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A novel FeS-NiS hybrid nanoarray: an efficient and durable electrocatalyst for alkaline water oxidation[†]

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It is highly important to develop cost-efficient electrocatalysts for the oxygen evolution reaction (OER). In this communication, we report a novel FeS-NiS hybrid nanosheet array on Ti mesh as a highly efficient non-noble-metal electrocatalyst for OER. This catalyst requires an overpotential of 260 mV to afford a current density of 10 mA cm⁻² in 1.0 M KOH, 100 and 110 mV less than those required for FeS and NiS, respectively. In addition, this catalyst shows good durability, with maintenance of its catalytic activity for at least 25 h.

With the exhaustion of fossil fuels, the accompanying environmental pollution is becoming increasingly serious.¹⁻⁴ Therefore, it is crucial to explore clean energy sources to achieve sustainable development.⁵ Hydrogen, a renewable and clean energy source, is regarded as an appealing alternative to traditional non-renewable fossil fuels.^{6,7} Electrochemical water splitting offers a promising approach to produce pure hydrogen; however, efficient electrocatalysts are required to facilitate the reaction rate of the oxygen evolution reaction (OER) process.⁸ Ru and Ir oxides are known to be the best OER electrocatalysts, but their scarcity and high price hinder their widespread application.⁹⁻¹¹ Consequently, it is highly desirable to develop earth-abundant high-performance electrocatalysts for OER.¹²⁻¹⁴

Over the last few years, inexpensive transition metal-based materials, such as transition metal sulfides,¹⁵ oxides,¹⁶ phosphides¹⁷ and layered double hydroxides (LDH),¹⁸ have been widely studied as electrocatalysts for OER.^{12,19–23} Among these materials, transition metal sulfides have emerged as an important class of compounds with high conductivity and facile fabrication processes, these characteristics are conducive

to the design of efficient electrocatalysts.^{22,24} Ni is a common and earth-abundant metal element; NiS has been reported as an efficient OER catalyst due to its high activity in alkaline media.^{25,26} Fe is also regarded as a promising transition metal element for designing OER electrocatalysts due to its costefficient catalytic power for OER.¹¹ In addition, it has been reported that combining different metal compounds can enhance their catalytic performance by virtue of synergistic effects.²⁷ Thus, we anticipate that the OER activity of NiS can be greatly enhanced by constructing a NiS-FeS hybrid structure, which, however, has not been reported.

In this communication, a novel FeS–NiS hybrid nanosheet array supported on Ti mesh (FeS–NiS/TM) was developed. FeS–NiS/TM showed an outstanding OER activity and only required an overpotential of 260 mV to drive a current density of 10 mA cm⁻² in 1.0 M KOH, which is less than those required for FeS/TM and NiS/TM. In addition, FeS–NiS/TM possessed good durability while maintaining its catalytic activity for at least 25 h.

FeS-NiS/TM was derived from an NiFe-LDH/TM precursor via a hydrothermal sulfuration reaction (see the ESI⁺ for preparation details). The X-ray powder diffraction (XRD) pattern of the precursor shows diffraction peaks, corresponding to NiFe-LDH/TM (JCPDS No. 38-0715, Fig. S1, ESI†).²⁸ As shown in Fig. 1a, the XRD pattern for the resulting FeS-NiS/ TM shows peaks at 29.9° , 43.1° , 53.1° , 63.2° and 70.7° , which can be assigned to the (110), (114), (300), (008) and (224) planes of the FeS phase (JCPDS No. 37-0477), respectively; moreover, the diffraction peaks at 18.4°, 35.7°, 37.3°, 40.4°, 52.6°, 57.4° and 75.6° can be indexed to the (110), (021), (220), (211), (401), (330) and (042) planes of the NiS phase (JCPDS No. 12-0041), respectively. The other peaks correspond to TM (JCPDS No. 44-1294). The scanning electron microscopy (SEM) image of NiFe-LDH/TM indicates full coverage of the bare TM with the nanosheet array (Fig. 1b). Fig. 1c shows the SEM image of FeS-NiS/TM, the sulfided product still maintains its nanosheet morphology. The transmission electron microscopy (TEM) images of NiFe-LDH (Fig. S2, ESI†) and FeS-NiS (Fig. 1d)

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Fig. 1 (a) XRD pattern of FeS–NiS/TM. SEM images of (b) NiFe–LDH/TM and (c) FeS–NiS/TM. (d) TEM image of an FeS–NiS nanosheet. (e) HRTEM image of an FeS–NiS nanosheet. (f) EDX elemental mapping images of Ni, Fe and S for FeS–NiS/TM.

further confirm their nanosheet natures. The high-resolution transmission electron microscopy (HRTEM) image (Fig. 1e) of the FeS–NiS nanosheet shows interplanar distances of 0.174 nm, 0.312 nm and 0.294 nm, corresponding to the (205) and (103) planes of FeS and the (101) plane of NiS, respectively (Fig. 1e). Note that the overlap of the lattice fringes of FeS and NiS results in atomic coupling, which may generate a synergistic effect between FeS and NiS and thus enhance the catalytic performance.²⁹ As shown in Fig. 1f, the energy-dispersive X-ray (EDX) spectrum of FeS–NiS/TM shows the existence of Ni, Fe and S elements and confirms the uniform distribution of Ni, Fe and S in the whole nanosheet array.

Fig. 2a shows the X-ray photoelectron spectroscopy (XPS) survey spectrum of FeS–NiS/TM, which further indicates the existence of Ni, Fe and S elements. As shown in Fig. 2b, the Ni 2p region exhibits two peaks at 873.5 and 855.6 eV, which can be assigned to Ni $2p_{3/2}$ and Ni $2p_{1/2}$, respectively,^{30,31} and the other peaks are satellite peaks (identified as "Sat."), which confirm the existence of Ni.^{30,32,33} The Fe 2p spectrum (Fig. 2c) shows two peaks at 711.7 and 723.5, which are assigned to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively. The other four peaks at around 705.5, 711.7, 716.2 and 723.5 confirm the existence of Fe–S bonds.^{34–36} In the S 2p region (Fig. 2d), two peaks at 164.9 and 169.4 eV were observed, which can be assigned to the S in NiS and a superficial oxidation of NiS in air, respectively.^{31,37}

The electrocatalytic OER performance of FeS-NiS/TM was evaluated in 1.0 M KOH using a standard three electrode



Fig. 2 (a) XPS survey spectrum of FeS–NiS/TM. XPS spectra of FeS–NiS/TM in the (b) Ni 2p, (c) Fe 2p and (d) S 2p regions.

system at a scan rate of 5 mV s⁻¹. The OER performances of RuO₂/TM, bare TM, FeS/TM and NiS/TM were also measured under the same conditions for comparison. Note that iR compensation was applied to all the initial data because ohmic resistance can affect the measured currents.^{12,38,39} Fig. 3a shows the representative linear sweep voltammetry (LSV) curves of bare TM, RuO₂/TM, NiS/TM, FeS/TM and FeS-NiS/TM. Apparently, RuO₂/TM shows an outstanding OER activity and only requires an overpotential of 250 mV to drive a current density of 10 mA cm⁻², while bare TM presents poor catalytic activity. It is worth mentioning that the FeS/TM and NiS/TM also show OER activity, with overpotentials of 360 and 370 mV to drive a current density of 10 mA cm⁻², respectively. As expected,



Fig. 3 (a) LSV curves of bare TM, RuO₂/TM, NiS/TM, FeS/TM, and FeS-NiS/TM with a scan rate of 5 mV s⁻¹ for OER in 1.0 M KOH at room temperature. (b) Tafel plots of RuO₂/TM, FeS-NiS/TM, NiS/TM and FeS/TM. (c) LSV curves of FeS-NiS/TM before and after 500 CV cycles. (d) Time-dependent current density curve of FeS-NiS/TM at a static overpotential of 299 mV for 25 h in 1.0 M KOH.



Fig. 4 (a) CVs for FeS–NiS/TM in the faradaic capacitance current range at scan rates from 10 to 70 mV s⁻¹ in 1.0 M KOH at room temperature. (b) Plot of the TOF of FeS–NiS/TM as a function of the overpotential.

FeS–NiS/TM presents enhanced OER catalytic activity and only requires an overpotential of 260 mV to drive the same current density. The enhanced catalytic performance of FeS–NiS/TM can be attributed to the synergistic effect caused by hybridizing NiS and FeS.^{40,41} In addition, the OER performance of FeS–NiS/TM is better than that of most reported non-noble-metal catalysts in the same media (Table S1, ESI†). Fig. 3b shows the Tafel plots of FeS–NiS/TM, FeS/TM, NiS/TM, and RuO₂/TM, and the Tafel values were calculated to be 80, 231, 219, and 58 mV dec⁻¹, respectively, implying superior OER catalytic kinetics on FeS–NiS/TM. The OER in alkaline solution consists of the following three steps:

$$M + H_2 O \rightleftharpoons M - OH + H^+ + e^-$$
(1)

$$M-OH \rightleftharpoons M-O + H^{+} + e^{-}$$
(2)

$$M-O \rightleftharpoons M + O_2 \tag{3}$$

where M represents the electrocatalyst.¹²

The multi-step chronopotentiometric curve of FeS-NiS/TM with increasing current density from 80 to 280 mA cm⁻² (20 mA cm⁻² per 500 s) indicates excellent mass transportation ability and conductibility of FeS-NiS/TM (Fig. S3, ESI†). Durability is also a crucial factor for measuring the performance of electrocatalysts. As shown in Fig. 3c, the LSV curve of FeS-NiS/ TM after 500 cyclic voltammetry (CV) cycles shows a slight change compared to its initial performance, indicating good stability of FeS-NiS/TM. Furthermore, we measured the timedependent current density curve of FeS-NiS/TM at a fixed overpotential of 299 mV; this catalyst presents good electrochemical durability, with its catalytic activity being maintained for at least 25 h (Fig. 3d). The SEM images and EDX elemental mapping of FeS-NiS/TM after durability tests were also investigated. After OER electrolysis, FeS-NiS/TM retained its array feature (Fig. S4a, ESI[†]). The EDX images further demonstrate the uniform presence of Ni, Fe, and S elements in the nanoarray (Fig. S4b, ESI⁺). These results suggest that this high-performance catalyst has good long-term OER test durability and can find practical application in real water-splitting devices. We also synthesized the material supported on carbon cloth (CC); the results showed a large improvement in the OER performance (Fig. S5, ESI[†]).

To measure the electrochemically active surface areas of FeS–NiS/TM, FeS/TM and NiS/TM, we calculated their electrochemical double-layer capacitances (C_{dl}) based on their

CVs.⁴¹⁻⁴³ The CVs were measured in the region from 0.774 to 0.874 V at different scan rates. According to the curves, the $C_{\rm dl}$ values for FeS/TM, NiS/TM, and FeS-NiS/TM were calculated as 1.61, 1.28, and 3.40 mF cm^{-2} , respectively, suggesting that FeS-NiS/TM possesses greater surface roughness and more exposed active sites (Fig. S6, ESI[†]).⁴⁴ The nanoarray structure with high surface area makes a great contribution to the high OER performance. We also measured the surface active sites for calculating the turnover frequency (TOF) using the electrochemistry method (see ESI[†] for calculation details).¹² Fig. 4a shows the CVs for FeS-NiS/TM at scan rates from 10 to 70 mV s^{-1} , and a linear dependence exists between the oxidation peak current density and scan rate (Fig. S7, ESI⁺). The TOF values for FeS-NiS/TM were calculated as 0.521 mol O2 s⁻¹ at overpotentials of 500 mV (Fig. 4b). This value is much higher than those of other reported catalysts (Table S2, ESI⁺). The enhanced OER activity of hybridized FeS and NiS can be ascribed to the following aspects: (a) higher surface roughness and more active sites;^{45,46} (b) electron interactions, which might have created synergistic effects to enhance the OER performance.^{47,48}

In summary, we synthesized an FeS–NiS nanosheet array on TM using NiFe–LDH/TM as a precursor *via* hydrothermal sulfurization and explored its OER catalytic performance in 1.0 M KOH. This catalyst requires an overpotential of 260 mV to afford a current density of 10 mA cm⁻². The enhanced OER catalytic performance might have originated from the synergistic effect caused by atomic coupling and electron interactions obtained by hybridizing FeS and NiS. Furthermore, this catalyst shows good durability. This study provides a novel earth-abundant catalyst for water oxidation and opens a new approach to design electrocatalysts with enhanced catalytic performance.

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Conflicts of interest

There are no conflicts to declare.

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