Sulphur doping of nickel ferrite nanosheet array for enhanced water oxidation

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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, heteroatom 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 transition 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 (CH2N2S) and potassium hydroxide (KOH) were purchased from Sinopharm Chemical Reagent Co., Ltd.,

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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 CH3N2S 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 CH3N2S 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 Kα 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 (η = 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 (Cdl), 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 Cdl. 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.](https://doi.org/10.1051/matecconf/202338201022)

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 ≈ 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.
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 2p3/2 and Fe 2p1/2, 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 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 2p1/2 and S 2p3/2, 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.

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
intrinsically surface-area activity, which is proportional to the C_{dl}. S-NiFe_{2}O_{4}/IF possess a C_{dl} value of 11.9 mF cm\(^{-2}\), which is larger than that for NiFe_{2}O_{4}/IF (7.2 mF cm\(^{-2}\)) and S-Fe_{3}O_{4} (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-NiFe_{2}O_{4}/IF is about 5.7 \(\Omega\), which is much smaller than those of NiFe_{2}O_{4}/IF (\approx 49.2 \Omega) and S-Fe_{3}O_{4} (\approx 20.0 \Omega) (Figure 5e), suggesting a rapid charge transfer rate in the S-NiFe_{2}O_{4}/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-NiFe_{2}O_{4}/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-NiFe_{2}O_{4}/IF via hydrothermal method. Benefitting from the rationally designed 3D hierarchical structure and optimized composition with good electrical conductivity, the as-synthesized S-NiFe_{2}O_{4}/IF has demonstrated a low overpotential of 287 mV at 100 mA cm\(^{-2}\) (Figure 5f), and there was no evident voltage increase. In conclusion, the S-NiFe_{2}O_{4}/IF catalyst has excellent OER stability in 1.0 M KOH.

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References


