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# PAPER



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# *In situ* chemical etching of tunable 3D Ni<sub>3</sub>S<sub>2</sub> superstructures for bifunctional electrocatalysts for overall water splitting<sup>+</sup>

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Three-dimensional (3D) nanomaterials are rendered with large specific surface areas as well as desired physicochemical, electrical and catalytic properties for a large variety of functional applications. In this work, 3D Ni<sub>3</sub>S<sub>2</sub> superstructures (needle array and leaf pattern) were created on nickel foams (NFs) through an *in situ* chemical etching (ICE) method. This anisotropic growth involves chemical dissolution, *in situ* nucleation and re-deposition processes, which endows the as-fabricated Ni<sub>3</sub>S<sub>2</sub> with large surface areas and warrants firm adhesion to the NF as well. Importantly, the Ni<sub>3</sub>S<sub>2</sub>@NF can directly serve as effective binder-free electrodes for hydrogen evolution reactions (HERs) and oxygen evolution reactions (OERs) from electrocatalytic water splitting.

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## Introduction

As compared to one-dimensional (1D) and two-dimensional (2D) nanostructures, 3D semiconducting nanomaterials are usually endowed with large specific surface areas in combination with unique physicochemical, electrical and catalytic properties.<sup>1,2</sup> Moreover, the spatial configuration of the interconnected networks of building subunits in the 3D structures can further expand specific properties, such as efficient mass transport and charge carrier transfer,3 making the relevant nano/microfunctional materials popular with diverse applications in energy storage, harvesting and conversion.4-8 However, fabrication of 3D functional nanostructures, especially those generated on underlying substrates, still remains a significant challenge because of the high complexity and diversity of the manufacturing process.9 For instance, some conventional chemical methods that have been applied to achieve 3D nanostructures either involve tedious experimental steps or lead to poor physical contact between the target materials and substrates.10-13

Chemical etching (chemical milling) is commonly employed in the industrial metal removal to obtain parts that cannot be machined easily through traditional machining methods. Usually, a strong chemical bath with regulated temperature is

applied to a metal surface, where metal ions are dissolved from the metal substrate into the chemical solution to achieve desired shapes.<sup>14-16</sup> Taking advantage of this technique, we speculate that fabrication of 3D nano/microstructures could be feasible in a hydro/solvo-thermal solution, because the exfoliated metal species may nucleate into crystal grains if a new phase can be formed at the metal-solution interface.17 Driven by the energy fluctuation, further growth of the as-formed grains may take place in the solution, which will grow into secondary architectures of target materials.18-20 Hence the chemical etching assisted growth involved process in a hydrothermal synthesis may bring about target materials with unique structural features, high surface areas, and excellent physical contact at a molecular level, thus conferring the materials with unique functionalities for diverse applications, such as electrocatalysis.21-25

3D nanostructures composed of transitional metal chalcogenides have been recently studied as bifunctional electrocatalysts for hydrogen evolution reactions (HERs) and oxygen evolution reactions (OERs) owing to their high electrocatalytic activity, good electric conductivity, low cost and abundance on earth.<sup>26-28</sup> For example, a recent study by Wang et al. presented nickel sulfide microsphere film on Ni foam as a bifunctional electrocatalyst for water splitting, in which superior activity with good durability has been demonstrated.29 Liu et al. demonstrated NiCo2S4 nanowires on carbon cloth serving as an efficient electrocatalyst for both HER and OER, where low overpotentials are reported to reach a current density of 100 mA cm<sup>-2</sup>.30 Therefore, it is of great importance to explore facile methods for the construction of 3D structures to enhance the bifunctional electrocatalytic properties. In this work, we present a facile design of in situ grown Ni<sub>3</sub>S<sub>2</sub> superstructures on nickel foams (NFs) via a one-step ICE approach. NF here plays dual roles of the



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nickel source and supporting scaffold, in which Ni atoms are dissolved into their ion derivatives when attacked by chemical etching, further reacting with thioacetamide (TAA), the sulfur source, to form well-defined Ni<sub>3</sub>S<sub>2</sub>. Simply tuning the solvent and the sulfur concentrations enables the manipulation of superstructures from needle arrays to leaf patterns. Significantly, these binder-free Ni<sub>3</sub>S<sub>2</sub>@NF systems are able to directly serve as bifunctional electrodes for HER and OER from overall water splitting with low overpotentials and good durability.

## Experimental section

#### Growth of Ni<sub>3</sub>S<sub>2</sub>@NF

3D Ni<sub>3</sub>S<sub>2</sub> superstructures on NF were prepared by a facile one-step hydrothermal method. A piece of NF was fixed by Teflon tape and dipped fully into a Teflon-lined stainless steel autoclave containing a 30 mL aqueous solution (DI water or ethanol) with a specific amount of thioacetamide (TAA,  $C_2H_5NS$ ). Subsequently, the autoclave was sealed and heated at 150 °C for 16 h to grow 3D Ni<sub>3</sub>S<sub>2</sub> superstructures with different morphologies, *e.g.* needle array and long leaf pattern, respectively. After the autoclave was rinsed with DI water and then dried in an electric oven at 60 °C for 12 h.

#### Characterizations

A field emission scanning electron microscope (FESEM, JEOL JSM-7001F) equipped with an energy dispersive X-ray spectroscope (EDX) and transmission electron microscope (TEM, Philips FEGCM300) were used to characterize the morphologies and compositions of all the samples. X-ray diffraction (XRD, Philips X-ray diffractometer, Cu K $\alpha$ ,  $\lambda = 0.15406$  nm) was employed to examine the XRD patterns of the samples. X-ray photoelectron spectroscopy (XPS) was performed using a VGSCALAB 220I-XL to study the elemental compositions.

#### **Electrochemical measurements**

Electrochemical measurements including linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS, frequency ranging from 0.01 to 100 kHz with 5 mV amplitude) and chronoamperometry (*j*-*t*) were performed on an electrochemical workstation (CHI 660E, CH Instruments Inc., Shanghai) using a three-electrode system in 1 M KOH aqueous solution. The reference electrode and counter electrode were a standard calomel electrode (SCE) and platinum foil, respectively. The Ni<sub>3</sub>S<sub>2</sub>@NF electrodes were then directly used as the anodes for oxygen evolution (operated within 1.2–1.8 V *vs.* RHE) or cathodes for hydrogen evolution (operated within -0.6-0 V *vs.* RHE), respectively. The working area of the electrode for HER or OER is ~1.5 cm<sup>-2</sup>.

## **Results and discussion**

Fig. 1 illustrates the formation of  $Ni_3S_2$  superstructures on NFs in different media, *i.e.* deionized water and ethanol. Initially, the chemical etching from TAA decomposition induces the release of Ni cations from NFs at an elevated temperature. Subsequently, these nickel ions react with surrounding  $S^{2-}$  anions to crystallize into nickel sulfide intermediate nanoparticles at the NF surfaces. The nanoparticles grow larger when their sizes are beyond the critical radius according to the Gibbs free energy formula below:<sup>31,32</sup>

$$G=rac{4}{3}\pi r^3 G_{
m v}+4\pi r^2\gamma$$

where  $G_v$  is the Gibbs volume energy,  $\gamma$  is the interfacial energy, and *r* is the critical radius, eventually forming distinct 3D superstructures of needle arrays (water) and leaf patterns (ethanol) at the microscale. The Ni<sub>3</sub>S<sub>2</sub> grown into needle array superstructures is labeled as NN@NF-1 (0.36 g TAA) and NN@NF-2 (0.18 g TAA), while that grown into leaf patterns as NL@NF-1 (0.36 g TAA) and NL@NF-2 (0.18 g TAA), respectively.



Fig. 1 Schematic formation of 3D Ni<sub>3</sub>S<sub>2</sub> superstructures on NFs in different solvents.

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The structures and chemical compositions of the Ni<sub>3</sub>S<sub>2</sub> superstructures are investigated (Fig. 2). As revealed in the scanning electron microscope (SEM) images of NN@NF-1 (Fig. 2a and b), NFs are fully covered with uniform needle arrays with an average length of 1.4  $\mu$ m and thickness of 400 nm, indicating an evident anisotropic growth behavior. A smaller dosage of TAA (0.18 g) can also lead to the formation of needle arrays despite their loose distribution, suggesting that chemical etching with different TAA concentrations will affect the growth of Ni<sub>3</sub>S<sub>2</sub> (Fig. S1a and b†). It should be noted that the needle

arrays are grown uniformly throughout the surface of the NF, which demonstrates NF supported array structures of the electrodes (Fig. S2†). In this case, the NF scaffolds with microholes are accessible to the electrolyte ions, which is important for the catalytic reactions. Elemental mappings of the needle arrays show an even dispersion of Ni and S elements (Fig. 2c–e), and the energy dispersive X-ray (EDX) analysis also confirms the existence of Ni and S (Fig. 2f), which manifests the successful formation of nickel sulfide on NFs. Meanwhile, NL@NF-1 with leaf-like ensembles is demonstrated from its SEM images and



Fig. 2 SEM images (a-c, g-i); elemental mapping (d, e, j, and k) and EDX patterns (f) of NN@NF-1 (a-f) and NL@NF-1 (f-k).



Fig. 3 TEM images (a-g); XRD patterns (h) and XPS spectrum (i) of NN@NF-1 (a-c, h, and i) and NL@NF-1 (d-i).

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EDX spectra (Fig. 2f-k). Noticeably, an individual micro-leaf with branched leaflets can grow up to 5.2  $\mu$ m in length, while shorter leaf patterns (2.5  $\mu$ m) are formed at half the TAA amount (Fig. S1c and d†). The elemental mapping results have clearly shown the profiles of the leaf pattern formed on the NF, demonstrating an anisotropic growth pattern. The distinct superstructures from different solvents possibly originate from the different crystallization kinetics in different solvents (water *vs.* ethanol). Hence, controlling the chemical etching parameters, such as TAA concentration or solvent, is capable of varying the superstructures.

To further examine the Ni<sub>3</sub>S<sub>2</sub> needle and leaf superstructures, transmission electron microscopy (TEM) characterizations and X-ray diffraction (XRD) are performed, as displayed in Fig. 3. An individual needle with a length of 1.38  $\mu$ m is presented in Fig. 3a, which is consistent with the SEM findings. Specifically, the high-magnification image of the needle tip area (Fig. 3b) shows an obvious porous character. The high-resolution TEM (HR-TEM) image in Fig. 3c identifies a lattice distance of 0.28 nm, which is attributed to the Ni<sub>3</sub>S<sub>2</sub> (110) crystal phase. Similarly, the profile of an individual micro-leaf is observed

from its TEM image (Fig. 3d-g), in which the branched leaflets are enveloped in a thin layer of ultrathin nanosheets, thus forming hierarchical 3D nanostructures. These unique structural features can only be found by TEM characterization because the nanosheets are too thin to be observed by SEM. It is also speculated that these nanosheets linked Ni<sub>3</sub>S<sub>2</sub> leaflets can serve as a whole for the solution based electrochemical reactions, hence possibly delivering unexpectedly good catalytic performance. XRD patterns in Fig. 3h confirm the formation of  $Ni_3S_2$  on NFs, where the peaks at  $2\theta = 21.7^\circ$ ,  $31.1^\circ$ ,  $37.8^\circ$ ,  $49.7^\circ$ and 55.2° correspond to (101), (110), (003), (113) and (122), respectively (JCPDS no. 44-1418),<sup>33</sup> and the characteristic peaks at  $2\theta = 44.5^{\circ}$  and  $51.8^{\circ}$  marked with an asterisk are from the NF (JCPDS no. 65-2865). The XRD patterns suggest that the crystal phases of Ni<sub>3</sub>S<sub>2</sub>, despite their distinct superstructures, are consistent in both solvents, water and ethanol. Furthermore, X-ray photoelectron spectroscopy (XPS) is used to analyze their surface composition (Fig. 3i). The characteristic peaks of Ni  $2p_{3/2}$ and Ni 2p<sub>1/2</sub> can be found at around 855.2 and 872.7 eV accompanied by their respective satellite peaks.34



Fig. 4 HER performances of the as-prepared  $Ni_3S_2@NF$  samples: LSV curves (a); Tafel plots (b); EIS curves with a digital photo inset (c) and long-term stability with a digital photo of gas evolution (d).

Given their high conductivity and reactivity, nickel sulfide materials have been intensively utilized as electrocatalysts for water splitting.35-37 In this case, the electrocatalytic activity of the as-prepared 3D Ni<sub>3</sub>S<sub>2</sub>(a)NF superstructures towards both HER and OER was evaluated in alkaline media (1 M KOH aqueous solution) using a typical three-electrode system, in which the Ni<sub>3</sub>S<sub>2</sub>(a)NF superstructures were directly used as the working electrodes. Fig. 4a shows the linear sweep voltammetry (LSV, operated within -0.6-0 V vs. RHE) curves of the Ni<sub>3</sub>S<sub>2</sub>@NF samples and pure NF, aiming to explore their HER performances. To deliver a current density of 10 mA cm<sup>-2</sup>, NL@NF-1 exhibits the lowest overpotential ( $\eta$ ) of 0.182 V among all the samples, while NN@NF-1 requires 0.199 V. The slightly lower overpotential of NL@NF-1 than that of NN@NF-1 could be due to the presence of the ultrathin leaflets in the NL (see previous TEM in Fig. 3e), which may have offered more electroactive sites for the catalytic reactions. It should also be noted that the average length of NL is much larger than that of NN (Fig. 2b vs. h), therefore providing additional surface area for the electrolyte ion adsorption. For the samples obtained with a lower amount of TAA (Fig. S3<sup>†</sup>), higher overpotentials are observed for

NL@NF-2 (0.203 V) and NN@NF-2 (0.238 V), respectively, suggesting that better growth of Ni<sub>3</sub>S<sub>2</sub> superstructures is favorable for the electrocatalytic reactions. Interestingly, the NL sample still exhibits better performance than NN when TAA is reduced, which again confirms that the NL structure is superior to NN in electrocatalysis. In contrast, pure NF shows inferior HER response with a much higher overpotential of 0.543 V, indicating that the grown Ni<sub>3</sub>S<sub>2</sub> plays a vital role in the enhanced electrocatalytic performances rather than NFs. The HER kinetics of NN@NF-1 and NL@NF-1 were fitted by Tafel plots  $(\log I - \eta)$  (Fig. 4b). Small Tafel slopes of 89 mV dec<sup>-1</sup> and 96 mV dec<sup>-1</sup> are calculated for NL@NF-1 and NN@NF-1, respectively, implying that the improved HER kinetics arise from enhanced electron transport. The HER performances of these Ni<sub>3</sub>S<sub>2</sub> superstructures are comparable to most of the reported nickel sulfide based electrocatalysts (Table S1<sup>†</sup>).

Electrochemical impedance spectroscopy (EIS) measurements were carried out to evaluate the conductivity of the samples, as shown in Fig. 4c. Ni<sub>3</sub>S<sub>2</sub>@NF electrodes (NL@NF-1 and NN@NF-1) with a geometric area of 4.5 cm<sup>-2</sup> (Fig. 4c inset) were measured in the frequency range from 0.01 to 100 kHz at



Fig. 5 OER performances of the as-prepared Ni<sub>3</sub>S<sub>2</sub>@NF samples: LSV curves (a); Tafel plots (b); a digital photo of gas evolution (c) and long-term stability test (d).

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an open circuit potential of 0 V with an amplitude of 5 mV. The Nyquist plots present a slightly smaller semicircle for NL@NF-1 than for NN@NF-1 within the high-frequency range, suggesting that NL@NF-1 shows enhanced electron mobility to improve the electrocatalytic performance.<sup>38</sup> Stability is critical to electrocatalysts, therefore the long-term stability of the representative samples was explored by chronoamperometry measurement (*j*-*t*) with constant overpotentials (185 mV for NL@NF-1 and 200 mV for NN@NF-1). Fig. 4d shows that a current density of 10 mA cm<sup>-2</sup> can be retained for 12 h by both samples, demonstrating their good electrocatalytic durability. The inset photo taken at an overpotential of 0.185 V indicates a stable evolution of gas bubbles on the electrode surface of sample NL@NF-1.

Next, the OER activities of the samples (NL@NF-1 and NN@NF-1) were evaluated in 1 M KOH on the same electrochemical setup. Fig. 5a shows their LSV curves operated within 1.2-1.8 V vs. RHE. Similar to the HER performance, NL@NF-1 delivers a lower overpotential than NN@NF-1 in OER. Overpotentials of 0.34 and 0.37 V are needed for NL@NF-1 and NN@NF-1, respectively, to achieve a current density of 10 mA cm<sup>-2</sup>. Comparatively, bare NF reaches the current density of 10 mA cm<sup>-2</sup> at a high potential of 1.73 V vs. RHE ( $\eta = 0.5$  V), further confirming that it is the Ni<sub>3</sub>S<sub>2</sub> superstructures that contribute to the enhanced electrocatalytic activity. Moreover, the Tafel slope for NL@NF-1 is 150 mV  $dec^{-1}$ , which is smaller than the 170 mV  $dec^{-1}$  of NN@NF-1 (Fig. 5b). We consider that the higher OER activity of NL@NF-1 compared to NN@NF-1 is related to the different structures of the two samples, where the large specific surface areas of ultrathin sheets in NL@NF-1 lead to more active sites for catalytic reactions.39,40 The wettability of the electrode surface is simply demonstrated by dropping a water droplet (5  $\mu$ L) onto the electrodes (Fig. S4<sup> $\dagger$ </sup>). Different from the hydrophobic pure NF surface, the water droplets are absorbed by Ni<sub>3</sub>S<sub>2</sub> based electrodes immediately (NL@NF-1 and NN@NF-1), showing the high hydrophilicity of the electrode surfaces. This hydrophilic property may facilitate diffusion of the electrolyte into the Ni<sub>3</sub>S<sub>2</sub> nanostructures and hence promote gas bubble evolution. A digital photo in Fig. 5c shows the extensive gas evolution of the NL@NF-1 electrode operated at an overpotential of 0.45 V. Similarly, both samples demonstrate excellent stability for OER for 12 h under an overpotential of 0.45 V (Fig. 5d), in which NL@NF-1 delivers a slightly higher current density than NN@NF-1. The observed current increase for both samples may arise from the activation process of the materials during the prolonged cycles.41 The as-reported OER performances are compared with some reported relevant results (Table S2<sup>†</sup>), and the electrocatalytic performances are comparable to some previous studies on Ni<sub>3</sub>S<sub>2</sub>. Collectively, bifunctional Ni<sub>3</sub>S<sub>2</sub>@NF electrodes for both HER and OER are demonstrated. We consider that the in situ growth method ensures the good adhesion of the Ni<sub>3</sub>S<sub>2</sub> superstructures to NF substrates for effective electron collection and rapid electron transfer, thus leading to the enhanced electrocatalytic kinetics and good cycling stability.42 In addition, the high hydrophilicity of the Ni<sub>3</sub>S<sub>2</sub> electrode surfaces has facilitated the diffusion of electrolyte ions during the catalytic reactions, which may be favorable for the gas bubble evolution.

## Conclusion

In summary, an ICE method was employed to construct Ni<sub>3</sub>S<sub>2</sub> superstructures on nickel foams, which can serve as bifunctional electrodes for overall water splitting. The superstructures of needle arrays and branched leaf patterns are achieved by simply tuning the etching parameters, such as the solvent and sulfur concentration. These Ni<sub>3</sub>S<sub>2</sub>@NFs perform effectively towards HER ( $\eta$  as low as 182 mV) and OER ( $\eta$  as low as 340 mV), which arises from their large specific surface area and good contact between the Ni<sub>3</sub>S<sub>2</sub> superstructures and NF substrates. This approach is feasible for a large variety of functional nanomaterials for electro-/photocatalytic applications.

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