic process. Another effective strategy aims to optimize the electronic conductivity and tune the electronic structures of catalytic centers. For example, introducing graphene, ^{10,13,23-} CNTs,²⁶ and so on or using metal sulfuration,¹⁷ seleniza-tion,^{14,18,22,27,28} nitridation,²⁹ phosphorization,^{30,31} and certain metal incorporation^{18,32} are effective ways. Notably, active materials directly grown on three-dimensional (3D) conductive substrates can also further enhance their electrocatalytic properties. The 3D free-standing OER electrode can observably promote the release of oxygen bubbles from the surface, facilitate electrolyte penetration, and increase conductivity without binder.^{18,21,33,34} Xu et al. reported metallic Ni₃N nanosheets for the first time, which exhibited a small Tafel slope (41 mV dec⁻¹) and high current density (52.3 mA cm⁻²) at a low overpotential (350 mV). The better performance was

 Received:
 March 19, 2016

 Accepted:
 July 12, 2016

 Published:
 July 12, 2016



Figure 1. Schematic illustration of the synthesis procedures for porous (Ni_{0.75}Fe_{0.25})Se₂ nanosheets on CFC.

mainly on account of the metal-like conductivity and more active sites derived from the disorderd structure.²⁹ Ma et al. showed that hybrid Co_3O_4 -carbon porous nanowire arrays grown on Cu foil possessed a stable current density of 10 mA cm⁻² at 1.52 V and an onset potential of 1.47 V for OER in 0.1 M KOH solution.¹⁶ Xia et al. presented the metallic (Ni, $Co)_{0.85}$ Se nanotube arrays grown on carbon fiber cloth (CFC), displaying a considerably low overpotential of 255 mV for OER at 10 mA cm⁻² in 1 M KOH solution.¹⁸ However, the efficiency of electrocatalysts mentioned above still needs to be raised to a higher level.

In the present work, we report a facile method to synthesize porous (Ni_{0.75}Fe_{0.25})Se₂ nanosheets on flexible and conductive CFC (Figure 1). First, the ultrathin NiFe-based nanosheet precursor is synthesized through a general solvothermal method,^{34,36,37} and then the porous (Ni_{0.75}Fe_{0.25})Se₂ nanosheets are achieved through direct selenization of the precusor by a secondary hydrothermal process.^{22,35} The as-synthesized porous (Ni_{0.75}Fe_{0.25})Se₂ nanosheets exhibit excellent electrocatalytic activity compared to those of Ni-based nanosheet precursor, NiFe-based nanosheet precursor, and porous NiSe₂ nanosheets. The performance of the (Ni_{0.75}Fe_{0.25})Se₂ nanosheets can be attributed to the porous nanostructure, good electronic conductivity, and large electrochemically active surface area derived from the Fe incorporation and selenization.

EXPERIMENTAL SECTION

Nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, >98%), iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, >98.5%), ammonium fluoride (NH₄F, >96%), urea (CH₄N₂O, >99%), ethylene glycol (C₂H₆O₂, >99%), sodium tetrahydroborate (>90%), and selenium (>99%) were purchased from Sinopharm Chemical Reagent Co., Ltd., 5 wt % Nafion solution was purchased from Sigma-Aldrich, and commercial IrO₂ (99.9% Ir) was purchased from Macklin Reagent. Carbon fiber cloth (CFC) was purchased from Shanghai He Seng Electric Co., Ltd.

Synthesis of the Ultrathin NiFe-Based Nanosheet Precursor. In a typical synthesis, 0.75 mmol of Ni(NO₃)₂·6H₂O, 0.25 mmol of Fe(NO₃)₃·9H₂O, 4 mmol of NH₄F, and 6 mmol of CO(NH₂)₂ were dissolved in 24 mL of deionized water (18.2 MΩ·cm). The solution was vigorously stirred for 20 min to form a clear solution; then 12 mL of ethylene glycol (EG) was added into the solution. After stirring for 15 min, the mixed solution was transferred into a 50 mL Teflon-lined autoclave. A piece of CFC (2.5 cm × 5 cm) was immersed into the autoclave and heated at 120 °C for 12 h. After cooling to room temperature, the substrate was washed with deionized water and ethanol and dried at 60 °C under vacuum. Mass loading of NiFe-based nanosheet precursor is ~0.82 mg cm⁻². Conversion of Ultrathin NiFe-Based Nanosheet Precursor into Porous ($Ni_{0.75}Fe_{0.25}$)Se₂ Nanosheets. A 1.0 mmol amount of NaBH₄ and 0.5 mmol of Se powder were dissolved in 3 mL of deionized water. After the Se powder was dissolved and formed a clear solution, 32 mL of deionized water was added into the solution. A piece of CFC (2.5 cm × 4 cm) covered with ultrathin NiFe-based nanosheets was immersed into the solution for 1 h and then transferred into a 50 mL Teflon-lined autoclave. The autoclave was heated at 180 °C for 24 h and then cooled to room temperature. The substrate was washed and dried at 60 °C under vacuum for 12 h. Mass loading of ($Ni_{0.75}Fe_{0.25}$)Se₂ is ~1.5 mg cm⁻².

Synthesis of the Ultrathin Ni-Based Nanosheet Precursor and Porous NiSe₂ Nanosheet. The synthesis process was the same as the above-mentioned one without adding $Fe(NO_3)_3$ ·9H₂O. A 1 mmol amount of Ni(NO₃)₂·6H₂O was used. Mass loading of Ni-based nanosheet precursor and NiSe₂ is ~0.86 and 1.4 mg cm⁻², respectively.

Preparation of IrO₂/CFC Electrode. A 10 mg amount of IrO₂ was dispersed in a mixed isopropanol (750 μ L) and deionized water (200 μ L) solution, and then 50 μ L of Nafion solution (5 wt %) was added. Sonication for 1 h was needed to form a relatively homogeneous suspension. Afterward, 150 μ L of catalyst ink was loaded on the CFC (IrO₂ mass loading is 1.5 mg cm⁻²).

Material Characterizations. XRD patterns were collected by a Bruker D8 Discover X-ray diffractometer with a Cu K α X-ray ($\lambda =$ 1.5418 Å) at room temperature. The morphologies of the samples were characterized with scanning electron microscopy (SEM, JEOL-7100F) at an acceleration voltage of 15 kV, transmission electron microscopy (TEM), and high-resolution TEM (HRTEM) images were recorded by a JEM-2100F microscope. EDS elemental mapping was recorded by an Oxford EDS IE250 system. X-ray photoelectron spectroscopy (XPS) analysis was done on VG Multilab 2000. Brunauer–Emmett–Teller (BET) surface area was measured by using a Tristar II 3020 instrument. The Ni/Fe ratio in the sample was characterized by inductively coupled plasma (ICP) test with the PerkinElmer Optima 4300DV spectrometer.

Electrochemical Measurements. The OER measurements were conducted at room temperature (25 °C) with a standard three electrode system (the counter electrode was platinum wire, and the reference electrode was saturated calomel electrode) and recorded using a CHI 760d electrochemical workstation. OER measurements were made in a 1 M KOH electrolyte solution with the active materials supported on the substrate at a scan rate of 5 mV s⁻¹. Linear sweep voltammetry (LSV) was measured from 0 to 0.8 V vs saturated calomel electrochemical impedance spectrum (EIS) was recorded at 1.6 V vs RHE over a frequency range from 10⁵ to 0.01 Hz.

RESULTS AND DISCUSSION

Crystal information on the as-synthesized samples are investigated by X-ray diffraction. The XRD patterns of Ni-



Figure 2. (a) XRD pattern of porous $(Ni_{0.75}Fe_{0.25})Se_2$ nanosheets on CFC. (b, c) SEM, (d) TEM, and (e) HRTEM images and (f) the corresponding elemental mapping of porous $(Ni_{0.75}Fe_{0.25})Se_2$ nanosheets on CFC.

based and NiFe-based nanosheet precursors are displayed in Supporting Information Figures S1 and S2, respectively. The peaks of Ni-based nanosheet precursor closely match Ni₅(CO₃)₄(OH)₂·4.5H₂O (JCPDS Card No. 00-046-1398; monoclinic phase), and NiFe-based nanosheet precursor can be indexed to the layer double hydroxide (LDH) for Ni_{0.75}Fe_{0.25}(CO₃)_{0.125}(OH)₂·0.38H₂O (JCPDS Card No. 00-040-0215; rhombohedral phase; a = b = 3.08 Å, c = 23.34 Å, α = β = 90°, and γ = 120°). The XRD patterns of porous selenide nanosheets are shown in Figure 2a and Figure S3a. The diffraction peaks of Ni-based porous selenide nanosheets can be indexed to cubic NiSe₂ (JCPDS Card No. 03-065-5016; cubic phase; a = b = c = 5.961 Å, and $\alpha = \beta = \gamma = 90^{\circ}$; Pa3). The XRD pattern of NiFe-based porous selenide nanosheets is almost the same as that of NiSe2, which means that the Fe element would have occupied certain positions of Ni in NiSe2like crystalline without structural change. From the comaprison of the peak positions, the relative intensity of the peaks at 30.04° and 33.71° of NiSe₂ are lower than those in the pattern of (Ni_{0.75}Fe_{0.25})Se₂ (Figure S4). This may be attributed to Fe incorporation. Fe element occupies the Ni lattice sites of NiSe₂ and causes the intensity changes. The actual elemental composition of NiFe-based porous selenide nanosheets is determined by ICP (Table S1), which shows that the molar ratio of Ni:Fe:Se is 2.91:1:8.54. The Ni:Fe ratio is consistent with that of the original NiFe-based nanosheet precursor, while the much more molar content of Se is derived from SeO₂ formed during the selenization process. SeO₂ can be dissolved in basic solution during the process of electrochemical activation without any further effect to the electrocatalytic performance. The formula of NiFe-based porous selenide nanosheets can be denoted as (Ni_{0.75}Fe_{0.25})Se₂.

In order to obtain the morphology and microstructural information on the as-synthesized nanosheet precursors and porous nanosheets, detailed microscopic characterizations are performed. As shown in SEM images (Figure 2b,c and Figure S5), the nickel—iron selenide nanosheets clearly exhibit many pores on the rough surface. Actually, the porous nanosheets consist of a large number of small particles, which can be fully exposed to the electrolyte with high surface area. There is a big phase shift between cubic phase and rhombohedral phase

together with the removal of carbonate and hydroxyl during the selenization process. The porous nanostructure may be caused by strain release due to the crystal mismatch after phase conversion. The conversion reaction can be written as reaction 2 together with the NaHSe formation reaction (reaction 1). This is similar to previous studies.^{22,35}

$$2Se + 4NaBH_{4} + 7H_{2}O$$

$$\rightarrow 2NaHSe + Na_{2}B_{4}O_{7} + 14H_{2}(g) \qquad (1)$$

$$Ni_{0.75}Fe_{0.25}(CO_{3})_{0.125}(OH)_{2} \cdot 0.38H_{2}O + 2NaHSe$$

$$\rightarrow (Ni_{0.75}Fe_{0.25})Se_{2} + 1.75NaOH + 0.125Na_{2}CO_{3}$$

$$+ 0.63H_2O + 0.875H_2(g)$$
 (2)

In comparison, the nickel selenide nanosheets show smaller pores and cracks on its relatively smooth surface (Figures S3 and S5d). As shown in Figure S7, the porous $(Ni_{0.75}Fe_{0.25})Se_2$ nanosheets possess a surface area of 60.3 $m^2 g^{-1}$, which is much higher than those of the NiFe-based nanosheet precursor (24.2 $m^2 g^{-1}$), the porous NiSe₂ nanosheets (20.5 $m^2 g^{-1}$), and the Ni-based nanosheet precursor (16.1 m² g⁻¹). The lattice space is measured to be 0.26 nm (Figure 2e) in the HRTEM image, which is in agreement with the (210) plane of cubic NiSe₂ (Figure S3g). This result further confirms that $(Ni_{0.75}Fe_{0.25})Se_2$ and NiSe₂ have the same crystal structure except for substitution of Ni by Fe element. The EDS mappings (Figure 2f) further reveal that Ni, Fe, and Se are homogeneously distributed on the nanosheets. In addition, the corresponding characterizations of commercial precious metal oxide IrO2 catalyst have also been done. As shown in Figure S6a, the diffraction peaks can be indexed to IrO₂ (JCPDS Card No. 01-088-0288). SEM images (Figure S6c) reveal that IrO₂ consists of nanoparticles. This morphology contributes a high surface area of 139.8 m² g⁻¹ (Figure S6b), which provides a high surface exposure of active sites for the OER. The lattice spaces are measured to be 0.26 and 0.32 nm from the HRTEM image (Figure S6d), which is in agreement with the (101) and (110) planes of IrO₂. The polycrystalline nature of the particles is confirmed by the selected area electron diffraction (SAED) pattern (Figure S6d, inset).

The surface element chemical states of the samples are determined by XPS analysis (Figure 3 and Figure S8). For



Figure 3. High-resolution (a) Ni 2p, (b) Fe 2p, (c) Se 3d, and (d) O 1s XPS spectra for porous $(Ni_{0.75}Fe_{0.25})Se_2$ nanosheets.

(N_{i0.75}Fe_{0.25})Se₂, the Ni 2p XPS spectrum (Figure 3a) shows that the peaks at 853.45, 855.84, 870.58, and 873.88 eV correspond to $Ni^{2+}2p_{3/2}$, $Ni^{3+}2p_{3/2}$, $Ni^{2+}2p_{1/2}$, and $Ni^{3+}2p_{1/2}$, respectively. Meanwhile, the satellite peaks are preserved in the Ni 2p region.^{18,28} The appearance of the peaks at 857.53 and 876.68 eV may be attributed to γ -NiOOH on the surface, which is a significant active phase for OER in the Ni-based catalysts.³² In the Fe 2p XPS spectrum (Figure 3b), the binding energy peaks at 705.78 and 712.52 eV are attributed to $Fe^{2+} 2p_{3/2}$ and $Fe^{3+} 2p_{3/2}$ signals, respectively.^{26,39} The ratio of $Fe^{3+}:Fe^{2+}$ is \sim 1.7. In addition, the peak fitting of Se 3d shows that peaks at 54.95 and 55.78 eV correspond to Se $3d_{5/2}$ and Se $3d_{3/2}$ (Figure 3c). The peaks at 59.2 and 59.7 eV are attributed to Se-O bonding structures which confirm the surface oxidation of Se species (SeO₂).^{18,39} The O 1s peak at 530.96 eV is attributed to oxygen in -OH groups which increases the hydrophilicity of the electrode (Figure 3d).^{18,34}

The electrocatalytic OER activities of the products are measured with a standard three electrode system in 1 M KOH. As comparison, the CFC substrate and the benchmark IrO₂ (deposited on CFC with the same mass loading) are also tested in the same condition. Figure 4a shows the *iR*-corrected LSV curves of as-prepared and control samples at a scan rate of 5 mV s^{-1} . As shown in Figure 4a, the current density of the bare CFC control sample is almost zero even with the increase of potential, which means that the bare CFC has no contribution to the OER activity. Meanwhile, all of the as-prepared samples exhibit considerable OER activity and certain oxidation reactions are observed before the onset of OER. For the Nibased nanosheet precursor, an anodic peak can be observed at 1.42 V (vs reversible hydrogen electrode, RHE), which corresponds to the reversible reactions of Ni(II)/Ni(III). Upon selenization, the corresponding peak of NiSe₂ shifts to lower position of 1.39 V vs RHE. The same phenomenon can be seen in NiFe-based samples. The anodic peak shifted from 1.47 to 1.45 V vs RHE after the selenization of NiFe-based nanosheet precursor. The oxidation peaks of selenides are



Figure 4. Electrochemical performances of Ni-based nanosheet precursor, porous NiSe₂ nanosheets, NiFe-based nanosheet precursor, and porous $(Ni_{0.75}Fe_{0.25})Se_2$ nanosheets for OER. (a) *iR*-corrected polarization curves in 1 M KOH solution at 5 mV s⁻¹. (b) Corresponding Tafel plots. (c) Charging current density differences plotted vs scan rates. The linear slope is twice that of the C_{dl} . (d) Chronopotentiometric curves of Ni-based nanosheet precursor and porous NiSe₂ nanosheets at 15 mA cm⁻², and NiFe-based precursor and porous $(Ni_{0.75}Fe_{0.25})Se_2$ nanosheets at 35 mA cm⁻².

broadened and shifted toward negative direction, suggesting that the catalysts possess low polarization. The redox potential shift may be attributed to the strength of charge transfer after selenization. Electrode materials will possess low polarization with more favorable charge transport kinetics. This can be drawn from previous studies.^{14,47,48} It should be pointed out that there is a positive shift in the redox potential for NiFebased samples compared with Ni-based samples. It indicates that the electrochemical oxidation of Ni(OH)₂ to NiOOH is suppressed by the presence of Fe, which is also observed in previous studies.^{40–42} It seems more difficult to oxidize Ni^{2+} to Ni³⁺ with Fe incorporation, which needs more oxidizing energy, and thus possibly strengthen OER kinetics. The enhanced performance after selenization and Fe incorporation is clearly shown from the LSV (Figure 4a). Specifically, porous NiSe₂ nanosheets exhibit an overpotential of 323 mV at the current density of 10 mA cm⁻². Meanwhile, the overpotential of Nibased nanosheet precursor is located at 368 mV at the same current density of 10 mA cm⁻². At a higher current density of 35 mA cm⁻², porous (Ni_{0.75}Fe_{0.25})Se₂ nanosheets exhibit a lower overpotential of 255 mV, which is 57 mV less than that of the benchmark IrO₂ on CFC. In comparison, the overpotential of NiFe-based nanosheet precursor is 281 mV at the same current density. Moreover, even at a much larger current density (such as 100 mA cm⁻²), the overpotential of porous (Ni₀₇₅Fe₀₂₅)Se₂ nanosheets is still as low as 277 mV. In comparison, the porous NiSe₂ nanosheets exhibit significantly inferior OER activity which reveals that the high catalytic activity is due to the synergistic effect between nickel and iron in the selenides.^{40,42,44} Mass activity is a relatively suitable activity parameter as reported by Fabbri et al.⁴⁶ The mass activity of the (Ni_{0.75}Fe_{0.25})Se₂, NiFe-based nanosheet precursor, NiSe₂, Ni-based nanosheet precursor, and IrO₂ catalysts at 1.6 V vs RHE is shown in Figure S14. The results reveal the same trends in catalytic activity as the LSV curves. The Ni/Fe ratio of nickel-iron selenide is 3, which is

consistent with the outstanding bimetallic (Ni, Fe) catalysts in previous studies. $^{43,44}_{\rm }$

The OER kinetics is estimated by the Tafel slope (Figure 4b). The Tafel slopes are 47.2, 66.2, 83.6, 86.0, and 63.3 mV dec⁻¹ for porous (Ni_{0.75}Fe_{0.25})Se₂ nanosheets, NiFe-based nanosheet precursor, porous NiSe2 nanosheets, Ni-based nanosheet precursor, and IrO2, respectively. The porous (Ni₀₇₅Fe₀₂₅)Se₂ nanosheets exhibit the smallest Tafel slope, which implies more favorable reaction kinetics during the OER process than the other samples. The improved kinetics is attributed to the richer active sites on the porous nanostructure, which can further be confirmed by the ECSA. The ECSA is evaluated through electrochemical double layer capacitance $(C_{\rm dl})$. As shown in Figure 4c and Figure S9, it can be observed that porous $(Ni_{0.75}Fe_{0.25})Se_2$ nanosheets have the largest C_{dl} value (about 30.2 mF cm⁻² at a potential window of 0.15-0.25 V vs saturated calomel electrode) when compared with the other products (16.4 mF cm⁻² for NiFe-based precursor, 4.1 mF cm⁻² for porous NiSe₂ nanosheets, 3.3 mF cm⁻² for Nibased precursor, and 1.4 mF cm⁻² for CFC). The C_{dl} value of CFC is very small and can be ignored compared with (Ni_{0.75}Fe_{0.25})Se₂ catalyst. The (Ni_{0.75}Fe_{0.25})Se₂ catalyst with porous nanostructure has a larger ECSA, revealing that the number of active sites for catalyzing the oxygen evolution reaction are increased obviously after Fe incorporation and selenization. The porous nanostructure formed by the transformation from ultrathin NiFe-based nanosheet precursor brings larger contact area between oxygen electrode and electrolyte, and the mass transport is enhanced. Meanwhile, the active sites can be abundantly exposed to the electrolyte. In addition, the charge transport kinetics would have been strengthened by the selenization process. This can be concluded from the EIS (Figure 5), which indicates that the



Figure 5. Nyquist plots of Ni-based precursor, NiSe₂, NiFe-based precursor, and $(Ni_{0.75}Fe_{0.25})Se_2$ at 1.6 V vs RHE, respectively.

porous $(Ni_{0.75}Fe_{0.25})Se_2$ nanosheets exhibit the lowest charge transfer resistance (R_{ct}) in comparison with the other samples (Table S4). It is worth mentioning that a low R_{ct} can endow an efficient pathway for electron transportation on the interface between electrode and electrolyte.¹⁸

Besides the improved electrocatalytic performance discussed above, it should be noted that the durability of the electrodes is also an important factor to evaluate the oxygen evolution performance. As shown in Figure 4d, the stability of NiFe-based precursor and porous $(Ni_{0.75}Fe_{0.25})Se_2$ nanosheets is tested at a constant current density of 35 mA cm⁻² by chronopotentiometric measurement. In comparison, the stability of Ni-based precursor and porous $NiSe_2$ nanosheets is tested at a current density of 15 mA cm⁻². Obviously, the $(Ni_{0.75}Fe_{0.25})Se_2$ nanosheets possess superior stability. This is probably due to the more obvious porous nanostructure (consists of a large number of small particles) and larger surface area in comparison with other samples, which can minimize the gas bubble growth and promote the detachment of small bubbles from the electrode. The electron transfer is temporarily blocked when the surface of the catalyst is covered by gas bubbles. That will generate a high local current density and damage the structure of the catalyst, which may result in materials loss from the electrode during the stability test.⁴⁶ In fact, the nickel—iron bimetallic selenide has a superior catalytic activity in comparison with non-noble metal catalysts as previously reported (Table S5).

The composition of selenide catalysts after OER electrolysis was probed by XPS and ICP measurement. As shown in Figure S10a, the high-resolution Ni 2p XPS spectrum exhibits two peaks at 855.18 and 872.92 eV, corresponding to the Ni³⁺ $2p_{3/2}$ and Ni³⁺ $2p_{1/2}$ binding energies, respectively. The appearance of the peaks at 857.41 and 874.79 eV can be attributed to oxvhvdroxide.^{14,18,38} The valence state of nickel changes during the OER process, which varies from mixed valence (Ni^{2+}/Ni^{3+}) to +3. The high-resolution Fe 2p spectrum displays two peaks at 705.82 and 712.64 eV, corresponding to the $Fe^{2+} 2p_{3/2}$ and $Fe^{3+} 2p_{3/2}$ binding energies, respectively (Figure S10b). In the meantime, it reveals that the ratio of Fe³⁺and Fe²⁺ increases from 1.7 to 4.3 after OER. This indicates that Fe^{2+} species is also oxidized during OER electrolysis. In addition, the peak intensity of O 1s increases (Figure S10d,e). Some selenide species still remain on the catalyst surface, which can be attributed to (Ni_{0.75}Fe_{0.25})Se₂. All of this information suggests that most of the surface of (Ni_{0.75}Fe_{0.25})Se₂ is oxidized into oxyhydroxides. It probably generates Ni1-xFexOOH on the surface, which corresponds to the reaction $(Ni_{1-x}Fe_x)^{2+}$ + $3OH^- \rightarrow Ni_{1-x}Fe_xOOH + H_2O + e^-$. This is similar to other Fe-doped Ni-based catalysts in previous studies.^{40,41,44} The Ni_{1-x}Fe_xOOH/(Ni_{0.75}Fe_{0.25})Se₂/CFC serves as the real active sites in the electrolysis. Meanwhile, (Ni_{0.75}Fe_{0.25})Se₂ can play a significant role in maintaining the electronic conductivity between the electrode and active oxyhydroxide layer and thus provides an effective electron path, which contributes to the great OER activity. Moreover, the XRD pattern of (Ni₀₇₅Fe₀₂₅)Se₂ after OER electrolysis exhibits broad peaks (Figure S12). This means the catalyst has low crystallinity and some structure changes occur after OER test, while the ratio of Ni and Fe has no change during the OER process (Figure S13 and Table S1-S3). The reason for the loss of Se may be attributed to the oxidation process. In comparison, the XPS characterization of post-OER NiSe₂ has also been done, which shows results similar to those of $(Ni_{0.75}Fe_{0.25})Se_2$ (Figure S11). Furthermore, Trotochaud et al. reported that Fe increases the conductivity of NiOOH, which might result in the enhanced activity of Ni1_,Fe,OOH relative to NiOOH.44 It may exert a partial charge transfer activation between Ni and Fe and modify the electronic properties of the Ni centers. Friebel et al. provided operando X-ray absorption spectroscopy (XAS) measurements to prove that Fe acts as the OER active site in (Ni, Fe) oxyhydroxide catalysts.⁴⁵ Combined with the above information, it is clear that the Fe incorporation plays an important role in the bimetallic (Ni, Fe) catalysts, which can significantly increase the electrocatalytic activity for OER.

ACS Applied Materials & Interfaces

CONCLUSIONS

In this work, porous (Ni_{0.75}Fe_{0.25})Se₂ nanosheets uniformly grown on CFC were successfully synthesized by direct conversion of NiFe-based nanosheet precursor. This oxygen evolution electrode exhibits efficient catalytic activity during OER: a small overpotential of ~255 mV at a current density of 35 mA cm⁻²; a Tafel slope as low as 47.2 mV dec⁻¹; and excellent durability. The impressive performance of the nickeliron bimetallic selenide is attributed to the porous nanostructure, good electronic conductivity, and high electrochemically active surface area derived from the Fe incorporation and selenization. The porous nanosheets consist of a large number of small particles, which can be fully exposed to the electrolyte with high surface area. Meanwhile, it can facilitate oxygen bubbles release from the electrode surface and prevent them from clustering and harming the catalysts. During the OER process, the Ni^{2+} and Fe^{2+} in the $(Ni_{0.75}Fe_{0.25})Se_2$ are oxidized into higher valence. It probably generates $Ni_{1-x}Fe_xOOH$ on the surface, which serves as the real active material in the electrolysis. Meanwhile, the good conductivity of (Ni0.75Fe0.25)-Se₂ contributes to the high-efficiency electron transport between electrode and reactive sites. Therefore, our work provides a simple and effective strategy to prepare nickel-iron bimetallic selenide with porous nanostructure, which would be beneficial for constructing a cost-effective and highly efficient bimetallic OER electrode.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b03392.

XRD patterns, SEM images, TEM images, EDS elemental mapping images, double layer capacitance measurements, EDS spectra, and nitrogen adsorption–desorption isotherms (Figures S1–S14) and XPS data, ICP data, mass activity, and comparison of different non-noble metal catalysts in alkaline electrolytes (Tables S1–S5) (PDF)

AUTHOR INFORMATION

Corresponding Authors

*(L.M.) E-mail: mlq518@whut.edu.cn. *(L.H.) E-mail: hel@whut.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Key Research Program of China (2016YFA0202603), the National Basic Research Program of China (Grant No. 2013CB934103), the International Science & Technology Cooperation Program of China (Grant No. 2013DFA50840), the National Natural Science Foundation of China (Grant Nos. 51521001, 51272197, and 51502227), the National Natural Science Fund for Distinguished Young Scholars (Grant No. 51425204), the China Postdoctoral Science (Grant No. 2015T80845), and the Foundation and the Fundamental Research Funds for the Central Universities (WUT; Grant Nos. 2014-IV-062 and 2014-IV-147).

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) Turner, J. A. Sustainable Hydrogen Production. Science 2004, 305, 972-974.

(3) Reece, S. Y.; Hamel, J. A.; Sung, K.; Jarvi, T. D.; Esswein, A. J.; Pijpers, J. J. H.; Nocera, D. G. Wireless Solar Water Splitting Using Silicon-Based Semiconductors and Earth-Abundant Catalysts. *Science* **2011**, 334, 645–648.

(4) Koper, M. T. M. Thermodynamic Theory of Multi-Electron Transfer Reactions: Implications for Electrocatalysis. *J. Electroanal. Chem.* **2011**, *660*, 254–260.

(5) Jiao, Y.; Zheng, Y.; Jaroniec, M.; Qiao, S. Z. Design of Electrocatalysts for Oxygen- and Hydrogen-Involving Energy Conversion Reactions. *Chem. Soc. Rev.* **2015**, *44*, 2060–2086.

(6) Lee, Y.; Suntivich, J.; May, K. J.; Perry, E. E.; Shao-Horn, Y. Synthesis and Activities of Rutile IrO_2 and RuO_2 Nanoparticles for Oxygen Evolution in Acid and Alkaline Solutions. *J. Phys. Chem. Lett.* **2012**, *3*, 399–404.

(7) Reier, T.; Oezaslan, M.; Strasser, P. Electrocatalytic Oxygen Evolution Reaction (OER) on Ru, Ir, and Pt Catalysts: A Comparative Study of Nanoparticles and Bulk Materials. *ACS Catal.* **2012**, *2*, 1765–1772.

(8) Gorlin, Y.; Jaramillo, T. F. A Bifunctional Nonprecious Metal Catalyst for Oxygen Reduction and Water Oxidation. *J. Am. Chem. Soc.* **2010**, *132*, 13612–13614.

(9) Subbaraman, R.; Tripkovic, D.; Chang, K. C.; Strmcnik, D.; Paulikas, A. P.; Hirunsit, P.; Chan, M.; Greeley, J.; Stamenkovic, V.; Markovic, N. M. Trends in Activity for the Water Electrolyser Reactions on 3d M (Ni,Co,Fe,Mn) Hydr(oxy)oxide Catalysts. *Nat. Mater.* **2012**, *11*, 550–557.

(10) Du, J.; Chen, C.; Cheng, F.; Chen, J. Rapid Synthesis and Efficient Electrocatalytic Oxygen Reduction/Evolution Reaction of $CoMn_2O_4$ Nanodots Supported on Graphene. *Inorg. Chem.* 2015, 54, 5467–5474.

(11) Kibria, M. F.; Mridha, M. S. Electrochemical Studies of the Nickel Electrode for the Oxygen Evolution Reaction. *Int. J. Hydrogen Energy* **1996**, *21*, 179–182.

(12) Deabate, S.; Henn, F. Structural Modifications and Electrochemical Behaviour of the β (II)-Ni(OH)₂/ β (III)-NiOOH Redox Couple upon Galvanostatic Charging/Discharging Cycling. *Electrochim. Acta* **2005**, *50*, 2823–2835.

(13) Wang, J.; Li, K.; Zhong, H. X.; Xu, D.; Wang, Z. L.; Jiang, Z.; Wu, Z. J.; Zhang, X. B. Synergistic Effect between Metal-Nitrogen-Carbon Sheets and NiO Nanoparticles for Enhanced Electrochemical Water-Oxidation Performance. *Angew. Chem., Int. Ed.* **2015**, *54*, 10530–10534.

(14) Tang, C.; Cheng, N.; Pu, Z.; Xing, W.; Sun, X. NiSe Nanowire Film Supported on Nickel Foam: An Efficient and Stable 3D Bifunctional Electrode for Full Water Splitting. *Angew. Chem., Int. Ed.* **2015**, *54*, 9351–9355.

(15) Li, Y.; Hasin, P.; Wu, Y. Ni_xCo_{3-x}O₄ Nanowire Arrays for Electrocatalytic Oxygen Evolution. *Adv. Mater.* **2010**, *22*, 1926–1929. (16) Ma, T. Y.; Dai, S.; Jaroniec, M.; Qiao, S. Z. Metal-Organic Framework Derived Hybrid Co₃O₄-Carbon Porous Nanowire Arrays as Reversible Oxygen Evolution Electrodes. *J. Am. Chem. Soc.* **2014**, *136*, 13925–13931.

(17) Liu, D.; Lu, Q.; Luo, Y.; Sun, X.; Asiri, A. M. $NiCo_2S_4$ Nanowires Array as an Efficient Bifunctional Electrocatalyst for Full Water Splitting with Superior Activity. *Nanoscale* **2015**, *7*, 15122–15126.

(18) Xia, C.; Jiang, Q.; Zhao, C.; Hedhili, M. N.; Alshareef, H. N. Selenide-Based Electrocatalysts and Scaffolds for Water Oxidation Applications. *Adv. Mater.* **2016**, *28*, 77–85.

(19) Li, S.; Wang, Y.; Peng, S.; Zhang, L.; Al-Enizi, A. M.; Zhang, H.; Sun, X.; Zheng, G. Co-Ni-Based Nanotubes/Nanosheets as Efficient Water Splitting Electrocatalysts. *Adv. Energy Mater.* **2016**, *6*, 1501661.

ACS Applied Materials & Interfaces

(21) Chen, S.; Duan, J.; Bian, P.; Tang, Y.; Zheng, R.; Qiao, S.-Z. Three-Dimensional Smart Catalyst Electrode for Oxygen Evolution Reaction. *Adv. Energy Mater.* **2015**, *5*, 1500936.

(22) Liang, H.; Li, L.; Meng, F.; Dang, L.; Zhuo, J.; Forticaux, A.; Wang, Z.; Jin, S. Porous Two-Dimensional Nanosheets Converted from Layered Double Hydroxides and Their Applications in Electrocatalytic Water Splitting. *Chem. Mater.* **2015**, *27*, 5702–5711.

(23) Long, X.; Li, J.; Xiao, S.; Yan, K.; Wang, Z.; Chen, H.; Yang, S. A Strongly Coupled Graphene and FeNi Double Hydroxide Hybrid as an Excellent Electrocatalyst for the Oxygen Evolution Reaction. *Angew. Chem.* **2014**, *126*, 7714–7718.

(24) Zhang, G.; Xia, B. Y.; Wang, X.; Lou, X. W. Strongly Coupled NiCo₂O₄-rGO Hybrid Nanosheets as a Methanol-Tolerant Electrocatalyst for the Oxygen Reduction Reaction. *Adv. Mater.* **2014**, *26*, 2408–2412.

(25) Tang, C.; Wang, H. S.; Wang, H. F.; Zhang, Q.; Tian, G. L.; Nie, J. Q.; Wei, F. Spatially Confined Hybridization of Nanometer-Sized NiFe Hydroxides into Nitrogen-Doped Graphene Frameworks Leading to Superior Oxygen Evolution Reactivity. *Adv. Mater.* **2015**, *27*, 4516–4522.

(26) Gong, M.; Li, Y.; Wang, H.; Liang, Y.; Wu, J. Z.; Zhou, J.; Wang, J.; Regier, T.; Wei, F.; Dai, H. An Advanced Ni-Fe Layered Double Hydroxide Electrocatalyst for Water Oxidation. *J. Am. Chem. Soc.* **2013**, *135*, 8452–8455.

(27) Liang, J.; Yang, Y.; Zhang, J.; Wu, J.; Dong, P.; Yuan, J.; Zhang, G.; Lou, J. Metal Diselenide Nanoparticles as Highly Active and Stable Electrocatalysts for the Hydrogen Evolution Reaction. *Nanoscale* **2015**, *7*, 14813–14816.

(28) Shi, J.; Hu, J.; Luo, Y.; Sun, X.; Asiri, A. M. Ni₃Se₂ Film as a Non-Precious Metal Bifunctional Electrocatalyst for Efficient Water Splitting. *Catal. Sci. Technol.* **2015**, *5*, 4954–4958.

(29) Xu, K.; Chen, P.; Li, X.; Tong, Y.; Ding, H.; Wu, X.; Chu, W.; Peng, Z.; Wu, C.; Xie, Y. Metallic Nickel Nitride Nanosheets Realizing Enhanced Electrochemical Water Oxidation. *J. Am. Chem. Soc.* **2015**, *137*, 4119–4125.

(30) Stern, L. A.; Feng, L.; Song, F.; Hu, X. Ni₂P as a Janus Catalyst for Water Splitting: The Oxygen Evolution Activity of Ni_2P Nanoparticles. *Energy Environ. Sci.* **2015**, *8*, 2347–2351.

(31) You, B.; Jiang, N.; Sheng, M.; Bhushan, M. W.; Sun, Y. Hierarchically Porous Urchin-Like Ni₂P Superstructures Supported on Nickel Foam as Efficient Bifunctional Electrocatalysts for Overall Water Splitting. *ACS Catal.* **2016**, *6*, 714–721.

(32) Han, N.; Zhao, F.; Li, Y. Ultrathin Nickel-Iron Layered Double Hydroxide Nanosheets Intercalated with Molybdate Anions for Electrocatalytic Water Oxidation. *J. Mater. Chem. A* **2015**, *3*, 16348–16353.

(33) Lu, Z.; Xu, W.; Zhu, W.; Yang, Q.; Lei, X.; Liu, J.; Li, Y.; Sun, X.; Duan, X. Three-Dimensional NiFe Layered Double Hydroxide Film for High-Efficiency Oxygen Evolution Reaction. *Chem. Commun.* **2014**, *50*, 6479–6482.

(34) Liu, X.; Wang, X.; Yuan, X.; Dong, W.; Huang, F. Rational Composition and Structural Design of in Situ Grown Nickel-Based Electrocatalysts for Efficient Water Electrolysis. *J. Mater. Chem. A* **2016**, *4*, 167–172.

(35) Shim, H. S.; Shinde, V. R.; Kim, J. W.; Gujar, T. P.; Joo, O. S.; Kim, H. J.; Kim, W. B. Diameter-Tunable CdSe Nanotubes from Facile Solution-Based Selenization of Cd(OH)₂ Nanowire Bundles for Photoelectrochemical Cells. *Chem. Mater.* **2009**, *21*, 1875–1883.

(36) Iveson, S. M.; Litster, J. D.; Hapgood, K.; Ennis, B. J. Nucleation, Growth and Breakage Phenomena in Agitated Wet Granulation Processes: A Review. *Powder Technol.* **2001**, *117*, 3–39.

(37) Jia, C.; Yang, P.; Zhang, A. Glycerol and Ethylene Glycol Co-Mediated Synthesis of Uniform Multiple Crystalline Silver Nanowires. *Mater. Chem. Phys.* **2014**, *143*, 794–800. (38) Bediako, D. K.; Lassalle-Kaiser, B.; Surendranath, Y.; Yano, J.; Yachandra, V. K.; Nocera, D. G. Structure-Activity Correlations in a Nickel-Borate Oxygen Evolution Catalyst. *J. Am. Chem. Soc.* **2012**, *134*, 6801–6809.

(39) Huang, S.; He, Q.; Chen, W.; Qiao, Q.; Zai, J.; Qian, X. Ultrathin FeSe₂ Nanosheets: Controlled Synthesis and Application as a Heterogeneous Catalyst in Dye-Sensitized Solar Cells. *Chem. - Eur. J.* **2015**, *21*, 4085–4091.

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

(41) Fominykh, K.; Chernev, P.; Zaharieva, I.; Sicklinger, J.; Stefanic, G.; Döblinger, M.; Müller, A.; Pokharel, A.; Böcklein, S.; Scheu, C.; Bein, T.; Fattakhova-Rohlfing, D. Iron-Doped Nickel Oxide Nanocrystals as Highly Efficient Electrocatalysts for Alkaline Water Splitting. *ACS Nano* **2015**, *9*, 5180–5188.

(42) Corrigan, D. A. The Catalysis of the Oxygen Evolution Reaction by Iron Impurities in Thin Film Nickel Oxide Electrodes. *J. Electrochem. Soc.* **1987**, *134*, 377–384.

(43) Burke, M. S.; Zou, S.; Enman, L. J.; Kellon, J. E.; Gabor, C. A.; Pledger, E.; Boettcher, S. W. Revised Oxygen Evolution Reaction Activity Trends for First-Row Transition-Metal (Oxy)hydroxides in Alkaline Media. J. Phys. Chem. Lett. **2015**, *6*, 3737–3742.

(44) Trotochaud, L.; Young, S. L.; Ranney, J. K.; Boettcher, S. W. Nickel-Iron Oxyhydroxide Oxygen-Evolution Electrocatalysts: The Role of Intentional and Incidental Iron Incorporation. *J. Am. Chem. Soc.* **2014**, *136*, 6744–6753.

(45) Friebel, D.; Louie, M. W.; Bajdich, M.; Sanwald, K. E.; Cai, Y.; Wise, A. M.; Cheng, M.; Sokaras, D.; Weng, T.; 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.

(46) Fabbri, E.; Habereder, A.; Waltar, K.; Kötz, R.; Schmidt, T. J. Developments and Perspectives of Oxide-Based Catalysts for the Oxygen Evolution Reaction. *Catal. Sci. Technol.* **2014**, *4*, 3800–3821. (47) Shi, Y.; Wen, L.; Li, F.; Cheng, H. M. Nanosized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ / Graphene Hybrid Materials with Low Polarization for High Rate Lithium Ion Batteries. *J. Power Sources* **2011**, *196*, 8610–8617.

(48) Wu, J. B.; Li, Z. G.; Lin, Y. Porous NiO/Ag Composite Film for Electrochemical Capacitor Application. *Electrochim. Acta* 2011, 56, 2116–2121.