Hierarchical Porous Ni₃S₄ with Enriched High-Valence Ni Sites as a Robust Electrocatalyst for Efficient Oxygen Evolution Reaction

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Electrochemical water splitting is a common way to produce hydrogen gas, but the sluggish kinetics of the oxygen evolution reaction (OER) significantly limits the overall energy conversion efficiency of water splitting. In this work, a highly active and stable, meso–macro hierarchical porous Ni₃S₄ architecture, enriched in Ni³⁺ is designed as an advanced electrocatalyst for OER. The obtained Ni₃S₄ architectures exhibit a relatively low overpotential of 257 mV at 10 mA cm⁻² and 300 mV at 50 mA cm⁻². Additionally, this Ni₃S₄ catalyst has excellent long-term stability (no degradation after 300 h at 50 mA cm⁻²). The outstanding OER performance is due to the high concentration of Ni³⁺ and the meso–macro hierarchical porous structure. The presence of Ni³⁺ enhances the chemisorption of OH⁻, which facilitates electron transfer to the surface during OER. The hierarchical porosity increases the number of exposed active sites, and facilitates mass transport. A water-splitting electrolyzer using the prepared Ni₃S₄ as the anode catalyst and Pt/C as the cathode catalyst achieves a low cell voltage of 1.51 V at 10 mA cm⁻². Therefore, this work provides a new strategy for the rational design of highly active OER electrocatalysts with high valence Ni³⁺ and hierarchical porous architectures.

1. Introduction

Hydrogen is an environmentally friendly and renewable energy carrier for green energy supply and storage.[1–3] Electrochemical water splitting is one way to produce hydrogen.[4,5] It involves two half-reactions, the hydrogen evolution reaction (HER), and the oxygen evolution reaction (OER) to produce hydrogen and oxygen, respectively.[6,7] However, the OER has sluggish kinetics because it is a four-electron transfer process resulting in a high overpotential, which limits the overall energy conversion efficiency of electrochemical water splitting.[8] Currently, IrO₂ and RuO₂ are considered as the best OER catalysts.[9–11] Nevertheless, the scarcity and high cost of Ir and Ru hamper their applications.[7,12,13] Hence, it is highly desirable to develop low cost and earth abundant electrocatalysts with high activity and long-term stability for the OER.

In the past years, substantial efforts have been devoted to exploring transition metal (Fe, Co, Ni)-based oxides, and hydroxides as noble-metal-alternative electrocatalysts for OER due to their abundance, low-cost, and high catalytic activity.[14–18] However, their electrochemical application is hindered by some severe obstacles: (1) low content of high valence state metal ions. The high valence state metal ions such as Co³⁺ and Ni³⁺ have been...
confirmed as the active sites for OER,[19–23] while most of the work is focused on Co²⁺ and Ni²⁺ based materials.[7,14,15] (2) Low utilization efficiency of active sites due to the low specific surface area. (3) Relatively low electrical conductivity of the transition metal-based oxides and hydroxides. In order to solve these issues, various nanostructured nickel sulfide-based materials, such as films of NiS microspheres,[24] Ni3S4 nanosheet arrays,[25] Ni3S4 nanosheets,[26] porous Ni3S4,[27] and hierarchical NiCo2S4 nanowires,[28] have been developed to achieve high electrocatalytic performance due to their diverse valence states, high specific surface area, and high electrical conductivity. For instance, Qiao and co-workers fabricated a Ni9S8/Ni foam electrode for OER which had an overpotential (η) of 340 mV at 30 mA cm⁻² with a catalyst loading of 11 mg cm⁻².[27] Wang and co-workers reported a NiS/Ni foam catalyst with an overpotential of 335 mV at 50 mA cm⁻² using a catalyst loading of 43 mg cm⁻².[24] When Ni3S4 (Ni²⁺, Ni³⁺) was used as an electrocatalyst, the current density reached 30 mA cm⁻² at η = 330 mV with a relatively low catalyst loading of 1.2 mg cm⁻².[26] Shanmugam and co-workers developed Ni3S2/Ni foam and NiCo2S4/Ni foam electrodes for OER. The NiCo2S4/Ni foam (η = 260 mV at 10 mA cm⁻², current density loss of 15% after 50 h) showed enhanced electrocatalytic activity and long-term stability compared to Ni3S4/Ni (η = 300 mV at 10 mA cm⁻², current density loss of 20% after 10 h).[28] Despite the significant progress, the electrocatalytic activities and long-term stability of the most developed nickel sulfides are not yet satisfactory. To this end, the development of alternative electrocatalysts with excellent electrocatalytic performance and durability for OER is highly challenging and intensively pursued.

In this work, meso–macro hierarchical porous Ni3S4 architectures enriched in Ni³⁺ species derived from Ni metal–organic framework (Ni-MOF) is developed as efficient OER electrocatalysts. MOFs with tunable structures and chemical compositions are interesting self-sacrificial templates for the synthesis of nickel sulfides. The as-prepared Ni3S4 architectures enriched in Ni³⁺ enhance the chemisorption of OH⁻, which facilitates the electron transfer. In addition, the obtained meso–macro porous structure increases the number of active sites and facilitates mass transport. Due to the enhanced chemisorption
of OH−, the high number of active sites, and the easy mass transport, the Ni3S4 architectures exhibit a remarkable OER performance. The Ni3S4 catalyst on Ni foam (NM50-Ni3S4/NF) electrode shows a relatively low overpotential of 257 mV at 10 mA cm−2, and 300 mV at 50 mA cm−2. The NM50-Ni3S4/NF electrode exhibits not only outstanding electrocatalytic activity but also excellent long-term stability even at a high current density (no degradation after 300 h at 50 mA cm−2). Furthermore, a water-splitting electrolyzer using NM50-Ni3S4/NF as the anode catalyst and Pt/C as the cathode catalyst achieves a low cell voltage of 1.51 V at 10 mA cm−2.

2. Results and Discussion

The Ni3S4 catalysts were synthesized as illustrated in Figure 1a. First, the Ni-MOFs were prepared by dissolving Ni salt and organic linkers in N,N-dimethylformamide (DMF) by a solvothermal method.[29,30] Scanning electron microscopy (SEM) images reveal that the Ni-MOFs consist of large round plates with an average diameter of around 100 µm and an average thickness of around 6 µm (Figure 1b,c; Figure S1, Supporting Information). Disk-like particles with a larger thickness could be obtained by increasing the growth temperature (Figure S1, Supporting Information).[31,32] X-ray diffraction (XRD) patterns of the obtained MOFs exhibit the same diffraction peaks as the theoretical pattern (Figure 1d),[29] indicating the successful synthesis of Ni-MOFs. Next, the Ni-MOFs underwent a solvothermal process to obtain Ni3S4. The as-synthesized NM50-Ni3S4 shows a large nanoflake structure resembling the Ni-MOF template (Figure 1e). Electron energy loss spectroscopy (EELS) spectra (Figure 1f) confirm that nickel sulfide was obtained by this solvothermal method with a uniform distribution of Ni and S. High-resolution transmission electron microscopy (HRTEM) images (Figure 1g) indicate that the nickel sulfide has good crystallinity. The lattice fringe distances were measured to be 0.536, 0.493, 0.551, and 0.242 nm, respectively, which are reminiscent of the cubic Ni3S4 phase (Table S1, Supporting Information). The magnified detail of the area highlighted in yellow and its corresponding power spectrum reveal that the structure of the selected region is in agreement with the cubic phase of Ni3S4 (space group: Fd3mS with a = b = c = 0.94570 nm).

XRD was employed to characterize the obtained nickel sulfide (Figure 2a; Figure S2, Supporting Information). The typical diffraction pattern of polydymite was observed. The diffraction peaks at 2θ of 26.6°, 31.2°, 37.9°, 47.0°, 49.9°, and 54.7° correspond to the (220), (311), (400), (422), (511), and (440) planes of cubic Ni3S4 (JCPDS: 00-047-1739), respectively.[33] The Ni3S4 sample derived from NM120 precursor shows an additional peak at ≈30°, which may be due to the incomplete sulfurization caused by its larger thickness (≈75 µm). Raman spectra (Figure 2b) reveal that the vibrational bands at 224, 286, 337, and 379 cm−1 in the low wavenumber region are attributed to Ni3S4.[34,35] confirming
that these samples are Ni$_3$S$_4$. Nitrogen adsorption/desorption isotherm and pore size distribution plots were used to investigate the porous structure of Ni$_3$S$_4$ catalysts (Figure 2c,d). The typical type-IV isotherms at a relative pressure of $\approx 0.5$–1.0 with an H3 hysteresis loop indicate a hierarchical porous structure and a broad pore-size distribution.[36–38] The specific surface areas of the obtained nickel sulfides are 34, 23, and 14 m$^2$ g$^{-1}$ for NM50-Ni$_3$S$_4$, NM80-Ni$_3$S$_4$, and NM120-Ni$_3$S$_4$, respectively.

X-ray photoelectron spectroscopy (XPS) was employed to investigate the elemental composition and chemical state of the surface of these Ni$_3$S$_4$ samples (Figure 3; Figure S4, and Tables S2–S4, Supporting Information). XPS detected C, N, O, S, and Ni. The C, N, and O come from the residue of the Ni-MOFs linkers. The rather high oxygen content in the samples might originate from the surface oxidation of Ni$_3$S$_4$.[39] The Ni 2p spectrum of NM50-Ni$_3$S$_4$ was deconvoluted into eight peaks, which were assigned to the Ni 2p $^{3/2}$, Ni 2p $^{1/2}$, and satellite peaks (Figure 3b). For the Ni 2p $^{1/2}$, the binding energies at 852.99, 852.93, 852.64, 852.64, and 852.80 eV and 856.57, 586.50, 855.59, 855.88, and 856.03 eV were assigned to Ni$^{2+}$ and Ni$^{3+}$, respectively.[40,41] The peaks at 860.35 $\pm$ 0.2 and 863.35 $\pm$ 0.2 eV were assigned to the satellite peaks (referred as “Sat.” in the figure), which indicate the presence of nickel–oxygen species.[42–44] The peak area of the Ni$^{3+}$ 2p was much larger than that of Ni$^{2+}$ 2p, demonstrating the much higher content of Ni$^{3+}$. Figure 3c summarizes the content of Ni$^{2+}$ and Ni$^{3+}$ in these samples, of which the Ni$^{3+}$ content is ten times higher than that of Ni$^{2+}$. The NM50-Ni$_3$S$_4$ exhibits the highest Ni content, as well as the highest Ni$^{3+}$ content. Ni$^{3+}$ improves the electrophilicity of adsorbed oxygen and therefore benefits the formation of NiOOH through nucleophilic attack during OER and is generally regarded as the active site for OER.[21,23] For the S 2p spectrum, the peaks at 161.3, 162.6, and 164.3 eV were attributed to the S 2p$^{3/2}$ of S$^{2-}$, S 2p$^{1/2}$ of S$^{2-}$, and the bridging S$^{2-}$ (referred to as “SO$_4^{2-}$”), respectively (Figure 3d).[39,45,46]

The electrocatalytic activity of the Ni$_3$S$_4$ catalysts for OER was investigated in 1.0 m KOH on a glassy carbon electrode (Figure 4; Figure S5, Supporting Information). The peaks at 1.38 and 1.28 V versus reference hydrogen electrode (RHE) refer to the redox reaction of Ni$^{2+}$ to Ni$^{3+}$ that goes forward and backward, respectively.[47–49] When scanning to more positive potentials than 1.5 V versus RHE, the current density rapidly increases due to oxygen evolution. The overpotential ($\eta$) at a current density of 10 mA cm$^{-2}$ was employed to evaluate the electrocatalytic activity of OER.[50] It is seen that all Ni$_3$S$_4$ catalysts show a lower overpotential than IrO$_2$ at a current density of 10 mA cm$^{-2}$ (Figure 4b). The NM50-Ni$_3$S$_4$ shows an overpotential of 0.307 V at a current density of 10 mA cm$^{-2}$ with a Tafel slope of 67 mV dec$^{-1}$ (Figure 4c).
A Tafel slope between 40 and 120 mV dec\(^{-1}\) indicates that the OER on NM50-Ni\(_3\)S\(_4\) may be controlled by the chemisorption of OH\(^-\) and the formation of *-O\(^-\) of the Krasil'shcikov path (Supporting Information).\(^{[51–53]}\) The charge transfer resistance \(R_{ct}\) of the Ni\(_3\)S\(_4\) catalysts for the OER was evaluated by electrochemical impedance spectroscopy (Figure S6, Supporting Information) at an applied potential of 1.61 V versus RHE. It can be seen that the NM50-Ni\(_3\)S\(_4\) sample shows the smallest charge transfer resistance (19 \(\Omega\)), resulting in the highest current density at high overpotential. The Faradaic efficiency of NM50-Ni\(_3\)S\(_4\) for the OER was found to be around 99%, indicating that nearly all of the current was used for the evolution of oxygen (Figure S7, Supporting Information).

The NM50-Ni\(_3\)S\(_4\) catalyst was coated on a Ni foam electrode (NM50-Ni\(_3\)S\(_4\)/NF) and tested for OER (Figure 4d; Figures S8 and S9, Supporting Information). The contribution of the Ni foam to the OER can be ignored (Figure 4d). The NM50-Ni\(_3\)S\(_4\)/NF electrode shows much higher OER performance than IrO\(_2\) and Ni foam. The NM50-Ni\(_3\)S\(_4\)/NF electrode reached a current density of 10, 50, and 100 mA cm\(^{-2}\) at an overpotential of 0.257, 0.300, and 0.340 V, respectively, making it one of the best nickel sulfide OER catalysts reported in literature (Table S5, Supporting Information). The NM50-Ni\(_3\)S\(_4\)/NF electrode shows excellent long-term stability at 50 mA cm\(^{-2}\), while the overpotential of IrO\(_2\) for OER rapidly increased by 73 mV after 4000 s (Figure 4e).

To gain further insights into the electrocatalytic OER activity of the Ni\(_3\)S\(_4\), density functional theory (DFT) was employed to calculate the chemisorption free energies of OH\(^-\) on the surface of Ni\(_3\)S\(_4\) (Figure 5). There are two kinds of coordinated Ni ions in the crystal structure of Ni\(_3\)S\(_4\), viz., the tetracoordinated Ni\(_4\) (a Ni atom coordinated with four S atoms, Ni\(^{2+}\)) and hexacoordinated Ni\(_6\) (a Ni atom coordinated with six S atoms, Ni\(^{3+}\)) (Figure 5a,b). The (110) plane of Ni\(_3\)S\(_4\) was selected to calculate the chemisorption free energies of OH\(^-\), due to the fact that this plane contains both kinds of Ni sites simultaneously. The hexacoordinated Ni\(_6\) exhibits an OH\(^-\) chemisorption free energy of 0.16 eV, which is much lower than 1.01 eV for that of the tetracoordinated Ni\(_4\), revealing the strong chemisorption capacity of hexacoordinated Ni\(_6\) (Figure 5b). The electron will be transferred from the adsorbed OH\(^-\) to the surface Ni sites during the OER process. The calculations show that the OH\(^-\) adsorbed on the hexacoordinated Ni\(_6\) exhibits a more positive charge density (red area around OH\(^-\)) than that of tetracoordinated Ni\(_4\), facilitating the electron transfer to the Ni surface sites. The O–H bond adsorbed on the hexacoordinated Ni\(_6\) shows an enhanced activation thus yielding a shorter Ni–O band distance (1.827 Å) and a longer O–H band (0.983 Å) (Figure 5c,d).

Therefore, the outstanding OER performance of the Ni\(_3\)S\(_4\) electrocatalyst is attributed to the following. First, the Ni\(^{3+}\) is beneficial for the chemisorption of OH\(^-\) on the surface of Ni\(_3\)S\(_4\), which facilitates the electron transfer from the OH\(^-\) to the...
surface Ni sites during OER. Second, the hierarchical porous structure provides more active sites per projected surface area and meanwhile enables faster mass transfer.

### 3. Conclusions
A hierarchical porous Ni\textsuperscript{3+}-rich Ni\textsubscript{3}S\textsubscript{4} material was synthesized and tested as an OER electrocatalyst. The Ni\textsubscript{3}S\textsubscript{4} architecture exhibits high electrocatalytic activity for OER (with an overpotential of 257 mV at 10 mA cm\textsuperscript{−2} and 300 mV at 50 mA cm\textsuperscript{−2}) and excellent long-term stability (no degradation after 300 h at 50 mA cm\textsuperscript{−2}). The outstanding OER performance is attributed to the high concentration of Ni\textsuperscript{3+} on the surface which favors the adsorption of OH\textsuperscript{−}, and the increased number of active sites and the fast mass transport originating from the hierarchical porous architectures. This work thus provides a strategy for the design of highly active OER electrocatalysts with enriched Ni\textsuperscript{3+} sites and hierarchical porous architectures, which can be extended to other transition metal sulfides for various applications not limited to OER.

### 4. Experimental Section
**Materials Preparation: Preparation of Ni-MOF:** The Ni\textsubscript{(HBTC)} (4,4′-bipy)-3DMF metal–organic framework was synthesized by a mild solvothermal method modified from previous work\textsuperscript{[29,30]}.

Typically, 8.73 g Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (99% purity, Acros Organics), 2.11 g trimesic acid (H\textsubscript{3}BTC, 98% purity, ABCR Germany), and 1.92 g 4,4-dipyridyl (98% purity, Acros Organics) were dissolved in 200 mL DMF (≥99%, Chem-Lab). This mixture was heated at 50, 80, and 120 °C for 72 h, respectively. The final light green products were washed with DMF and ethanol (EtOH, 99.9% purity, VWR France) and dried in air at 60 °C overnight. The Ni-MOFs synthesized at 50, 80, and 120 °C were denoted as NM50, NM80, and NM120, respectively.

**Preparation of Ni\textsubscript{3}S\textsubscript{4} Catalysts:** The Ni-MOFs were converted into Ni\textsubscript{3}S\textsubscript{4} through a solvothermal method in EtOH at 150 °C for 12 h using sodium sulfide (Na\textsubscript{2}S·9H\textsubscript{2}O, >98%, Acros Organics) as a sulfur source. The molar ratio of the Ni-MOFs to Na\textsubscript{2}S·9H\textsubscript{2}O was 1:8. After reaction, the obtained suspension was centrifuged and the solids were washed with EtOH and deionized water, and dried in air at 60 °C overnight. The resulting black powders were denoted as NM50-Ni\textsubscript{3}S\textsubscript{4}, NM80-Ni\textsubscript{3}S\textsubscript{4}, and NM120-Ni\textsubscript{3}S\textsubscript{4}, respectively.

**Physicochemical Characterizations:** XRD patterns were recorded on a Bruker AXS D8 diffractometer using Cu K\textalpha (λ = 0.15405 nm) and Ni filter with 2θ ranging from 5° to 80° with a step size of 0.02° (1.0 s per step) at 40 kV. XPS was performed with a PHI quantum-2000 (monochromatic Al K\textalpha with 1486.6 eV operating at 15 kV and 300 W). The morphologies and microstructures were observed on an FEI Tecnai F20 field emission gun microscope operated at 200 kV with a point-to-point resolution of 0.19 nm. The pore structures of samples were probed by nitrogen adsorption/desorption isotherms at 77 K (Micromeritics ASAP 2020, US). Prior to the measurements, the
samples were outgassed at 100°C for 12 h. The specific surface area was determined by the Brunauer–Emmett–Teller model, while the pore size and volume were calculated by the DFT method of the built-in software.

**Electrochemical Measurements:** All the electrochemical properties were characterized using an Autolab electrochemical workstation at room temperature (25°C). A three-electrode system with a graphite plate (1 cm × 5 cm) as the counter electrode and a Hg/HgO electrode (Tianjin Aida Hengsheng Technology Co. Ltd., China) as the reference electrode was used. The obtained Ni₃S₄ catalysts coated on a glassy carbon disk (5.0 mm in diameter, Pt/INE) or Ni foam (Suzhou Taili Material Technology Co., Ltd., China) was employed as the working electrode. The OER polarization curve of IrO₂ (P40V020, particles from Premetec Co.) was recorded for comparison. To evaluate the electrocatalytic activity of the OER, the cyclic voltammograms were recorded at 10 mV s⁻¹ in the potential range between 0.98 and 1.73 V versus RHE on a rotating disk electrode at a rotating speed of 1600 rpm in oxygen-saturated 1.0 M KOH solution. The long-term stability was carried out with an NM50-Ni₃S₄/NF electrode (NM50-Ni₃S₄ coated on Ni foam) by chronoamperometry at 50 mA cm⁻² from the anode in a water-splitting electrolyzer using Pt/C on Ni foam as the cathode, operating at 20 mA cm⁻². The EIS measurements were recorded in a frequency range from 100 kHz to 0.1 Hz with an amplitude of 5 mV (peak-to-peak) at an applied potential of 1.61 V versus RHE.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

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