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Tree-Like NiS-Ni₃S₂/NF Heterostructure Array and Its Application in Oxygen Evolution Reaction

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Abstract: In the past decade, fossil fuel resources have been exploited and utilized extensively, which could lead to increasing environmental crises, like greenhouse effect, water pollution, etc. Accordingly, many coping strategies have been put forward, such as water electrolysis, metal-air batteries, fuel cell, etc. Among the strategies mentioned above, water electrolysis is one of the most promising. Water splitting, which can achieve sustainable hydrogen production, is a favorable strategy due to the abundance of water resources. Splitting of water includes two half reactions integral to its operation: hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). However, its practical application is mainly impeded by the sluggish anode reaction. Simultaneously, noble metal oxides (IrO₂ and RuO₂) and Pt-based catalysts have been recognized as typical OER catalysts; however, the scarcity of noble metals greatly limits their development. Hence, designing an alternative electrocatalyst plays a vital role in the development of OER. However, exploring a highly active electrocatalyst for OER is still difficult. Herein, a miraculous construction of a tree-like array of NiS/Ni₃S₂ heterostructure, which is directly grown on Ni foam substrate, is synthesized via one-step hydrothermal process. Since NiS and Ni₃S₂ have shown great OER performance in previous investigations, this novel NiS-Ni₃S₂/Nikel foam (NF) heterostructure array has tremendous potential as a practical OER catalyst. Upon application in OER, the NiS-Ni₃S₂/NF heterostructure array catalyst exhibits excellent activity and stability. More specifically, this novel tree-like NiS-Ni₃S₂ heterostructure array shows extremely low overpotential (269 mV to achieve a current density of 10 mA·cm⁻²) and small Tafel slope for OER. It also shows extraordinary stability in alkaline electrolytes. Compared with the Ni₃S₂ nanorods array, the NiS-Ni₃S₂ heterostructure array has a synergistic effect that can improve the OER performance. Due to the secondary structure (Ni₃S₂ nanosheets), the tree-like NiS-Ni₃S₂ array provides more active sites could have higher specific surface area. The greater activity of the NiS/Ni₃S₂ heterostructure may also stem from the tight conjunction between tree-like NiS/Ni₃S₂ and the Ni foam substrate, which is beneficial for electronic transmission. Hydroxy groups can accumulate in large amounts on the surface of the tree-like array, and it also generates some Ni-based oxides that are favorable to OER. Moreover, the synergistic effect of such heterostructure can intrinsically improve the OER activity. The unique tree-like NiS-Ni₃S₂ heterostructure array has great potential as an alternative OER electrocatalyst.

Key Words: Heterostructure; Tree-like array; NiS-Ni₃S₂; Oxygen evolution reaction

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NiS-Ni₃S₂ 树状异质结阵列在析氧反应中的应用

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摘要: 在过去的几十年里, 数以万计化石能源的开发和利用导致了一系列的环境问题, 例如温室效应和水污染等。许多应对的策略被提出以应对环境问题, 可再生氢气是其中一个最为瞩目的能源。而在其中, 电解水是为了获得可在生氢气最为环保的方案。在阳极发生反应过于低效则限制着这项技术的发展, 所以研究开发高效的阳极电催化剂变得尤为重要。在本文中, 我们通过一步水热法合成了一种直接生长在泡沫镍基底的NiS-Ni₃S₂树状异质结阵列。这个材料在实际电解水的阳极反应中表现出巨大的潜能, 表现出高效的电催化性能和超强的稳定性能。NiS-Ni₃S₂树状异质结阵列比纳米棒状Ni₃S₂表现出更好的性能。因为其拥有更高的比表面积和NiS-Ni₃S₂之间协同效应展现。NiS-Ni₃S₂树状异质结阵列的高性能也可能是因为其紧密地与泡沫镍基地连接, 拥有较好的电子传输路径。同时, 在反应的过程中, 一些羟基氢氧化镍的产生也有利于催化效果的提升。毫无疑问, NiS-Ni₃S₂树状异质结阵列作为电解水的阳极催化剂拥有极大的前景。

关键词: 异质结结构; 树状阵列; NiS-Ni₃S₂; 析氧反应

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1 Introduction

Nowadays, companying with the high demands of energy and the depletion of fossil fuels, it has been an urgent task to explore sustainable and clean energy to replace fossil fuels. Water electrolysis, metal-air batteries, fuel cell, have emerged as coping strategies. Among those, water splitting that under the condition of electric or sunlight pulse, is consider as a most promising technology for the generation of alternative energy¹. As we all know, the splitting of water includes two half reactions, hydrogen evolution reaction and oxygen evolution reaction. Both hydrogen-evolution reaction (HER) and the oxygen-evolution reaction (OER) play an integral part of water splitting systems, so that it is a key factor to improve the efficiencies of HER and OER². Many catalysts have been put forward for hydrogen evolution reaction and most of them demonstrate considerable catalytic performance³. However, the reaction kinetic of OER is sluggish, frustrating the advance and development of water splitting. Actually, the above mentioned technologies (water electrolysis, metal-air batteries and fuel cell) may be complicated in industrial design, but the essential methods are same. Typically, they consist of two-electrode systems, which includes HER or oxygen reduction reaction (ORR) in cathode and OER or the oxidation of carbon-based fuels in anode. In this regard, the slow reaction process of OER impedes these technologies in practical application⁴. Thus, the OER plays a critical role in energy fields.

To date, noble metal oxides (IrO₂ and RuO₂) are recognized as the typical OER catalysts. However, they will be suffering from oxidation and dissolution during the OER. What is more, the high cost and scarcity of these precious metals hinder their large scale application. To solve these problems, enormous effort has been devoted to advancing the development of oxygen evolution reaction. Different electrocatalysts for OER are

designed and put forward in last decade, such as, the transition metal-based oxides (Co₃O₄⁵, NiCo₂O₄⁶, NiO⁷, Ni-Fe layered double hydroxides⁸, Ni-Co layered double hydroxides⁹, etc.), metal chalcogenides (CoSe₂¹⁰, NiSe¹¹, NiS¹²), metal pnictides¹³ and metal-organic framework¹⁴ have been intensively studied as alternative materials for OER catalysts. It is worthwhile to mention that metal chalcogenides are one of the most attractive branches due to their high performance and good stability for HER/OER. Besides, the raw materials of metal chalcogenides are earth-abundant and low-cost. Comparing with transition metal-based oxides, metal chalcogenides possess higher intrinsic electroconductivity which leads to considerable OER activities. Among the metal chalcogenides, nickel sulfides (e.g. NiS, NiS₂, Ni₃S₂) are one class that has great potential for OER catalysts. As previous studies reported, nickel sulfides have been widely investigated as supercapacitors¹⁵, lithium-ion batteries¹⁶ and OER catalysts. It is noted that NiS and Ni₃S₂ demonstrate low overpotentials and good stability for OER in alkaline electrolyte. Particularly, Ni₃S₂¹⁷, a metal-rich form of nickel sulfides, shows a superior performance towards OER comparing with the NiS. However, most studies of OER performance about nickel sulfides are mainly focused on single phase. Recently, Zhou *et al.*¹⁸ reported the synthesis of MoSe₂-NiSe vertical heteronanostructures with a colloidal epitaxial growth strategy. The MoSe₂-NiSe heterostructure shows excellent performance for HER. Zhang *et al.*¹⁹ synthesized MoS₂/Ni₃S₂ heterostructure, which shows an extremely low overpotential for water splitting. However, the literature about heterostructure with nickel sulfides for the enhanced OER performance is scarce.

Herein, we synthesized tree-like NiS-Ni₃S₂ heterostructure array on nickel foam with epitaxial growth strategy²⁰. Such a tree-like NiS-Ni₃S₂ heterostructure is synthesized by hydrothermal method. Ni₃S₂ nanorods array being grown on

nickel foam, at the same time, the delicate heterostructure are constructed by *in situ* growth of NiS nanosheets on Ni₃S₂ nanorods. Both NiS and Ni₃S₂ shows good performance for OER in the previous investigations. Thus, we applied this novel tree-like NiS-Ni₃S₂ heterostructure array material in OER, and it exhibits fairly high catalytic activities for OER with an extremely low overpotential and a small Tafel slope. Meanwhile, it shows an extraordinary stability in the alkaline electrolyte. The high electrochemical performances of NiS-Ni₃S₂/NF array may originate from the synergetic effect between NiS nanosheets and Ni₃S₂ nanorods. In addition, the three-dimensional NiS-Ni₃S₂ array grown on nickel foam is a binder-free catalyst which is beneficial to electronic transmission and conversion reaction for OER²¹. Moreover, the rich-branches architecture would provide more active sites for OER. We anticipate that this material has tremendous potential in different fields.

2 Experimental

2.1 Synthesis of the tree-like NiS-Ni₃S₂ heterostructure array

In a typical synthesized method for the tree-like NiS-Ni₃S₂ heterostructure array, 1.162 g Ni(NO₃)₂·6H₂O (98%) and 0.474 g Na₂S₂O₃ (97%) are successively dissolved into 20 mL of deionized (DI) water. And then, 10 mL ethylene glycol (98%) and 1 mL oxalic acid (95%) were slowly added. After stirring for 30 min, the prepared mixed solution and a piece of pretreated nickel foam (~1 × 2.5 cm, remove the surface oxides of NF with 1 mol·L⁻¹ HCl) were transferred into a Teflon-lined stainless-steel autoclave (50 mV), then, which was sealed tightly and maintained at 180 °C for 24 h in an electric oven. After the reaction, the nickel foam was taken out and washed with DI water and ethanol for several times. Finally, the product was prepared.

2.2 Synthesis of the Ni₃S₂ nanorods array

The synthesized procedure of the Ni₃S₂ nanorods is similar to that of the tree-like NiS-Ni₃S₂ heterostructures array. The Ni₃S₂ nanorods array was synthesized without oxalic acid, and we reduce the reaction time to 18 h. While the intermediate state of the tree-like NiS-Ni₃S₂ heterostructure array was synthesized by reducing the addition of oxalic acid to 0.3 mL.

2.3 Characterization

The samples were identified by X-ray diffraction (XRD, PANalytical D8 with Cu K α). The morphology and structure of the samples were investigated by transmission electron microscopy (TEM, philips, tecnai, F30, 200 kV) and field emission scanning electron microscopy (FESEM, JEOL, JSM-7800F, 5 kV) which equipped with an Oxford INCA X-sight energy dispersive X-ray spectrometer (EDX). X-ray photoelectron spectroscopy (XPS) that equipped with an Al K α X-ray source was applied to analyze the valence state of products.

2.4 Electrochemical measurements

All electrochemical measurements were performed by

electrochemical workstation (CHI 760D, Shanghai Chenhua Instrument) in a standard three-electrode system at the room temperature. A platinum foil and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The as-prepared electrodes (NiS-Ni₃S₂/NF or Ni₃S₂/NF) were regarded as working electrode. The loading mass of sample is about (1.7 ± 0.2) mg·cm⁻². All measured potentials were calibrated to RHE following the equation: $E(\text{RHE}) = E(\text{SCE}) + 0.059\text{pH} + 0.244$. Linear sweep or cyclic voltammetry of samples were tested in 1 mol·L⁻¹ KOH electrolyte. Electrochemical impedance spectroscopy (EIS) measurements were employed at 0.35 V (vs SCE) with frequency from 100 kHz to 0.01 Hz and an AC voltage of 5 mV.

3 Results and discussion

The samples are synthesized by one-pot hydrothermal method with precise control. Ni₃S₂ nanorods array is directly grown on nickel foam. Simultaneously, NiS nanosheets in suit grow on the surface of Ni₃S₂ nanorods. Previous studies proved that the similar crystalline structure of NiS nanosheets and Ni₃S₂ nanorods would realize the NiS-Ni₃S₂ heterostructure theoretically. However, the epitaxial growth of the NiS nanosheets at the radial direction of the Ni₃S₂ nanorods is hindered kinetically reaction²². According to previous studies²³, certain substance would be activated on the surface of Ni₃S₂ nanorods and controls the morphology of the sample. Since tremendous efforts have been devoted to the exploration of certain activator, we consider that acetic acid plays a crucial role in the formation process of NiS-Ni₃S₂ heterostructure²⁴. Specifically, Ni₃S₂ nanorods array (Fig. S1a, Supporting Information) was prepared in almost the same condition except acetic acid. Accordingly, all peaks of the X-ray diffraction (XRD) pattern of Ni₃S₂ nanorods (Fig. S1b) can be well match with the standard card of Ni₃S₂ (JCPDS No. 44-1418), which proves that the as-synthesized sample is high pure material.

To observe the morphology details and hierarchical structure of the as-synthesized NiS-Ni₃S₂ heterostructure under the control of acetic acid, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and XRD were carried out. The FESEM images are presented in Fig. 1. Tree-like NiS-Ni₃S₂ array, which consists of Ni₃S₂ nanorods and NiS nanosheets, was fabricated in large-scale (Fig. 1a). The side profile of the NiS-Ni₃S₂ array is clearly detected in Fig. 1b, which shows that tree-like NiS-Ni₃S₂ array tightly adheres on the surface of nickel foam. As shown in Fig. 1c, the length of Ni₃S₂ nanorods is about 4 μm while the thickness of NiS nanosheets is 100 nm. The XRD pattern of NiS-Ni₃S₂ heterostructure is shown in Fig. 1d, which indicates that the product is composed of two phases. The diffraction peaks can be indexed to rhombohedral NiS (JCPDS card No. 12-0041, $a = 0.962$ nm, $b = 0.962$ nm, $c = 0.314$ nm) and rhombohedral Ni₃S₂ (JCPDS card No. 44-1418, $a = 0.57454$ nm, $b = 0.57454$ nm, $c = 0.713$ nm), respectively. By comparing the FESEM and XRD

Fig. 1 Different magnification FESEM images of tree-like NiS-Ni₃S₂ heterostructure array (a)–(c) and the corresponding XRD pattern (d).

pattern of Ni₃S₂ nanorods array without the control of acetic acid, this means that the Ni₃S₂ nanorods array grow at first, ensuing the epitaxial growth of NiS nanosheets. What's more, it proves that the backbone of tree-like NiS-Ni₃S₂ is Ni₃S₂ nanorods. The other peaks can be fit to associate with nickel foam. Fig. 2 is the TEM image of NiS-Ni₃S₂ heterostructure, which clearly shows that each tree-like structure consist of backbone and branch. High-resolution TEM images are presented to reveal the heterostructure directly. The HRTEM images from branch and backbone of the NiS-Ni₃S₂ heterostructure are presented, respectively. The measured lattice fringes of 0.251 nm corresponds to the (021) inter planer of NiS (Fig. 2b), while the lattice fringes of 0.238 nm is in accordance with the (003) inter planer of Ni₃S₂ (Fig. 2c). Furthermore, two kinds of lattice fringes are detected in a continuous interface region of the NiS-Ni₃S₂ heterostructure. As shown in Fig. 2d, lattice fringes with 0.294 nm corresponds to the (101) plane of rhombohedral NiS, while the interplanar of 0.408 nm can be

Fig. 2 (a) TEM image of tree-like NiS-Ni₃S₂ heterostructure and the corresponding HRTEM images in different region. (b) HRTEM image of branched NiS nanosheets. (c) HRTEM image of backbone Ni₃S₂ nanorods. (d)–(e) HRTEM image of different interface region of tree-like NiS-Ni₃S₂ heterostructure.

indexed to (101) plane of rhombohedral Ni₃S₂. Another HRTEM image (Fig. 2e) distinctly shows the interface between NiS and Ni₃S₂, which proves that NiS-Ni₃S₂ heterostructure was successfully synthesized.

The energy-dispersive X-ray spectroscopy (EDX) suggests that the atomic ratio of Ni : S is around 1.3 (Fig. S2, Supporting Information), which is in accordance with the mixed atomic ratio of NiS-Ni₃S₂. To further analyze the different part composition of tree-like NiS-Ni₃S₂ array, an intermediate state of the tree-like NiS-Ni₃S₂ heterostructure array (Fig. S3a, Supporting Information) whose EDX data are collected in different region (branch and backbone) is synthesized under the control of acetic acid. It is obvious that the atomic ratio of Ni : S is 1 : 1 for branch (Fig. S3b), while the value is about 1.5 : 1 for backbone (Fig. S3c). The elemental mapping analysis (Fig. 3) shows that the uniform distribution of Ni and S elements. These results well prove the composition of backbone (Ni₃S₂) and branche (NiS) architectures. What is more, the high-quality sample is the guarantee of high electrochemical performance.

Furthermore, the surface chemical state of NiS-Ni₃S₂ heterostructure is investigated by X-ray photoelectron (XPS). From the spectrum of Ni 2p (Fig. 4a), it consists of four easily identifiable characters, namely two spin-orbit satellites and four shakeup satellites. The fitting peaks are marked at 854.2 and 872.2 eV, properly indexed to Ni²⁺, while 855.9 and 873.9 eV corresponds to Ni³⁺. Additionally, the intense peaks at 861.3 and 879.9 eV are the satellite peaks of Ni species, which associates with the surface oxidation states of Ni species. As shown in Fig. 4b, the peaks at 161.4 and 163.7 eV assign to the S 2p_{1/2} and S 2p_{3/2}, respectively²⁵. The peak located at 168.8 eV belongs to sulfur-oxygen bond.

The electrocatalytic performance on OER of tree-like NiS-Ni₃S₂ heterostructure array is measured in alkaline electrolyte (O₂-saturated, 1 mol·L⁻¹ KOH), using a standard three-electrode systems. For comparison, the OER performances of Ni₃S₂ nanorods and bare nickel foam are investigated in the same set. Their linear sweep voltammetry (LSV) curves is shown in Fig. 5a. The oxidation peaks (around in 1.39 V vs RHE (Reversible Hydrogen Electrode)) could be ascribed to the oxidation of Ni^{II} to Ni^{III}, which have been studied in detail for Ni-based electrocatalysts²⁷. As shown in LSV curves, the tree-like NiS-Ni₃S₂ heterostructure catalyst needs an overpotentials of 269 mV to achieve a current density of 10 mA·cm⁻², while the Ni₃S₂ nanorods require an overpotentials of 338 mV to afford current

Fig. 3 FESEM image of tree-like NiS-Ni₃S₂ heterostructures array and the corresponding EDX-mapping.

Fig. 4 XPS survey spectra of tree-like NiS-Ni₃S₂ heterostructure array that before OER, (a) Ni 2p and (b) S 2p.

Fig. 5 (a) Polarization curve of Nickel foam (blue), Ni₃S₂ nanorods array (black) and tree-like NiS-Ni₃S₂ heterostructure array (red) at a scan rate of 5 mV·s⁻¹. (b) Tafel plot of Ni₃S₂ nanorods array (red) and tree-like NiS-Ni₃S₂ heterostructure array (black) for OER. (c) Stability measurement of the tree-like NiS-Ni₃S₂ heterostructure array for 1000 CV cycles. (d) Chronopotentiometric curve of tree-like NiS-Ni₃S₂ heterostructure array at constant current density of 50 mA·cm⁻². All the measurements were performed in 1.0 mol·L⁻¹ KOH.

density of 10 mA·cm⁻². Besides, the bare nickel foam shows a poor OER performance. The high electrochemical property of NiS/Ni₃S₂ attributes to the heterostructure. Tafel slope is an important parameter to evaluate OER reaction kinetics. Generally speaking, the lower value of Tafel slope indicates facile catalytic activity for OER. The corresponding Tafel plots (Fig. 5b) reveal that the tree-like NiS-Ni₃S₂ heterostructure array shows the smaller Tafel slope value than Ni₃S₂ nanorods. It suggests that tree-like NiS-Ni₃S₂ heterostructure, comparing with Ni₃S₂ nanorods, shows a higher intrinsic electrocatalytic activity for OER. It is believed that the exposed active sites act as a crucial factor for high OER performance. The durability of the tree-like NiS-Ni₃S₂ heterostructure for OER is examined. After continuous cyclic voltammetric (CV) scanning, the polarization curve demonstrates a negligible decrease in current

density (Fig. 5c). The long-term electrochemical stability of NiS-Ni₃S₂ heterostructure is also tested (Fig. 5d), which suggests that a potential of about 1.642 V is required to deliver 50 mA·cm⁻² after continues 12 h reaction (only increase a potential about 20 mV).

In order to understand the electrochemically active surface areas (ECSA) of the samples, the double-layer capacitances (C_{dl}) are measured by cyclic voltammetry in non-faradaic potential region (Fig. 6). It is obvious that the C_{dl} value of the tree-like NiS-Ni₃S₂ heterostructure array (Fig. 6b, 16.5 mF) is higher than Ni₃S₂ nanorods (Fig. 6d, 5.5 mF), which suggests that the tree-like NiS-Ni₃S₂ heterostructure array has a higher active surface area. We hypothesize that the Ni₃S₂ nanorods is the main catalytic group for OER catalyst, since the C_{dl} value of Ni₃S₂ nanorods is fairly high and it has lower onset overpotentials. In

Fig. 6 Electrochemical double layer capacitance analysis (a) cyclic voltammogram (CV) curves of tree-like NiS-Ni₃S₂ heterostructure array at different scan rates. (b) Scan rate dependence of the current density of tree-like NiS-Ni₃S₂ heterostructure array which could estimate double layer capacitance (C_{dl}). (c) CV curves of Ni₃S₂ nanorods array at different scan rates. (d) Scan rate dependence of the current density of Ni₃S₂ nanorods array which could estimate C_{dl} .

Fig. 7 (a) FESEM image of tree-like NiS-Ni₃S₂ heterostructure array that after long-term OER test and (b) the corresponding XRD pattern. XPS data in (c) Ni 2p region and (d) S 2p region of tree-like NiS-Ni₃S₂ heterostructure array after OER

NiS-Ni₃S₂ heterostructure, the electronic modulation of hierarchical heterostructure may induce the electrons transferred from metallic Ni₃S₂ to NiS, achieving the synergistic effect between NiS and Ni₃S₂. Thus, such heterostructure would improve the electrical conductivity of the sample. As supporting evidence, the EIS of samples is conducted. As shown in Fig. S4

(Supporting Information), the tree-like NiS-Ni₃S₂ heterostructure array exhibits lower charge transfer resistance than Ni₃S₂ nanorods, which suggests that the heterostructure can efficiently lower the charge transfer resistance of the Ni₃S₂ nanorods.

After the long-term OER test, FESEM image (Fig. 7a), XRD

pattern (Fig. 7b) and XPS (Fig. 7c, d) are carried out to further analyze the stability of samples. The XPS spectrum of Ni 2p shows slight shift after the OER (~0.2 eV, Fig. 7c), and the satellite peaks of the Ni 2p become intensive after the OER. The spectrum of S 2p is shown in Fig. 7d after the OER, and it is obvious that the peak of S—O bond become fairly strong. It suggests that the surface oxidation of the samples may occur during the OER. As previously reported, the nickel hydroxides (NiOOH or NiO) are efficient OER catalysts, which can rationally enhance the OER²⁶. However, XRD pattern was presented to analyze the sample after OER. The diffraction peaks are in accordance with previous XRD pattern, which mean that the nickel hydroxides layer is fairly thin. A HRTEM image of the sample after OER is carried out (Fig. S5, Supporting Information). The lattice fringes of 0.238 nm belongs to the (003) plane of Ni₃S₂. Furthermore, an oxide layer (~4 nm) at the edge of sample can be distinctly observe. There is no clear that lattice fringes can be detect in oxide layer, which means the oxide layer is amorphous. We believed that the NiS-Ni₃S₂ heterostructure would generate some amorphous nickel-base oxides (NiO/NiOOH) on the main catalytic group (metal-rich Ni₃S₂) during the OER, and it would highly enhance the OER performance.

4 Conclusions

In summary, 3D tree-like NiS-Ni₃S₂/NF heterostructure array is synthesized by simple and facile one-pot hydrothermal method. The novel tree-like NiS-Ni₃S₂/NF heterostructure boasts much interesting properties, which has a great potential in various fields. Herein, one of the examples is given. It shows a high electrochemical performance and good stability when we applied it for OER catalyst. The improvement of OER performance may be attributed to: (1) the NiS/Ni₃S₂ heterostructure would have a synergistic effect that facilitates the electron transfer, which can improve the entire electrical conductivity of the sample. (2) During the OER reaction, some nickel hydroxides (NiOOH or NiO) would generate, which have been widely reported as good OER catalyst. The synergistic effect between them may highly improve the OER performance. (3) Such branched nanorod architectures, which are constructs by primary structure (Ni₃S₂ nanorods) and secondary structures (NiS nanosheets), would provide more actives site for OER. (4) The three-dimensional NiS-Ni₃S₂ array growing on foam is some kind of binder-free catalyst which is beneficial to enhancing the intrinsic kinetics and conversion reaction for OER. Based on our research, it has broader applications in the coming future, such as photocatalysis, supercapacitor and sensor.

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Supporting Information: available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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