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Article

Selective Se doping of NiFe_2O_4 on an active NiOOH scaffold for efficient and robust water oxidation

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ABSTRACT

There remains a challenge in designing electrocatalysts for water oxidation to create highly efficient catalytic sites for the oxygen evolution reaction (OER) while maintaining their robustness at large outputs. Herein, an etching-assisted synthesis approach was developed to integrate highly active NiFe_2O_4 nanoparticles with a robust and active NiOOH scaffold directly on commercial stainless steel. A precise selenization strategy was then introduced to achieve selective Se doping of NiFe_2O_4 to further enhance its intrinsic OER activity while maintaining a three-dimensional NiOOH nanosheet array as a robust scaffold for prompt mass transfer and gas evolution. The resulting $\text{NiFe}_2\text{O}_4\text{-xSe}_x/\text{NiOOH}$ electrode exhibited superior electrocatalytic activity with low overpotentials of 153 and 259 mV to deliver benchmark current densities of 10 and 500 mA cm^{-2} , respectively. More importantly, the catalyst exhibited remarkable durability at a stable current output of 100 mA cm^{-2} for hundreds of hours. These findings may open up opportunities for exploring efficient and robust electrocatalysts for scalable hydrogen production with practical materials.

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1. Introduction

Hydrogen has attracted increasing attention because of its essential role in several important industrial processes, particularly as a new-style energy carrier in energy conversion [1–3]. Compared with reforming fossil fuels, water splitting using

renewable energy resources such as solar and hydropower is a promising alternative method for hydrogen production without CO_2 emissions [4]. Because of the sluggish kinetics involving a four-electron process, the oxygen evolution reaction (OER) is the efficiency-limiting step for water splitting and other energy devices such as fuel cells and metal-air batteries [5,6]. Although

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noble metal-based catalysts such as iridium and ruthenium oxides (IrO_2 and RuO_2) have shown high activity for OER [7,8], their high cost and scarcity impede their practical application, which calls for the development of efficient, nonprecious-metal electrocatalysts.

Although enormous efforts have been made to explore cost-effective electrocatalysts, including oxides, oxyhydroxides, and chalcogenides, it is still challenging to develop highly active catalysts while meeting durability requirements [9–18]. Recently, metal sulfides or selenides have been reported as efficient catalysts for OER because they can evolve into S- or Se-doped oxides and oxyhydroxides as highly active sites under the strong oxidative conditions of OER [19,20]. Unfortunately, such evolution and conversion processes usually lead to severe structural distortion and collapse, causing inevitable stability issues. Therefore, the rational design of one unit with a robust scaffold decorated with highly efficient active sites may be an effective way to create high-performance OER catalysts.

In general, oxyhydroxides exhibit remarkable stability during OER owing to their “self-healing” process [21,22]. For example, NiOOH has been considered the true catalytic active site for $\text{Ni}(\text{OH})_2$, NiSe , and NiS electrocatalysts, although its OER activity needs to be further improved [18,23]. NiFe_2O_4 with an inverse-spinel-structure is regarded as a more active electrocatalyst for OER because of its good conductivity and appropriate adsorption/desorption of intermediate species of OER [24–26]. In particular, the vulcanization or selenization of NiFe_2O_4 would further enhance its electrocatalytic activity for OER [19]. Therefore, the combination of active NiOOH as a robust scaffold and NiFe_2O_4 as the active site, followed by the precise selenization of NiFe_2O_4 , would be a good option to create the abovementioned heterostructures as highly efficient OER catalysts. However, the energy difference between the two phases, which is mainly determined by temperature and ligand molecules, makes it challenging to fabricate heterostructures of NiOOH and NiFe_2O_4 and, needless to say, to carry out the subsequent selective selenization. Herein, we developed a one-step KOH etching-assisted method for the direct fabrication of three-dimensional (3D) $\text{NiFe}_2\text{O}_4/\text{NiOOH}$ heterostructures on a commercial stainless-steel mesh consisting of NiOOH nanosheet arrays decorated by NiFe_2O_4 nanocrystals. The precise selenization of NiFe_2O_4 into $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x$ was further achieved to create highly active Se-doped catalytic sites while keeping the 3D NiOOH nanosheet array intact as a robust scaffold, endowing the heterostructure electrode with remarkable electrocatalytic activity and stability for OER.

2. Experimental

2.1. Chemicals and materials

A stainless-steel mesh was purchased from Wuxi Xinmeihui Metal Technology Co., Ltd. Sodium borohydride, potassium hydroxide, ethanol, and acetone were obtained from the National Reagent Company. Se powder, commercial RuO_2 , and Nafion™ (5 wt%) were provided by Sigma-Aldrich. Milli-Q water (18.2 M Ω cm at 25 °C) was used for all the experiments. All

reagents were of analytical grade and were used without further purification.

2.2. Preparation of $\text{NiFe}_2\text{O}_4/\text{NiOOH}$ heterostructures

A stainless-steel mesh containing several inherent transition metal elements (Fe, Ni, Mn), which are potentially catalytically active, was selected as the back electrode and the metal source for the growth of $\text{NiFe}_2\text{O}_4/\text{NiOOH}$ heterostructures owing to its excellent conductivity and 3D structure, allowing the electrolyte to fully contact the surface of the catalyst and enable fast mass transfer. A piece of stainless-steel mesh (1 × 3 cm, 600 mesh) was ultrasonically cleaned in acetone, HCl, distilled water, and ethanol successively for 30 min and then kept in a vacuum oven at 40 °C for 24 h. Typically, the pretreated stainless steel was transferred to a 50 mL autoclave containing 6 M KOH solution and maintained at 160 °C for 16 h. The KOH concentration, reaction temperature, and reaction duration were varied to control the morphology and composition of the products. Bare NiOOH nanosheets were obtained at 150 °C in 6 M KOH, and bare NiFe_2O_4 nanoparticles were formed at 200 °C in 12 M KOH.

2.3. Selenization of $\text{NiFe}_2\text{O}_4/\text{NiOOH}$ heterostructures

The NaHSe solution was prepared by adding Se powder (65 mg) to deionized water (30 mL) containing NaBH_4 (65 mg) under N_2 flow while stirring. In a typical process, the solution was transferred to a 50-mL autoclave with a piece of $\text{NiFe}_2\text{O}_4/\text{NiOOH}$ on stainless steel and maintained at 180 °C for 24 h in an oven. For different degrees of selenization, samples were prepared using different hydrothermal times (16 h, 24 h). For comparison, samples of bare NiFe_2O_4 were selenized under the same selenization conditions. The final product was defined as $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x$.

2.4. Materials characterization

The crystal structure was studied by X-ray power diffraction (XRD) on a Bruker D8 Advance Power X-ray diffractometer at 40 kV and 40 mA for monochromatized $\text{Cu K}\alpha$ ($\lambda = 0.15406$ nm). The morphology, composition, and structure were studied using field emission scanning electron microscopy (FESEM, HITACHI S-4800) and high-resolution transmission electron microscopy (HRTEM) with a JEOL JEM 2100 microscope operating at 200 kV. Raman spectroscopy was performed on a confocal microscopic Raman spectrometer (HORIBA LabRAM HR Evolution) with an excitation laser at 532 nm and a low laser power of 1 mW. The contact angles were measured under ambient conditions on a JC2000D optical contact angle measuring device. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific ESCALab 250 instrument using 200 W monochromatic $\text{Al K}\alpha$ radiation. Inductively coupled plasma (ICP) analysis was carried out using a Thermo iCAP 7200 ICP-OES instrument. The composition of the stainless-steel mesh was measured using an electron probe micro-analyzer (EPMA-1720).

2.5. Electrochemical measurements

All electrochemical measurements were performed using a standard three-electrode cell on an electrochemical workstation (CHI660E, Shanghai Chen Hua Instruments Co., China), with a platinum plate as the counter electrode and a Ag/AgCl (3.3 M KCl) electrode as the reference electrode. The active area of the prepared electrodes for electrochemical tests was 1×1 cm. Linear sweep voltammetry (LSV) curves for all the electrocatalysts were recorded after 20 cycles of cyclic voltammetry (CV) until a stable CV curve was obtained. To exclude the effect of the reference electrode in the alkali solution, the performance of $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x/\text{NiOOH}$ was evaluated with a Hg/HgO electrode as the reference electrode, and nearly identical LSV curves were obtained (Fig. S1), confirming its outstanding electrocatalytic activity.

LSV curves were recorded in a 1 M KOH solution at a scan rate of 5 mV s^{-1} without iR-correction. Because $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x/\text{NiOOH}$ exhibited a current density of 10 mA cm^{-2} at 1.41 V vs. RHE, electrochemical impedance spectroscopy (EIS) tests of all catalysts were carried out at the same potential (1.41 V vs. RHE) over a frequency range of 0.01– 10^5 Hz and an AC amplitude of 5 mV in 1 M KOH to study the charge transfer resistance and solution resistance. The electrochemical active surface areas (ECSAs) were obtained via a series of CV measurements at various scan rates (20, 40, 60, 80, 100, and 120 mV s^{-1}) in a potential window of 0.8–0.9 V vs. RHE. The 6000-cycle stability test was carried out at a scan rate of 50 mV s^{-1} . The Faraday efficiency test of $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x/\text{NiOOH}$ was carried out at an overpotential of 330 mV vs. RHE.

To exclude the influence of ECSA on performance comparisons, the OER curves were normalized by the ECSAs. The ECSA-normalized current density for the as-prepared catalysts was calculated as follows:

ECSA-normalized current density = current density $\times C_s/C_{dl}$ where C_s is the specific capacitance. Here, 0.04 mF cm^{-2} was adopted as the value of C_s based on previously reported OER catalysts in alkaline solution [27], and C_{dl} is the electrochemical double-layer capacitance value of different electrocatalysts.

For comparison, $\sim 5 \text{ mg}$ of commercial RuO_2 was ultrasonically dispersed in a mixture of 550 μL ethanol, 450 μL water, and 50 μL of 5% NafionTM. The dispersion (40 μL) was transferred onto a stainless-steel substrate for electrochemical measurements. The RuO_2 loading was $\sim 0.2 \text{ mg cm}^{-2}$.

2.6. Density functional theory calculation

Geometry optimization and frequency analysis of the constructed systems were carried out using density functional theory (DFT) implemented in the Vienna Ab Initio Simulation Package (VASP). The Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was employed to model the electronic exchange-correlation energy. Projector augmented wave (PAW) pseudo-potentials were adopted to describe the ionic cores. The energy cutoff and Gaussian smearing were set to 600 and 0.05 eV, respectively. The convergence criteria for self-consistent field and geometry

optimization were set to 10^{-7} eV and $0.01 \text{ eV/\AA}$, respectively. The DFT+U method was used to describe the 3d orbitals of Fe and Ni. The k-point sampling of the Brillouin zone was obtained using a $4 \times 4 \times 1$ grid. The mechanisms employed for OER are listed below:

The Gibbs free-energy change of the elementary steps was calculated as follows:

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S + \int C_p dT \quad (5)$$

where ΔE , ΔZPE , ΔS , and $\int C_p dT$ are the reaction energies obtained in the geometry optimization, the zero-point energy correction, the entropy change, and the free-energy correction obtained in the frequency analysis, respectively.

3. Results and discussion

3.1. Preparation and characterization of $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x/\text{NiOOH}$ hybrid catalyst

In a typical experiment, a commercial 304 stainless-steel (SS) mesh with the morphology and composition shown in Fig. S2 and Table S1, respectively, were treated in a KOH solution at 160°C to grow $\text{NiFe}_2\text{O}_4/\text{NiOOH}$ heterostructures. NiFe_2O_4 was then partially selenized while keeping NiOOH unchanged via a hydrothermal process to obtain $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x/\text{NiOOH}$. The details are presented in the experimental section. A possible formation mechanism is proposed in Fig. 1(a).

In general, Fe^{2+} and Ni^{2+} were formed from the stainless-steel substrate during alkali etching and then oxidized. Initially, NiOOH nucleated and grew gradually to form nanosheets because of the low critical concentration of Ni^{3+} . With extended reaction time, the level of Fe^{3+} approached the critical concentration and Fe^{3+} reacted with Ni^{2+} to form NiFe_2O_4 nanoparticles, thus generating $\text{NiOOH}/\text{NiFe}_2\text{O}_4$ heterostructures. Therefore, the ratio of the two phases can be readily controlled by tuning the leaching rates of Fe and Ni ions via the temperature and concentration of OH^- . In two extreme cases, pure NiOOH nanosheets were obtained at 150°C in 6 M KOH, and pure NiFe_2O_4 nanocrystals were formed at 200°C in 12 M KOH (Fig. S3). The well-defined heterostructures can be obtained in a narrow temperature window of approximately 160°C . The XRD results (Fig. S4) suggested that the higher temperature and concentration of KOH were favorable for the formation of NiFe_2O_4 , with a color change from pale yellow to black (140 to 180°C , Fig. S5). ICP analysis (Table S2) of the etching solution after the reaction revealed that the mass fraction of Fe was much higher than that in stainless steel. The pale yellow color of the reaction solution was due to the high concentration of Fe^{3+} (Fig. S6). The mass fractions of Ni, Cr, and Mn were much lower, supporting the suggested formation mechanism. The etching and recrystallization regulated by the temperature and concentration of KOH were likely responsible for the formation of the $\text{NiOOH}/\text{NiFe}_2\text{O}_4$ heterostructures.

Typical samples were characterized first by XRD. As depict-

Fig. 1. (a) Scheme for the preparation of $\text{NiFe}_2\text{O}_{4-x}\text{Se}_y/\text{NiOOH}$. XRD patterns (b) and Raman spectra (c). (I) $\text{NiFe}_2\text{O}_{4-x}\text{Se}_y/\text{NiOOH}$; (II) $\text{NiFe}_2\text{O}_4/\text{NiOOH}$; (III) stainless steel. High-resolution XPS spectra of $\text{NiFe}_2\text{O}_{4-x}\text{Se}_y/\text{NiOOH}$ and $\text{NiFe}_2\text{O}_4/\text{NiOOH}$. (d) Fe 2p; (e) Ni 2p; (f) O 1s; (g) Se 3d.

ed in Fig. 1(b), a set of peaks at 30.3° , 35.7° , 57.4° , 63.0° , and 74.5° were observed for the $\text{NiFe}_2\text{O}_4/\text{NiOOH}$ sample, which corresponded to the (220), (311), (511), (440), and (533) crystallographic planes of cubic NiFe_2O_4 [JCPDS No. 54-0964], respectively [28]. The diffraction peaks at 43.5° , 50.8° , and 74.7° are attributed to the steel substrate (JCPDS No. 33-0397). This result indicates the formation of NiFe_2O_4 on stainless steel. No clear peak from NiOOH was observed, probably owing to its low crystallinity. To probe NiOOH species, Raman spectroscopy was performed (Fig. 1(c)). The two main peaks at ~ 482 and 554 cm^{-1} can be ascribed to the e_g bending vibration and the A_{1g} stretching vibration of Ni–O of NiOOH [29–31], which remained clear after the sample was kept for more than 14 d, suggesting the good stability of NiOOH under ambient conditions (Fig. S7). Two other weak peaks at ~ 335 and 669 cm^{-1} can be indexed to the classic Raman vibration of NiFe_2O_4 [24,32]. The Raman results thus indicated the presence of NiOOH and NiFe_2O_4 . It is noted that two weak peaks at 725 and 786 cm^{-1} appeared, which can be attributed to Cr–O bonding from the oxidation of Cr impurities in the steel substrate [33,34]. After selenization, all the XRD peaks remained at a slightly reduced intensity, indicating that no crystalline impurities were introduced (Fig. 1(b)). The Raman spectra remained nearly unchanged (Fig. 1(c)), implying that NiOOH did not change during the selenization process.

The composition and elemental chemical states of the $\text{NiFe}_2\text{O}_4/\text{NiOOH}$ heterostructures were further studied by XPS

(Figs. 1(d–g) and Fig. S8). The Fe 2p spectrum were fitted with two doublet peaks and two satellite peaks, which shifted to slightly higher energies as compared to those of the steel substrate (Fig. S9). The doublet peaks at 706.7 and 719.8 eV are assigned to metallic Fe from the stainless steel, and the other doublet peaks at higher energies (711.5 and 725.0 eV) are attributed to Fe^{3+} from NiFe_2O_4 [24,25]. In contrast, prominent peaks at 855.7 and 856.8 eV corresponding to Ni^{2+} and Ni^{3+} correspond well to Ni in NiFe_2O_4 and NiOOH [14,33]. In the O 1s spectrum, the peak at 531.4 eV corresponds to hydroxides, indicating the formation of NiOOH [14,24]. After selenization, a clear Se signal was observed in the Se 3d XPS spectrum, with peaks at 58.1 and 54.3 eV assigned to Se–O and Se–metal (Se–M), respectively (Fig. 1(g)) [35]. The binding energies of Ni 2p and Fe 2p shifted slightly to lower energies owing to the modulation of Se doping (Figs. 1(d,e)), as N or P-doping has been previously reported [36,37].

The formation of heterostructures is also owing to morphological evolution. After etching, the smooth surface of the stainless steel was covered by 3D heterostructures consisting of nanoparticles with diameters of 200–400 nm and vertical nanosheets with a lateral size of 1–3 μm and a thickness of $\sim 15\text{ nm}$ (Figs. 2(a,b) and Fig. S10). The STEM-EDS elemental mapping results (Fig. S11) corroborated that the nanosheets and nanoparticles were NiOOH and NiFe_2O_4 , respectively. The selective selenization process did not change the product morphology (Fig. 2(c) and Fig. S12). The TEM image confirmed the

Fig. 2. Typical SEM images of stainless steel (a), NiFe₂O₄/NiOOH (b), and NiFe₂O_{4-x}Se_x/NiOOH (c); (d) TEM image of NiFe₂O_{4-x}Se_x/NiOOH; (e) HRTEM image of the nanoparticle in (d); HRTEM image (f) and SAED pattern (g) of the nanosheet in (d); (h) STEM image and corresponding elemental mapping images of NiFe₂O_{4-x}Se_x/NiOOH.

presence of nanoparticles with diameters of 200–400 nm with darker contrast decorated on the nanosheet (Fig. 2(d)). The lattice fringes of the nanoparticles with a d -spacing of 0.29 nm (Fig. 2(e)) are well indexed to the (220) planes of cubic NiFe₂O₄, confirming that the nanoparticles were NiFe₂O₄. No ordered lattice fringe (Fig. 2(f)) was observed from the nanosheet, indicating the amorphous nature of NiOOH. The selected area electron diffraction (SAED) pattern (Fig. 2(g)) showed no discernible diffraction spots or rings, consistent with the above observations. In the STEM-EDS elemental mapping images, an additional Se signal appeared only in the nanoparticles (Fig. 2(h) and Fig. S13). This result, together with the XRD and Raman results, suggests that NiFe₂O₄ nanoparticles were partially selenized into NiFe₂O_{4-x}Se_x, whereas the NiOOH scaffold did not change, probably owing to the different strengths of the Ni–O bond in NiOOH and NiFe₂O₄, allowing us to achieve selective selenization by controlling the hydrothermal conditions.

3.2. Electrochemical performance of electrocatalysts

The OER electrocatalytic activity of the heterostructure electrodes was evaluated using a standard three-electrode system in O₂-saturated 1 M KOH. The LSV polarization curves without iR-correction for all samples are presented in Fig. 3(a) to evaluate the performance for the practical application of water splitting for hydrogen production. The undoped NiFe₂O₄/NiOOH exhibits excellent OER activity with low overpotentials (η) of 259 and 346 mV at current densities of 10 and 50 mA cm⁻², respectively, significantly outperforming commercial RuO₂ on stainless steel (RuO₂/SS, Figs. S14(a,b)). Pure NiFe₂O₄ and NiOOH samples on SS were prepared in parallel for comparison (Fig. S3). As shown in Fig. 3(a), both NiFe₂O₄ and NiOOH showed reasonable OER activity, and the former was more active. However, the NiFe₂O₄/NiOOH heterostructure delivered appreciably enhanced OER activity, as shown by the 49 and 75 mV lower overpotential at 10 mA cm⁻² than NiFe₂O₄

and NiOOH, respectively. This suggests that the present strategy for combining them is effective for improving the OER activity.

After selective selenization, the NiFe₂O_{4-x}Se_x/NiOOH exhibited remarkably enhanced OER activity, with overpotentials of 182 and 267 mV to drive current densities of 10 and 50 mA cm⁻², respectively. These values are 77 and 79 mV less than those of undoped NiFe₂O₄/NiOOH. Slowing the scanning rate from 5 to 1 mV s⁻¹, the OER activity did not change (Fig. S14(c)), indicating its good electrocatalytic kinetics [38]. This improvement can be ascribed to the electronic modulation of Se doping on the catalytic sites to modulate the adsorption/desorption of intermediates [19,20]. This doping effect can be corroborated by control experiments. (1) The pure NiFe₂O₄ sample was also selenized in parallel under the same conditions. Similarly, the doped NiFe₂O_{4-x}Se_x exhibited enhanced OER activity after Se doping (Fig. S15). (2) With the present doping strategy, the Se dopant content can be easily tuned by varying the reaction time. As shown in Fig. S16, the OER activity increased appreciably as the amount of Se doping increased. Therefore, it is clear that the significantly improved OER activity is owing to the selective Se doping of NiFe₂O_{4-x}Se_x/NiOOH. It should be noted that if both NiFe₂O₄ and NiOOH are selenized via a gas-phase method, the NiOOH scaffold becomes unstable and starts to peel off during OER. This suggests the necessity of precise selenization of NiFe₂O₄ while keeping NiOOH intact.

To assess the electrocatalytic kinetics, Tafel analyses of various catalysts were derived from their LSV polarization curves. NiFe₂O_{4-x}Se_x/NiOOH exhibited the smallest Tafel slope (42.5 mV dec⁻¹), substantially smaller than those of NiFe₂O₄/NiOOH (82.4 mV dec⁻¹) and RuO₂/SS (106.2 mV dec⁻¹) (Fig. 3(b) and Fig. S14(b)), indicating that it had the fastest kinetics. To compare the OER activity of the NiFe₂O_{4-x}Se_x/NiOOH heterostructure with those of reported electrocatalysts, iR-correction was applied to evaluate the present NiFe₂O_{4-x}Se_x/NiOOH electrode. As shown in Fig. 3(a), a benchmark current density of 10 mA cm⁻² was achieved at an ultralow overpotential of 153 mV. Of more interest, it delivered an industrial-level current density of 500 mA cm⁻² at an extremely low overpotential of 259 mV. The Tafel slope after iR-correction was reduced to 22.2 mV dec⁻¹. These results outperformed those of most state-of-the-art analogs (Fig. 3(c) and Table S3) [35,39–44]. Interestingly, the NiFe₂O_{4-x}Se_x/NiOOH electrode exhibited pH-dependent OER activity (Fig. S17), suggesting that lattice oxygens may also have taken part in the OER process [45,46].

To determine whether the recorded current was truly from the OER process, the Faraday efficiency was evaluated by measuring the evolved oxygen gas volumes and comparing them with theoretical values. As shown in Fig. 3(d), the experimental results for NiFe₂O_{4-x}Se_x/NiOOH agreed well with the theoretical analysis, giving a Faraday efficiency of over 98%. This suggests that the observed current and gas originated from the OER rather than from other processes.

Chronoamperometric experiments were then performed at applied potentials of 1.41 and 1.56 V (vs. RHE) to evaluate the electrocatalytic stability of NiFe₂O_{4-x}Se_x/NiOOH. Fig. 3(e)

Fig. 3. (a) LSV polarization curves of various catalysts for OER without iR-correction. The orange dashed line and the inset are LSV curves of $\text{NiFe}_2\text{O}_{4-x}\text{S}_x/\text{NiOOH}$ with iR-correction. (b) Corresponding Tafel plots. (c) Comparison of overpotentials and Tafel slopes of $\text{NiFe}_2\text{O}_{4-x}\text{S}_x/\text{NiOOH}$ with state-of-the-art analogs. (d) OER Faradaic efficiency of $\text{NiFe}_2\text{O}_{4-x}\text{S}_x/\text{NiOOH}$. (e) Stability test of $\text{NiFe}_2\text{O}_{4-x}\text{S}_x/\text{NiOOH}$ for OER at different potentials. (f) Multi-chronoamperometric curves for $\text{NiFe}_2\text{O}_{4-x}\text{S}_x/\text{NiOOH}$ recorded at various overpotentials.

shows that $\text{NiFe}_2\text{O}_{4-x}\text{S}_x/\text{NiOOH}$ delivered steady current densities of approximately 10 and 100 mA/cm^2 for hundreds of hours, indicating its impressive durability. Furthermore, multi-step chronoamperometric measurements suggested that $\text{NiFe}_2\text{O}_{4-x}\text{S}_x/\text{NiOOH}$ can steadily deliver current densities up to hundreds of mA/cm^2 (Fig. 3(f)). LSV measurements indicated that no detectable degradation was observed after 6000 cycles (Fig. S18).

After the stability test, the catalyst was systematically characterized. SEM images showed that the morphology and structure of $\text{NiFe}_2\text{O}_{4-x}\text{S}_x/\text{NiOOH}$ were well preserved after the test (Fig. S19). The XRD pattern (Fig. S20) still displayed clear diffraction signals from the cubic NiFe_2O_4 . These results corroborate the superior stability of $\text{NiFe}_2\text{O}_{4-x}\text{S}_x/\text{NiOOH}$ during OER. XPS analyses indicated that the Fe^{3+} , Ni^{2+} , and Ni^{3+} signals showed negligible changes before and after the test (Fig. S21). It is noted that the Cr signal, which was the main impurity in the stainless-steel substrate, completely disappeared after the test (Fig. S21(c) and Table S4). To identify the effect of chromium content on the OER activity of $\text{NiFe}_2\text{O}_{4-x}\text{S}_x/\text{NiOOH}$, the chromium content was measured during the stability test. The chromium content decreased from 6.65% to 0.76% within 24 h and approached 0.13% after 96 h (Table S5 and Fig. S22) while the performance of $\text{NiFe}_2\text{O}_{4-x}\text{S}_x/\text{NiOOH}$ remained unchanged (Fig. S23), suggesting that chromium doping or leaching had a negligible effect on its electrocatalytic activity for OER [38]. However, the effect of Cr may be traded off by the formation of more (oxy)hydroxide species to some extent. In the Se 3d spectra (Fig. S21(d)), the peak at 54.3 eV assigned to the Cr–Se bond completely disappeared after long-term testing, and thus the Se content decreased from 8.3% to ~2%, consistent with previous reports [35,47]. In addition, the peak ascribed to Se–Fe or Se–Ni shifted from 55.1 to 55.7 eV after long-term testing, likely ow-

ing to partial oxidation, which is consistent with the minor broad peak at 58.1 eV attributed to Se–O [35]. Similar to Cr, the portion of Se bonded with Cr may have had a negligible contribution to the OER activity, and only the portion of Se bonded with Ni or Fe in NiFe_2O_4 had a positive effect on the electrocatalytic process by affecting the adsorption/desorption of intermediates and the interaction between Ni and Fe, which is generally favorable for OER. In contrast, the Mn content remained nearly unchanged.

3.3. Mechanism analysis

To further understand the enhanced OER activity by selective Se doping, the charge transfer process, the ECSA, and the surface wettability were studied for samples with and without Se doping. EIS analyses (Fig. 4(a) and Table S6) indicated that the solution resistance (R_s) did not change significantly by Se doping (1.59 vs. 1.69 Ω). However, the charge transfer resistance (R_{ct}) for $\text{NiFe}_2\text{O}_{4-x}\text{S}_x/\text{NiOOH}$ (4.29 Ω) was reduced five and nine times compared with $\text{NiFe}_2\text{O}_4/\text{NiOOH}$ (22.90 Ω) and RuO_2/SS (38.40 Ω), respectively. This suggests that Se doping significantly enhanced the charge transport ability and thus accelerated the catalytic process. The double-layer capacitance (C_{dl} , Fig. S24) analyses via CV at different scan rates (Fig. S25) illustrated that $\text{NiFe}_2\text{O}_{4-x}\text{S}_x/\text{NiOOH}$ had a larger ECSA (37.50 mF/cm^2) than $\text{NiFe}_2\text{O}_4/\text{NiOOH}$ (32.75 mF/cm^2) and RuO_2/SS (23.60 mF/cm^2). In view of their similar morphologies, this difference means that selective Se doping created new active sites such as defects and/or remarkably enhanced the intrinsic activity of the catalytic sites [48,49]. To compare the intrinsic activity before and after Se doping, the LSV curves were normalized by the ECSAs. As shown in Fig. 4(b), $\text{NiFe}_2\text{O}_{4-x}\text{S}_x/\text{NiOOH}$ still showed much better OER activity

Fig. 4. Nyquist plots (the inset is the model of equivalent circuit) (a) and ECSA-normalized LSV curves (b) of $\text{NiFe}_2\text{O}_4/\text{NiOOH}$, $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x/\text{NiOOH}$, and RuO_2/SS . Contact angle images of $\text{NiFe}_2\text{O}_4/\text{NiOOH}$ (c) and $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x/\text{NiOOH}$ (d) at different contact times.

than $\text{NiFe}_2\text{O}_4/\text{NiOOH}$ and RuO_2/SS , even after ECSA normalization, indicating that Se doping enhanced the intrinsic OER activity.

The surface wettability was then investigated by measuring the contact angle between the electrolyte and the electrocatalyst in view of its important role in mass transfer [50]. As shown in Figs. 4(c,d), both $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x/\text{NiOOH}$ and $\text{NiFe}_2\text{O}_4/\text{NiOOH}$ showed superhydrophilic surfaces. However, the droplet completely spread out on the former within 20 ms, whereas it could be detected for as long as 50 ms on the latter. This reveals that selective selenization delivered a more hydrophilic surface, which is beneficial for mass transfer. Moreover, a comparison with the steel substrate, which had a contact angle of 116.34° (Fig. S26), suggests the importance of 3D heterostructures in improving surface wettability.

To obtain deeper insight into the effect of Se doping on the OER activity, DFT simulations were performed to analyze the modulation of Se doping on the electronic structure and local coordination environment of NiFe_2O_4 . Two possible Se-doped crystalline structural models were constructed, as shown in Fig. 5(a). The intermediates, including OH^* , O^* , and OOH^* , were constructed on the basis of the optimized structures (Fig. S27). The simulation results are presented in Table S7. As shown in Fig. 5(b) and Table S8, the rate-limiting step for undoped NiFe_2O_4 is the step $^*\text{OOH}$ to O_2 in terms of the largest energy barrier (3.64 eV). In contrast, the rate-limiting step is the formation of OOH^* from O^* after Se doping, as is commonly observed [6,49]. Such a difference may be caused by structural distortion on the NiFe_2O_4 surface owing to Se doping. As shown in Fig. S28, the $^*\text{OOH}$ species was bound strongly with Fe and Ni on the surface of NiFe_2O_4 , whereas this interaction was significantly reduced because of the evident steric hindrance introduced by Se doping. More importantly, the energy barriers

Fig. 5. (a) Structures of NiFe_2O_4 and Se-doped NiFe_2O_4 . Fe atom (golden), Ni atom (gray), O atom (red), Se atom (green). (b) The free-energy landscape of NiFe_2O_4 and Se-doped NiFe_2O_4 for OER.

were substantially reduced to 2.11 eV for $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x-1$ and 2.05 eV for $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x-2$, leading to a significant reduction in overpotentials from 2.28 V for undoped NiFe_2O_4 to 0.76 and 0.68 V, respectively. This observation is in good agreement with the experimental results, rationalizing the significant enhancement of Se doping on OER.

4. Conclusions

In summary, $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x/\text{NiOOH}$ on stainless steel with a unique 3D heterostructure of Se-doped NiFe_2O_4 nanocrystals decorated on a vertically aligned NiOOH nanosheet scaffold was rationally developed via direct alkaline etching of the substrate followed by facile precise solution selenization. Systematic experiments indicated that integrating NiFe_2O_4 nanocrystals with the NiOOH nanosheet scaffold appreciably enhanced the OER electrocatalytic activity. The selective selenization of NiFe_2O_4 further significantly promoted the OER activity by electronic modulation of the active centers. Together with improved surface wettability and mass transfer from 3D heterostructures, these features enabled $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x/\text{NiOOH}$ to achieve an industrial-level OER current density of 500 mA cm^{-2} at an ultralow overpotential of 259 mV with a small Tafel slope of 22.2 mV dec^{-1} . This performance was better than those of state-of-the-art OER catalysts. More importantly, the $\text{NiFe}_2\text{O}_{4-x}\text{Se}_x/\text{NiOOH}$ catalyst showed outstanding durability in terms of steady current output at various current densities up to hundreds of mA cm^{-2} . These results suggest that the present strategy provides a new avenue to advance the development of high-efficiency and scalable electrocatalysts for cost-effective hydrogen production from water splitting.

Electronic supporting information

Supporting information is available in the online version of this article.

Graphical Abstract

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Selective Se doping of NiFe₂O₄ on an active NiOOH scaffold for efficient and robust water oxidation

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The rational fabrication of selectively Se-doped NiFe₂O₄ nanoparticles on active NiOOH nanosheet arrays enables efficient and robust OER electrocatalysts for scalable hydrogen production with commercial stainless steel.

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选择性硒掺杂提高NiFe₂O₄/NiOOH异质结电催化析氧性能

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摘要: 氢能具有能量密度高、清洁无污染等优势, 被认为是理想的能源, 受到越来越多的关注. 利用太阳能和风能等可再生能源电解水制氢是一种极具发展前景的可以规模化获取清洁氢气的能源技术, 其挑战在于如何降低电能消耗并实现稳定地高速电解制氢. 由于电解水阳极析氧反应(OER)涉及四电子转移, 动力学过程缓慢, 是电解水过程的决速步骤. 因此, 开发高效、廉价、稳定的OER电催化剂对于推动电解水制氢的应用至关重要. 硫族化合物具有良好的导电性, 对OER中间体表现出适宜的吸附/脱附能力, 是一类高活性的析氧电催化剂. 但在析氧反应中硫族化合物会不可避免地发生氧化, 导致其结构坍塌, 使其性能发生大幅衰减. NiOOH被认为是Ni(OH)₂、NiSe和NiS等镍基电催化剂析氧过程中的真实催化活性位点, 在析氧反应过程中表现出优异的稳定性. 因此, 结合硫族化合物的高催化活性和羟基氧化物的稳定性, 将有望获得高效稳定的析氧电催化剂.

本文提出了一种选择性硒掺杂的策略, 实现了不锈钢基底上NiFe₂O₄/NiOOH异质结的选择性硒掺杂, 获得了硒掺杂浓度可调的NiFe₂O_{4-x}Se_x/NiOOH异质结电催化剂, 大幅提升了其电催化析氧性能. 采用X射线衍射技术、拉曼光谱、扫描电镜和透射电镜技术等对NiFe₂O₄/NiOOH异质结的结构、形貌和组分进行了表征. 利用X射线光电子能谱和透射电镜的能量色散光谱仪对硒掺杂产物的元素组成和分布进行了分析. 结果表明, 硒元素仅掺杂到NiFe₂O₄纳米颗粒中, 而NiOOH纳米片骨架保持不变, 保证了催化剂在析氧过程的稳定性. NiFe₂O_{4-x}Se_x/NiOOH异质结电极在1 M KOH溶液中表现出较好的析氧性能, 达到10和500 mA cm⁻²电流密度所需要的过电位分别仅为153和259 mV, 塔菲尔斜率为22.2 mV dec⁻¹. 更重要的是, NiFe₂O_{4-x}Se_x/NiOOH电催化剂的电化学性能稳定性, 计时电流测试表明, 在10~400 mA cm⁻²电流密度下可稳定工作. 稳定性测试表明, 催化剂在100 mA cm⁻²的电流密度下可稳定工作至少300 h. 电催化过程研究表明, 选择性硒掺杂提高了界面间电荷运输能力, 改善了电极表面的浸润性, 优化了活性位点的电子结构, 从而大幅提高催化剂的电催化性能. 密度泛函理论计算结果表明, 硒掺杂会导致NiFe₂O₄表面晶格发生畸变, 显著改善了反应中间体的吸附过程, 因此明显降低了析氧反应决速步骤的能垒. 本研究结果将为未来探索高效和稳定的电催化剂提供新的研究思路.

关键词: 水氧化反应; 选择性硒化; 镍铁尖晶石; 羟基氧化镍; 异质结

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