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Arousing the Reactive Fe Sites in Pyrite (FeS₂) via Integration of **Electronic Structure Reconfiguration and in Situ Electrochemical Topotactic Transformation for Highly Efficient Oxygen Evolution** Reaction

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5 Supporting Information

ABSTRACT: Despite significant advances in the development of highly efficient and robust oxygen evolution reaction (OER) electrocatalysts to replace noble-metal catalysts, commercializing OER catalysts with high catalytic activity for sustainable development still remains a great challenge. Especially, transition-metal Fe-based OER catalysts, despite their earth-abundant, cost-efficient, and environmentally benign superiorities over Co- and Ni-based materials, have received relatively insufficient attention because of their poor apparent OER activities. Herein, by rational design, we report Ni-modified pyrite (FeS₂) spheres with yolk-shell structure that could serve as pre-electrocatalyst precursors to induce a highly active nickel-iron oxyhydroxide via in situ electrochemical topological transformation under the OER process. Notably, as confirmed by the results of X-ray absorption spectroscopy, X-ray



photoelectron spectroscopy, and density functional theory (DFT) calculations, Ni doping could effectively regulate the intrinsic electronic structure of FeS₂ to realize a semiconductor-to-semimetal transition, which endows FeS₂ with dramatically improved conductivity and water adsorption ability, providing prequisites for subsequent topological transformation. Moreover, systematic post-characterizations further reveal that the optimal Ni-FeS₂-0.5 sample completely converts to amorphous Nidoped FeOOH via an in situ electrochemical transformation with volk-shell structure well-preserved under the OER conditions. The electronic structure modulation combined with electrochemical topotactic transformation strategies well stimulate the reactive Fe sites in Ni-FeS₂-0.5, which show impressively low overpotentials of 250 and 326 mV to drive the current densities (j) of 10 and 100 mA cm⁻², respectively, and a Tafel slope as small as 34 mV dec⁻¹ for the OER process. When assembled as a water electrolyzer for the overall water splitting, Ni-FeS2-0.5 can display a low voltage of 1.55 V to drive a current density of 10 mA cm⁻², outperforming most of the transition-metal-based bifunctional electrocatalysts to date. This work may provide new insight into the rational design of other high-performance Fe-based OER electrocatalysts and inspire the exploration of cost-effective, ecofriendly electrocatalysts to meet the demand for future sustainable development.

1. INTRODUCTION

The energy crisis and environmental pollution have stimulated the development of diverse sustainable energy conversion and storage technologies. Among these technologies, electrochemical water splitting, which is a vital section of numerous energy conversion techniques (such as rechargeable metal-air batteries and regenerated fuel cells), has been recognized as one of the most promising strategies to alleviate future energy demands and environmental issues. However, the kinetically sluggish oxygen evolution reaction (OER), owing to its complex four-electron reaction pathway, severely hinders the enhancement of efficiency for water splitting, which is the bottleneck of water electrolysis. Noble-metal-based catalysts, represented by IrO_2 and RuO_2 , are well-recognized as the most

efficient OER electrocatalysts. Nevertheless, their natural scarcity and high cost impede further applications.

For these reasons, transition-metal-based (Ni, Co, Fe, etc.) nonoxide materials involving their phosphides, selenides, sulfides, and borides, etc., have been widely studied as alternative OER electrocatalysts owing to their earth-abundant, highly active, and low-cost features.¹⁻⁴ However, most researchers mainly focus on Co- and Ni-based materials, with literature referring to Fe-based materials rarely reported,^{5,6} although they are more abundant and environmentally benign. Indeed, Fe is used more as a dopant to enhance the

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performance of Ni/Co-based OER catalysts⁷⁻⁹ rather than a host phase to accelerate the OER process, which is attributed to the inferior activity of Fe-based OER catalysts caused by their intrinsically low electrical conductivity and less exposed active sites.^{6,10,11} Recently, many reports demonstrated by combining experimental and theoretical studies that Fe is also the active site for OER. For instance, Bell and co-workers investigated the origin of dramatically enhanced activity of mixed nickel-iron oxyhydroxides via operando X-ray absorption spectroscopy (XAS) and density functional theory (DFT) calculation.¹² The results show that Fe^{3+} in $Ni_{1-x}Fe_xOOH$ exhibits unusually short Fe-O bond distances and meanwhile the OER intermediates have nearly optimal binding energy at the Fe sites, confirming that Fe³⁺ species are the active sites for OER. Boettcher and co-workers studied the roles of Fe and Co in electrodeposited cobalt-iron (oxy)hydroxides through in situ electrical measurements coupled with ex situ XRD and Xray photoelectron spectroscopy (XPS) characterizations and drew the conclusion that Fe acts as a catalytic center, while Co provides an electrically conductive, chemically stable host.¹⁰ Chen et al. synthesized an Fe-based OER electrocatalyst, namely, ultrathin pyrrhotite (Fe_7S_8) nanosheets with a mixedvalence state and intrinsic metallic character, which shows an onset overpotential (η) of 270 mV at 10 mA cm⁻² with a Tafel slope of 43 mV decade⁻¹, demonstrating highly active Fe sites in the OER process.¹³ Song et al. also prepared a highly efficient mono-Fe OER electrocatalyst, which displays an η of 283 mV at 10 mA $\rm cm^{-2}$ with a Tafel slope of 41.4 mV decade⁻¹, further confirming the activity of the Fe sites toward OER.14

Inspired by the numerous contributions made above, we attempted to design an Fe-based electrocatalyst with a highefficiency OER performance by addressing the factors that cause its inferior apparent activity. We chose the earthabundant pyrite (FeS₂) as the research subject for the OER process although it is rarely studied as an OER catalyst because of its poor performance. In view of the restraining factors in the electrocatalytic process,¹⁵ namely, the intrinsic electrical conductivity, the number of active sites, and the reaction energy barrier, we sought to promote the OER property of FeS₂ from these aspects. Given that semiconductor characteristics and less exposed active sites are the main factors that cause the poor performance of FeS₂,^{16,17} yolk-shell-structured FeS₂ spheres were first constructed to ensure more exposed active sites, and then through a composition modulation strategy, we introduce Ni into the lattice of FeS₂ so as to regulate its intrinsic properties like the electrical conductivity and hydrophilicity.^{18–20} Meanwhile, considering the previous reports that transition-metal sulfides/phosphides can be in situ partially or entirely transformed into highly active metal (oxy)hydroxides during the OER process,^{14,21,22} we anticipate that the Ni doping strategy, together with sulfidation process, will endow the catalyst with more rapid charge and mass transfer, a more hydrophilic surface, and an optimal composition so as to induce the entire conversion to the most active nickel-iron (oxy)hydroxide species.²³ Moreover, it is believed that the sulfides are promising bifunctional catalysts, and thus we also expect that sulfidation will benefit the watersplitting process.⁶

Herein, we demonstrate a facile strategy to obtain yolkshell-structured Ni-doped FeS_2 (Ni-FeS₂) spheres as a highefficency OER precatalyst. The optimized Ni-FeS₂-0.5 spheres can induce an entire conversion to highly active nickel—iron

oxyhydroxide via in situ electrochemical topological transformation during the OER process. This electrochemical reconstruction-derived catalyst could deliver current densities of 10 and 100 mA cm^{-2} at low overpotentials of 250 and 326 mV, respectively, and a Tafel slope as low as 34 mV dec^{-1} for the OER process, and this performance even surpasses those of the benchmark IrO₂ catalyst and most transition-metal-based (Ni, Co, Fe, etc.) OER catalysts recently reported. XPS and synchrotron-based XAS as well as DFT calculations were conducted to manifest the effective reconfiguration of the electronic structure of FeS₂ by Ni doping, and the results indicate that Ni doping induces a transition from semiconductor to semimetal and a promoted adsorption ability of H_2O for FeS₂. To gain deep insight into the active form of the catalyst during the catalytic process, Ni-FeS2-0.5 after longterm OER testing was elaborately characterized by comprehensive ex situ measurements, which reveal that the Ni-doped FeS₂ spheres undergo a topotactic conversion during the electrochemical oxidation process and transform into hierarchical Ni-FeOOH spheres with the original frameworks and Fe/Ni molar ratio retained. Finally, the water-splitting performance of Ni-FeS₂-0.5 was also evaluated, and, excitingly, the Ni-FeS₂-0.5 catalyst demonstrates an activity superior to most of the transition-metal-based bifunctional electrocatalysts to date. This work may inspire the exploration and design of highly active Fe-based catalysts and provide a better understanding of the role that Fe plays in the OER process.

2. EXPERIMENTAL SECTION

Synthesis of Ni-FeS₂-0.5. In a typical synthesis of a nickel--iron alkoxide precursor, 8 mL of glycerol was dissolved in 42 mL of isopropyl alcohol (IPA) to form a transparent colorless solution. Then 0.125 mmol of Ni(NO₃)₂·6H₂O and 0.25 mmol of Fe(NO₃)₃·9H₂O were added to the above solution under vigorous stirring. After that, the obtained solution was transferred into a Teflon-lined stainless steel autoclave and kept at 140 °C for 12 h. Finally, the autoclave was cooled naturally, and then the faint yellow precipitate was collected by centrifugation, alternatively washed with absolute ethanol and water, and dried. For the preparation of Ni-FeS₂-0.5, the precursor and S powder were placed in a quartz tube furnace, with the precursor in the center of the tube, while the S powder was upstream. With a heating rate of 5 °C min⁻¹, the sample was then annealed at 370 °C and maintained for 4 h under a N₂ atmosphere.

Synthesis of Ni-FeS₂-**1.** Ni-FeS₂-1 was prepared with a procedure similar to that of the Ni-FeS₂-0.5 sample, except that the molar ratio of Ni-to-Fe was changed to 1:1 [n(Ni) + n(Fe) = 0.375 mmol].

Synthesis of Ni-FeS₂**-0.25.** Ni-FeS₂-0.25 was prepared with a procedure similar to that of the Ni-FeS₂-0.5 sample, except that the molar ratio of Ni-to-Fe was changed to 1:4 [n(Ni) + n(Fe) = 0.375 mmol].

Synthesis of FeS₂. FeS₂ was prepared with a procedure similar to that of the Ni-FeS₂-0.5 sample, except that Ni(NO₃)₂·6H₂O was not used and the molar amount of Fe(NO₃)₃·9H₂O was increased to 0.375 mmol.

Synthesis of NiS₂. NiS₂ was prepared with a procedure similar to that of the Ni-FeS₂-0.5 sample, except that $Fe(NO_3)_3$ ·9H₂O was not used and the molar amount of Ni(NO₃)₂·6H₂O was increased to 0.375 mmol and the holding time at 370 °C was reduced to 2.5 h.

The Pt/C catalyst was commercially purchased from Johnson Matthey Co. Ltd. (20 wt % Pt in C, crystallite size 3.5 nm, and carbon black XC72R), and the IrO_2/C catalyst was synthesized according to the literature.²⁴

Materials Characterization. The morphology and structure of the samples were characterized by scanning electron microscopy (SEM; JSM-6490LV) and transmission electron microscopy (TEM; JEOL JEM-2010) as well as high-resolution transmission electron microscopy (HRTEM). High-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images and elemental mapping were conducted on a JEOL JEM-2100F microscope (200 kV). Powder X-ray diffraction (XRD) was conducted to analyze the crystal structure, which was in the range of $10-80^{\circ}$ (2 θ) on a Bruker D8 Advance diffractometer. N₂ sorption measurements were measured at liquid-nitrogen temperature (77 K) on a Belsorp-max sorption analyzer. Before the experiments, the sample was degassed at 200 °C for 5 h. The surface area and pore-size distribution were calculated by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively, from the adsorption branch. X-ray photoelectron spectroscopy (XPS) was exploited to identify the chemical states by using an ESCALAB 250 spectrometer (PerkinElmer), and the C 1s level at 284.8 eV was taken as a reference to calibrate the binding energies. Fourier transform infrared (FT-IR) spectra were collected on a Bruker VECTOR 22 spectrometer with the KBr disk method. The X-ray absorption nearedge structure (XANES) was measured in transmission mode using a Si(111) double-crystal monochromator at 1W1B station in Beijing Synchrotron Radiation Facility (BSRF). The acquired extended X-ray absorption fine structure (EXAFS) data collected in ambient conditions were analyzed with the ATHENA module, implemented in the IFEFFIT software packages. Raman spectra were obtained on an Invia Raman spectrometer with a laser excitation of 532 nm.

Computational Methods. The electronic structure calculations based on the generalized gradient approximation (GGA)-Perdew-Burke-Ernzerhof (PBE) method with spin polarization were performed in the Vienna ab initio simulation package (VASP) code. The projected-augmented-wave potential together with the DFT+U method was used with $U_{\rm Fe}$ = 2 eV for the Fe d orbitals and $U_{\rm Ni}$ = 3 eV for the Ni d orbitals. The cutoff energy was 400 eV, and the K-point mesh was $3 \times 6 \times 6$. For the structure optimization, the residual forces on all atoms were less than 0.01 eV $Å^{-1}$. In this paper, we explored the $2 \times 1 \times 1$ supercells with and without Ni-doped FeS₂. The densities of states (DOSs) of all systems were calculated. Firstprinciples DFT calculations were performed using Dmol^{25,26} in the Materials Studio 5.5 package from Accelrys Inc. Numerical basis sets of double- ζ -quality plus polarization functions, which is the numerical equivalent of the Gaussian basis, 6-31G**, but is much more accurate, were used in calculations of the water adsorption energies. The cores were treated using DFT semilocal pseudopotentials, specifically designed for DFT calculations.²⁶ The GGA-PBE functional^{27,28} was employed in the calculations. Spin-unrestricted calculations were performed using a Fermi broadening²⁹ of 0.005 Ha to smear the occupation of bands around the Fermi energy, and the results were extrapolated to T = 0 K. The convergence criteria in energy, force, and displacement were set to 2×10^{-5} Ha, 0.004 Ha Å⁻¹, and 0.005 Å, respectively. The subsequent results are based on using a Brillouin zone sampling by a Γ -centered Monkhorst–Pack scheme³⁰ with a 4 × 4×1 k-point grid. A geometry-optimized FeS₂ cell was used to build Fe-terminated slabs (with and without Ni doping) of thickness 4.4 Å and a vacuum slab of 15 Å both above and below the layer. The water adsorption energies of bare and Ni-doped (210) FeS₂ slabs were calculated based on the following equation:

 $E_{\text{water ads}} = E_{\text{FeS}_2/\text{water complex}} - (E_{\text{water}} + E_{\text{FeS}_2})$

where $E_{\rm water\ ads}$ is the water adsorption energy of the surface, $E_{\rm FeS_2/water\ complex}$ is the total energy obtained for the water-adsorbed FeS_2 surface, $E_{\rm water}$ is the total energy of the water molecule, and $E_{\rm FeS_2}$ is the total energy of the FeS_2 surface.

Electrochemical Measurements. The working electrode was prepared by dispersing a catalyst powder of 4 mg into 1 mL of solution containing 900 μ L of ethanol and 100 μ L of a Nafion solution (5 wt %). Afterward, the slurry was mixed by ultrasonication to obtain a homogeneous ink. Then 30 μ L of ink was extracted, coated onto a glassy carbon (GC) electrode (D = 3 mm), and left to dry naturally.

The hydrogen evolution reaction (HER) and OER performances were evaluated in a standard three-electrode configuration using a

CHI 760E electrochemical workstation (CH instrument, Chenhua, China), wherein a graphite rod and a Hg/HgO (KOH-saturated) electrode were used as the counter and reference electrodes, respectively. The potentials measured were referenced to a reversible hydrogen electrode (RHE) according to the Nernst equation E(RHE)= E(Hg/HgO) + 0.098 + 0.059pH, and all current densities were normalized to the geometrical surface area. Linear-sweep-voltammetry (LSV) measurements were conducted, if not specified, at a scan rate of 5 mV s⁻¹ in a N_2/O_2 -saturated 1 M KOH solution by using IR compensation with a degree of 90%. The Tafel slope was obtained from the corresponding LSV curves according to the Tafel equation η = $b \log(j/j_0)$. Electrochemical impedance spectroscopy (EIS) tests were carried out from 500000 to 0.01 Hz with an amplitude of 5 mV at an applied potential of 1.5 V versus RHE. An electrochemical surface area (ECSA) was determined by the tested electrochemical double-layer capacitance (C_{dl}) obtained from cyclic voltammetry (CV) measurement. When $\Delta j (j_a - j_c)$ was plotted against the scan rate, a linear slope that is twice C_{dl} was acquired. The long-term durability was conducted by a chronoamperometric curve in a 1 M KOH solution.

With regard to the overall water-splitting measurements, Ni foam (NF) was preprocessed by HCl, water, and ethanol, in turn, so as to eliminate the oxides and impurities. Then, the catalyst was dropped onto NF with a loading of 2 mg cm⁻² and used as both the anode and cathode. The polarization curve was recorded in N₂-saturated 1 M KOH at a scan rate of 5 mV s⁻¹.

3. RESULTS AND DISCUSSION

In the current work, we developed a facile solvothermal approach coupled with subsequent sulfidation to synthesize highly uniform yolk-shell-structured Ni-FeS₂ spheres. As schematically illustrated in Figure 1, the synthesis strategy



Figure 1. Schematic illustration of the fabrication of yolk-shellstructured Ni-FeS₂ spheres.

mainly consists of two steps. The first step is to prepare uniform nickel—iron alkoxide solid spheres as the precursor by using $Fe(NO_3)_3.9H_2O$ as the Fe source, $Ni(NO_3)_2.6H_2O$ as the Ni source, and glycerol together with IPA as a mixed solvent. Later on, by means of a nonequilibrium heat treatment process, the nickel—iron alkoxide solid spheres could be easily transformed into yolk—shell-structured nickel—iron sulfides



Figure 2. SEM images of the Ni-Fe-0.5 precursor (a) and Ni-FeS₂-0.5 (b and c). (d and e) TEM images of Ni-FeS₂-0.5. (f) HRTEM image of Ni-FeS₂-0.5. The inset is the corresponding SAED pattern. (g and h) HAADF-STEM image of Ni-FeS₂-0.5 and the corresponding line-scan profiles. (i) Elemental mapping images.

(denoted as Ni-Fe-X for precursors and Ni-FeS2-X for sulfurized products; X represents the Ni/Fe molar ratio of raw materials). Previously, numerous synthetic strategies and associated formation mechanisms had been proposed as guidances for the design of hollow structures.³¹⁻³³ Here, we assume that the rational evolution might be that the large temperature gradients along the radial direction will drive the formation of the core-shell structure in the final product when the heating rate was set at a relatively high degree (5 °C min⁻¹).³⁴ Hence, on the interface between the shell and core, there will exist two forces in opposing directions, namely, the contraction force (F_c) induced by the oxidative degradation of the organic species and the adhesion action (F_a) from the relatively dense shell.³⁵ F_c results in the inward shrinkage of the nickel-iron alkoxide core, while F_a hinders the inward contraction of the precursor core. When F_c is dominant, the inner core will proceed to shrink as a consequence of the loss of the organic species and thus a yolk-shell structure will be generated. Synchronously, the S powder loaded in the combustion boat will react with the precursor to form metal sulfides.

The morphologies and microstuctures of the as-prepared nickel-iron alkoxide precursor and corresponding sulfurized products (Ni-FeS₂) were investigated by an electron microscopy technique (Figure 2a-e and Figures S1-S4). The SEM (Figure 2a) and TEM (Figure S3) images clearly show that the Ni-Fe-0.5 precursor was featured with a highly uniform spherical morphology with an average diameter of 680 nm and that the spheres in nature are solid with a fairly smooth surface. After sulfuration treatment, the resultant product still

maintains the spherical morphology of the precursor but with a rougher surface. Meanwhile, the sulfurized product may possess a yolk-shell structure from individual broken spheres (marked by arrows; Figure 2b,c). Moreover, TEM images further confirm that the yolk-shell structure is successfully obtained via the sulfuration treatment (Figure 2d,e). The HRTEM image (Figure 2f) recorded on the edge of a single yolk-shell sphere shows clear lattice fringes with a spacing of 0.244 nm, which can be assigned to the (210) plane of FeS₂. The selected-area electron diffraction (SAED) pattern (the inset in Figure 2f) displays a polycrystalline nature of the yolkshell spheres. Energy-dispersive X-ray spectroscopy (EDS) line-scan results demonstrate a well-defined yolk-shell structure for Ni-FeS₂-0.5 (Figure 2g), while the EDS mapping images (Figure 2h,i) not only show a homogeneous distribution of Fe, Ni, and S elements but also reveal that the core and shell have the same components. Furthermore, the specific surface area and porous nature of Ni-FeS₂-0.5 were also investigated by nitrogen sorption measurements. The BET surface area was tested to be $45 \text{ m}^2 \text{ g}^{-1}$, and the pore sizes are mostly below 10 nm (Figure S5). All of the results above indicate that well-defined yolk-shell-structured Ni-FeS2 spheres were achieved, and they might provide fast transfer channels for electrons and more accessible active sites to the electrolyte ions.

Powder XRD and FT-IR spectroscopy (Figures S6 and S7) were conducted to investigate the crystal structure and composition of the Ni-Fe-0.5 precursor spheres. As revealed in Figure S6, the XRD pattern of the Ni-Fe-0.5 spheres shows a weak diffraction peak at 10.5°, which is characteristic of metal



Figure 3. (a) XRD patterns of the as-prepared Ni-FeS₂-0.5, Ni-FeS₂-0.25, and FeS₂. The inset is magnified XRD patterns of the (200) peak. (b) XPS survey spectrum of Ni-FeS₂-0.5. (c) Comparison of high-resolution Fe 2p between bare FeS₂ and Ni-FeS₂-0.5. High-resolution XPS spectra of Ni 2p (d) and S 2p (e) for Ni-FeS₂-0.5.



Figure 4. (a) Fe K-edge XAFS $k^3[\chi(k)]$ oscillation curves and (b) normalized Fe K-edge XANES spectra of Ni-doped FeS₂ and FeS₂ (the inset is an enlarged view of peak B). FT-EXAFS spectra of (c) Fe and (d) Ni in Ni-doped and bare FeS₂.

glycerate.^{37,38} Meanwhile, the FT-IR absorption peaks located at 3335, 2920, and 2855 cm⁻¹ are in good accordance with the hydrogen-bonded hydroxyl groups and typical C–H stretching vibrations,³⁸ further confirming the existence of the organic alkoxide in the precursor. Therefore, the as-formed Ni-Fe-0.5 precursor spheres are composed of amorphous metal alkoxide. Figure 3a displays the XRD patterns of sulfurized samples with different Ni/Fe molar ratios, all of which could be readily indexed to cubic-phase FeS₂ with the $Pa\overline{3}$ space group (JCPDS 42-1340). Particularly, no diffraction peaks related to Ni-based phases could be detected. Also, the diffraction peaks of Ni-FeS₂-X (X = 0.25, 0.5) shift to lower angles compared with their counterparts in FeS₂ [magnified (200) peak in Figure 3a]. Such a negative shift indicates a lattice expansion, further proving the substitution of Ni atoms at the Fe sites within the materials.¹⁸ When the Ni/Fe molar ratio is increased to X = 1, additional peaks belonging to ternary Ni_{0.5}Fe_{0.5}S₂ are detected at 32.1°, 39.6°, and 54.6°, indicating the occurrence of phase



Figure 5. (a) Structure representations and the corresponding DOSs of pristine FeS_2 , Ni-FeS₂-0.25, and Ni-FeS₂-0.5. (b) Geometry-optimized structures and relevant water adsorption energies of water-adsorbed pristine FeS_2 , Ni-FeS₂-0.25, and Ni-FeS₂-0.5, wherein the yellow spheres denote S, the bluish-violet spheres Fe, the rose spheres Ni, the red spheres O, and the white spheres H.

separation in the Ni-FeS₂-1 sample (Figure S8).¹⁷ Furthermore, the inductively coupled plasma atomic emission spectroscopy (ICP-AES) and EDS analysis for Ni-FeS₂-X (X = 0.25, 0.5) samples demonstrate that the actual Fe/Ni atom ratios in Ni-FeS₂-0.25 and Ni-FeS₂-0.5 are 6.0 and 2.7, respectively (Table S1 and Figure S9). The results above suggest that the Ni atoms, in the form of the doping state, are probably stabilized in the FeS₂ lattice.

XPS was carried out to investigate the effect of Ni doping on the chemical state of Ni-FeS₂-0.5. The survey XPS spectrum reveals the presence of Fe, Ni, and S elements (Figure 3b), consistent with the result from the elemental mapping images (Figure 2i). Furthermore, as depicted in Figure 3c, the highresolution Fe 2p XPS spectrum displays two peaks located at about 707.2 and 720.0 eV, which could be assigned to the spin-orbit doublet of the 2p orbital of Fe²⁺ in FeS₂.¹⁶ Especially, these two peaks both show an obvious downshift in contrast to those of pure FeS2, suggesting that the electrical potential environment of the Fe centers has been modified through Ni doping.^{39–41} The broad shoulder peak at 711.1 eV possibly belongs to the Fe³⁺ species from the surface oxidation under ambient air.⁴² In high-resolution Ni 2p XPS spectrum (Figure 3d), the doublets located at 853.6 and 870.8 eV have binding energies between nickel metal and nickel oxides, indicative of the presence of nickel sulfides, 43-46 while the other two peaks situated at 855.5 and 873.3 eV, respectively, are attributable to oxidized Ni species.^{41,47} The remaining two peaks are satellite peaks. With regard to the S 2p spectrum, the

two sharp peaks appearing at about 162.4 and 163.6 eV (Figure 3e) are assigned to S $2p_{3/2}$ and S $2p_{1/2}$, respectively.⁴⁸⁻⁵⁰ The minor peak occurring at about 164.5 eV is due to polysulfides (S_n^{2-}) ,⁵¹ while the weak peak at 168.7 eV could be recognized as a S–O bond derived from surface oxidization.^{52–54}

Synchrotron XAS was performed to further investigate the local structure and electronic nature of Ni-FeS₂-X (X = 0.25, 0.5). As displayed in Figure 4a, the Fe K-edge $k^3[\chi(k)]$ oscillation curve of Ni-FeS $_2$ -X is very similar in profile to that of FeS₂, confirming the good maintenance of the FeS₂ structure after Ni incorporation.¹⁸ XANES was exploited to evaluate the effect of Ni doping on the electronic structure of Ni-FeS2-X. As indicated in the Fe K-edge XANES spectra (Figure 4b), the profiles of Ni-FeS₂-X are consistent with that of pristine FeS₂, further suggesting that the Ni-FeS₂-X samples have structures analogous to that of FeS₂. In addition, the Fe K-edge XANES spectra of Ni-FeS2-X involve three main excitations, which are labeled as A-C, respectively. Here, peak A is a pre-edge peak generally arising from a Fe 1s \rightarrow 3d dipole-forbidden transition, which becomes allowed in the condition of distorted FeO_6 octahedral or deviation from centrosymmetric coordination.^{55,56} The shoulder peak marked as B represents a ligand-to-metal charge transfer, and peak C is due to a Fe 1s \rightarrow 4p electric dipole-allowed transition.⁵⁵ For all of the samples, peak A shows a weak signal intensity ascribed to the transition from the Fe 1s core level to the 3d unoccuped state, which emerged as a result of a distorted FeO₆



Figure 6. (a) OER polarization curves and (b) the corresponding Tafel plots of Ni-FeS₂-0.5, Ni-FeS₂-0.25, FeS₂, Pt/C, and IrO₂/C at 5 mV s⁻¹ in 1 M KOH. (c) Summary and comparison of the overpotentials at 10 mA cm⁻² and Tafel slopes for Ni-FeS₂-0.5, Ni-FeS₂-0.25, FeS₂, Pt/C, and IrO₂/C, respectively. (d) C_{dl} of Ni-FeS₂-0.5, Ni-FeS₂-0.25, and FeS₂. (e) Nyquist plots of post-OER Ni-FeS₂-0.5, Ni-FeS₂-0.25, and FeS₂ at an overpotential of 270 mV. The inset shows a partial zoomed-in image. (f) Durability test of Ni-FeS₂-0.5 at an overpotential of 250 mV. The inset displays the SEM image for Ni-FeS₂-0.5 after a 15 h stability test.

octahedron and the Fe 3d-4p orbital mixing enabled by deviation from centrosymmetric coordination.^{17,56} However, a relatively obvious distinction is detected at peak B among these three materials (the inset in Figure 4b). Notably, Ni-FeS₂-0.5 exhibits the lowest intensity, followed by Ni-FeS2-0.25 and FeS₂, revealing an increased occupancy of the Fe valence state after Ni doping. This result further demonstrates that a secondary charge transfer has taken place from Ni to Fe in the Ni-FeS₂-X samples,^{58,59} which well matches with the result from previous XPS measurements. Moreover, the bonding environment of Fe atoms was further investigated by Fouriertransformed (FT-)EXAFS at the Fe edge for Ni-FeS₂-0.5, which shows a dominant peak at approximately 1.85 Å (Figure 4c), corresponding to the Fe-S coordination,^{17,60} whereas as in the case with Ni-FeS₂-0.25, the peak intensity of Ni-FeS₂-0.5 is slightly decreased compared with FeS2, implying surface disorder caused by Ni incorporation (Figure S10).⁶¹ Figure 4d shows Ni K-edge EXAFS spectra of Ni-FeS₂-X in the R space, which reveal a main peak assigned to Ni-S bonding at about 1.93 Å.62 Moreover, no Ni-Ni bonding is found in the coordination shells. Besides, the Ni K-edge XANES spectra and $k^3[\chi(k)]$ oscillation curve of Ni-FeS₂-X are also dissimilar to that of Ni foil (Figure S11). These results above confirm not only the successful doping of Ni into the crystal structure of FeS₂ but also the electronic structure changes of Ni-doped FeS₂, which might offer more active sites to promote the catalytic performance of FeS₂.

To further get through the role of Ni in the electronic structure reconfiguration of FeS₂, the optimized crystal structures of FeS₂, Ni-FeS₂-0.25, and Ni-FeS₂-0.5 were constructed and the corresponding electronic DOS of these three samples were calculated (Figure 5a). The calculation results reveal that the pristine FeS₂ is a semiconductor with a band gap close to the experimental value of 0.95 eV.⁶³ Upon the substitution of Ni in FeS₂, a transition from a semi-

conductor to a semimetal is observed for both Ni-FeS₂-0.25 and Ni-FeS₂-0.5, indicating an enhanced charge-transfer kinetics. Such a transition behavior might be caused by the electron transfer from Ni to Fe, as elaborated by the XPS and XANES results above (Figures 3c and 4b), where new energy levels of Ni are induced within the forbidden zone of FeS₂ and are close to overlapping with the conduction band.¹⁹ Moreover, considering that the adsorption energy of water plays a vital role in estimating the HER and OER activity of a catalyst in an alkaline solution, DFT calculations were further conducted to study the effect of Ni doping on the water adsorption ability of FeS₂. As displayed in Figure 5b, geometryoptimized structures for FeS2, Ni-FeS2-0.25, and Ni-FeS2-0.5 were established. The derived water adsorption energies on Ni- FeS_2 -0.5 and Ni-FeS_2-0.25 are -1.43 and -1.2 eV, respectively, which are much lower than that of FeS_2 (-0.93 eV), indicating a favorable water activation process on the surface of Nimodified FeS2. The enhanced conductivity combined with good hydrophilicity of Ni-FeS2-0.5 might accelerate in situ electrochemical transformation to obtain highly active nickeliron (oxy)hydroxide species.

To evaluate the effects of electronic structure modification of FeS₂ by Ni on its electrocatalytic performance, the OER activities of Ni-FeS₂-*X*, FeS₂, Pt/C, and IrO₂/C were measured using a standard test system in alkaline media (pH = 14). The LSV curves (Figure 6a) suggest that both the FeS₂ and Pt/C electrodes exhibit low OER activities. However, after the introduction of Ni in FeS₂, the electrocatalytic activity toward OER is enhanced dramatically, even surpassing the state-ofthe-art IrO₂/C and most transition-metal-based (Ni, Co, Fe, etc.) OER catalysts reported to date (Table S2). More specifically, Ni-FeS₂-0.5 that outperforms the rest of the catalysts can readily achieve an onset η of 206 mV and requires η values of 250 and 326 mV to drive the current densities (*j*) of 10 and 100 mA cm⁻², respectively. Subsequently, only 300 mV

Figure 7. High-resolution XPS spectra of (a) S 2p, (b) Fe 2p, and (c) Ni 2p before and after long-term OER tests. (d) Normalized Fe K-edge XANES spectra and (e) Fe K-edge FT-EXAFS spectra of Ni-FeS₂-0.5 before and after long-term OER tests. (f) Fe K-edge XAFS $k^3[\chi(k)]$ oscillation curves of Ni-FeS₂-0.5 after long-term OER tests together with Fe foil, Fe₂O₃, and FeOOH. (g) Normalized Ni K-edge XANES spectra and (h) Ni K-edge FT-EXAFS spectra of Ni-FeS₂-0.5 before and after long-term OER tests. (i) Ni K-edge XAFS $k^3[\chi(k)]$ oscillation curves of Ni-FeS₂-0.5 before and after long-term OER tests. (i) Ni K-edge XAFS $k^3[\chi(k)]$ oscillation curves of Ni-FeS₂-0.5 before and after long-term OER tests. (i) Ni K-edge XAFS $k^3[\chi(k)]$ oscillation curves of Ni-FeS₂-0.5 after long-term OER tests together with Ni foil and Ni(OH)₂.

is required for Ni-FeS₂-0.25 to reach a current density (j) of 10 mA cm⁻², which also precedes the benchmark IrO₂/C, further proving the superiority of Ni-doped FeS₂ toward OER. Meanwhile, the reaction kinetics of the catalysts, which are reflected by their Tafel slopes, also follow the same trend. As depicted in Figure 6b, the Ni-FeS2-0.5 catalyst exhibits the lowest Tafel slope of about 34 mV dec⁻¹, rather close to that of NiFe LDH (32 mV dec⁻¹), by which Ni-FeS₂-0.25 (68 mV dec⁻¹), IrO_2/C (73 mV dec⁻¹), Pt/C (94 mV dec⁻¹), and FeS₂ (151 mV dec⁻¹) are followed. Distinct comparisons with regard to the overpotentials at 10 mA cm^{-2} and the corresponding Tafel slopes for all of the samples are illustrated in Figure 6c, which further indicates the overwhelming advantage for Ni-doped FeS2. To further improve the OER performance of Ni-FeS₂-0.5, we utilized a NF as the substrate to support Ni-FeS₂-0.5 and measured its activity toward the OER performance under different scan rates (Figure S12). As expected, the NF-supported Ni-FeS2-0.5 shows an enhanced OER catalytic activity, yielding a much lower overpotential of 230 mV and a negligible change in the performance at different scan rates, which might benefit from the metallic nature and 3D nanostructure of NF.^{64,65} In addition to these, the OER performance was also assessed by comparing the ECSAs through the tested electrochemical C_{dl} (Figure S13). As shown in Figure 6d, C_{dl} of Ni-FeS₂-0.5 (27.3 mF cm⁻²) is 5.3 times

larger than that of pure FeS_2 (5.2 mF cm⁻²), indicating more accessible catalytic sites and higher current densities. However, given the fact that Ni-FeS2-0.5 has the smallest specific surface area of 45 m² g⁻¹ compared with those of Ni-FeS₂-0.25 (49 m²) g^{-1}) and FeS₂ (76 m² g⁻¹) (Figure S14), it might make more sense to attribute the enhanced active sites to the role of Ni in the electronic structure modification of Fe insead of the contribution of the specific surface area. EIS (Figure 6e) unravels a remarkably favorable conductivity for post-OER Ni- FeS_2 -X (X = 0.25, 0.5) in contrast to the post-OER FeS_2 , indicating enhanced charge-transfer kinetics during the OER process. This further supports an effective optimization of the catalyst and also proves an inheritance of the conductivity from the optimal sulfide precursor. The durability and long-term stability of Ni-FeS2-0.5 toward OER were further tested to manifest its practical applications. As displayed in Figure S15, the polarization curve of Ni-FeS2-0.5 suffers a negligible difference after 2000 CV cycles in comparison with the original data, proving its good durability. The chronoamperometry curve (Figure 6f) at a constant *j* of 10 mA cm⁻² was observed with a slight decline at first and then a continuous increase, which probably results from the electrochemical selfreconstruction of the Ni-FeS2-0.5 catalyst during the OER conditions (more details will be discussed later). The SEM image (the inset in Figure 6f) for Ni-FeS₂-0.5 after the stability

Figure 8. (a) HER polarization curves of Ni-FeS₂-0.5, Ni-FeS₂-0.25, FeS₂, and Pt/C at 5 mV s⁻¹ in 1 M KOH. (b) Durability test of Ni-FeS₂-0.5 at an overpotential of 258 mV. (c) Polarization curves of a two-electrode alkaline electrolyzer using Ni-FeS₂-0.5 loaded onto NF as both the cathode and anode at a scan rate of 5 mV s⁻¹ in N₂-saturated 1.0 M KOH. Optical photograph presenting the generation of H₂ and O₂ bubbles during the overall water-splitting process. (d) Durability test of Ni-FeS₂-0.5 ||Ni-FeS₂-0.5 electrodes for water splitting at 1.57 V. (e) Comparison of the water-splitting performance of Ni-FeS₂-0.5 with other transition-metal-based bifunctional electrocatalysts. Data in the graph: 10% VNS/NF;¹⁸ Ni₁₅Fe_{0.5}P/CF;⁷⁶ Fe-CoP/Ti;⁷⁷ NiSe/NF;⁷⁸ NiCo₂O₄/NF;⁷⁹ CoP/GO-400;⁸⁰ Co_{0.85}Se@NC/NF.⁸¹

test shows the typical (oxy)hydroxide-like nanosheets, and this phenomenon preliminarily reveals self-reconstruction, which might be responsible for the activated process.^{39,66,67}

To gain deep insight into the origin for the remarkable OER activity of Ni-FeS₂-0.5, a series of ex situ measurements were conducted for analysis from aspects in the structure, component, and chemical state for Ni-FeS2-0.5 after the stability test. The XRD pattern of post-OER Ni-FeS2-0.5 indicates an obvious phase change after electrocatalysis (Figure S16), and the as-formed amorphous phase resulting from the in situ electrochemical transformation may be explained by disorder of the crystal structure. TEM images of Ni-FeS₂-0.5 after the stability test (Figure S17) further reveal that an in situ electrochemical topological transformation has happened, during which the yolk-shell structure is well-preserved. More interestingly, the outer single shell has transformed into a double-layer shell, and many in situ generated small nanosheets could also be distinguished from the shell, which may benefit the contact with electrolyte ions. ICP-AES tests were exploited to detect the change in the composition after a long-term OER test (Table S3). As listed in the chart, the atom

ratio of Fe-to-Ni remains nearly the same as the case before the OER process (Table S1), indicating a well-controlled compositional modulation. Considering that the Ni content cannot be neglected for the post-OER catalysts, we further prepared NiS₂ by a similar method and tested its OER performance (Figure S18,S19). As displayed in Figure S19, Ni-FeS₂-0.5 only requires an η of 250 mV to drive the *j* of 10 mA cm⁻², while NiS₂ needs an η of 283 mV. This further proves the effective modification of FeS₂ by Ni, which dramatically stimulates the activity of Fe toward the OER process. XPS techniques were further utilized to investigate the chemical composition and surface valence state in pristine and galvanostatic activation (GA)-treated Ni-FeS₂-0.5. Notably, the survey XPS survey spectrum shows that the S content on the surface of GA-treated Ni-FeS2-0.5 decreases distinctly while the O content increases to a dominant role, suggesting the generation of excessive O-containing species (Figure S20). High-resolution S 2p lines in Figure 7a also indicate that the signal intensity of the S element on the surface significantly decreases after the OER test but with the relatively increased peak intensity of S-O in the S 2p region.⁶⁸ In the highresolution Fe 2p spectra (Figure 7b), the signal from Fe–S almost disappears for Ni-FeS₂-0.5 after a long-term OER test,¹⁴ while the two peaks at 711.3 and 724.4 eV, which occupy the dominant content after the OER process, may be indexed to Fe $2p_{3/2}$ and $2p_{1/2}$ of FeOOH.^{22,69} Likewise, the Ni–S peaks after the OER test also could not be detected, and only peaks assigned to oxidized Ni species are recognized (Figure 7c). The results above demonstrate that Ni-FeS₂-0.5 on the surface is reconstructed and Fe, Ni, and S species have been oxidized to high-valence states, which might be responsible for the high OER activity.

To further identify the active form of the catalyst during the OER process, XAS measurements were performed. As presented in the Fe K-edge XANES spectra (Figure 7d), Ni-FeS₂-0.5 is oxidized with increased Fe valence after the OER test. Furthermore, in the FT-EXAFS spectra, the local structure around the Fe sites that previously feature Fe-S coordination has transformed into Fe-O coordination, indicating a distinct structural evolution (Figure 7e). Besides, the Fe k-space oscillation of post-OER Ni-FeS2-0.5 shows obvious differences from that of Fe_2O_3 but is more similar to that of FeOOH (Figure 7f), confirming that the Fe component in the Ni-FeS₂-0.5 catalyst has been in situ oxidized to FeOOH. This deduction is in accordance with the XPS results above (Figure 7a), and it has been further verified by Raman spectra. As shown in Figure S21, there are five peaks, located at around 243, 300, 398, 498, and 691 cm⁻¹, respectively, all of which show a slight shift compared with those of the literaturereported FeOOH.^{20,22,70,71} In addition, the characteristic bands ascribed to Ni-based vibration modes are not detected. This result suggests that the Ni atoms also exist in a doping form in the in situ formed FeOOH. In order to confirm the hypothesis above, ex situ Ni K-edge XAFS analyses were carried out to identify the oxidation states and local atomic structure of Ni in post-OER Ni-FeS₂-0.5 (Figure 7g-i). As indicated in Figure 7g, the Ni K-edge of Ni-FeS₂-0.5 undergoing the long-term OER test shifts to a higher energy close to the oxidation state 2+. Furthermore, the XANES profile of Ni-FeS₂-0.5 after the OER test well resembles to that of Ni(OH)₂, suggesting that the post-OER Ni-FeS₂-0.5 exhibits a structure similar to that of $Ni(OH)_2$.⁷² This result is further supported by the Ni *k*-space oscillations (Figure 7i). Notably, Ni-FeS₂-0.5 after the OER test and Ni(OH)₂ exhibit well-matched EXAFS oscillations, demonstrating that both of them share an analogous structure. FT-EXAFS analysis at the Ni K-edge also reveals that Ni-S bonds in GA-treated Ni-FeS₂-0.5 are destroyed and oxidized to Ni–O bonds (Figure 7h). Considering that the oxidation state of Ni after OER catalysis still remains in 2+ without a transition from $Ni(OH)_2$ to NiOOH, a rational explanation for this discrepancy might be that Ni is incorporated into the as-formed FeOOH host and stabilized in a lower oxidation state as previously reported.^{73,74} Thus, the actual active state during OER catalysis could be described as Ni²⁺Fe³⁺OOH. From the systematic postcharacterizations implemented above, we may draw the conclusion that the optimized Ni-doped FeS₂ spheres undergo a topotactic conversion during the electrochemical oxidation process and transform into hierarchical Ni-doped FeOOH spheres with the original frameworks and Fe/Ni molar ratio retained. Also, the hierarchical structure, yolk-shell-structured framework, and optimal metal composition of Ni-doped FeOOH are responsible for its remarkable OER performance. As for the occurrence of such a transformation, we consider that it is

possibly attributed to the following: (1) the precatalyst of FeS_2 is a metastable material,⁷⁵ which may easily experience selfreconstruction under the OER conditions; (2) the optimized Ni-doped FeS_2 yolk–shell spheres are endowed with superior conductivity, hydrophilicity (proven by the DFT calculations mentioned above), and many accessible active sites, which may accelerate complete conversion to amorphous Ni-FeOOH species;²³ (3) the loss of S may also facilitate the progress of reconstruction.

Another critical factor for water splitting, the HER activities of Ni-FeS₂-X, FeS₂, and Pt/C were also studied in N₂-saturated alkaline media (pH = 14). The results obtained from the LSV curves indicate that the incorporation of Ni in FeS₂ not only dramatically promotes the OER performance but also induces enhanced HER activities. As shown in Figure 8a, Ni-FeS₂-0.5 delivers a lower overpotential with 258 mV at 10 mA cm⁻² in contrast to bare FeS_2 (332 mV) but still larger than that of Pt/ C (30 mV). To further improve the HER performance, we utilized NF as a substrate to support Ni-FeS₂-0.5 and measured its activity toward HER. As shown in the LSV curves, Ni-FeS₂-0.5 on NF exhibits a much smaller overpotential of 164 mV compared with the one on the GC electrode (258 mV), which might benefit from the good conducitivity and 3D porous nanostructure of NF (Figure S22). The electrochemical stability of Ni-FeS2-0.5 for HER was also evaluated. Figure 8b demonstrates that Ni-FeS₂-0.5 could be retained at a j of 10 mA cm⁻² within 14 h, proving its excellent long-term durability for practical applications. In view of the excellent OER and HER performances of Ni-FeS₂-0.5, a water electrolyzer with a two-electrode configuration was assembled, in which the catalyst was loaded onto NF as both the anode and cathode. As depicted in Figure 8c, the Ni-FeS₂-0.5 couple is capable of delivering a water-splitting j of 10 mA cm⁻² at an applied potential of 1.55 V, which even surpasses the conventional noble-metal-based electrocatalysts (1.60 V for $Pt/C-IrO_2/C$). Meanwhile, the ever-bubbling H_2 and O_2 could be observed on both electrodes (the inset in Figure 8c). Furthermore, the stable i-t curve indicates that the electrolyzer exhibits negligible degradation in a period of 22 h, demonstrating its superior durability (Figure 8d). In addition, compared with the other transition-metal-based bifunctional electrocatalysts reported so far, Ni-FeS₂/NF also shows a better or comparable performance for water splitting (Figure 8e). These results suggest that the Ni-modified Fe-based catalyst with a remarkable performance toward the overall water splitting is promising for further applications.

4. CONCLUSIONS

In summary, we have demonstrated a novel approach to stimulating reactive Fe sites by integrating the electronic structure reconfiguration and in situ electrochemical topotactic transformation strategies so as to accelerate the sluggish OER kinetics at low overpotential. The obtained Ni-FeS₂-0.5 spheres can transform into nickel—iron oxyhydroxide via an in situ electrochemical reconstruction that could exhibit a remarkable OER performance with overpotentials of 250 and 326 mV to drive *j* values of 10 and 100 mA cm⁻², respectively, and a Tafel slope as small as 34 mV dec⁻¹. In addition, when used as a bifunctional catalyst for the overall water splitting, the Ni-FeS₂-0.5 sample also shows a better or comparable performance (1.55 V at j_{10}) in contrast to other transition-metal-based bifunctional electrocatalysts reported so far. The experimental results combined with the DFT calculations demonstrate that

the introduction of Ni not only could effectively modulate the electronic structure of FeS_2 with a semimetallic characteristic but also could promote its water adsorption ability, which offers the conditions for the entire reconstruction. Further characterizations on post-OER Ni-doped FeS₂ confirm that the catalyst experiences a reconstruction to evolve into hierarchical Ni-FeOOH yolk—shell spheres. These results would expand understanding of the Fe-based OER catalysts and provide guidance in the design of other highly active Fe-based catalysts for future energy applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01017.

Field-emission SEM images of the Ni-Fe-0.25 precursor, Fe precursor, Ni-FeS₂-0.25, and FeS₂, TEM images of the Ni-Fe-0.5 precursor, Ni-FeS2-0.25, and FeS2, N2 adsorption-desorption isotherms of Ni-FeS2-0.5, Ni-FeS₂-0.25, and FeS₂, XRD patterns of the Ni-Fe-0.5 precursor and Ni-FeS₂-1, FT-IR spectra of the asprepared Ni-Fe-0.5 precursor, EDS spectrum of Ni-FeS2-0.5, Fe K-edge k^3 -weighted EXAFS spectra, Ni K-edge XANES spectra and XAFS k^3 -weighted oscillation curves, OER polarization curves of NF and Ni-FeS2-0.5 on NF and of Ni-FeS₂-0.5 on NF at different scan rates, CV curves of Ni-FeS2-0.5, Ni-FeS2-0.25, and FeS2 at the different scan rates, XPS survey spectra of Ni-FeS₂-0.5 before and after OER tests, Raman spectrum and XRD pattern of Ni-FeS2-0.5 after OER tests, and HER polarization curves of NF and Ni-FeS₂-0.5 on NF in 1 M KOH (PDF)

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Notes

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