Self-Assembled Ultrathin NiCo₂S₄ Nanoflakes Grown on Ni Foam as High-Performance Flexible Electrodes for Hydrogen Evolution Reaction in Alkaline Solution

Lianbo Ma,^a Yi Hu,^a Renpeng Chen,^a Guoyin Zhu,^a Tao Chen,^a Hongling Lv,^a Yanrong Wang,^a Jia Liang,^a Haixia Liu,^a Changzeng Yan,^a Hongfei Zhu,^a Zuoxiu Tie,^a Zhong Jin,^{*a} and Jie Liu^{*ab}

^a Key Laboratory of Mesoscopic Chemistry of MOE and Collaborative Innovation Center of Chemistry for Life Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, China

^b Department of Chemistry, Duke University, Durham, North Carolina, 27708, USA

*Corresponding authors.

Email addresses of corresponding authors: zhongjin@nju.edu.cn (Z. Jin), j.liu@duke.edu (J. Liu).

Abstract

Considerable efforts have been devoted on the design and fabrication of non-platinum electrocatalysts with high performance and low cost for hydrogen evolution reaction (HER). However, the catalytic activity of existing electrocatalysts usually subjects to the limited amount of exposed active sites. Herein ,we propose that self-assembled ultrathin NiCo_2S_4 nanoflakes grown on nickel foam ($\text{NiCo}_2\text{S}_4/\text{Ni}$ foam) can serve as excellent electrocatalyst for HER in alkaline solution with high activity and stability. The $\text{NiCo}_2\text{S}_4/\text{Ni}$ foam electrodes were prepared by the complete sulfidation of networked ultrathin NiCo-layered double hydroxide nanoflakes grown on Ni foam ($\text{NiCo-LDH}/\text{Ni}$ foam). The advantages of this unique architecture are that the ultrathin and porous NiCo_2S_4 nanoflakes can provide a huge number of exposed active sites, the highly-conductive Ni foam can promote the transfer of electrons, and the three-dimensional-networked structure can facilitate the diffusion and penetration of electrolyte. Electrochemical measurements reveal that $\text{NiCo}_2\text{S}_4/\text{Ni}$ foam electrodes exhibit greatly improved performance than $\text{NiCo-LDH}/\text{Ni}$ foam for HER in alkaline solution with low onset overpotential (17 mV), small Tafel slope (84.5 mV/dec) and excellent long-duration cycling stability (maintaining an onset overpotential of ~20 mV and an overpotential of 155 mV at $50 \text{ mA}/\text{cm}^2$ after testing for 100,000 seconds). In addition, the highly-flexible $\text{NiCo}_2\text{S}_4/\text{Ni}$ foam electrodes show no obvious catalytic degradation after bending for 200 times, confirming the high flexibility and robustness under severe conditions.

KEYWORDS: Hydrogen evolution reaction; Ultrathin NiCo_2S_4 nanoflakes; Layered double hydroxide; Three-dimensional-networked structure; Alkaline solution

Introduction

Hydrogen has been considered as a clean resource to replace the diminishing fossil fuels due to its ultrahigh gravimetric energy density among existing fuels [1,2]. The reforming of nature gas or methane is a conventional approach of hydrogen generation for industrial purposes [3,4], but the problem of CO₂ release during this process seriously restricts its extensive application [5]. In recent years, hydrogen generation from water splitting has presented an alternative eco-friendly and carbon-free strategy for hydrogen production [6], but a necessity for carrying out the hydrogen evolution reaction (HER, In acidic solution: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$; In alkaline solution: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$) is the use of electrocatalysts [7–9]. Platinum (Pt) and other Pt-group metals have been considered as the best catalysts for HER [10]. Unfortunately, the low natural abundance and high cost of Pt-group noble metals restrict their massive deployment for hydrogen production. Therefore, the design and fabrication of novel electrocatalysts for HER with minimum noble metal usage is in urgent demand.

To realize this goal, various electrocatalysts have been developed. Until now, metal alloys [11,12], transition metal chalcogenides [13,14], nitrides [15,16], carbides [17,18], and phosphides [19,20] are the most widely investigated catalysts for replacing Pt-group metals because of their high stability, high abundance and low cost. However, these catalysts usually suffer from lower electrical conductivity and/or limited number of exposed active sites, which seriously limit their catalytic performance toward HER [21]. Recently, it was acknowledged that two effective

strategies to improve the HER performance of electrocatalysts are: (1) the incorporation of catalytic materials with conductive networks; (2) the construction of special structures, such as hollow, porous, or hierarchical architectures [22–25]. Benefiting from their structural advantages, rationally-designed electrocatalysts may exhibit enhanced catalytic activity and stability (Table S1) [5,23,24,26–44].

As we know, normally much larger overpotentials are needed to trigger the HER process in alkaline solution as compared with those in neutral and acidic solutions [8,24,27], and the exploration of novel electrocatalysts with high catalytic activity in alkaline solution remains a great challenge. With the merits of high surface-to-volume ratio, short diffusion length for carrier transport, composition versatility, easily-tailored properties and low cost, transition-metal layered double hydroxides (LDHs) have emerged as a novel class of electrocatalysts in alkaline solution [26,45,46]. Interestingly, we have noticed that LDHs also can serve as versatile precursors to produce a variety of other multicomponent transition-metal compounds that may exhibit even better electrocatalytic performance than LDHs for HER in alkaline solution. Recently, it has been confirmed that the coordination structure of transition-metal dichalcogenides is similar to the active centers in hydrogenase [47], and the charged states of metals and sulfur in metal sulfides are similar to those of hydride-acceptors and proton-acceptors in hydrogenase and its analogues [35,48]. In addition, it is expected that the different electrocatalytic components would exhibit beneficial synergistic effect. Inspired by these, we then decide to take advantage of the unique structure of multi-metallic LDHs in the design of new electrocatalysts with

further improved HER activity and stability. Herein, we demonstrate that three-dimensional-networked (3D-networked) NiCo-layered double hydroxide nanoflakes grown on Ni foam (NiCo-LDH/Ni foam) can be converted to ultrathin and porous NiCo₂S₄ nanoflakes on Ni foam (NiCo₂S₄/Ni foam) by a sulfidation process. Electrochemical measurements revealed that the binder-free, self-supported and highly-flexible NiCo₂S₄/Ni foam electrode exhibited much better electrocatalytic activity than NiCo-LDH/Ni foam in alkaline solution with low onset overpotential, small Tafel slope, and excellent catalytic retention during long-term tests (100,000 seconds) (Table S1). Remarkably, the mechanically flexible and robust characteristics of Ni foam ensure the widely application of NiCo₂S₄/Ni foam electrodes for HER under harsh circumstances.

Experimental

Chemicals

All the chemicals were purchased from Sinopharm Chemical Reagent Corp. with analytical grade and were used without further purification.

Synthesis of NiCo-LDH/Ni foam

Ni foams were cleaned in 1.0 M HCl solution with sonication for 10 min to remove nickel oxide on the surface, and subsequently washed with excessive deionized water and ethanol. In a typical synthesis, 290 mg of Co(NO₃)₂·6H₂O, 145 mg of Ni(NO₃)₂·6H₂O and 600 mg of hexamethylenetetramine (HMT) were dissolved into 30 mL of methanol solution under stirring to form a clear solution. Then a piece of Ni

foam (2 cm × 1 cm) was put into the solution, and transferred into a Teflon-lined stainless steel autoclave. After heating at 180 °C for about 12 h, the Ni foam was taken out and cleaned by sonication in deionized water for 2 min to remove any possible contamination on the surface.

Synthesis of NiCo₂S₄/Ni foam

Typically, the as-obtained NiCo-LDH/Ni foam was added into 30 mL of aqueous solution containing 300 mg of thioacetamide, and then the mixture was transferred into an autoclave and heated at 140 °C for 5 h. After cooling down to room temperature naturally, the product was washed with deionized water and ethanol for three times, respectively, and dried at 60 °C overnight.

Characterizations

The morphology, size and structure of the products were examined by field-emission scanning electron microscopy (FESEM, JSM-6480), transmission electron microscopy (TEM, JEM-2100) and Energy-dispersive X-ray spectroscopy (EDX) attached to the FESEM. The crystallinity of as-synthesized samples were characterized by powder X-ray diffraction (XRD) on a Bruker D-8 Advance diffractometer using Cu $K\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation at a scanning rate of 6 °/min. X-ray photoelectron spectra (XPS) were obtained using a PHI-5000 VersaProbe X-ray photoelectron spectrometer with an Al $K\alpha$ X-ray radiation. Raman spectra were collected with a Horiba JY H800 Raman spectrometer using a 532 nm laser source.

Electrochemical Measurements

The catalytic performances of the as-prepared samples toward HER were conducted

on a typical three-electrode setup using a CHI 760D electrochemical analyzer (Chenhua Instruments, Shanghai) at room temperature. Ni foam, NiCo-LDH/Ni foam or NiCo₂S₄/Ni foam were separately used as the working electrodes. Saturated calomel electrode (SCE) and Pt foil were used as the reference and counter electrodes, respectively. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), chronoamperometry measurements and chronopotentiometric measurements were conducted, and linear sweep voltammetry (LSV) was performed at a scan rate of 2 mV/s. During the electrochemical measurements, the electrolyte (1.0 M KOH, pH = 14.0) was degassed by bubbling high-purity nitrogen to eliminate the dissolved oxygen. During the HER stability tests, the pH value usually only slightly change from 14.0 to approximately 14.2 after HER testing for 6 h, this tiny increment of pH value has very little influence on the electrochemical results. In addition, to eliminate the influence of the pH variation, a pH detector was employed to monitor the pH value of electrolyte, and a certain amount (~5 mL) of deionized water was added into the reaction system with a time interval of 6 h to maintain a relatively stable pH value of 14.0 in the reaction system. The calculation of current densities was based on the actual area of electrode that immersed in the electrolyte, and the height of electrode was carefully adjusted according to the height of electrolyte level. All the potentials measured in our work were calibrated with the reversible hydrogen electrode (RHE) according to the equation: $E_{\text{RHE}} = E_{\text{SCE}} + 0.2412 + 0.05916 \times \text{pH}$.

Figure 1. (a) Schematic illustration of the two-step strategy for preparing 3D-networked NiCo-LDH/Ni foam and NiCo₂S₄/Ni foam electrodes. Optical images of (b) initial Ni foam, (c) as-prepared NiCo-LDH/Ni foam and (d) NiCo₂S₄/Ni foam, respectively.

Results and Discussion

As schematically illustrated in Figure 1a, the 3D-networked NiCo₂S₄/Ni foam electrode was fabricated *via* a two-step strategy. In the first hydrothermal synthesis step, Ni foam was immersed into an aqueous solution containing Ni^{2+} and Co^{2+} . The OH^- ions gradually released by the hydrolysis of hexamethylenetetramine (HMT) at high temperature facilitated the formation and uniform assembly of NiCo-layered double hydroxide (NiCo-LDH) nanoflakes on the entire surface of the Ni foam. In the second sulfurization process, the as-prepared NiCo-LDH nanoflakes on Ni foam were converted to ultrathin and porous NiCo₂S₄ nanoflakes with well-retained morphology. The optical images of initial Ni foam and the as-prepared products after two

sequential steps are also provided in **Figure 1b-d**, which suggest the high structural integrity and the color changes of the products with 3D-networked architectures.

Figure 2. (a-c) FESEM images of the NiCo-LDH/Ni foam, revealing that the ultrathin NiCo-LDH nanoflakes interconnected and intersected with each other to form a networked structure. The red arrows in (c) indicate the void spaces between the NiCo-LDH nanoflakes. (d-f) FESEM images and (g-i) TEM images of the 3D-networked NiCo₂S₄/Ni foam architecture. The morphology of NiCo₂S₄/Ni foam is similar to that of NiCo-LDH/Ni foam, but with numerous pores formed in the nanoflakes. (i) The HRTEM image of NiCo₂S₄/Ni foam indicates two lattice distances of 0.23 and 0.28 nm, corresponding to the (400) and (311) planes of NiCo₂S₄, respectively.

Field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were applied to examine the morphology and microstructure of the products. The typical FESEM image of bare Ni foam is presented in [Figure S1](#), which shows networked structure and clean surface. [Figure 2a-c](#) present the FESEM images of NiCo-LDH/Ni foam. It could be seen that the surface of Ni foam was evenly covered by NiCo-LDH nanoflakes ([Figure 2a](#)), and no exposed surface of Ni foam was observed. FESEM images with higher magnification ([Figure 2b,c](#)) revealed that densely-packed, highly-ordered NiCo-LDH nanoflakes were grown on Ni foam surface. The NiCo-LDH nanoflakes were interconnected and intersected with each other to form a 3D-networked structure with plenty of void spaces (marked by red arrows in [Figure 2c](#)). Further TEM characterization ([Figure S2](#)) reveals that the thickness of NiCo-LDH sheets is in the range of 3–5 nm. After the sulfurization process, the interconnected and intersected structure was well retained, as shown in the FESEM images of NiCo₂S₄/Ni foam ([Figure 2d-f](#)). Numerous pores were formed in the NiCo₂S₄ nanoflakes, which may be attributed to the formation of H₂S released from the decomposition of thioacetamide during the sulfurization step. [Figure 2g-i](#) present the TEM images of the NiCo₂S₄/Ni foam architecture. Wrinkled nanoflakes composed of agglomerative NiCo₂S₄ nanoparticles were observed ([Figure 2g](#)), and the fine particles of NiCo₂S₄ showed a size range of 10–15 nm ([Figure 2h](#)). The high-resolution TEM (HRTEM) image ([Figure 2i](#)) reveals two distinct lattice spacings of 0.23 and 0.28 nm corresponding to the (400) and (311) planes of NiCo₂S₄,

respectively, confirming the formation of NiCo_2S_4 nanocrystals. The 3D-networked and porous $\text{NiCo}_2\text{S}_4/\text{Ni}$ foam is reckoned to be very beneficial for electrocatalysis process because: (i) the ultrathin and porous NiCo_2S_4 nanoflakes provide a great number of exposed active sites for expediting the HER process, (ii) the abundant pores and void spaces between nanoflakes facilitate the diffusion and penetration of ions and electrons during the electrochemical reactions [49], and (iii) the Ni foam provides strong mechanical strength and excellent electrical conductivity for the transport of electrons [50].

Figure 3. (a) XRD pattern, high-resolution XPS spectrum of (b) Ni 2p region, (c) Co 2p region, and (d) S 2p region of the 3D-networked ultrathin $\text{NiCo}_2\text{S}_4/\text{Ni}$ foam architecture.

The as-prepared NiCo-LDH/Ni foam and $\text{NiCo}_2\text{S}_4/\text{Ni}$ foam products were

comprehensively characterized by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The XRD characterization (Figure S3) of NiCo-LDH/Ni foam indicates the successful preparation of NiCo-LDH (JCPDS card No. 33-0429, space group: $R^{**}(166)$, $a = 3.038$, $b = 3.038$, $c = 22.790$). Figure 3a shows the XRD pattern of 3D-networked ultrathin NiCo₂S₄/Ni foam product, except the strong diffraction peaks of Ni foam, all other diffraction peaks can be accordingly indexed to the cubic phase NiCo₂S₄ (JCPDS card No. 20-0782, space group: $Fd-3m(227)$, $a = 9.387$, $b = 9.387$, $c = 9.387$), confirming the formation of NiCo₂S₄ in the sulfurization process. The EDX spectrum of NiCo-LDH/Ni foam (Figure S4) demonstrates the co-existence of Ni, Co, and O elements; while in the EDX spectrum of NiCo₂S₄/Ni foam (Figure S5), the O element almost disappeared and the S element was detected instead. Moreover, further Raman characterizations (Figure S6 and S7) confirmed the preparation of NiCo-LDH and NiCo₂S₄, respectively. The survey XPS spectrum of NiCo₂S₄/Ni foam (Figure S8) is consistent with the above result of EDX. In the high-resolution XPS spectrum of Ni 2p region (Figure 3b), two spin-orbit doublets can be deconvoluted by using the Gaussian fitting method, which are attributed to the characteristics of Ni²⁺ and Ni³⁺, and two shake-up satellite peaks, respectively. The intense satellite peaks indicate that the majority of Ni element in the final product is Ni²⁺ cations [51], which is in good agreement with that of NiCo₂S₄. As regards the Co 2p region (Figure 3c), it shows two distinguished doublets located at a low energy band (Co 2p_{3/2}) and a high energy band (Co 2p_{1/2}), respectively. The difference of binding energy between the two

doublets is over 15 eV, suggesting the co-existence of Co^{2+} and Co^{3+} [52]. Figure 3d shows the core-level spectrum of S 2p region, and the binding energy of 161.8 eV is corresponding to S $2p_{3/2}$. In detail, the deconvoluted peak at 163.6 eV is originated from the sulfur-metal bonds, while the binding energy at 161.8 eV is attributed to the S^{2-} in low coordination at the surface [49,53,54]. The high energy of 168.7 eV is attributed to the S^{4+} species at the surface and/or edges of NiCo_2S_4 nanoflakes with highly oxidized state [53].

Figure 4. (a) LSV polarization curves and (b) the corresponding Tafel slopes of bare

Ni foam, NiCo-LDH/Ni foam and NiCo₂S₄/Ni foam electrodes. (c) The capacitive currents at 0.15 V as a function of scan rate for bare Ni foam, NiCo-LDH/Ni foam and NiCo₂S₄/Ni foam. (d) Chronopotentiometric measurements of long-term stability of bare Ni foam, NiCo-LDH/Ni foam and NiCo₂S₄/Ni foam at a current density of 50 mA/cm². (e) Chronopotentiometric measurements of long-term stability of NiCo₂S₄/Ni foam electrodes at various current densities (50, 100 and 200 mA/cm²). (f) Chronoamperometry curves of long-term stability of NiCo₂S₄/Ni foam electrodes under various overpotentials (0.2, 0.3 and 0.4 V).

The samples with unique compositions and 3D-networked structure were then investigated as free-standing electrodes for electrocatalytic HER in 1.0 M KOH electrolyte. The linear sweep voltammetry (LSV) measurements were performed to estimate the HER activity of NiCo₂S₄/Ni foam, and control experiments on NiCo-LDH/Ni foam and bare Ni foam were also conducted for comparison. As shown in Figure 4a, the LSV polarization curve of NiCo₂S₄/Ni foam exhibit an onset overpotential of only 17 mV, which is much smaller than those of NiCo-LDH/Ni foam (67 mV) and bare Ni foam (150 mV). This result suggests that the surface of NiCo₂S₄/Ni foam is much more active for HER. The overpotential at the cathodic current density of 10 mA/cm² (η_{10}) can be used to evaluate the HER activity of electrocatalysts [55]. The η_{10} of NiCo₂S₄/Ni foam was approaching 65 mV, significantly lower than those of NiCo-LDH/Ni foam (140 mV) and bare Ni foam (240 mV). Based on the LSV polarization curves in Figure 4a, corresponding Tafel

plots were calculated (Figure 4b). The Tafel plots of these catalysts fitted very well with the Tafel equation ($\eta = b \times \log j + a$, where j is the current density and b is the Tafel slope) at different overpotential ranges. The Tafel slopes of NiCo₂S₄/Ni foam, NiCo-LDH/Ni foam and bare Ni foam were *ca.* 84.5, 124.2 and 328.5 mV/dec, respectively. It proves that the 3D-networked NiCo₂S₄/Ni foam electrode exhibits the highest catalytic activity toward HER among all these samples. According to the previous reports [56–58], the mechanism of HER process in alkaline solution can be regarded as a combination of three basic steps: (1) the electroreduction of water molecules and hydrogen adsorption (Volmer reaction: $M + H_2O + e^- \rightarrow M-H_{ads} + OH^-$), (2) the electrochemical hydrogen desorption (Heyrovsky reaction: $M-H_{ads} + H_2O + e^- \rightarrow M + H_2 + OH^-$), and/or (3) the chemical desorption (Tafel reaction: $2M-H_{ads} \rightarrow 2M + H_2$), where M stands for an metal atom, and H_{ads} represents a H atom absorbed at an active site of the catalyst. The relative low Tafel slope indicates that the HER process with NiCo₂S₄/Ni foam as the electrocatalyst in alkaline solution is more facile. Moreover, compared to the previously-reported electrocatalysts for HER in alkaline solution (Table S1) [5,23,24,26–44], the NiCo₂S₄/Ni foam electrode in this work shows remarkable electrocatalytic activity.

It is known that the HER catalytic activity of electrocatalysts depends largely on the electrochemically-active surface area (ECSA) [59, 60]. To estimate the effective ECSA of these samples, we measured the electric double layer capacitance (EDLC) at the solid/liquid interface of all electrodes. The CV curves were collected in the region of 0.1–0.2 V, where the current responses should only be due to the

charging/discharging of electrical double layers on the surface of electrodes (Figure S9). Figure 4c shows the capacitive currents at 0.15 V as a function of scan rate for all samples, the EDLCs of NiCo₂S₄/Ni foam, NiCo-LDH/Ni foam and bare Ni foam were *ca.* 6.47, 2.37, and 0.79 mF/cm², respectively, showing that NiCo₂S₄/Ni foam has a much higher effective ECSA than other samples. It indicates that the much better HER catalytic activity of NiCo₂S₄/Ni foam may be associated with its higher effective surface area and larger amount of active sites.

The estimation of turnover frequency (TOF) for each active sites makes it possible to compare the catalytic activity of NiCo₂S₄/Ni foam with other reported HER catalysts. The number of the active sites was quantified following the previous literature [35,61]. Figure S10 shows the cyclic voltammetry (CV) curve at 50 mV s⁻¹ in phosphate buffered saline (PBS, pH = 7.0) solution. Assuming a one-electron process occurred for both reduction and oxidation, the upper limit of active sites could be calculated. Figure S11 displays the polarization curve at pH = 14.0, normalized by the active sites and expressed in terms of TOF. As the most active catalyst, Pt shows a TOF of 0.8 s⁻¹ at the overpotential of 0 mV [13], while NiCo₂S₄/Ni foam needs an overpotential of 35 mV. To achieve the TOF values of 4.0 and 7.0 s⁻¹, NiCo₂S₄/Ni foam needs overpotentials of 110 and 155 mV, respectively. The as-obtained TOF values are higher than those of other reported HER catalysts under the same overpotentials [35,62–65], further suggesting the remarkable HER catalytic activity of NiCo₂S₄/Ni foam.

We also applied electrochemical impedance spectroscopy (EIS) measurements to

further verify the conductivity advantages of NiCo₂S₄/Ni foam. As shown in [Figure S12](#), bare Ni foam exhibits the best ionic and Ohmic resistances due to its highly-conductive nature, and the NiCo₂S₄/Ni foam electrode displays much better impedance characteristics as compared with NiCo-LDH/Ni foam. The greatly enhanced ionic conductance and electronic conductivity of NiCo₂S₄/Ni foam electrode can be partly attributed to its unique compositions of bimetallic sulfide, of which the conductivity is much higher than transition-metal LDHs.

To evaluate the electrochemical stability of these electrodes, chronopotentiometric measurements of HER based on NiCo₂S₄/Ni foam, NiCo-LDH/Ni foam and bare Ni foam samples were carried out at a constant current density of 50 mA/cm², as shown in [Figure 4d](#). Remarkably, the NiCo₂S₄/Ni foam exhibited a overpotential slightly decreased from 178 mV to 165 mV after an long testing time of 100,000 seconds, indicating its increased catalytic activity toward HER. In contrast, under the same conditions, the NiCo-LDH/Ni foam showed an overpotential slightly increased to 300 mV, and the overpotential of bare Ni foam remained almost unchanged at a high value (400 mV). The galvanostatic measurements of NiCo₂S₄/Ni foam were also carried out at 100 and 200 mA/cm², respectively, as shown in [Figure 4e](#). It shows that the overpotential of NiCo₂S₄/Ni foam during long-term tests at each current density remained almost stable, demonstrating an ultra-high electrochemical stability compared to other existing electrocatalysts ([Table S1](#)) [[5,23,24,26-44](#)]. The long-duration chronoamperometric studies of NiCo₂S₄/Ni foam at 0.2, 0.3, and 0.4 V were performed, as shown in [Figure 4f](#). No obvious decrease in current density during

long-term tests under different overpotential values was observed, further suggesting the excellent stability of NiCo₂S₄/Ni foam. The surface morphology and microstructure of the NiCo₂S₄/Ni foam electrode was retained very well after long-duration test for 100,000 seconds (Figure S13), which confirms its high structural stability.

According to the above results, the NiCo₂S₄/Ni foam exhibits much higher electrocatalytic performance than NiCo-LDH/Ni foam, which may be attributed to the special compositions and unique nanostructure of NiCo₂S₄: (1) the first-row transition-metal dichalcogenides possess coordination structure similar to the active centers in effective hydrogenase [47], and the charged natures of metals and sulfur in metal sulfides are similar to those of hydride-acceptors and proton-acceptors in hydrogenase and its analogues [35,48]. (2) NiCo₂S₄ has much better electrical conductivity than NiCo-LDH (according to the EIS measurements in Figure S12), which can promote the transfer of electrons, and thus boosting the HER process. (3) The hierarchical and porous characteristics of NiCo₂S₄ nanoflakes (as compared in Figure 2c and 2f) can facilitate the penetration and migration of electrolyte, provide shorten pathways for electrons transfer, and exhibit much more exposed active sites for HER.

Figure 5. Photographs of NiCo₂S₄/Ni foam electrodes during testing at (a) initial state (without bending) and after bending for (b) 50, (c) 100 and (d) 200 times, respectively. (e) The LSV polarization curves of NiCo₂S₄/Ni foam electrode at initial state and after bending for different times. (f) Long-term chronopotentiometric measurements of NiCo₂S₄/Ni foam electrode at a current density of 50 mA/cm² after bending for 200 times.

To further identify its high flexibility and structural integrity inherited from bare Ni foam [66,67], we investigated the HER performance of NiCo₂S₄/Ni foam electrode after bending for different times (Figure 5a-d). As shown in Figure 5e, the electrochemical activity of NiCo₂S₄/Ni foam electrode remained almost unchanged at the initial state (without bending) or after bending for 50, 100 and 200 times. The long stability test of NiCo₂S₄/Ni foam electrode after bending for 200 times was conducted at a constant current density of 50 mA/cm² (Figure 5f). Compared with the stability

tests in Figure 4d, the NiCo₂S₄/Ni foam after bending for 200 times shows comparable long time cycling stability. In Figure 4d, the NiCo₂S₄/Ni foam exhibited an overpotential decreased slightly from 178 mV to 165 mV after a long testing time of 100,000 seconds at a constant current density of 50 mA/cm². However, when the NiCo₂S₄/Ni foam was tested as electrocatalysts for HER after bending for 200 times, it has already been fully activated in the electrolyte owing to the previous LSV tests at initial state and after bending for 50, 100 and 200 times (Figure 5e), therefore, the initial overpotential values in Figure 4d and Figure 5f are slightly different. During the long time stability tests after bending for 200 times, the overpotential of NiCo₂S₄/Ni foam increases from an initial value of 156 mV to 166 mV eventually. This corresponds to a potential increase of only 6.4% after a long period time (100,000 seconds), suggesting the excellent electrocatalytic stability of NiCo₂S₄/Ni foam and the great robustness against external intervention. The high flexibility and structural durability of electrode are expected to be very beneficial to various applications, such as flexible photoelectrodes for photoelectrocatalysis, flexible fuel cells, portable hydrogen fuel device and so on.

Conclusions

In summary, we have rationally designed and fabricated 3D-networked NiCo₂S₄/Ni foam electrode as a high-performance HER electrocatalyst through the sulfidation of NiCo-LDH/Ni foam. Electrochemical measurements prove that the ultrathin and porous NiCo₂S₄/Ni nanoflakes on Ni foam can provide a high number of exposed

active sites and facilitate the transport of electrons and ions. Therefore, the NiCo₂S₄/Ni foam electrode exhibits greatly enhanced catalytic performance in alkaline solution as compared with NiCo-LDH/Ni foam. Moreover, flexible NiCo₂S₄/Ni foam electrode shows almost no catalytic degradation after long-duration testing or after bending for many times. The high activity and stability make NiCo₂S₄/Ni foam a promising electrocatalyst, and the fabrication strategy can be extended to prepare other hierarchical and multicomponent compound electrodes for diverse electrochemical applications.

Acknowledgements

This work was supported by the National Thousand Young Talents Program of China, the Young Scientists Project of National Basic Research Program of China (973 Program No. 2015CB659300), the National Natural Science Foundation of China (NSFC Grant No. 21403105; No. 21573108), National Science Foundation for Post-doctoral Scientists of China (Grant No. 2015M581769, No. 2015M580413, No. 2015M580408), the Jiangsu Province Science Foundation for Youths (Project No. BK20150571; No. BK20150583), the Fundamental Research Funds for the Central Universities and a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2015.XX.XXX>.

References

- [1] J. A. Turner, *Science* 305 (2004) 972–974.
- [2] S. Han, Y. L. Feng, F. Zhang, C. Q. Yang, Z. Q. Yao, W. X. Zhao, F. Qiu, L. Y. Yang, Y. F. Yao, X. D. Zhuang, X. L. Feng, *Adv. Funct. Mater.* 25 (2015) 3899–3906.
- [3] M. A. Rosen and D. S. Scott, *Int. J. Hydrogen Energy* 23 (1998) 653–659.
- [4] D. Trommer, F. Noembrini, A. Fasciana, D. Rodriguez, A. Morales, M. Romero and A. Steinfeid, *Int. J. Hydrogen Energy* 30 (2005) 605–618.
- [5] T. W. Lin, C. J. Liu and C. S. Dai, *Appl. Catal. B* 154 (2014) 213–220.
- [6] T. R. Cook, D. K. Dogutan, S. Y. Reece, Y. Surendranath, T. S. Teets, D. G. Nocera, *Chem. Rev.* 110 (2010) 6474–6502.
- [7] M. Dresselhaus, I. Thomas, *Nature* 414 (2001) 332–337.
- [8] A. J. Bard, M. A. Fox, *Acc. Chem. Res.* 28 (1995) 141–145.
- [9] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* 110 (2010) 6446–6473.
- [10] D. Merki, X. Hu, *Energy Environ. Sci.* 4 (2011) 3878–3888.
- [11] J. Greeley, T. F. Jaramillo, J. Bonde, I. B. Chorkendorff, J. K. Nørskov, *Nat. Mater.* 5 (2006) 909–913.
- [12] Q. Yuan, Z. Y. Zhou, J. Zhuang, X. Wang, *Chem. Commun.* 46 (2010)

1491–1493.

- [13] T. F. Jaramillo, K. P. Jorgensen, J. Bonde, J. H. Nielsen, S. Horch, I. Chorkendorff, *Science* 317 (2007) 100–102.
- [14] H. Tang, K. P. Dou, C. C. Kaun, Q. Kuang, S. H. Yang, *J. Mater. Chem. A* 2 (2014) 360–364.
- [15] W. F. Chen, K. Sasaki, C. Ma, A. I. Frenkel, N. Marinkovic, J. T. Muckerman, Y. M. Zhu and R. R. Adzic, *Angew. Chem., Int. Ed.* 51 (2012) 6131–6135.
- [16] M. Nagai, Y. Goto, O. Uchino and S. Omi, *Catal. Today* 45 (1998) 335–340.
- [17] D. V. Esposito, S. T. Hunt, A. L. Stottlemeyer, K. D. Dobson, B. E. McCandless, R. W. Birkmire, J. G. G. Chen, *Angew. Chem., Int. Ed.* 49 (2010) 9859–9862.
- [18] Y. Liu, T. G. Kelly, J. G. G. Chen, W. E. Mustain, *ACS Catal.* 3 (2013) 1184–1194.
- [19] P. Xiao, M. A. Sk, L. Thia, X. M. Ge, R. J. Lim, J. Y. Wang, K. H. Lim and X. Wang, *Energy Environ. Sci.* 7 (2014) 2624–2629.
- [20] E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak, *J. Am. Chem. Soc.* 135 (2013) 9267–9270.
- [21] X. L. Zheng, J. B. Xu, K. Yan, H. Wang, Z. L. Wang, S. H. Yang, *Chem. Mater.* 26 (2014) 2344–2353.
- [22] Z. C. Xing, Q. Liu, A. M. Arisi, X. P. Sun, *Adv. Mater.* 26 (2014) 5702–5707.
- [23] K. Xiong, L. Li, L. Zhang, W. Ding, L. S. Peng, Y. Wang, S. G. Chen, S. Y. Tan, Z. D. Wei, *J. Mater. Chem. A* 3 (2015) 1863–1867.
- [24] X. M. Geng, W. Wu, N. Li, W. W. Sun, J. Armstrong, A. Al-hilo, M. Brozak, J. B.

- Cui, T. Chen, *Adv. Funct. Mater.* 24 (2014) 6123–6129.
- [25] D. S. Kong, H. T. Wang, Z. Y. Lu, Y. Cui, *J. Am. Chem. Soc.* 136 (2014) 4897–4900.
- [26] H. F. Liang, L. S. Li, F. Meng, L. N. Dang, J. Q. Zhuo, A. Forticaux, Z. C. Wang, S. Jin, *Chem. Mater.* 27 (2015) 5702–5711.
- [27] Y. Zheng, Y. Jiao, L. H. Li, T. Xing, Y. Chen, M. Jaroniec, S. Z. Qiao, *ACS Nano* 8 (2014) 5290–5296.
- [28] M. Ledendecker, G. Clavel, M. Antonietti, M. Shalom, *Adv. Funct. Mater.* 25 (2015) 393–399.
- [29] H. Vrubel, X. L. Hu, *Angew. Chem. Int. Ed.* 124 (2012) 12875–12878.
- [30] L. G. Feng, H. Vrubel, M. Bensimon, X. L. Hu, *Phys. Chem. Chem. Phys.* 16 (2014) 5917–5921.
- [31] C. Tang, N. Y. Cheng, Z. H. Pu, W. Xing, X. P. Sun, *Angew. Chem. Int. Ed.* 54 (2015) 9351–9355.
- [32] C. G. Morales-Guio, L. Liardet, M. T. Mayer, S. D. Tilley, M. Gratzel, X. L. Hu, *Angew. Chem. Int. Ed.* 54 (2015) 664–667.
- [33] H. C. Zhang, Y. J. Li, G. X. Zhang, P. B. Wan, T. H. Xu, X. C. Wu, X. M. Sun, *Electrochim. Acta* 148 (2014) 170–178.
- [34] L. L. Feng, G. T. Yu, Y. Y. Wu, G. D. Li, H. Li, Y. H. Sun, T. Asefa, W. Chen, X. X. Zou, *J. Am. Chem. Soc.* 137 (2015) 14023–14026.
- [35] J. Q. Tian, Q. Liu, A. M. Asiri, X. P. Sun, *J. Am. Chem. Soc.* 136 (2014) 7587–7590.

- [36] D. N. Liu, Q. Lu, Y. L. Luo, X. P. Sun, A. M. Asiri, *Nanoscale* 7 (2015) 15122–15126.
- [37] X. J. Fan, H. Q. Zhou, X. Guo, *ACS Nano* 9 (2015) 5125–5134.
- [38] L. M. Lang, Y. Shi, J. Wang, F. B. Wang, X. H. Xia, *ACS Appl. Mater. Interfaces* 7 (2015) 9098–9102.
- [39] J. L. Shi, Z. H. Pu, Q. Liu, A. M. Asiri, J. M. Hu, X. P. Sun, *Electrochim. Acta* 154 (2015) 345–351.
- [40] J. Wang, H. X. Zhong, Z. L. Wang, F. L. Meng, X. B. Zhang, *ACS Nano* 10 (2016) 2342–2348.
- [41] Y. Feng, X. Y. Yu, U. Paik, *Chem. Commun.* 52 (2016) 1633–1636.
- [42] X. Zhang, H. M. Xu, X. X. Li, Y. Y. Li, T. B. Yang, Y. Y. Liang, *ACS Catal.* 6 (2016) 580–588.
- [43] J. M. McEnaney, T. L. Soucy, J. M. Hodges, J. F. Callejas, J. S. Mondschein, R. E. Schaal, *J. Mater. Chem. A* 4 (2016) 3077–3081.
- [44] H. B. Zhang, Z. J. Ma, J. J. Duan, H. M. Liu, G. G. Liu, T. Wang, K. Chang, M. Li, L. Shi, X. G. Meng, K. C. Wu, J. H. Ye, *ACS Nano* 10 (2016) 684–694.
- [45] M. F. Shao, F. Y. Ning, M. Wei, D. G. Evans, X. Duan, *Adv. Funct. Mater.* 24 (2014) 580–586.
- [46] W. Ma, R. Z. Ma, C. X. Wang, J. B. Liang, X. H. Liu, K. C. Zhou, T. Sasaki, *ACS Nano* 9 (2015) 1977–1984.
- [47] D. S. Kong, J. J. Cha, H. T. Wang, H. R. Lee, Y. Cui, *Energy Environ. Sci.* 6 (2013) 3553–3558.

[48] Y. G. Li, H. L. Wang, L. M. Xie, Y. Y. Liang, G. S. Hong, H. J. Dai, *J. Am. Chem. Soc.* 133 (2011) 7296–7299.

[49] L. Yu, L. Zhang, H. B. Wu, X. W. Lou, *Angew. Chem. Int. Ed.* 53 (2014) 3711–3714.

[50] S. K. Lee, M. J. Song, J. H. Kim, T. S. Kan, Y. K. Lim, J. P. Ahn, D. S. Lim, *NPG Asia Mater.* 6 (2014) e115.

[51] X. H. Xiong, G. Waller, D. Ding, D. C. Chen, B. Rainwater, B. Zhao, Z. X. Wang, M. L. Liu, *Nano Energy* 16 (2015) 71–80.

[52] J. Xu, P. Gao, T. S. Zhao, *Energy Environ. Sci.* 5 (2012) 5333–5339.

[53] W. Chen, C. Xia, H. N. Alshareef, *ACS Nano* 8 (2014) 9531–9541.

[54] Q. Liu, J. T. Jin, J. Y. Zhang, *ACS Appl. Mater. Interfaces* 5 (2013) 5002–5008.

[55] Z. P. Huang, Z. B. Chen, Z. Z. Chen, C. C. Lv, C. Zhang, *ACS Nano* 8 (2014) 8121–8129.

[56] N. Krstajic, M. Popovic, B. Grgur, M. Vojnovic, D. Sepa, *J. Electroanal. Chem.* 512 (2001) 16–26.

[57] B. M. Jovic, V. D. Jovic, U. C. Lacnjevac, L. Gajic-krstajic, N. V. Krstajic, *Int. J. Hydrogen Energy* 40 (2015) 10480–10490.

[58] F. Safizadeh, E. Ghali, G. Houlachi, *Int. J. Hydrogen Energy* 40 (2015) 256–274.

[59] C. C. L. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, *J. Am. Chem. Soc.* 135 (2013) 16977–16987.

[60] J. Q. Tian, Q. Liu, N. Y. Cheng, A. M. Asiri, X. P. Sun, *Angew. Chem. Int. Ed.* 53 (2014) 9577–9581.

- [61] D. Merik, S. Fierro, H. Vrubel, X. Hu, Chem. Sci. 2 (2011) 1262–1267.
- [62] Z. B. Chen, D. Cumminst, B. N. Reineche, E. Clark, M. K. Sunkara, T. F. Jaramillo, J. Am. Chem. Soc. 11 (2011) 4168–4175.
- [63] J. R. McKone, B. F. Sadtler, C. A. Werlang, N. S. Lewis, H. B. Gray, ACS Catal. 3 (2013) 166–169.
- [64] P. Xiao, W. Chen, X. Wang, Adv. Energy Mater. 5 (2015) 1500985.
- [65] T. R. Hellstern, J. D. Benck, J. Kibsgaard, C. Hahn, T. F. Jaramillo, Adv. Energy Mater. 6 (2016) 1501758.
- [66] Q. F. Wang, X. F. Wang, B. Liu, G. Yu, X. J. Hou, D. Chen, G. Z. Shen, J. Mater. Chem. A 1 (2013) 2468–2473.
- [67] H. Wang, G. Wang, Y. Liang, F. Qian, Y. Song, X. Lu, S. Chen, Y. Tong, Y. Li, Nanoscale 7 (2013) 10283–10290.

Graphic Abstract