

Article

Highly Efficient Oxygen Evolution on the Tubular Array of the Mesoporous NiMoO₄@NiFeS Heterostructure

Xinyue Hou, Hao Wu , Juan Li, Xiaoyu Jiang, Yacong Zhang and Yongfu Lian 

Key Laboratory of Functional Inorganic Material Chemistry (Ministry of Education of China), School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China; 2231480@s.hljju.edu.cn (X.H.); 2241551@s.hljju.edu.cn (J.L.); 2241719@s.hljju.edu.cn (X.J.); 2241557@s.hljju.edu.cn (Y.Z.)

* Correspondence: haowu@hlju.edu.cn (H.W.); chyflian@hlju.edu.cn (Y.L.)

Abstract

Developing efficient and stable oxygen evolution reaction (OER) electrocatalysts is crucial to the practical application of water electrolysis for hydrogen production. Herein, a tubular array of a mesoporous NiMoO₄@NiFeS heterostructure was anchored on nickel foam through successive hydrothermal processing, liquid etching and direct sulfur vulcanization. The efficient charge transfer, phase transition and full exposure of active sites at the heterostructure's interfaces, as well as its superhydrophilic surface, endow NiMoO₄@NiFeS with exceptional OER activity. A series of electrochemical experiments indicate that in 1.0 mol·L⁻¹ KOH, NiMoO₄@NiFeS delivers overpotentials as low as 180 and 223 mV at current densities of 10 and 100 mA cm⁻², respectively, and that a Tafel slope of merely 25.9 mV dec⁻¹ is achieved on NiMoO₄@NiFeS, evidencing that the tubular array of the mesoporous NiMoO₄@NiFeS heterostructure significantly facilitates the interfacial transfer of charge/mass and the decrease in the energy barrier of the rate-determining step. This work provides valuable insights for the construction of an efficient and low-cost electrocatalyst with hierarchical mesoporous core-shell structures.

Keywords: hierarchical heterostructure; nickel molybdate; nickel-iron disulfide; phase transformation; oxygen evolution

1. Introduction

Hydrogen energy represents a major clean energy carrier. Its large-scale production relies largely on the exploitation of efficacious and low-cost water electrolysis [1]. The oxygen evolution reaction (OER), the anode half-reaction for water electrolysis, comes to a four-electron transfer process. Because of its sluggish kinetics and as it requires a high overpotential to be maintained, OER constitutes a key bottleneck limiting the whole energy efficiency [2]. Currently, IrO₂ and RuO₂ are the benchmarked OER catalysts. However, their scarcity and high cost prevent them from large-scale utilization in industrial water electrolysis. Thus, the development of high-efficiency non-precious metal-based electrocatalysts for OER is of great significance [3,4].

In recent ten years, significant attention has been devoted to exploring efficient transition metal-based catalysts, particularly those involving 3d transition metals such as nickel molybdate (NiMoO₄) [5]. The unique d-orbital electron configuration and the presence of high-valence Mo in NiMoO₄ can promote electron migration and create active sites, thereby enhancing its electrochemical OER performance [6,7]. However, the practical application of NiMoO₄ still faces several bottlenecks, including an insufficient current density, short cycle



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life, and low utilization of active sites [8]. Constructing heterostructures may represent an effective strategy to overcome these limitations. Integrating NiMoO_4 with NiFe-based compounds, such as NiFe phosphides (NiFeP), has led to remarkable progress [9]. NiFeP undergoes rapid and complete surface reconstruction under OER conditions, in situ transforming into highly active NiFeOOH species and thereby delivering excellent initial activity. Nevertheless, the complete leaching of P atoms often results in catalyst framework collapse and severe agglomeration of active species, posing substantial stability challenges during prolonged operation [10].

Substituting NiFeP with nickel–iron sulfides (NiFeS) to construct a heterojunction of NiMoO_4 and NiFeS is an interesting strategy to reach a balance of activity and stability. Unlike NiFeP, NiFeS undergoes a partial and controlled surface reconstruction during OER, in which S anions are not entirely leached but are partially retained in the lattice as sulfate/sulfite species [11,12]. These residual sulfur species stabilize the reconstructed NiFeOOH layer, preventing excessive crystallization and uncontrolled agglomeration, thus forming a unique sulfur-stabilized active phase [13]. This regulated reconstruction mechanism not only endows the catalyst with high intrinsic activity comparable to that of NiFeP but also dramatically enhances its long-term operational stability [13]. Fan et al. [14] prepared a $\text{NiMoO}_4/\text{NiFeS}$ heterostructure enriched in crystalline–amorphous interfaces via hydrothermal processing and electrochemical deposition. The synergistic interaction between the $\text{NiMoO}_4/\text{NiFeS}$ core and surface-reconstructed NiFeOOH shell profoundly enhanced the OER catalytic activity. Moreover, it is also evidenced that in the $\text{NiMoO}_4/\text{NiFeS}$ heterostructure, the true active sites are ascribed to the lattice oxygen centers other than the metal centers upon the formation of a reconstructed NiFeOOH layer, thereby switching the OER mechanism from the adsorbate evolution mechanism (AEM) to the lattice oxygen oxidation mechanism (LOM) and largely improving the OER kinetics [12]. Nonetheless, the as-prepared $\text{NiMoO}_4/\text{NiFeS}$ still exhibited sluggish reaction kinetics and inferior long-term stability and durability.

The microstructural engineering of the heterojunction of NiMoO_4 and NiFeS is equally decisive for its practical catalytic performance [14]. Specifically, constructing self-supported electrodes by growing hierarchical porous nanoarrays (e.g., nanorods or nanosheets) in situ on a conductive skeleton serves a dual purpose [15,16]. First, the high-surface-area porous structure not only maximizes the exposure of active sites but also facilitates rapid mass transport and efficient bubble detachment, which are critical for maintaining high performance [9]. Second, a superhydrophilic surface is imperative to ensure complete electrolyte permeation and sufficient OH^- adsorption at the electrode/electrolyte interface, thereby fully exploiting the active sites. All these features collectively make self-supported, micro-arrayed NiMoO_4 and NiFeS heterostructures with superhydrophilic surfaces highly promising candidates for efficient OER electrocatalysts, unlocking new possibilities for sustainable water splitting [17].

Herein, a tubular array of a mesoporous $\text{NiMoO}_4@/\text{NiS}_2/\text{FeS}_2$ heterostructure (denoted as $\text{NiMoO}_4@/\text{NiFeS}$) was designed and grown in situ on conductive nickel foam (NF) by successive hydrothermal processing, liquid deposition/etching and direct sulfur vulcanization [14]. The hierarchical heterostructure, with its mesoporous tubular array architecture, not only facilitates active site exposure and charge/mass transfer but also provides a superhydrophilic surface that ensures efficient utilization of the active sites [17]. As a result, the well-designed $\text{NiMoO}_4@/\text{NiFeS}$ electrode exhibits excellent OER activity and stability. Similar to other reported high-performance NiFe-based electrodes, it holds promise for practical application in alkaline water electrolysis systems [12]. Furthermore, the surface reconstruction of $\text{NiMoO}_4@/\text{NiFeS}$ during OER was investigated, and density functional

theory (DFT) calculations were performed to analyze the effects of the heterojunction on the electronic structure, catalytic center, and OER reaction pathway [7].

2. Results

2.1. Electrode Characterization

2.1.1. Morphological Observation

The scanning electron microscopy (SEM) image (Figure 1(a₁)) shows that the NiMoO₄ electrode exhibits an ordered flower-like array composed of irregular square-shaped microrods. High-resolution SEM images (Figure 1(a₂,a₃)) reveal that these microrods are solid with smooth and clean surfaces. This ordered flower-like array morphology is preserved in the NiMoO₄@NiFe-PBA (Figure 1(b₁)) and NiMoO₄@NiFeS (Figure 1(c₁)) electrodes. However, notable morphological evolution is observed from higher-resolution SEM images. In the NiMoO₄@NiFe-PBA electrode, the microrods transform into partially hollow, irregular square-shaped structures featuring radial open pores and rough surfaces (Figure 1(b₂,b₃)). More strikingly, in the NiMoO₄@NiFeS electrode, the microrods develop a markedly hollow and porous architecture with abundant interfaces, a significantly expanded central cavity, and considerably roughened surfaces containing enlarged penetrating pores (Figure 1(c₂,c₃)). This hierarchical porous structure is distinctly different from previously reported NiMoO₄-based core-shell morphologies (microrods, nanorods, or nanoneedles) [9,14,18] and provides a robust physical framework that facilitates electrolyte penetration, active site exposure, charge/mass transfer, bubble release, and favorable surface wettability.

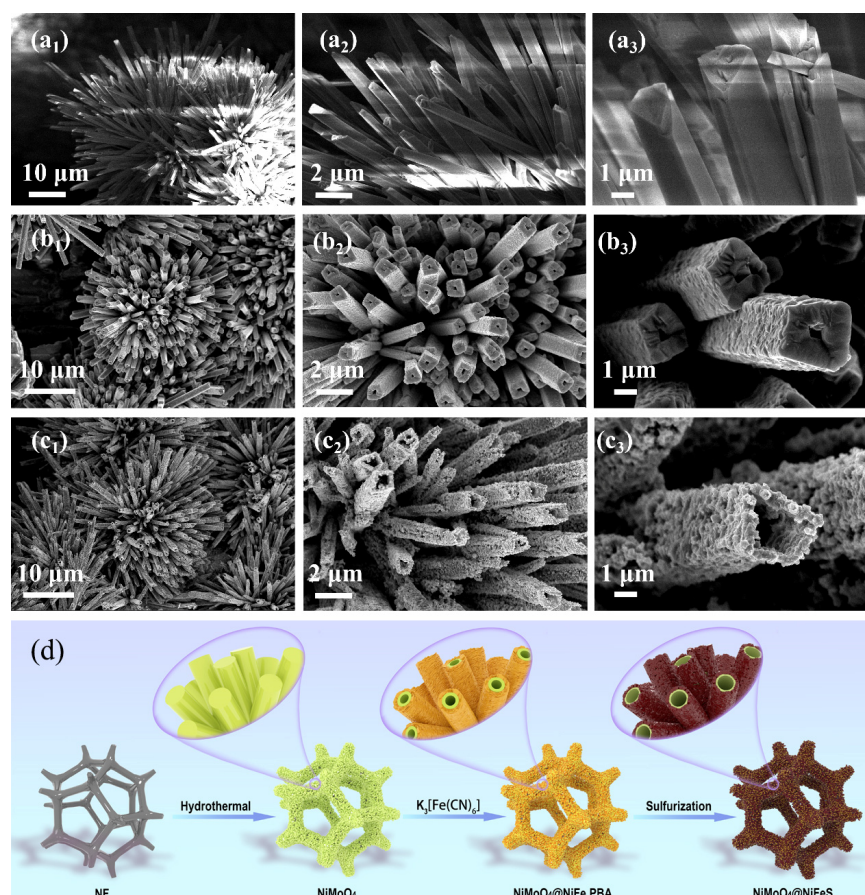


Figure 1. SEM images of (a₁–a₃) NiMoO₄, (b₁–b₃) NiMoO₄@NiFe-PBA and (c₁–c₃) NiMoO₄@NiFeS. (d) Schematic illustration of the synthesis procedure for NiMoO₄@NiFeS.

To clarify the cavity evolution during sulfurization, time-dependent SEM characterization was conducted on the samples achieved by sulfurization of $\text{NiMoO}_4@\text{NiFe}$ PBA precursor for 0, 5, 15, 30 and 60 min, respectively. As shown in Figure S1, the tubular size grows larger and larger and the surface becomes rougher and rougher with the extension of sulfurization time, confirming the gradual expansion of the tubular size owing to a Kirkendall-type diffusion process and the transformation from NiFe-PBA to NiFeS . Based on the SEM observations, a possible morphological evolution of the synthesized electrodes is proposed in Figure 1d. Under hydrothermal conditions, typical irregular solid quadrangular prism-shaped NiMoO_4 microrods grow in situ and form an ordered flower-like array on a piece of NF. Subsequently, during the etching process in $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution, the difference in diffusion rates between K^+ and Ni^{2+} leads to faster dissolution of the inner NiMoO_4 and slower deposition of the outer NiFe-PBA nanoflakes. This kinetic mismatch is responsible for the formation of hollow, porous $\text{NiMoO}_4@\text{NiFe-PBA}$ core-shell structures with rough surfaces. The shell thickness can be tuned by adjusting the precursor dosage, water bath temperature and reaction time. Finally, a uniform NiFe PBA shell with a thickness of approximately 75 nm was grown on the surface of NiMoO_4 microrods (Figure S3). Upon sulfidation under a nitrogen atmosphere, the reaction between sulfur (S) and $\text{NiMoO}_4@\text{NiFe-PBA}$ generates irregular square $\text{NiMoO}_4@\text{NiFeS}$ microtubes with multilevel structures. As presented in Figure S4, the apparent color evolution of the materials (from yellow to dark orange and then to deep black) further confirms the successful construction of $\text{NiMoO}_4@\text{NiFeS}$.

For comparison, NiMoO_4 was directly sulfidized to obtain S-NiMoO_4 . It can be seen from Figure S5a that S-NiMoO_4 completely maintains the morphology of NiMoO_4 without hollow cavities or rough surfaces. S atoms could not penetrate the interior of solid NiMoO_4 microrods without the assistance of the diffusion channels created by $\text{K}_3[\text{Fe}(\text{CN})_6]$ etching, and the formed compact layers of metal sulfides on the surfaces of NiMoO_4 block the inward diffusion of S and the outward migration of metal ions, restricting the reactions of S and metal atoms to an extremely shallow surface depth. On the other hand, $\text{NiMoO}_4@\text{NiFeO}$ was fabricated by direct calcination of $\text{NiMoO}_4@\text{NiFe-PBA}$ without the addition of S powder. As shown in Figure S5b, the ordered flower-like arrays assembled by NiMoO_4 microrods collapse in $\text{NiMoO}_4@\text{NiFeO}$, and the hollow porous irregular square-shaped $\text{NiMoO}_4@\text{NiFe-PBA}$ microrods convert to tabular solid ones, which are constructed by the close stacking of flake-like metal oxides.

2.1.2. Crystalline Structure Characterization

The crystalline structure of the synthesized $\text{NiMoO}_4@\text{NiFeS}$ was initially probed via transmission electron microscopy (TEM) observation. The low-resolution TEM images (Figure 2a,b) evidence the successful fabrication of the integrated $\text{NiMoO}_4@\text{NiFeS}$ irregular square microtubes. The light exterior corresponds to the partially crystalline metal sulfides (MS_2 , $\text{M} = \text{Ni}$ or Fe), and the dark edges and uneven interior correspond to the highly crystalline NiMoO_4 and the tubular cavity, respectively, confirming the presence of multiple interfaces within the $\text{NiMoO}_4@\text{NiFeS}$ microtubes [19]. In addition, the uneven stacking of the partially crystalline MS_2 on the outside surfaces of the highly crystalline NiMoO_4 accounts for the significantly rough surface and the extremely strong hydrophilicity of the $\text{NiMoO}_4@\text{NiFeS}$ microtubes. Moreover, in line with the high-resolution TEM (HRTEM) image shown in Figure 2c, the observed lattice fringe with a spacing of 0.324 nm is in good agreement with the d-spacing corresponding to the strongest diffraction peak of $\text{NiMoO}_4 \cdot 2.8\text{H}_2\text{O}$ (JCPDS No. 04-017-0338) identified in the following XRD pattern, and the lattice spacings measuring 0.281 and 0.269 nm correspond to the (200) lattice plane of NiS_2 (JCPDS No. 11-0099) and the (101) lattice planes of FeS_2 (JCPDS No. 74-1051), respectively.

The EDX elemental mapping profiles of NiMoO₄@NiFeS (Figure 2d–i) confirm the coexistence of Ni, Mo, Fe, O and S elements and the tubular structure of the NiMoO₄@NiFeS composite. It should be noted that Ni, Fe and S are uniformly co-distributed in the outside layers, and Ni, Mo and O in the inner layers of the microtube, confirming the formation of an external NiFeS shell and an internal NiMoO₄ core. Thus, the flower-like NiMoO₄@NiFeS multilevel heterostructure was successfully prepared by the simultaneous self-sacrifice of well-aligned NiMoO₄ microrods and phase transformation from PBA to MS₂, which facilitates electron transfer across the interfaces of NiMoO₄ and sulfides.

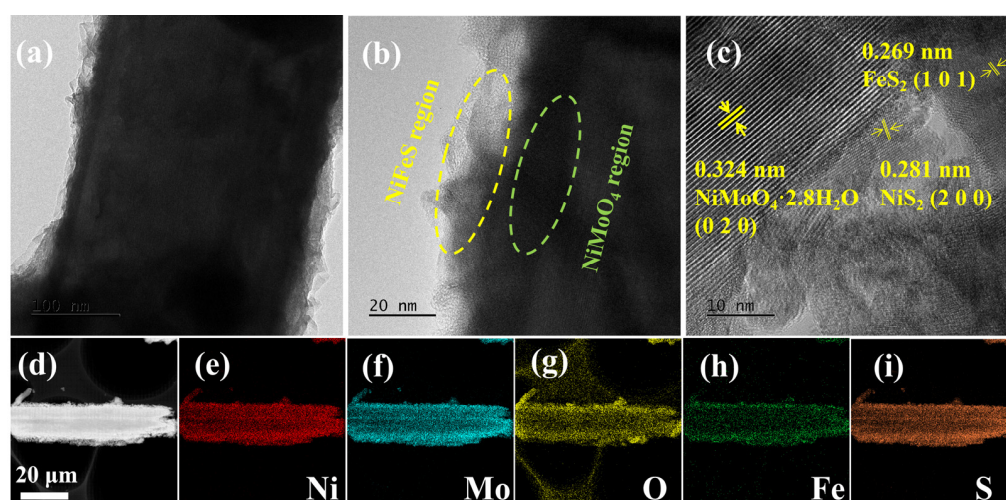


Figure 2. (a,b) Low-resolution and (c) high-resolution TEM images and (d–i) EDX elemental mapping images of the NiMoO₄@NiFeS microtube.

Figure 3a shows the powder X-ray diffraction (XRD) patterns of NiMoO₄, NiMoO₄@NiFe-PBA and NiMoO₄@NiFeS, respectively. The three strong peaks that appeared at $2\theta = 44.5^\circ$, 51.8° and 76.4° are indexed to the (111), (200) and (220) crystal facets of the metallic NF substrate (JCPDS No. 04-0850), respectively. The XRD pattern of NiMoO₄ is in good agreement with previously reported data [20–22]. The peaks at 13.5° , 21.1° , 22.8° , 23.0° , 23.5° , 27.2° and 27.5° correspond to the (100), $(-1-11)$, (-111) , (112), (102), (210) and (020) crystal planes of NiMoO₄·2.8H₂O (JCPDS No. 04-017-0338) [23], respectively. In the XRD pattern of NiMoO₄@NiFe-PBA, the diffraction peaks observed near 17.6° , 25.0° , 35.8° and 51.4° correspond to the (200), (220), (400) and (440) crystal planes of K₂FeNi(CN)₆ (JCPDS No. 20-0915), evidencing the partial conversion of NiMoO₄ to NiFe-PBA. In the XRD pattern of NiMoO₄@NiFeS, the detectable diffraction peaks except those of Ni and NiMoO₄ correspond well to the crystal planes of FeS₂ and NiS₂. The diffraction peaks detected at 25.9° , 33.3° , 37.3° and 52.1° correspond to the (110), (101), (111) and (211) crystal planes of FeS₂ (JCPDS No. 74-1051), and those detected at 31.6° , 35.3° , 38.8° , 45.3° and 53.6° correspond to the (200), (210), (211), (220) and (311) crystal planes of NiS₂ (JCPDS No. 11-0099) [20], confirming the formation of FeS₂ and NiS₂ via sulfidation of NiMoO₄@NiFe-PBA. The phase composition obtained from Rietveld refinement of the XRD pattern of NiMoO₄@NiFeS indicates that the crystallite sizes of NiMoO₄, FeS₂, and NiS₂ are estimated to be approximately 12.8 nm, 21.0 nm, and 14.0 nm, with corresponding phase contents of 38.8%, 4.2%, and 29.7%, respectively (Figure S6). It is noted that the XRD pattern of NiMoO₄@NiFeS shows broader and weaker diffraction peaks as well as more unstable baselines with respect to that of NiMoO₄, indicating the reduced crystallite size and increased structural disorder of NiMoO₄@NiFeS, which aligns with the aforementioned SEM and TEM analytical outcomes. Undoubtedly, the poor crystallization of NiMoO₄@NiFeS

can lead to more active site exposure and more pathways for electron and ion transport, thereby contributing significantly to the improvement in its OER performance.

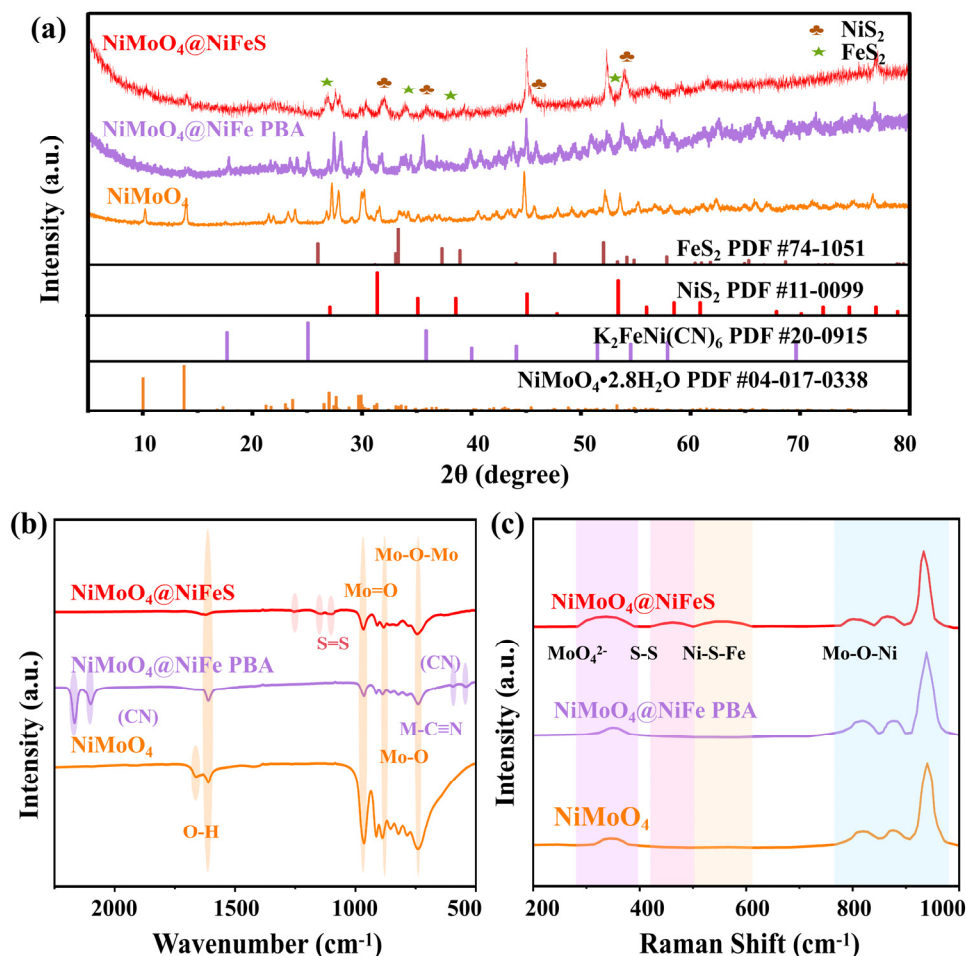


Figure 3. (a) XRD patterns, (b) FTIR spectra and (c) Raman spectra of NiMoO₄, NiMoO₄@NiFe–PBA and NiMoO₄@NiFeS.

Regarding vibrational properties, both Fourier transform infrared (FTIR) and Raman spectroscopy were performed for NiMoO₄, NiMoO₄@NiFe-PBA and NiMoO₄@NiFeS, which were removed from NF by extensive ultrasonication in alcohol and analyzed after drying. In the FTIR spectra shown in Figure 3b, the absorption peaks observed at 742, 887 and 965 cm⁻¹ are attributed to the Mo-O-Mo bending, Mo-O stretching, and Mo=O stretching vibrations of molybdates [24–26], respectively. For NiMoO₄, the bands detected at 1609 and 1665 cm⁻¹ are assigned to the δ(OH) bending vibrations of surface-adsorbed water and lattice water coordinated with Ni²⁺/MoO₄²⁻ [27], respectively. In sharp contrast, the former completely disappears for NiMoO₄@NiFe-PBA and NiMoO₄@NiFeS, indicative of the transformation of NiMoO₄·2.8H₂O to NiMoO₄. Moreover, those characteristic peaks of MoO₄²⁻ detected within the 700–1000 cm⁻¹ wavenumber range are significantly weakened for NiMoO₄@NiFeS, which may partly stem from the loss of coordinated water molecules. In the FTIR spectrum of NiMoO₄@NiFe-PBA, the characteristic peaks at 587, 2095 and 2164 cm⁻¹ correspond to the cyanide (C≡N⁻) moieties derived from K₂FeNi(CN)₆, and the signal at 537 cm⁻¹ is linked to the M–C≡N (M = Fe or Ni) stretching mode [9]. Significantly, the specific peaks detected at 1098, 1145 and 1253 cm⁻¹ for NiMoO₄@NiFeS correspond to the asymmetric/symmetric stretching modes of S atoms [28], verifying the generation of MS₂.

To further verify the generation of NiMoO_4 , $\text{NiMoO}_4@\text{NiFe-PBA}$ and $\text{NiMoO}_4@\text{NiFeS}$, Raman spectroscopy was employed to analyze their scattering features. As illustrated in Figure 3c, each specimen displays a broad peak near 346 cm^{-1} , linked to the symmetrical stretching mode of MoO_4^{2-} units in NiMoO_4 , whereas the Raman signals within $800\text{--}1000\text{ cm}^{-1}$ correspond to Mo-O-Ni linkages [29], verifying the presence of NiMoO_4 in these samples. For $\text{NiMoO}_4@\text{NiFeS}$, the special Raman bands appeared at ca. 460 and 553 cm^{-1} , aligning with the stretching pertaining to S-S linkage within NiS_2 [30] and the vibration of the Ni-S-Fe linkage band [31], respectively, offering further support for the formation of FeS_2 and NiS_2 on the surface of a self-sacrificial template (NiMoO_4).

2.1.3. Chemical States and Surface Composition

X-ray photoelectron spectroscopy (XPS) was employed to characterize the chemical states and surface composition of $\text{NiMoO}_4@\text{NiFeS}$. Consistent with the results from above EDX analyses, the survey XPS spectrum reveals the presence of Mo, Ni, Fe, O, C, N and S within $\text{NiMoO}_4@\text{NiFeS}$ (Figure 4a). As indicated in Figure 4b, the deconvoluted Ni 2p profile for $\text{NiMoO}_4@\text{NiFeS}$ reveals the characteristic features of Ni^0 , Ni^{2+} , Ni^{3+} and a shakeup satellite [32], respectively. Similar features are also observed for the high-resolution Fe 2p profiles derived from $\text{NiMoO}_4@\text{NiFeO}$ as well as $\text{NiMoO}_4@\text{NiFeS}$ (Figure 4c), from which the typical peaks assignable to Fe^0 , Fe^{2+} , Fe^{3+} and a shakeup satellite are deconvoluted, respectively. The appearance of Ni^{3+} and Fe^{3+} was clearly ascribed to surface oxidation, whereas the presence of Ni^0 and Fe^0 could be ascribed to the reduction of Ni^{2+} and Fe^{2+} by CN^- at an elevated temperature, respectively [33]. In contrast, no Ni^0 and Fe^0 species are detected for NiMoO_4 and $\text{NiMoO}_4@\text{NiFe-PBA}$. Herein, sharp and discrete “two-part” peaks are observed in the XPS spectrum of PBA, correlating strongly with its high crystallinity coupled with a uniform coordination environment [34].

From the core-level Mo 3d (Figure 4d) profile for $\text{NiMoO}_4@\text{NiFeS}$, the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ signals appear at 232.5 and 235.6 eV , respectively, alongside a peak separation of 3.1 eV . The same peak separation is also observed for NiMoO_4 and $\text{NiMoO}_4@\text{NiFe-PBA}$, indicating the formation of Mo^{6+} species. From the high-resolution S 2p scan of $\text{NiMoO}_4@\text{NiFeS}$ (Figure 4e), the S $2p_{1/2}$ and S $2p_{3/2}$ features emerge at 164.0 and 162.9 eV , assignable to the configurations of apical S^{2-} and bridging S_2^{2-} , respectively [35]. Additionally, the peaks at 168.7 and 169.9 eV arise from the formation of S-O bonds [36–38], also originating from surface oxidation. Within the core-level O 1s profile for $\text{NiMoO}_4@\text{NiFeS}$ (Figure 4f), signals appearing at 530.3 , 530.8 , 531.7 and 533.4 eV match the binding energies of crystal lattice oxygen (O_L), coordination-unsaturated oxygen (O_V), surface adsorbed hydroxide oxygen (O_A), and physical adsorbed water, respectively. In comparison with NiMoO_4 and $\text{NiMoO}_4@\text{NiFe-PBA}$, $\text{NiMoO}_4@\text{NiFeS}$ displays significantly enhanced O_V and O_A species and a dramatically reduced O_L one, suggesting that O_L is effectively activated to O_V and O_A at the interfaces of NiMoO_4 and NiFeS and that the abundant vacancies in $\text{NiMoO}_4/\text{NiFeS}$ are capable of absorbing more OH^- ions to accelerate the lattice oxygen oxidation–reduction reaction.

On the other hand, it is of interest to note that the Ni 2p, Fe 2p and Mo 3d peaks of $\text{NiMoO}_4@\text{NiFeS}$ are systematically shifted toward higher binding energy relative to those of $\text{NiMoO}_4@\text{NiFe-PBA}$ [9], whereas its S 2p and O 2p peaks are negatively shifted relative to the S 2p of S-NiMoO_4 and O 2p of $\text{NiMoO}_4@\text{NiFe-PBA}$, respectively. These results suggest strong electronic interactions and efficient charge redistribution at the interfaces of NiMoO_4 and NiFeS . In addition, the Mo 3d peaks shift systematically to the higher energy end in the sequence of NiMoO_4 , $\text{NiMoO}_4@\text{NiFe-PBA}$ and $\text{NiMoO}_4@\text{NiFeS}$, even though Mo remains in a constant valence state. Such a rigid shift in binding energy for a redox-inert element is attributed to the modulation of the Fermi level position in oxides resulting

from oxygen vacancy formation [35]. It is expected that both the activation of O_L and the charge redistribution at the hetero-structured $NiMoO_4@NiFeS$ interfaces can modulate the catalyst's adsorption energy towards reaction intermediates and redox processes of metal ions, thereby enhancing interfacial transfer of charge/mass and lowering the kinetic barrier of the potential-limiting step.

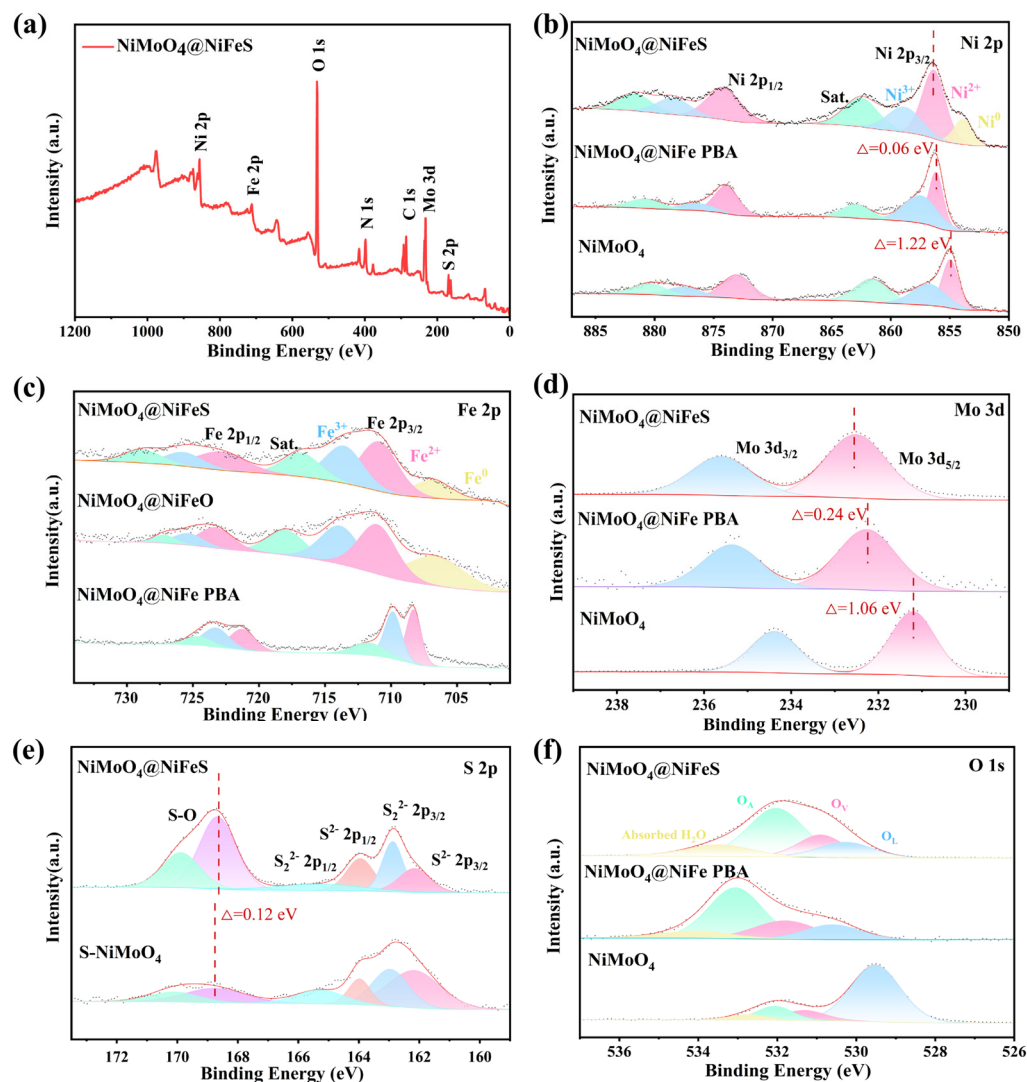


Figure 4. (a) Survey XPS spectrum of $NiMoO_4@NiFeS$, (b) the deconvoluted Ni 2p XPS spectra of $NiMoO_4$, $NiMoO_4@NiFe$ -PBA and $NiMoO_4@NiFeS$, (c) the deconvoluted Fe 2p XPS spectra of $NiMoO_4@NiFe$ -PBA, $NiMoO_4@NiFeO$ and $NiMoO_4@NiFeS$, (d) the deconvoluted Mo 3d XPS spectra of $NiMoO_4$, $NiMoO_4@NiFe$ -PBA and $NiMoO_4@NiFeS$, (e) the deconvoluted S 2p XPS spectra of S- $NiMoO_4$ and $NiMoO_4@NiFeS$, and (f) the deconvoluted O 1s XPS spectra of $NiMoO_4$, $NiMoO_4@NiFe$ -PBA and $NiMoO_4@NiFeS$.

2.1.4. BET Analysis and Surface Wettability Property

BET analysis provided further evidence of surface area enhancement. In line with the nitrogen adsorption–desorption isotherms shown in Figure 5a, $NiMoO_4$, $NiMoO_4@NiFe$ -PBA and $NiMoO_4@NiFeS$ demonstrate the characteristic type-IV nitrogen sorption profiles featuring H3-type hysteresis within the P/P₀ interval spanning 0.5 to 1.0, suggesting that the stacking of individual particles generates abundant irregular and open mesopores. The BET specific surface areas yielded values of 4.7645, 11.7876 and 43.3591 m²·g^{−1} for $NiMoO_4$, $NiMoO_4@NiFe$ -PBA and $NiMoO_4@NiFeS$, respectively. It should be pointed out here that the BET specific surface area of $NiMoO_4@NiFeS$ is twice as much as that of the previously

reported $\text{NiMoO}_4/\text{NiFeS}$ [14]. Displayed in Figure 5b are the BJH pore size distribution profiles originating from the adsorption branch of isotherms. Clearly, $\text{NiMoO}_4@\text{NiFeS}$ exhibits the largest cumulative pore volume ($0.1078 \text{ cm}^3 \cdot \text{g}^{-1}$ versus 0.0218 and $0.1038 \text{ cm}^3 \cdot \text{g}^{-1}$ for NiMoO_4 and $\text{NiMoO}_4@\text{NiFe-PBA}$, respectively) and the smallest average diameter (9.9436 nm versus 18.3233 and 35.2085 nm for NiMoO_4 and $\text{NiMoO}_4@\text{NiFe-PBA}$, respectively) (Table S1). Moreover, the dominant pores of $\text{NiMoO}_4@\text{NiFeS}$ are distributed in the range of mesopores, and those of NiMoO_4 and $\text{NiMoO}_4@\text{NiFe-PBA}$ in the range of macropores. The dominant mesopore, large BET surface area and high porosity of $\text{NiMoO}_4@\text{NiFeS}$ promote the accessibility of electrochemical catalytic centers, charge migration, electrolyte penetration and evolved gas release during the electrocatalysis process, which are expected to benefit the OER activity of $\text{NiMoO}_4@\text{NiFeS}$.

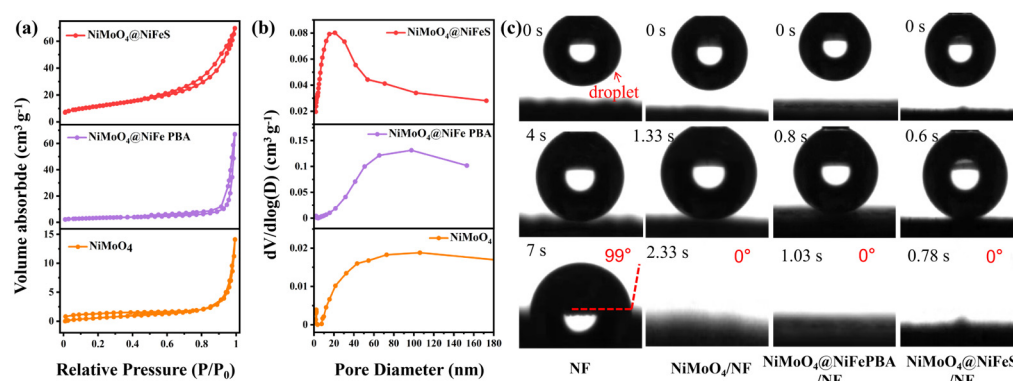


Figure 5. (a) N_2 adsorption–desorption isotherms and (b) BJH pore size distributions of NiMoO_4 , $\text{NiMoO}_4@\text{NiFe-PBA}$ and $\text{NiMoO}_4@\text{NiFeS}$. (c) Digital images of dynamic interfacial behaviors of droplets on the surfaces of NF, NiMoO_4 , $\text{NiMoO}_4@\text{NiFePBA}$ and $\text{NiMoO}_4@\text{NiFeS}$.

To estimate the surface wettability property of $\text{NiMoO}_4@\text{NiFeS}$, contact-angle measurements were performed. As demonstrated in Figure 5c, aqueous droplets disperse instantaneously upon contact with the $\text{NiMoO}_4@\text{NiFeS}$ substrate, and the wetting angle was determined to be 0° . Conversely, the contact angle of NF measured 99° . The contact angle of $\text{NiMoO}_4@\text{NiFeS}$ is markedly lower than that of pristine NF, suggesting that water molecules can more readily wet the surface of this electrode, thereby demonstrating better wettability. The in situ growth of $\text{NiMoO}_4@\text{NiFeS}$ effectively modified the surface properties of NF and created abundant highly active sites. The superhydrophilic surface of $\text{NiMoO}_4@\text{NiFeS}$ plays a significant role for the electrocatalytic reactions that take place at the interfaces of the solid electrode, liquid electrolyte and generated gas bubbles. The wetting time on the surface of $\text{NiMoO}_4@\text{NiFeS}$ (0.78 s) is significantly faster than that of $\text{NiMoO}_4@\text{NiFe-PBA}$ (1.03 s) and NiMoO_4 (2.33 s). When the electrode surface is hydrophilic, a uniform and stable water film forms on the surface, and gas bubbles tend to detach preferentially, facilitating rapid wetting and permeation of the electrolyte throughout the electrode matrix via mesoscopic and microscopic pores. This efficiently promotes the transport of electrolyte ions to active sites, ultimately improving the overall electrochemical performance.

2.2. OER Performance in Alkaline Media

2.2.1. LSV Curve Analysis

The oxygen evolution reaction (OER) behavior of $\text{NiMoO}_4@\text{NiFeS}$ was systematically evaluated in a conventional three-electrode setup in 1 M KOH solution. Consistent with the LSV profiles displayed in Figure 6a, $\text{NiMoO}_4@\text{NiFeS}$ exhibits superior OER activity featuring minimal overpotentials of 180, 223 and 297 mV at current densities of

10, 100 and 500 mA cm^{-2} , respectively. These values are significantly lower than those of $\text{NiMoO}_4/\text{NiFeO}$ (184, 243 and 360 mV), S-NiMoO_4 (193, 248 and 320 mV), $\text{NiMoO}_4/\text{NiFe-PBA}$ (203, 260 and 320 mV), and NiMoO_4 (209, 290 and 493 mV) (Figure 6b). The redox peaks around the overpotential of 0.2 V are assigned to the Ni (II)/Ni (III) redox process, whose integrated areas reflect the total charge transferred from Ni^{2+} to Ni^{3+} species. It is noted that the ratio of oxidized Ni decreases dramatically in the order of $\text{NiMoO}_4/\text{NiFeS}$, $\text{NiMoO}_4/\text{NiFeO}$, S-NiMoO_4 , $\text{NiMoO}_4/\text{NiFe-PBA}$ and NiMoO_4 , which is inversely correlated with their overpotential needed to reach a current density of 10 mA cm^{-2} , indicating that the resultant Ni (III) phase play a role of the catalytic center of these electrocatalysts.

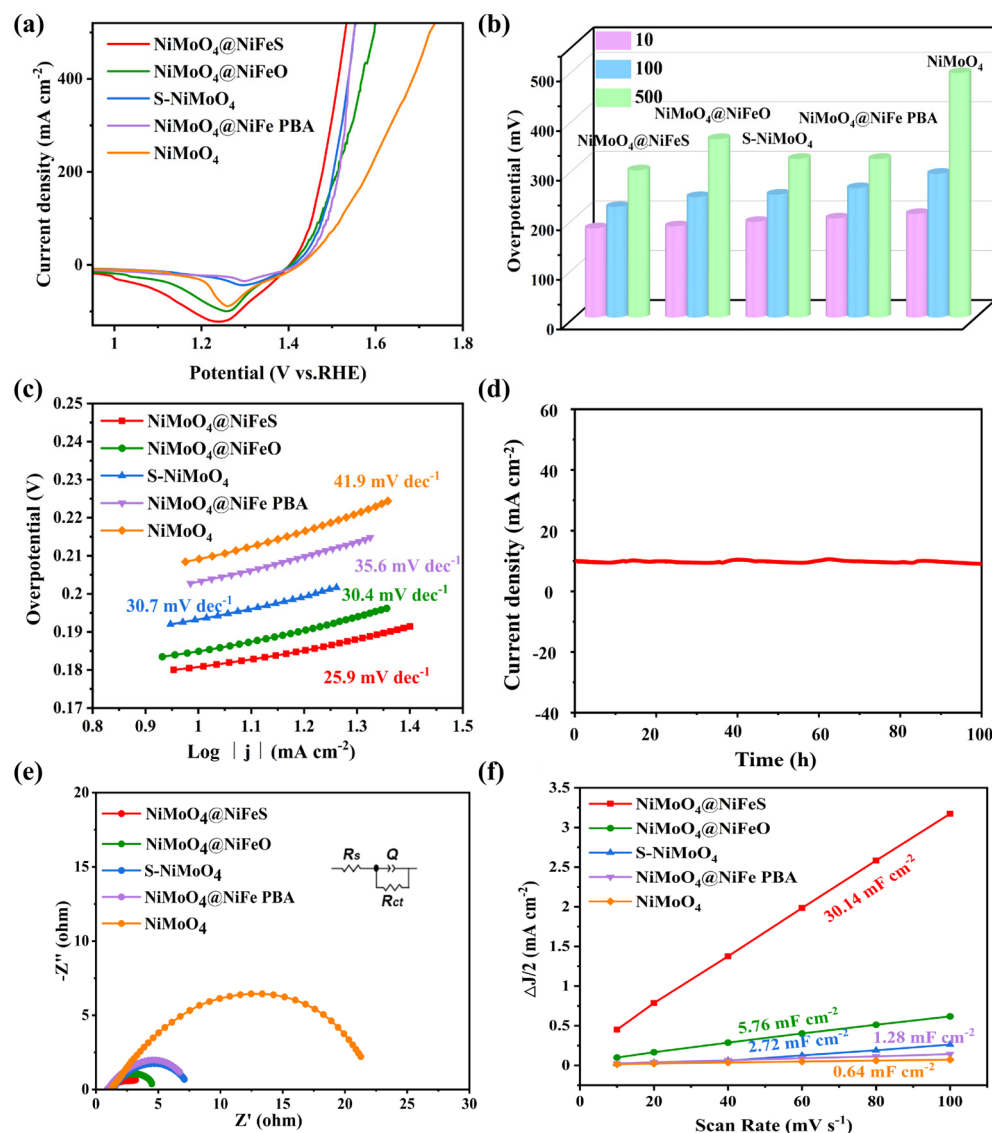


Figure 6. (a) LSV polarization curves, (b) overpotentials and (c) Tafel plots of the as-prepared electrodes; (d) $I-t$ curve of $\text{NiMoO}_4/\text{NiFeS}$; (e) Nyquist plots and (f) calculated ECSA of the as-prepared electrodes. The inset in (e) shows the equivalent circuit model applied to fit the Nyquist plots, where R_s is the electrolyte resistance, R_{ct} is the charge-transfer resistance and Q represents the constant phase element.

2.2.2. Tafel Curve Analysis

The OER reaction kinetics of the synthesized electrodes were assessed by Tafel slope analyses. As evidenced by Figure 6c, the Tafel slope of $\text{NiMoO}_4/\text{NiFeS}$ is as low as 25.9 mV dec^{-1} , markedly smaller than that of $\text{NiMoO}_4/\text{NiFeO}$ (30.4 mV dec^{-1}), S-NiMoO_4

(30.7 mV dec^{−1}), NiMoO₄@NiFe-PBA (35.6 mV dec^{−1}), NiMoO₄ (41.9 mV dec^{−1}) and the previously reported NiMoO₄/NiFeS (36.5 mV dec^{−1}), confirming that the construction of the NiMoO₄@NiFeS heterostructure significantly facilitates the OER reaction process. In particular, the superhydrophilic nature of the electrode ensures an intimate, molecular-level interaction with the electrolyte, greatly diminishing the resistance for ion transport and thereby accelerating the reaction kinetics at the solid/liquid interface. As shown in Table 1, the NiMoO₄@NiFeS electrode exhibits exceptional OER activity in alkaline media, surpassing many state-of-the-art NiFe-based OER catalysts. Moreover, the activity of NiMoO₄@NiFeS at industrial operating temperatures (e.g., 60 or 80 °C) is significantly superior to that at room temperature, indicating its potential for application in actual alkaline water electrolysis processes (Figure S7).

Table 1. Comparison of OER performance between the as-prepared NiMoO₄@NiFeS and other recently reported NiFe-based catalysts.

Catalysts	η_{10} (mV)	η_{100} (mV)	Tafel Slope	Reference
NiMoO ₄ @NiFeS	180	223	25.9	This work
NiMoO ₄ /NiFeS	155	230	36.5	[14]
NiMoO ₄ @NiFeP	194	244	41	[9]
NiMoO ₄ @Fe-NiOOH	227	-	48.7	[18]
R-NiFeOOH@SO ₄	-	251	56	[12]
NiMoO ₄ @NiFe LDH	-	238	32	[39]
NiFe@Ni/Fe-MnOOH	230	-	39	[40]
FeNi ₃ /NiFeO _x -250	246	-	30	[41]
NiFe/NiMo	-	233	15.4	[42]
S-NiFeOOH	182	219	20	[43]
NiFe-LDH@S-NiFeO _x	-	220	54.6	[44]
Co-Co@Ni-Fe PBA@WS ₂ -P	280	-	70	[45]
FeOOH/Mo-NiS _x	-	239	61	[46]
FeOOH/Ni ₃ S ₂ /Ni(OH) ₂	212	248	33.64	[47]
NiFeOOH/LNFO	250	-	63.7	[48]
NiFe@NVC	245	-	36.2	[49]
NiFe-LDH/Ni ₄ Mo	192.5	264	42	[50]
NiFeV/Ni ₃ Fe	249	-	48	[51]
NiFeS/NIF	220	254	28.1	[52]

2.2.3. Stability Analysis

Furthermore, both the chronoamperometry (CA) and CV cycling were conducted to assess the durability of NiMoO₄@NiFeS within alkaline electrolytes. As shown in Figure 6d, the catalyst can operate stably for over 100 h at a current density of 10 mA·cm^{−2} without clear current decay. It operates stably at a current density of 500 mA cm^{−2} for 50 h with only 2% decay (Figure S8). Moreover, the OER LSV curves of NiMoO₄@NiFeS demonstrated negligible degradation after continuous 1000 CV cycles (Figure S9). Thus, NiMoO₄@NiFeS exhibits admirable long-term stability and durability in alkaline solutions. The ratio of Ni to Fe in NiMoO₄@NiFeS, which can be adjusted by the added amount of K₃[Fe(CN)₆] during the preparation process, also influences the OER stability. As shown in Figure S6, the optimized dosage of 0.012 M adopted in this work achieves a well-balanced structure and stability.

2.2.4. EIS and ECSA Analyses

Initially, the electron-transfer properties of the synthesized materials were probed via electrochemical impedance spectroscopy (EIS). As shown in Figure 6e and Table S2, NiMoO₄@NiFeS exhibits the lowest interfacial resistance (R_{ct}) (2.45 Ω), indicating its

excellent electrical conductivity and interfacial electron transfer kinetics, which may be attributed to its abundant heterointerfaces and mesoporous architecture serving as pathways for efficient charge transfer. Subsequently, a series of cyclic voltammograms (CVs) were acquired within a non-Faradaic potential window (Figure S10), and then the electrochemical active surface areas (ECSAs) of the obtained electrodes were quantified based on their double-layer capacitance (Cdl) values to probe the density of accessible catalytic sites [53,54]. As depicted in Figure 6f, the recorded Cdl magnitude for NiMoO₄@NiFeS is as high as 30.14 mF cm⁻², which is 5.2, 11.1, 23.5, and 47.1 times that of NiMoO₄@NiFeO (5.76 mF cm⁻²), S-NiMoO₄ (2.72 mF cm⁻²), NiMoO₄@NiFe-PBA (1.28 mF cm⁻²), and NiMoO₄ (0.64 mF cm⁻²), respectively, suggesting that it has a greater abundance of active sites and superior electrolyte accessibility. Apart from its abundant heterointerfaces and mesoporous architecture, the electrode's superhydrophilic property also contributes largely to the ECSA by turning its total surface area into accessible three-phase reaction interfaces, thereby greatly increasing the number of accessible active sites. All in all, the expedited charge migration and enlarged electroactive surface area of the NiMoO₄@NiFeS heterostructure are collectively accountable for its exceptional OER behavior, rendering NiMoO₄@NiFeS a highly promising catalyst for OER.

2.3. Surface Phase Reconstruction/Transition of NiMoO₄@FeNiS

To investigate the evolution of surface chemical states of the catalyst during the electrocatalytic process, XPS characterizations were performed on the NiMoO₄@NiFeS electrode after stability testing. It can be seen from the survey XPS spectrum (Figure S11) that the N, Mo and S peaks are no longer detectable, owing to their leaching from the surface of catalyst after the OER test. Within the core-level Ni 2p profile of NiMoO₄@NiFeS (Figure 7a), the three deconvoluted spin-orbit split components correspond to the Ni 2p_{3/2} and Ni 2p_{1/2} orbitals associated with Ni²⁺, Ni³⁺ and corresponding shake-up satellites, respectively. It is noted that the deconvoluted Ni 2p peaks are systematically shifted toward higher binding energy relative to those before stability testing (Figure 4b), and that the peak corresponding to Ni⁰ disappears, indicating the presence of Ni in a high oxidation state. The enhanced intensity of the Ni³⁺ peak (Table S3) suggests the formation of NiOOH, whose higher valence state is known to provide favorable adsorption configurations and energetics for OER [55,56]. Similarly, the three deconvoluted spin-orbit doublet peaks observed in Figure 7b represent the Fe 2p_{3/2} and Fe 2p_{1/2} states of Fe²⁺, Fe³⁺ and corresponding shake-up satellites, respectively, and the marked increase in the Fe³⁺ signal (Table S3) also indicates the formation of FeOOH during the electrochemical process. Nonetheless, the deconvoluted Fe 2p peaks are systematically shifted toward a lower binding energy relative to those before stability testing (Figure 4c), and the peak corresponding to Fe⁰ still exists, which could be ascribed to an intermetallic charge transfer effect [57]. With strong electron depletion around Ni sites due to electrons transferring to adjacent oxygen intermediates, the Fe center maintains a relatively reduced state acting as an electron sink. Thus, the Fe center is conducive to maintaining the higher valence state of the Ni one. Within the core-level Mo 3d profile (Figure 7c), the near-surfaced Mo signal disappears, implying their leaching into the electrolyte as soluble MoO₄²⁻ ions. Similarly, the near-surfaced S signal is not detected within the high-resolution S 2p scan (Figure 7d) either, indicating that the sulfur species on the outermost layer undergo complete oxidative dissolution under OER operation and then leach into the electrolyte as soluble SO₄²⁻ ions [58]. There is no doubt that the leaching of Mo and S out from NiMoO₄@NiFeS not only provides an exceptionally porous architecture with an amplified surface area but also enlarges the number of active sites via exposure of more nickel sites and the generation of surface γ-NiOOH species. Remarkably, the O 1s core-level profile (Figure 7e) reveals a continued elevation in the O_A

intensity along with a great decrease in that of O_L relative to those before OER (Figure 4d), suggesting the occupancy of oxygen vacancies by OH^- ions from the electrolyte and the formation of more hydroxyl-rich (oxy)hydroxide species associated with active $NiFeOOH$ intermediates [14]. This finding is in good agreement with the increased proportion of high-valence metal species observed in the Ni 2p and Fe 2p spectra, as well as the disappearance of the Mo 3d and S 2p signals, supporting that the OER process occurs following the LOM mechanism. Electron paramagnetic resonance (EPR) measurements (Figure S12) were further performed on $NiMoO_4@NiFeS$ before and after OER catalysis. The characteristic paramagnetic signal at $g = 2.003$ originating from oxygen vacancies is remarkably elevated after OER, demonstrating massive lattice oxygen loss during the phase transformation of sulfides into (oxy)hydroxides and the consequent formation of abundant oxygen vacancies, which is consistent with the XPS analysis.

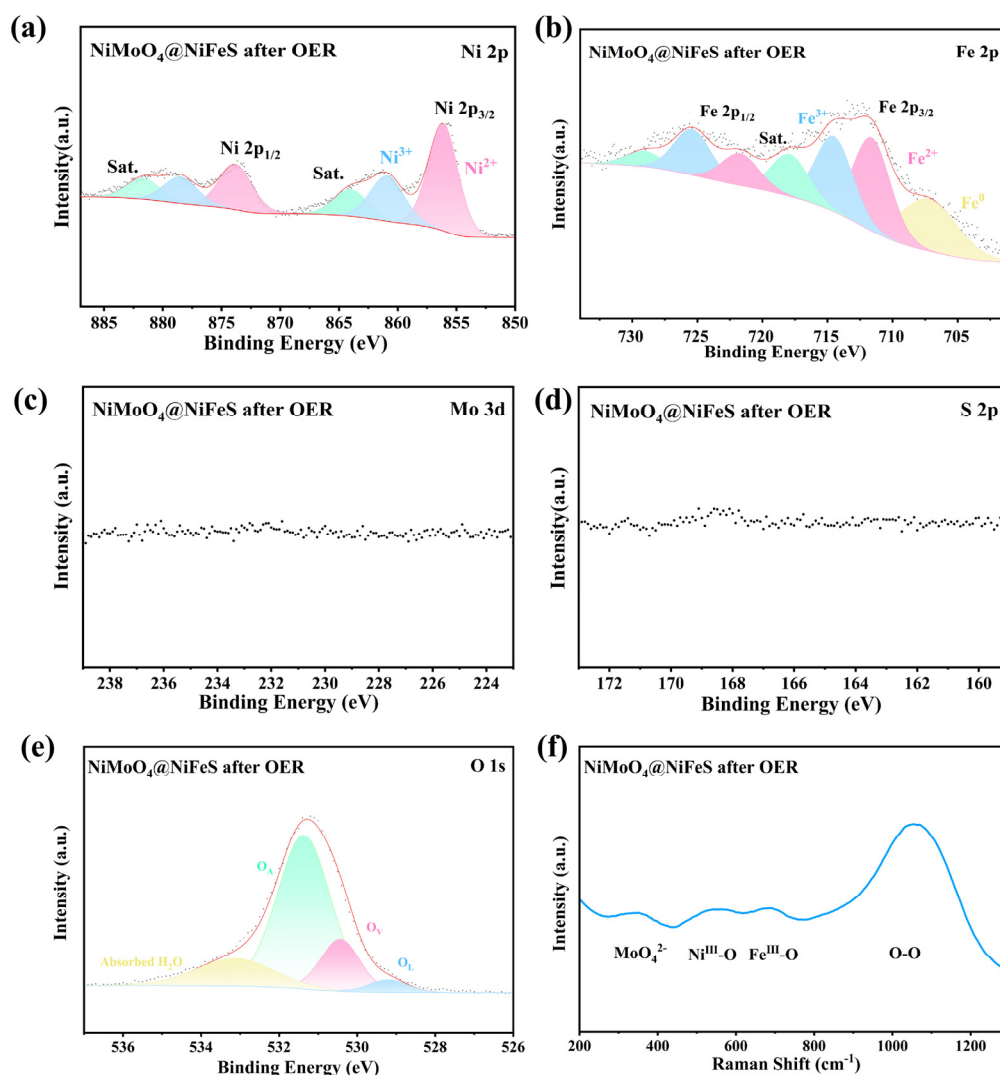


Figure 7. High-resolution (a) Ni 2p, (b) Fe 2p, (c) Mo 3d, (d) S 2p and (e) O 1s XPS spectra and (f) Raman spectrum of $NiMoO_4@NiFeS$ after stability testing.

Aiming at elucidating the structural evolution of $NiMoO_4@NiFeS$ during the OER process, Raman scattering characterization was also performed on the $NiMoO_4@NiFeS$ electrode after stability testing. From the Raman spectrum shown in Figure 7f, it can be observed that the original sulfide characteristic peaks (S-S, Ni-S-Fe) (Figure 3c) have disappeared, confirming the leaching or oxidative restructuring of sulfur species. Instead, a new set of broad peaks emerges, which offers compelling spectroscopic evidence for the

formation of γ -Fe/NiOOH species. Among them, the broad peak near 553 cm^{-1} might originate from the $\text{Ni}^{\text{III}}\text{-O}$ stretching vibration of γ -NiOOH, and the one at 690 cm^{-1} from the $\text{Fe}^{\text{III}}\text{-O}$ stretching vibration of γ -FeOOH [43,59]. Moreover, a broad and strong “active oxygen” O-O stretching mode appears dominantly around 1079 cm^{-1} . In contrast, neither $\text{Fe}^{\text{III}}\text{-O}$ stretching vibration nor an “active oxygen” O-O stretching mode was detected for the in situ Raman spectra of the previously reported $\text{NiMoO}_4/\text{NiFeS}$ [14]. Therefore, Raman analysis confirms the presence of α - NiMoO_4 , γ -NiOOH and γ -FeOOH in $\text{NiMoO}_4@\text{NiFeS}$ after stability testing. For the LOM pathway, the formed O-O bonds are responsible for the generation of oxygen vacancies, indirectly reflecting that lattice oxygen is involved in the OER process [60,61]. It should be pointed out that the $\text{Ni}^{\text{III}}\text{-O}$, $\text{Fe}^{\text{III}}\text{-O}$ and O-O moieties detected herein are neither protonated nor bonded to a neighboring OH group, indicating that the immediate participation of lattice oxygen leads to a reduced energy barrier for activating the (oxy)hydroxide surface. Furthermore, the significant broadening of these peaks indicates that the newly generated active phase possesses lower crystallinity or amorphous structure, which is a typical feature of highly efficient electrocatalysts.

In order to deeply investigate the structural stability and active phase evolution, the $\text{NiMoO}_4@\text{NiFeS}$ electrode after stability testing was investigated by SEM and TEM observation. Moreover, the SEM images shown thereafter (Figure 8a,b) reveal that the $\text{NiMoO}_4@\text{NiFeS}$ electrode after stability testing perfectly maintains the same multileveled flower-like morphology assembled by microtubes as before stability testing (Figure 1(c₁–c₃)), and no clear aggregation or structural collapse is observed even after undergoing severe anodic oxidation and gas bubble evolution, indicating that the as-prepared self-supported electrode also possesses outstanding mechanical structural stability and excellent corrosion resistance. The low-resolution TEM image (Figure 8c) reveals an uneven and amorphous coating layer on the solid body, evidencing the multiple interfaces between the poorly crystalline MOOH (M = Ni or Fe) and the highly crystalline NiMoO_4 . Moreover, from the HRTEM image (Figure 8d), two distinct lattice fringes are clearly distinguished, to elucidate the microstructure of the coating layer. The one with 0.248 nm spacing corresponds to the (101) crystalline plane of NiOOH [62], and that with 0.225 nm spacing to the (002) crystalline plane of FeOOH [63], confirming the in situ formation of FeOOH and NiOOH active species during the OER process. Meanwhile, the EDS mapping revealed the uniform dispersion of Mo, Ni, Fe, S and O elements (Figure 8e–j). In comparison with those before stability testing (Figure 2d–i), the signal intensities of Mo and S reduce to some extent, confirming their leaching as soluble species under an alkaline and oxidative environment. In contrast, no clear change is observed for the signal intensities of Ni, Fe and O, owing to the generation of a bimetallic Fe-Ni (oxy)hydroxide via in situ reconstruction of $\text{NiMoO}_4@\text{NiFeS}$.

2.4. DFT Calculations

Density functional theory (DFT) calculations were performed to elucidate the origin of the intrinsic catalytic activity for the oxygen evolution reaction (OER). Both the electronic structures of the catalysts and the adsorption energetics of key intermediates were systematically investigated. As evidenced above, the core-shell-shell structured $\text{NiMoO}_4@\text{NiFeS}/\text{NiFeOOH}$ was formed via the surface phase reconstruction of $\text{NiMoO}_4@\text{NiFeS}$ during OER. Accordingly, theoretical models of NiMoO_4 , NiFeS , $\text{NiFeS}/\text{NiFeOOH}$, and $\text{NiMoO}_4@\text{NiFeS}/\text{NiFeOOH}$ were constructed for comparative analysis (Figure S13). Charge density difference analysis reveals an electron transfer of approximately 0.81 e^- from NiFeS to the surface-reconstructed NiFeOOH active layer in the $\text{NiFeS}/\text{NiFeOOH}$ heterojunction (Figures 9a and S14a). In contrast, the $\text{NiMoO}_4@\text{NiFeS}/\text{NiFeOOH}$ composite material exhibits a substantially enhanced electron transfer of about 1.5 e^- from the inner $\text{NiMoO}_4@\text{NiFeS}$ heterojunction towards the

outer NiFeOOH layer (Figures 9b and S14b), showing the distribution of enriched electrons and holes on NiMoO₄@NiFeS/NiFeOOH. These results indicate that the formation of heterojunctions and interfacial charge rearrangement collectively facilitate charge transport and modulate the electronic structure of NiFeOOH.

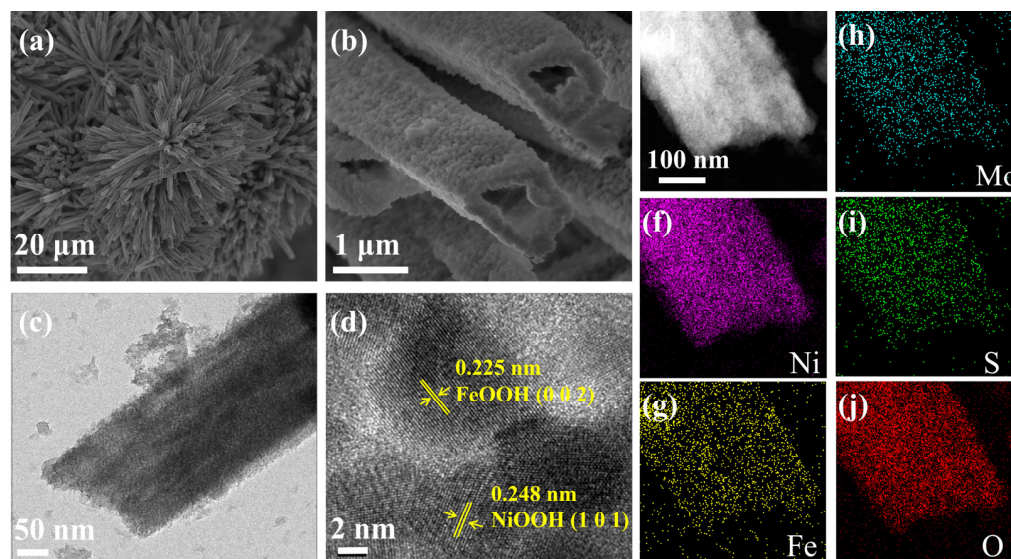


Figure 8. (a,b) SEM, (c) TEM, (d) HRTEM and (e–j) EDX elemental mapping images of NiMoO₄@NiFeS after stability testing.

The effect of electronic structure modulation on the O 2p band center (ϵ_{2p}) of NiMoO₄@NiFeS/NiFeOOH was analyzed by projected density of states (PDOS) (Figure 9c). Relative to pristine NiMoO₄, the ϵ_{2p} of NiFeS/NiFeOOH and NiMoO₄@NiFeS/NiFeOOH shift upward to -2.62 eV and -2.16 eV, respectively. This upshift results in deeper penetration of the Fermi level into the O 2p band, which facilitates electrons flowing away from oxygen sites under an applied anodic potential, thereby promoting lattice oxygen release [59,64,65]. Consequently, the higher ϵ_{2p} positions in NiFeS/NiFeOOH and NiMoO₄@NiFeS/NiFeOOH facilitate oxygen vacancy formation more readily than in pristine NiMoO₄, favoring the lattice oxygen oxidation mechanism (LOM) pathway for OER. The traditional adsorbate evolution mechanism (AEM) pathway [14,66] on Ni sites is illustrated in Figures 9d and S15. Initially, OH[−] is adsorbed at the active site (*), generating a *OH radical and releasing one electron. This *OH intermediate subsequently undergoes proton-coupled electron transfer to form *O, accompanied by the release of a water molecule and an additional electron. Nucleophilic attack of OH[−] on *O then yields the *OOH intermediate, along with one electron. Finally, *OOH reacts with OH[−] to produce O₂, a water molecule, an electron, and a regenerated active site. The corresponding free energy diagrams reveal that the formation of *OOH from *O is the rate-determining step (RDS) for pristine NiMoO₄, NiFeS, and NiFeS/NiFeOOH, with overpotentials (η s) of 0.62, 0.55 and 0.51 eV, respectively (Figures 9e and S16).

In contrast, for the Ni sites in the reconstructed NiMoO₄@NiFeS/NiFeOOH catalyst, the RDS shifts to the formation of *O from *OH, and the corresponding η decreases to 0.46 eV (Figure 9e). On the other hand, the lattice oxygen-mediated LOM pathway for NiFeS/NiFeOOH and NiMoO₄@NiFeS/NiFeOOH was further analyzed (Figures 9f and S17). This pathway can be divided into five steps: (i) deprotonation of the electrocatalyst to generate exposed lattice oxygen; (ii) nucleophilic attack of OH[−] on lattice oxygen; (iii) O–O coupling; (iv) release of O₂, leaving behind oxygen vacancies (*O_{vac}); and (v) replenishment of oxygen vacancies by OH[−] [67,68]. As shown in Figure 9g, the energy barriers for the RDS of the LOM pathway for NiFeS/NiFeOOH and

NiMoO₄@NiFeS/NiFeOOH are 0.47 and 0.41 eV, respectively. These values are lower than those for the corresponding AEM pathways (0.51 eV and 0.46 eV). The lower energy barriers for the LOM pathway can be attributed to the direct O-O coupling from lattice oxygen, which avoids the formation of high-energy *OOH intermediates required in the AEM pathway. This computational finding is consistent with the experimental results (Figure S18), where the OER activity shows a strong pH dependence, further confirming that the OER preferentially proceeds via the LOM route on these catalysts. For NiFeS/NiFeOOH, the RDS of the LOM pathway is the O-O coupling step. Notably, after the introduction of NiMoO₄, the substantial interfacial electron injection (1.5 e^-) from the inner core-shell structured NiMoO₄@NiFeS to the NiFeOOH layer significantly elevates the O 2p band center (ϵ_{2p}) and then promotes the formation of oxygen vacancies and the release of lattice oxygen, which effectively reduces the energy barrier of this step and shifts the RDS to the *OOH formation step, revealing a deep activation effect of NiMoO₄ on the LOM pathway.

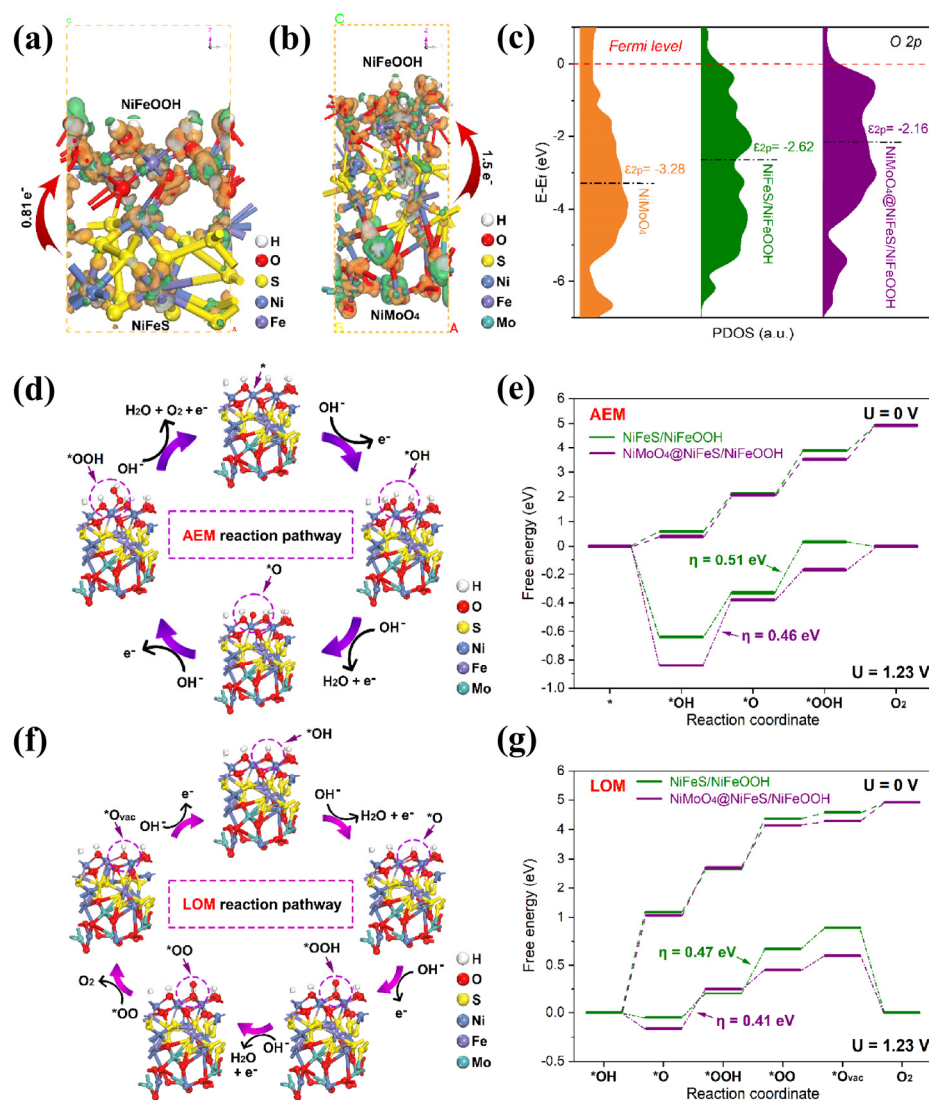


Figure 9. (a,b) Charge density difference in NiFeS/NiFeOOH (a) and NiMoO₄@NiFeS/NiFeOOH (b); (c) calculated PDOS and corresponding ϵ_{2p} of O 2p orbitals in NiMoO₄, NiFeS/NiFeOOH, and NiMoO₄@NiFeS/NiFeOOH; (d,f) schematic illustration of the AEM (d) and LOM (f) reaction pathway on NiMoO₄@NiFeS/NiFeOOH; (e,g) free-energy diagrams for the AEM reaction pathway on Ni sites (e) and the LOM reaction pathway on O sites (g) of NiFeS/NiFeOOH and NiMoO₄@NiFeS/NiFeOOH.

3. Materials and Methods

3.1. Materials

Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Tianjin Guangfu Technology Development Co., Ltd., Tianjin, China), ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, Shanghai Macklin Biochemical Technology Co., Ltd., Shanghai, China), potassium ferri-cyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$, Tianjin Bodi Chemical Co., Ltd., Tianjin, China), sulfur powder (Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China), potassium hydroxide (KOH, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), and hydrochloric acid (HCl, ~36.0–38.0% aqueous solution, Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China) were of analytical grade and applied as received. Commercial nickel foam (NF, Wuzhou Sanhe New Materials Technology Co., Ltd., Wuzhou, China) and deionized water (18.2 M Ω .cm, Shanghai Hitech Instruments Co., Ltd., Shanghai, China) were utilized throughout the experiments.

3.2. Synthesis of NiMoO_4/NF

Preparation of NiMoO_4 : Typically, NiMoO_4 microrod arrays were grown in situ on NF via a hydrothermal method. First, a piece of NF (2×2 cm) was sequentially ultrasonicated in acetone and 0.5 M HCl for 10 min each, followed by thorough rinsing with deionized water and ethanol. Subsequently, 1.16 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.7 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were ultrasonically dissolved in 50 mL of deionized water. The resulting green solution together with the cleaned NF was then transferred into a 100 mL Teflon-lined autoclave and kept at 150 °C for 6 h. After the autoclave had cooled to room temperature, the as-prepared NiMoO_4/NF electrode was collected and alternately washed with ethanol and deionized water. Finally, after drying at 60 °C for 12 h, an electrode with a yellow surface (denoted as NiMoO_4) was obtained.

Preparation of NiMoO_4/NF -based Prussian blue analogues (NiMoO_4/NF -PBA): In this step, 0.2 g of $\text{K}_3[\text{Fe}(\text{CN})_6]$ was completely dissolved in 50 mL of deionized water. Then, the as-synthesized NiMoO_4 was immersed in this solution. The reaction was carried out in a water bath at 90 °C for 30 min. After that, the product was carefully collected and rinsed three times alternately with deionized water and ethanol. Finally, it was dried at 60 °C for 12 h, yielding the dark orange NiMoO_4/NF -PBA electrode.

Preparation of NiMoO_4/NF -S: Typically, the as-prepared NiMoO_4/NF -PBA electrode and 100 mg of sulfur powder were placed in two separate ceramic boats. These boats were then positioned in a tube furnace with a distance of 5 cm between them, where the sulfur powder was placed upstream and the NiMoO_4/NF -PBA electrodes downstream. Subsequently, the tube furnace was heated to 350 °C at a ramp rate of 5 °C min^{−1} and maintained at this temperature for 1 h under a flowing N_2 atmosphere (60 mL min^{−1}). After the furnace had cooled to room temperature, the deep black NiMoO_4/NF -S electrode was obtained. For comparison, NiMoO_4/NF -O and S- NiMoO_4 were also prepared following the same procedure, except that no sulfur powder was added for the former and NiMoO_4 was used instead of NiMoO_4/NF -PBA for the latter, respectively.

3.3. Characterizations

The morphology of the synthesized electrodes was observed using scanning electron microscopy (SEM, Hitachi S-4800, Hitachi, Tokyo, Japan), and their crystalline structure and lattice fringes were investigated via transmission electron microscopy (TEM, JEM-2010, JEOL, Tokyo, Japan) operating at an accelerating voltage of 200 kV. Elemental mapping was conducted on an energy-dispersive X-ray (EDX) spectrometerscope attached to the TEM. Powder X-ray diffraction (XRD, Bruker D8 Advanced diffractometer, Bruker AXS GmbH, Karlsruhe, Germany) equipped with Cu K α radiation ($\lambda = 1.5418$ Å) was employed

to analyze the crystal phases. The chemical composition and oxidation states were examined by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD, Kratos Analytical, Manchester, UK), and the binding energies were calibrated with reference to the C 1s peak at 284.8 eV. Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer 100FT-IR (Waltham, MA, USA) spectrometer using KBr pellets for background correction. Raman scattering spectra were collected using a Jobin Yvon (Palaiseau, France) HR 800 micro-Raman spectrometer with 458 nm excitation. Nitrogen adsorption–desorption isotherms were measured using a volumetric adsorption analyzer (BET, Micromeritics TRISTAR II 3020, Micromeritics Instrument Corp, Norcross, GA, USA), and the specific surface area and pore size distribution were calculated. The water contact angle on the material surface was measured using a contact angle tester (Theta Flex, Biolin Scientific, Gothenburg, Sweden) to evaluate its hydrophilic/hydrophobic properties and surface wetting characteristics.

3.4. Electrochemical Measurements

Electrochemical measurements were performed on a Bio-Logic SP-300 workstation (Bio-Logic, Seyssinet-Pariset, France) using a conventional three-electrode configuration in 1 M KOH. The working electrode was the as-prepared NiMoO₄@NiFeS electrode (along with the control electrode) with a geometric area of 1.0 cm². An Hg/HgO (1 M KOH) electrode and a Pt plate (1 cm²) served as the reference and counter electrodes, respectively. All measured potentials were converted to the reversible hydrogen electrode (RHE) scale using the following equation:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.059 \times \text{pH}, \quad (1)$$

Linear sweep voltammetry (LSV) curves were recorded at a scan rate of 1 mV·s^{−1} with iR-correction. The Tafel slope is obtained from the Tafel equation as follows: $\eta = b \times \log(j/j_0)$, where η is the overpotential, b is the Tafel slope, j is the current density, and j_0 is the exchange current density, respectively. The electrochemical double-layered capacitance (C_{dl}) was determined by the CV method with a N₂-saturated 1.0 M KOH aqueous solution and in a non-Faradaic region at different scan rates (10, 20, 40, 60, 80 and 100 mV s^{−1}). Electrochemical impedance spectroscopy (EIS) measurements were conducted over a frequency range from 100 kHz to 0.01 Hz with amplitude of 10 mV.

3.5. Theoretical Calculations

DFT calculations were performed by using the CASTEP code. The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional was used with the generalized gradient approximation (GGA) and a plane-wave cutoff energy of 500 eV. The ion–electron interaction was modelled by the frozen core projector augmented wave (PAW) pseudopotentials. A 3 × 4 × 2 k-point mesh was used for Brillouin zone sampling. Spin-polarized calculations were enabled, and DFT-D (TS scheme) dispersion correction was applied to account for van der Waals interactions at the heterointerface. DFT with the Hubbard-U approach (DFT+U) was employed with effective U values of 4.0, 4.3, and 4.0 eV for Ni, Fe, and Mo, respectively. The models of NiMoO₄, NiFeS, NiFeS/NiFeOOH, and NiMoO₄@NiFeS/NiFeOOH were constructed with optimized total thicknesses of ~4.2 Å, ~4.4 Å, ~8.1 Å, and ~12.6 Å, respectively. A vacuum layer of thickness 15 Å was employed to isolate periodic effects. All structural models were thoroughly optimized with convergence criteria of 1.0 × 10^{−5} eV atom^{−1} for total energy and 0.02 eV Å^{−1} for maximum force. Detailed computational parameters are provided in the Supporting Information.

4. Conclusions

In summary, a self-supporting electrode composed of the arrays of mesoporous NiMoO₄@NiFeS microtubes was fabricated by gas-phase sulfidation of NiMoO₄@NiFe-PBA microrods. The mesoporous structure and superhydrophilic nature of these microtube arrays contribute an enlarged electrochemical active surface area for easy electrolyte penetration and rapid bubble release. The interfacial electronic coupling between NiMoO₄ and NiFeS induces in situ surface reconstruction and the generation of a bimetallic Fe-Ni (oxy)hydroxide phase (γ -Ni/FeOOH) with an increased number of oxygen vacancies and accessible nickel sites under anodic potential. Identified as virtual active species, the thermodynamically stable high-valence metal (oxy)hydroxides are responsible for the marvelous OER performance of the heterogeneous electrocatalyst. A series of electrochemical measurements evidenced that the self-supporting NiMoO₄@NiFeS electrode outperformed most of the state-of-the-art non-precious metal-based OER electrocatalysts. DFT calculations further reveal the charge redistribution at the hierarchical interfaces of the core-shell-shell structured NiMoO₄@NiFeS/NiFeOOH after the OER test, which leads to the O 2p band center being elevated significantly towards the Fermi level and thereby promotes the formation of oxygen vacancies and the release of lattice oxygen. Theoretical calculations also support the contribution of a self-sacrificing template (NiMoO₄) to the optimization of the energy barrier of the RDS step. Therefore, both experimental and theoretic results support that the LOM pathway takes precedence over the traditional AEM one. This work presents a rational design strategy that integrates heterojunction engineering with microstructural tailoring to develop cost-effective and durable OER electrocatalysts.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal16070621/s1>, Figure S1. Scanning electron microscopy (SEM) images of the NiMoO₄@NiFeS samples achieved by sulfurization of NiMoO₄@NiFe PBA precursor for (a) 0, (b) 5, (c) 15, (d) 30 and (e) 60 min, respectively; Figure S2. (a–c) Low-magnification SEM images of (a) NiMoO₄, (b) NiMoO₄@NiFe-PBA and (c) NiMoO₄@NiFeS; (d–i) TEM images of NiMoO₄@NiFeS observed from one (a–c) and the other (d–f) regions; Figure S3. (a) Low-resolution and (b) high-resolution TEM images and (c–j) EDX elemental mapping images of the NiMoO₄@NiFe PBA microtube; Figure S4: Optical images of the electrodes at different preparation stages: (a) NiMoO₄, (b) NiMoO₄@NiFe PBA, and (c) NiMoO₄@NiFeS; Figure S5: SEM images of (a) S-NiMoO₄ and (b) NiMoO₄@NiFeO; Figure S6. Rietveld refinement profile for the powder XRD data of NiMoO₄@NiFeS; Figure S7: (a) LSV polarization curves, (b) Tafel plots of NiMoO₄@NiFeS measured in 1 M KOH at temperatures of 25, 60 and 80 °C, respectively; Figure S8. Chronoamperometric stability test of the NiMoO₄@NiFeS/NF at a current density of 500 mA cm^{−2} in 1.0 M KOH; Figure S9. LSV curves of NiMoO₄@NiFeS electrodes prepared with different concentrations of K₃[Fe(CN)₆] (0.006 M, 0.012 M, and 0.024 M) before and after 1000 cyclic voltammetry cycles; Figure S10: CV curves of (a) NiMoO₄@NiFeS, (b) NiMoO₄@NiFeO, (c) S-NiMoO₄, (d) NiMoO₄@NiFe PBA, and (e) NiMoO₄ at various scan rates; Figure S11: The survey XPS spectrum of NiMoO₄@NiFeS after OER test; Figure S12. EPR spectra of NiMoO₄@NiFeS before and after OER performance; Figure S13: The optimized side view structural models for NiMoO₄ (a), NiFeS (b), NiFeS/NiFeOOH (c) and NiMoO₄@NiFeS/NiFeOOH (d). The white, red, yellow, royal blue, purple and turquoise balls represent H, O, S, Ni, Fe and Mo atoms, respectively; Figure S14: Bader charge analyses for NiFeS/NiFeOOH (a) and NiMoO₄@NiFeS/NiFeOOH (b). The white, red, yellow, royal blue, purple and turquoise balls represent H, O, S, Ni, Fe and Mo atoms, respectively; Figure S15: Schematic illustration of the AEM reaction pathway on NiMoO₄ (a), NiFeS (b) and NiFeS/NiFeOOH (c); Figure S16: Free-energy diagrams for the AEM reaction pathway on Ni sites of NiMoO₄ (a) and NiFeS (b); Figure S17: Schematic illustration of the LOM reaction pathway on NiFeS/NiFeOOH; Figure S18: The OER current densities of NiMoO₄@NiFeS at different pH values. Typically, a ρ value approaching 1 suggests a preference for LOM, indicating that NiMoO₄@NiFeS predominantly follows the

LOM instead of the AEM, while lattice oxygen plays a direct role in the reaction; Table S1: Surface area, pore volume, and pore size of NiMoO₄, NiMoO₄@NiFe PBA, and NiMoO₄@NiFeS; Table S2: Parameters obtained by fitting the Nyquist plots of NiMoO₄@NiFeS, NiMoO₄@NiFeO, S-NiMoO₄, NiMoO₄@NiFe PBA and NiMoO₄ using the equivalent circuit in Figure 6e. The impedance of Q is defined as $ZQ = 1/[T(j\omega)^n]$, where T is the CPE constant (CPE-T) with units of F·s(n − 1) and n is the CPE exponent (CPE-P, $0 \leq n \leq 1$); Table S3: XPS area ratios of Ni 2p and Fe 2p for NiMoO₄@NiFeS before and after OER test.

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