

Sulphur doping of nickel ferrite nanosheet array for enhanced water oxidation

Haijun Liu, Bin Dong

College of Chemistry and Chemical Engineering, State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao 266580, China.

Abstract. Industrial water electrolysis requires highly-active and ampere-current-bearing oxygen evolution reaction (OER) catalysts, but achieving such a large operating current density at low overpotentials in available OER catalysts still remains a grand challenge. Herein, we report a facile and conventional strategy to grow vertically non-metallic modified nickel ferrite nanosheets on Fe foam (S-NiFe₂O₄/IF) as large-current-density OER catalysts. The vertically aligned nanosheet arrays can offer large electrochemical surface area, and the spacing between nanoarrays can allow for effective electrolyte access to the active sites. The introduction of S enhanced the adsorption and dissociation to water and optimized the adsorption of OER intermediates. As a result, S-NiFe₂O₄/IF exhibits superior OER activity with an overpotential of 287 and 326 mV to achieve 100 and 500 mA cm⁻², respectively, and displays robust stability in alkaline media. In addition, the synthesis strategy developed here can be applied to other mixed transition metal oxides with similar self-supported earth-abundant nanoarrays for advanced electrocatalysis in energy-related reactions.

Keywords: Nickel ferrite, Sulphur doping, Nanosheet array, Water oxidation.

1. Introduction

Oxygen evolution reaction (OER) is the key to limit the efficiency of water electrolysis due to its slow kinetic process, and the development of efficient electrocatalysts is regarded as an effective way to overcome this bottleneck [1]. Currently, the research hotspots for high-efficiency electrolytic water catalysts focus on the noble metals and transition metal compounds. Precious metal OER catalysts, such as IrO₂, RuO₂, etc., are currently considered as the best materials for OER catalysts. However, they are expensive, scarce in resources, and not available for large-scale industrial applications [2]. Therefore, it is important to explore low-cost, high-activity non-precious metal catalysts to improve OER efficiency [3].

In recent years, transition metal oxides (TMOs), such as spinel, perovskite, and hydroxide have emerged as promising OER catalysts due to their rich intrinsic redox pairs, abundant reserves, and low-cost [4]. However, TMOs have inherent low electrical conductivity and limited active sites that still need to be addressed to further boost the catalytic activity. Various methods, such as fine inter-surface design [5], coupling with carbon materials [6], and doping with heteroatoms [7] have been used to improve the OER electrocatalytic performance of TMOs. Among these methods, heteroatoms doping is considered to be the most promising method to improve the electrocatalytic performance of TMOs. In addition, self-

supported nanoarrays can offer large electrochemical surface area, and the spacing between nanoarrays can allow for effective electrolyte access to the active sites [8]. Moreover, in situ growth of the nanoarray on a conducting substrate allows for rapid charge transfer between the current collector and the active site while preventing delamination of the active material [9].

Inspired by these criteria, we herein highlight the synthesis of sulfur-incorporated nickel ferrite nanosheets array built grown on IF (S-NiFe₂O₄/IF) via hydrothermal reaction. As a free-standing electrode, S-NiFe₂O₄/IF exhibits remarkable catalytic activity and durability for water oxidation in alkaline medium. Moreover, the facile synthetic approach proposed in this study can be easily extended as a general approach for producing other mixed metal oxides for various applications, such as supercapacitors, metal-air batteries, and photocatalysis.

2. Experimental Procedures

2.1 Materials Preparation

Chemicals: Iron foam (IF, 1.0 mm in thickness) was purchased from Kunshan Lvchuang Electrical Co Ltd. Nickel chloride hexahydrate (NiCl₂·6H₂O), thiourea (CH₄N₂S) and potassium hydroxide (KOH) were purchased from Sinopharm Chemical Reagent Co., Ltd.,

Shanghai, China. Deionized (DI) water was used in all experiments.

Preparation of S-NiFe₂O₄/IF: The solution was prepared by dissolving 0.1 mmol of NiCl₂·6H₂O into 60 mL of 0.4 M CH₄N₂S aqueous solution, then gentle stirring for 10 min to form a homogeneous solution. Then solution was transferred into a 100 mL Teflonlined stainless steel autoclave with a piece of IF (20 mm × 50 mm) and maintained at 160 °C for 2 h in an oven. After the autoclave cooled slowly to room temperature, the sample was taken out and washed with water and ethanol thoroughly, followed by vacuum drying.

Preparation of NiFe₂O₄/IF: For comparison, NiFe₂O₄/IF was also prepared by hydrothermal method. The NiFe₂O₄/IF was synthesized using a similar procedure to S-NiFe₂O₄/IF, except for the removal of CH₄N₂S during the hydrothermal treatment.

2.2 Physical Characterization

The crystalline structures of the samples were confirmed by powder X-ray diffraction (XRD) using a Philips X'Pert diffractometer with Cu K α radiation (λ = 0.15418 nm). The structures and morphologies were collected on a scanning electron microscope (Hitachi S-4800) and a high resolution transmission electron microscope (FEI Tecnai G2, 200 kV). The corresponding energy-dispersive spectroscopy (EDS) mapping analyses were performed on representative areas. X-ray photoelectron spectroscopy (XPS) were carried out on an Escalab 250Xi system.

2.3 Electrochemical measurements

OER tests were conducted in a three-electrode configuration with an electrochemical workstation (Gamry Reference 1000 Instrument) at room temperature. The obtained sample, platinum column and Hg/HgO (1.0 M KOH) electrode served as the working electrode, counter electrode and reference electrode, respectively. All of the electrochemical measurements were conducted in 1.0 M KOH solution for OER. The recorded potentials were converted to the potential versus reversible hydrogen electrode (RHE) according to the Nernst equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \times \text{pH} + 0.098$. Linear sweep voltammetry (LSV) measurements were performed with a scan rate of 5.0 mV·s⁻¹. The Tafel plots (log j vs η) were obtained from the corresponding LSV curves, according to the Tafel equation ($\eta = b \log j + a$, where η is the overpotential, j is the current density and b is the Tafel slope). The electrochemical active surface area of catalyst is estimated from electrochemical double-layer capacitance (C_{dl}), which is obtained by measuring double-layer charging from the CVs at different scan rates in non-Faradaic potential range in 1.0 M KOH. The plots then fit to linear regression and the slope is just the C_{dl}. Electrochemical impedance spectroscopy (EIS) measured in the frequency from 10⁵ Hz to 0.01 Hz. The durability of catalysts was obtained by conducting chronopotentiometry curve.

3. Results and Discussion

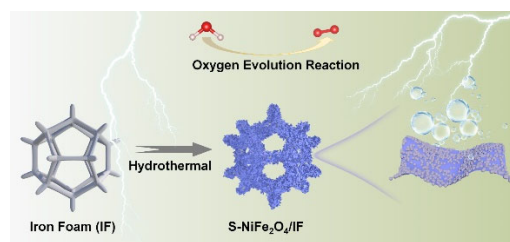


Figure 1: Schematic illustration of the preparation of S-NiFe₂O₄/IF.

Typically, self-supported S-NiFe₂O₄/IF nanosheet arrays on IF were prepared by a one-step synthesis, the hydrothermal reaction, as shown in Figure 1. IF was used as the substrate because it provides a large surface area and a high conductivity. The morphological, structural, and compositional features of the as-prepared S-NiFe₂O₄/IF were characterized. The structural information of the as-fabricated S-NiFe₂O₄/IF was studied by X-ray diffraction (XRD), as shown in the Figure 2a. The XRD pattern shows sharp diffraction peaks at 30.3°, 35.7°, 43.4°, 57.4°, and 63.0°, which can be ascribed to (220), (311), (400), (511) and (440) reflections from NiFe₂O₄ (JCPDS card no. 00-054-0964), respectively [10]. In addition, the diffraction peak located at 44.7° is attributed to the (110) plane of Fe (03-065-4899) from IF. Due to the low sulfur source utilization of the sulfur-containing material and the low hydrothermal reaction temperature, no additional peaks were observed [11]. Figure 2b displays the scanning electron microscopy (SEM) images of the IF. It can be seen that the surface of IF is smooth. SEM image of S-NiFe₂O₄/IF (Figure 2c, and Figure 3) exhibit full coverage of bare IF with the S-NiFe₂O₄ nanosheet composed with uniform separated nanoparticles. This type of catalytic arrangement is conducive to fast electron transfer kinetics, mainly due to its high surface exposure and sufficient interfacial contact. In order to examine the specific microstructure of S-NiFe₂O₄, transmission electron microscopy (TEM) observations were carried out. TEM image of S-NiFe₂O₄/IF product (Figure 2d) reveals that the S-NiFe₂O₄ NPs with size of $\approx$ 50 nm are uniformly loaded on the IF substrate without obvious aggregation. This construction of nanosheets composed of nanoparticles can increase the exposed active sites and thus improve the catalytic activity of OER. The high-resolution TEM (HRTEM) image (Figure 2e) exhibits the typical lattice fringes with distance of 0.147 nm and 0.251 nm, corresponded to the NiFe₂O₄ (440) and (311) crystal plane, respectively. The SAED pattern exhibits several light circles attributed to (440) and (311) planes of NiFe₂O₄ phase, demonstrating the well-crystalline structure (Figure 2f). The energy dispersive spectrum (EDS) mapping (Figure 2g) indicates the homogeneous distribution of Ni, Fe, O and S elements within the 2D nanosheets. In addition, the uniform distribution of S elements in the entire section demonstrates the successful doping of heteroatoms into NiFe₂O₄/IF.

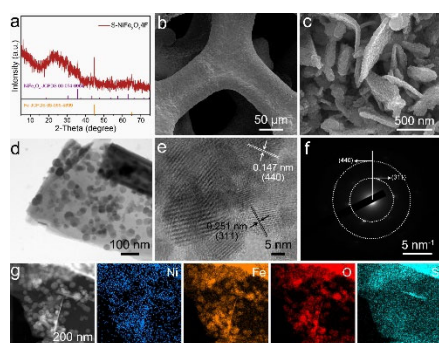


Figure 2: (a) XRD pattern of S-NiFe₂O₄/IF. (b) SEM image of IF. (c) SEM image of S-NiFe₂O₄/IF. (d) TEM image of S-NiFe₂O₄/IF. (e) HRTEM image of S-NiFe₂O₄/IF. (f) SAED image of S-NiFe₂O₄/IF. (g) HAADF-STEM-EDS mapping of S-NiFe₂O₄/IF.

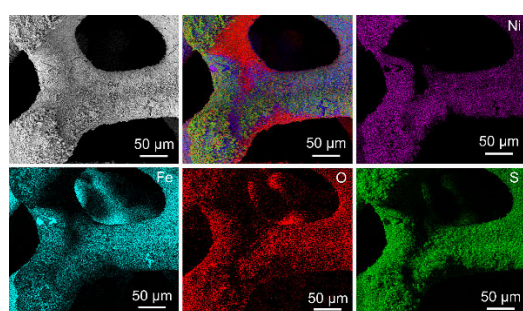


Figure 3: The SEM mapping of S-NiFe₂O₄/IF.

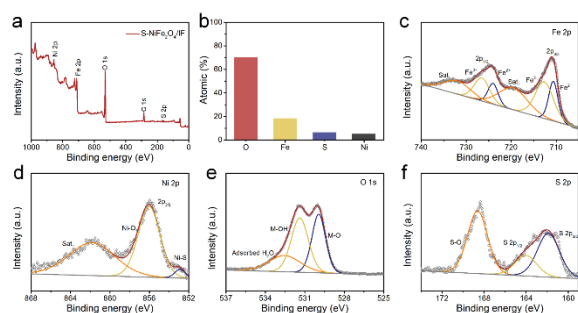


Figure 4: (a) XPS survey of S-NiFe₂O₄/IF. (b) The content of O, Fe, S and Ni elements. XPS spectra of S-NiFe₂O₄/IF in (c) Fe 2p region, (d) Ni 2p region, (e) O 1s region and (f) S 2p region.

To determine the surface chemical state and electronic structure, an X-ray photoelectron spectroscopy (XPS) survey was recorded. The resulting high-resolution spectra from the Fe 2p, Ni 2p, O 1s and S 2p core level regions are collected in Figure 4. According to the XPS spectra of S-NiFe₂O₄/IF, Ni, Fe, S, O elements are proved in S-NiFe₂O₄/IF (Figure 4a), agreeing with the EDX-mapping results. The content of O, Fe, S and Ni in the as-prepared S-NiFe₂O₄/IF determined by XPS (Figure 4b) were 70.3 %, 18.3 %, 6.4 %, and 5.0 %, respectively. In the Fe 2p high-resolution XPS spectrum of S-NiFe₂O₄/IF (Figure 4c), two spin-orbit doublets at binding energies at ca. 711.0 and 724.6 eV can be attributed to the Fe 2p_{3/2} and Fe 2p_{1/2}, respectively. One doublet of which at 710.6 and 724.0 eV was belonged to Fe²⁺ and another one

located at 712.6 and 726.5 eV was belonged to Fe³⁺. The other peaks at 719.5 and 732.0 eV were attributed to satellite peak for S-NiFe₂O₄/IF. Furthermore, the profile of the Ni 2p_{3/2} spectrum can be deconvoluted into three peaks, where the bonding energies at 852.9, 856.0 and 861.8 eV attributed to the characteristic of Ni-S, Ni-O species and shake-up satellites (denoted Sat.), respectively. As shown in Figure 4e, the O 1s spectrum is further fitted with four doublets, including M-O at 529.9 eV, M-OH at 531.4 eV, and adsorbed H₂O at 532.5 eV, respectively. A clear chemisorbed water signal appears, showing the excellent adsorption capacity of as-prepared catalyst for oxygen-containing intermediates. Figure 4f shows S 2p high-resolution spectra of S-NiFe₂O₄. The peak at the binding energy of 164.0 eV and 161.9 eV in S-NiFe₂O₄ is owing to the S 2p_{1/2} and S 2p_{3/2}, respectively. The other peaks of S 2p at the higher binding energy (~168.6 eV) are recognized as the oxidized S species (S-O). All the above results demonstrate the successful introduction of S atoms into NiFe₂O₄ crystal on the surface of the IF.

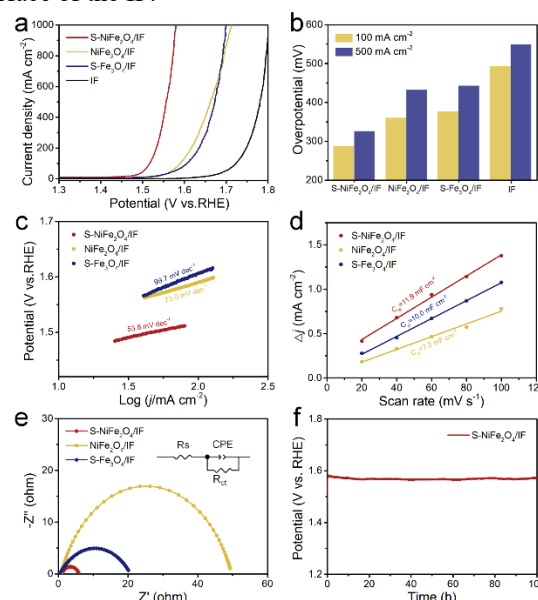


Figure 5: OER electrochemical properties of S-NiFe₂O₄/IF and other contrast samples in 1.0 M KOH. (a) Polarization curves; (b) overpotentials under 100 and 500 mA cm⁻²; (c) Tafel plots; (d) the double layer capacitances (C_{dl}) for estimating electrochemical specific area (ECSA); (e) Nyquist plots; (f) the Chronoamperometry curve of S-NiFe₂O₄/IF for 100 h.

The electrocatalytic performance of S-NiFe₂O₄/IF catalyst for OER was evaluated on a conventional three-electrode system under alkaline pH conditions of 1.0 M KOH. The S-NiFe₂O₄/IF electrode requires the lowest overpotential (≈ 287 mV) to reach 100 mA cm⁻² compared to the other electrodes (Figure 5a,b). OER is related to electrochemical kinetics: The smaller the slope of the Tafel plot, the faster the reaction rate. The Tafel slopes of S-NiFe₂O₄/IF, NiFe₂O₄/IF and S-Fe₃O₄ were 53.8 mV dec⁻¹, 73.0 mV dec⁻¹, and 99.7 mV dec⁻¹, respectively, indicating the fastest OER rates of S-NiFe₂O₄/IF electrode (Figure 5c). We further evaluated the ECSA of as-prepared catalysts to understand the

intrinsic surface-area activity, which is proportional to the C_{dl} . S-NiFe₂O₄/IF possess a C_{dl} value of 11.9 mF cm⁻², which is larger than that for NiFe₂O₄/IF (7.2 mF cm⁻²) and S-Fe₃O₄ (10.0 mF cm⁻²) (Figure 5d). This shows that the sulfidation process can increase the ECSA value, and sulfidation process is beneficial to further increase the number of exposed active sites. EIS at a constant overpotential of 0.55 V (Hg/HgO) was further applied to probe the electrode kinetics under the OER process. As shown in Figure 4e, the Nyquist plots in the high-frequency range present standard semicircles, whose diameters are determined by the charge-transfer resistance (R_{ct}). The R_{ct} of S-NiFe₂O₄/IF is about 5.7 Ω , which is much smaller than those of NiFe₂O₄/IF ($\approx$ 49.2 Ω) and S-Fe₃O₄ ($\approx$ 20.0 Ω) (Figure 5e), suggesting a rapid charge transfer rate in the S-NiFe₂O₄/IF catalyst. OER electrochemical stability is another critical factor in evaluating catalysts' performance [12]. Fig. 3e shows the long-term OER process stability test was carried out for 100 h at a fixed current density of 100 mA cm⁻² (Figure 5f), and there was no evident voltage increase. In conclusion, the S-NiFe₂O₄/IF catalyst has excellent OER stability in 1.0 M KOH.

4. Conclusion

In conclusion, a facile and reliable strategy was proposed and successfully demonstrated to synthesize S-NiFe₂O₄/IF via hydrothermal method. Benefitting from the rationally designed 3D hierarchical structure and optimized composition with good electrical conductivity, the as-synthesized S-NiFe₂O₄/IF has demonstrated a low overpotential of 287 mV at 100 mA cm⁻², a small Tafel slope of 53.8 mV dec⁻¹, and long-term stability over 200 h in alkaline OER process. The cost-effective Fe-based catalyst materials and low-cost facile preparation for mass production enable its potential application in practical water splitting.

Acknowledgements

This work is financially supported by National Natural Science Foundation of China (52174283 and 52274308).

References

1. Y. Sun, J. Wu, Y. Xie, et al. Dynamics of both active phase and catalysis pathway for spinel water-oxidation catalysts, *Advanced Functional Materials*, vol. 32 (2022), 2207116.
2. C. Kou, J. Zhou, H. Wang, et al. Boron pretreatment promotes phosphorization of FeNi catalysts for oxygen evolution, *Applied Catalysis B: Environmental*, vol. 330 (2023), 122598.
3. Y. Yan, K. Huang, J. Lin, et al. Charge redistribution in FeOOH nanoarray by ecological oxygen-reduction deposition for boosting electrocatalytic water oxidation, *Applied Catalysis B: Environmental* vol. 330 (2023), 122595.
4. J. Liu, M. Zheng, J. Li, et al. Lithiation-induced defect engineering to promote oxygen evolution reaction, *Advanced Functional Materials*, vol. 33 (2023), 2209753.
5. C. Wang, H. Lu, Z. Mao, et al. Bimetal schottky heterojunction boosting energy-saving hydrogen production from alkaline water via urea electrocatalysis, *Advanced Functional Materials*, vol. 30 (2020), 2000556.
6. L. Yan, Y. Xu, P. Chen, et al. A freestanding 3D heterostructure film stitched by MOF-derived carbon nanotube microsphere superstructure and reduced graphene oxide sheets: a superior multifunctional electrode for overall water splitting and Zn-air batteries, *Advanced Material*, vol. (2020), 2003313.
7. L. Yu, L. Wu, B. McElhenny, et al. Ultrafast room-temperature synthesis of porous S-doped Ni/Fe (oxy)hydroxide electrodes for oxygen evolution catalysis in seawater splitting, *Energy & Environmental Science*, vol. 13 (2020), 3439.
8. J. Liu, D. Zhu, Y. Zheng, et al. Self-supported earth-abundant nanoarrays as efficient and robust electrocatalysts for energy-related reactions, *ACS Catalysis*, vol. 8 (2018), 6707–6732.
9. T. Ma, S. Dai, S. Qiao, Self-supported electrocatalysts for advanced energy conversion processes, *Materials Today*, 19 (2016), 265-273.
10. Z. L. Cao, Z. Li, K. Su, et al. Rational design of hollow oxygen deficiency-enriched NiFe₂O₄@N/rGO as bifunctional electrocatalysts for overall water splitting, *Journal of Energy Chemistry*, vol. 54 (2021), 595–603.
11. H. Liu, R. Luan, L. Li, et al. Sulphur-dopant induced breaking of the scaling relation on low-valence Ni sites in nickel ferrite nanocones for water oxidation with industrial-level current density, *Chemical Engineering Journal*, vol. 461 (2023), 141714.
12. J. Chi, X. Zeng, X. Shang, Embedding RhPx in N, P co-doped carbon nanoshells through synergetic phosphorization and pyrolysis for efficient hydrogen evolution, *Advanced Functional Materials*, vol. 29 (2019), 1901790.