



International Journal of Hydrogen Energy

Volume 102, 10 February 2025, Pages 909-917



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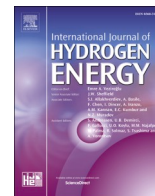
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Atomically doped carbon on highly porous nickel sulfide for efficient hydrogen evolution reaction

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ARTICLE INFO

Handling Editor: Dr J Ortiz

Keywords:

Hydrogen evolution reaction

Nickel sulfide

Carbon doping

Porous structure

ABSTRACT

The development of efficient hydrogen evolution reaction (HER) has been directed toward high-performance of non-noble electrocatalysts for sustainable future energy supply. Herein, we introduce a novel one-pot synthesis strategy to fabricate a carbon-doped porous Ni_3S_2 ($\text{Ni}_3\text{S}_2\text{-C}$) directly from Ni foam via a straightforward hydrothermal reaction. Highly porous grass-like structured $\text{Ni}_3\text{S}_2\text{-C}$ electrocatalysts through one-pot synthesis display enhanced charge mobility, more active sites of Ni^{3+} and low Gibbs free energy on their surface which is required for high performance HER. As a result, the $\text{Ni}_3\text{S}_2\text{-C}$ electrocatalyst exhibits excellent catalytic activity with onset potential of -14 mV, low overpotential of -70 mV at 10 mA/cm^2 , small Tafel slope of 76 mV/dec with remarkable long-term stability for 77 h and durable catalytic properties after 1000 cycles. This work highlights a cost-effective and scalable approach to develop highly efficient HER electrocatalysts, offering significant potential for future energy conversion systems.

1. Introduction

The current climate and environmental issues have prompted a strong interest in identifying various renewable and sustainable energy sources to replace traditional fossil fuels for energy conversion and storage [1–3]. For the generation of hydrogen, electrolytic water splitting with sustainable energy input, such as renewable solar and wind energy, has recently emerged as a potential technique [4,5]. Effective electrocatalysts are required for efficient water splitting because the electrochemical processes of water reduction and hydrogen evolution alone are insufficient to achieve high-energy utilization efficiency. Although Pt-based materials are widely recognized as the most advanced electrocatalysts for the hydrogen evolution reaction (HER), large-scale hydrogen production is substantially impeded by the high cost and scarcity of Pt [6]. In addition, the acidic electrolyte contaminates the generated hydrogen gas as well as causes severe chemical corrosion of the Pt electrode during electrocatalytic process [7,8]. Therefore, highly effective and stable electrocatalysts are required based on low-cost and earth-abundant alternative metal or metal compound catalysts for HER [9,10].

Various non-noble metal-based electrocatalysts like transition metal compounds have been proposed as potential HER electrocatalysts

because of their excellent electrocatalytic activity and abundant reserves, including metal sulfides, nitrides, phosphides, and carbon-based materials [11–15]. In particular, the nickel derivatives have specific active sites such as Ni^{3+} , which demonstrate an effective electrocatalytic performance as a result of their specific electron configuration [16]. Among these nickel derivatives, Ni_3S_2 , a transition metal sulfide, is one of the promising HER catalysts because of its excellent electrical conductivity, low cost, and ease of preparation. However, Ni_3S_2 exhibits significantly lower intrinsic activity for HER with its suboptimal surface electronic structure compared to that of Pt metal [17–20]. So far, some strategies have been studied to enhance the surface electronic structure by introducing metallic or non-metallic dopants such as copper, zinc, iron, vanadium, phosphorus, and nitrogen into Ni_3S_2 [21–29]. Meanwhile, C doping is a relatively unexplored strategy, despite its potential to modify the surface electronic structure and improve the intrinsic activity of Ni_3S_2 for HER. Incorporating carbon atoms could introduce new active sites or alter the electronic properties in a way that enhances catalytic performance, making it a promising avenue for future research [30,31]. Further studies focusing on C doping are likely to provide valuable insights into optimizing Ni_3S_2 as an effective and efficient HER electrocatalyst.

In another point of view, an optimal structure of electrocatalyst with

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<https://doi.org/10.1016/j.ijhydene.2024.12.480>

Received 24 June 2024; Received in revised form 19 November 2024; Accepted 29 December 2024

Available online 12 January 2025

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a rationally designed reaction interface is essential, to further promote the catalytic reaction kinetics and improve the energy efficiency for hydrogen generation. Previously synthesized nanoarchitectures, such as nanorods, nanosheets, nanowires, and nanoparticles have demonstrated the superiority of well-designed configurations [32–35]. Moreover, significant breakthroughs in nanostructure synthesis and stabilization of these electrocatalysts on carbon substrates have revealed even more active areas while improving electrical conductivity [36,37]. Nonetheless, the complexity and high cost of nanomaterials in the manufacturing process remain challenge for large area application. Porous nanostructured electrodes with intrinsically effective strategies, on the other hand, feature increased catalytic active sites, charge transfer areas, and gas release through 3D architecture [38]. Furthermore, porous foams can be considered a promising alternative nanostructure template due to its low manufacturing price, high conductivity, and rich macro-porosity regarding the fabrication of electrocatalysts for large area application [39].

In this study, a highly porous, carbon-doped Ni_3S_2 foam is proposed, which exhibits excellent HER performance, including high hydrogen adsorption and desorption ability, high electrical conductivity, large surface area, and high durability in alkaline media. The synthesized $\text{Ni}_3\text{S}_2\text{-C}$ electrocatalyst shows a low overpotential of 70 mV at 10 mA/cm² with a Tafel slope of 76 mV/dec, which is comparable to the benchmark Pt/C catalyst. Additionally, the $\text{Ni}_3\text{S}_2\text{-C}$ electrode displayed a higher density of Ni^{3+} chemical state, which significantly promoted HER performance. Comprehensive theoretical study on the HER performance of $\text{Ni}_3\text{S}_{2-x}\text{C}_x$ is also conducted using density functional theory (DFT), including the electronic properties of low-index surfaces with various terminations. The results support that $\text{Ni}_3\text{S}_2\text{-C}$ improves the electrocatalytic efficiency because of the low Gibbs free energy of its surface.

2. Experimental

2.1. Chemicals and materials

Sodium sulfide hydrate ($\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$), potassium hydroxide (KOH), Acetone ($\text{C}_3\text{H}_6\text{O}$, >99%) and Ethanol ($\text{C}_2\text{H}_6\text{O}$, >99%) were purchased from Thermofisher Scientific. The Oxalic acid dihydrate ($\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$) and Hydrochloric acid (HCl, 36.5–38.0%) were purchased from Sigma-Aldrich. A piece of nickel foam (2 mm of thickness, bulk density of 450 g/cm³, Goodfellow Co. Ltd, England) was used as a substrate. Before fabrication, the piece of nickel foam was immersed into 6 M HCl solution and stirred for 30 min to remove oxide layer on nickel foam substrate. After then, the nickel foam was thoroughly washed with deionized water several times and dried at 80 °C.

2.2. Fabrication of porous Ni_3S_2 and $\text{Ni}_3\text{S}_2\text{-C}$ electrocatalysts

The 70 mL of deionized water that contains 1 M Na_2S was transferred into a Teflon-lined stainless-steel autoclave, and a piece of cleaned nickel foam was placed into. Next, the autoclave is sealed and kept at 170 °C for 10 h. Then, the nickel foam is cooled down to room temperature, followed by washing with deionized water repeatedly and drying at 70 °C; the resulting material was denoted as Ni_3S_2 . The $\text{Ni}_3\text{S}_2\text{-C}$ catalyst is fabricated by reaction with 1 M oxalic acid in 9:1 v/v % of deionized water and ethanol at 45 °C for 2 h. After the reaction a part of the Ni_3S_2 was changed to the $\text{Ni}_3\text{S}_2\text{-NiC}_2\text{O}_4$ foam, and it was washed several times with deionized water and dried at 70 °C for 2 h. The $\text{Ni}_3\text{S}_2\text{-NiC}_2\text{O}_4$ foam was heated to 400 °C at heating rate of 5 °C/min in Ar atmosphere and annealed at 400 °C for 2 h; the resulting material was denoted as $\text{Ni}_3\text{S}_2\text{-C}$ catalyst.

2.3. Structural characterization

X-ray diffraction (XRD) patterns of Ni, Ni_3S_2 and porous $\text{Ni}_3\text{S}_2\text{-C}$

catalysts were obtained using X'Pert PRO MPD (PANalytical, NLD) with Cu K α radiation in the range of $2\theta = 5^\circ\text{--}80^\circ$ at a scanning rate of $5^\circ/\text{min}$, and the patterns were indexed with standard data (JCPDS file. 44–1418 of Ni_3S_2). The microstructure of Ni, Ni_3S_2 and $\text{Ni}_3\text{S}_2\text{-C}$ was investigated using field emission scanning electron microscopy (FE-SEM) images using an NNS-40 microscope (FEI, US) operating at 30 kV. Transmission electron microscopy (TEM) with electron energy loss spectroscopy (EELS) and high-angle annular dark-field (HAADF) images were obtained on TEM (JEM-ARM200F, JEOL Ltd, Japan) at an acceleration voltage of 200 kV. The chemical state and surface species of Ni, Ni_3S_2 and $\text{Ni}_3\text{S}_2\text{-C}$ were analyzed using X-ray photoelectron spectroscopy (XPS) by ESCALAB 250Xi. The specific surface area of as-synthesized $\text{Ni}_3\text{S}_2\text{-C}$ was analyzed with a Brunauer-Emmett-Teller (BET) surface area and pore size analyzer (ASAP 2020, Micromeritics Co.).

2.4. Electrochemical measurement

The electrochemical measurements were performed with an Ivium-n-Stat electrochemical analyzer at 25 °C in 1 M KOH solution. As-prepared Ni, Ni_3S_2 and $\text{Ni}_3\text{S}_2\text{-C}$ catalysts were directly used as the working electrode by cutting with a size of $W30 \times L10$ mm, which the mass was measured as approximately 0.1 g. The saturated calomel electrode and net-type of Pt was used as the reference electrode and the counter electrode, respectively. The Pt/C electrode was prepared by dispersion of Pt/C powder into ethanol and 10 μL of 5 wt% Nafion solution after then the mixture was sonicated for 1 h. Linear sweep voltammetry (LSV) with a scan rate of 5 mV/s was used to record polarization curves. Electrochemical impedance spectroscopy (EIS) was monitored at an overpotential of 200 mV in a frequency range of 0.01–10 kHz with an amplitude of 5 mV. All used potentials were converted to the reversible hydrogen electrode (RHE) based on equation $E(\text{RHE}) = E(\text{SCE}) + (0.242 + 0.059 \text{ pH}) \text{ V}$.

2.5. Computational details

All density functional theory (DFT) calculations were carried out by utilizing the ORCA package [40,41]. The B3LYP global hybrid functional was used in combination with Ahlrichs family def2-TZVP basis set. The RIJCOSX approximation with tight self-consistent field convergence was employed for reducing computational costs. The crystal plane of Ni_3S_2 was modeled as (001) facet. Visualization of the optimized atomic structures was made by using VESTA code [42]. The projected density of states (DOS) and d-band center values were generated by Multiwfn code [43]. The free energy of hydrogen adsorption (ΔG_{H^*}) was calculated as follows:

$$\Delta G_{\text{H}^*} = \Delta E_{\text{H}^*} + \Delta \text{ZPE} - T\Delta S \quad (1)$$

where, ΔE_{H^*} , ΔZPE , T and ΔS represent the hydrogen adsorption energy, zero-point energy difference between the adsorbed and gaseous hydrogen, temperature, and entropy change of hydrogen adsorption, respectively [44]. In this work, the hydrogen adsorption energy (ΔE_{H^*}) on Ni_3S_2 was calculated as follows:

$$\Delta E_{\text{H}^*} = E_{\text{Ni}_3\text{S}_2+\text{H}} - E_{\text{Ni}_3\text{S}_2} - 1/2 E_{\text{H}_2} \quad (2)$$

where, $E_{\text{Ni}_3\text{S}_2+\text{H}}$, $E_{\text{Ni}_3\text{S}_2}$ and E_{H_2} represent the total energies of hydrogen adsorbed Ni_3S_2 , clean Ni_3S_2 , and isolated H_2 molecule, respectively. The entropy change ΔS was calculated by using equation $\Delta S = S_{\text{H}} - 1/2 S_{\text{H}_2} \approx -S_{\text{H}_2}$, since the vibrational entropy contribution of the hydrogen adsorbed state is very small [20]. The reported value of $T\Delta S_{\text{H}^*}$ is -0.204 eV. The zero-point energy difference was also calculated as $\Delta \text{ZPE} = \text{ZPE}_{\text{H}} - 1/2 \text{ZPE}_{\text{H}_2}$ [45].

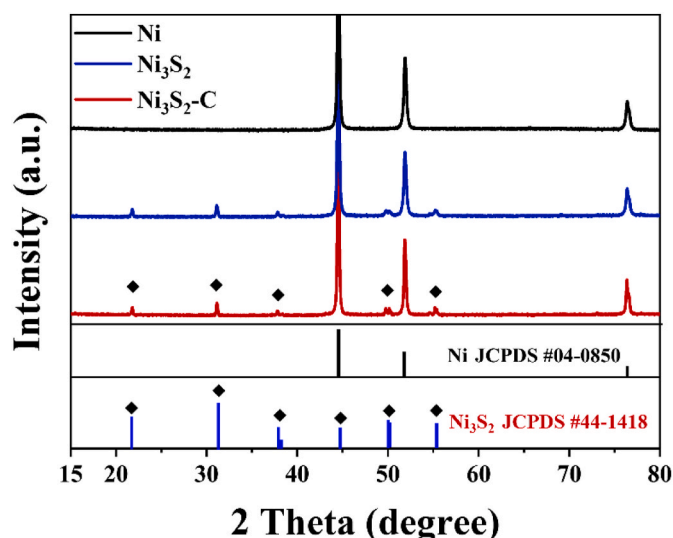


Fig. 1. The XRD patterns of Ni, Ni_3S_2 , and highly porous $\text{Ni}_3\text{S}_2\text{-C}$ electrocatalysts correspond to JCPDS #44–1418.

3. Results and discussion

The highly porous $\text{Ni}_3\text{S}_2\text{-C}$ electrocatalyst was characterized by XRD with respect to the corresponding electrocatalysts (Ni and Ni_3S_2) (Fig. 1). For the pristine Ni foam, the XRD pattern indicates three crystalline peaks, at $2\theta = 44.6^\circ$, 51.9° , and 76.3° . After the hydrothermal reaction, the Ni foam successfully changed to Ni_3S_2 foam with five new peaks at $2\theta = 21.1^\circ$, 31.1° , 38.2° , 50.1° , and 55.1° , which are in good agreement with the heazlewoodite phase of Ni_3S_2 (JCPDS no.

44–1418) [46]. In Fig. A.1, the diffraction peak at 18.9° corresponding to the (202) crystal plane of NiC_2O_4 (JCPDS no. 25–0581), had emerged with Ni_3S_2 peaks indicating that Ni_3S_2 was partially transformed to NiC_2O_4 after the reaction with oxalic acid. However, this peak was not observed after annealing at 400°C implying that NiC_2O_4 was successfully decomposed. In addition, the main Ni peaks corresponding to (111) and (200) as shown in Fig. A.2 for the $\text{Ni}_3\text{S}_2\text{-C}$ electrocatalyst were slightly shifted to higher angles compared to those of the Ni_3S_2 foam, indicating a lattice contraction. The peak shifts can be ascribed to the successful incorporation of carbon atoms into the Ni_3S_2 lattice, leading to a reduction in lattice parameters due to the smaller atomic radius of carbon compared to sulfur [47,48]. As shown in Fig. A.3, the XRD pattern of electrocatalyst did not include the NiO peaks at 37.2° and 43.4° , implying that the surface of Ni_3S_2 foam is transformed to $\text{Ni}_3\text{S}_2\text{-C}$ when treated at 400°C , rather than NiO although it is exposed to oxygen species [49,50].

Fig. 2(a–f) and Fig. A.4 show the morphological changes of Ni foam to the nanostructures of the $\text{Ni}_3\text{S}_2\text{-C}$ after sulfurization and carbon doping of our process, respectively. This is attributed to the fact that the nickel ion form a nickel oxalate complex thorough the self-complex formation mechanism in oxalic acid involving H^+ and OH^- ions; this allows for fabrication of a porous structure with an increased amount of nickel oxalate complex [51]. Thus, the surface of the $\text{Ni}_3\text{S}_2\text{-C}$ electrocatalyst was fully covered by grass-like nanorods/nanowires to form a 3D hierarchical structure, which is expected to effectively facilitate rapid electron transport and proton accessibility to the surface of the active materials.

TEM equipped with EELS analysis exhibits the cross-sectional microstructure and elemental distribution of the as-prepared $\text{Ni}_3\text{S}_2\text{-C}$ electrocatalyst (Fig. 3 and Fig. A.5). $\text{Ni}_3\text{S}_2\text{-C}$ completely covered on the surface of Ni foam which was sulfurization of the Ni surface under considerable amount of exposure (Fig. 3(a)). The observed voids are

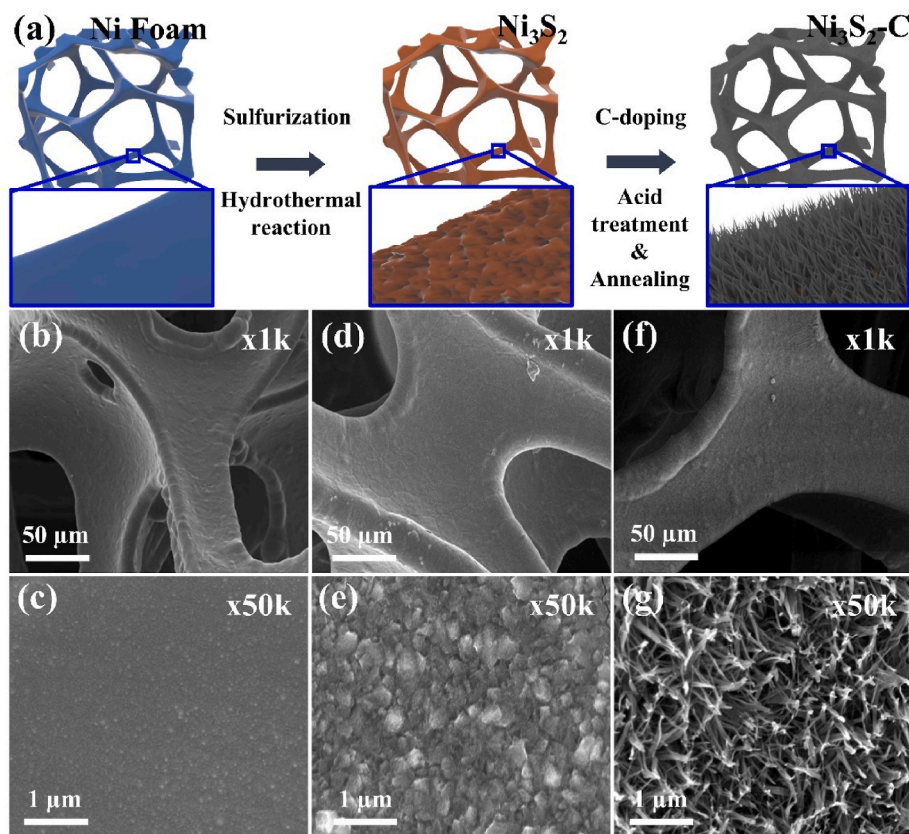


Fig. 2. (a) Schematic process for manufacturing $\text{Ni}_3\text{S}_2\text{-C}$. SEM images of (a, b) Ni, (c, d) Ni_3S_2 , and (e, f) $\text{Ni}_3\text{S}_2\text{-C}$ electrocatalysts at low and high magnifications. The morphology of $\text{Ni}_3\text{S}_2\text{-C}$ changed to a highly porous surface after sulfurization and carbon doping in Ni foam.

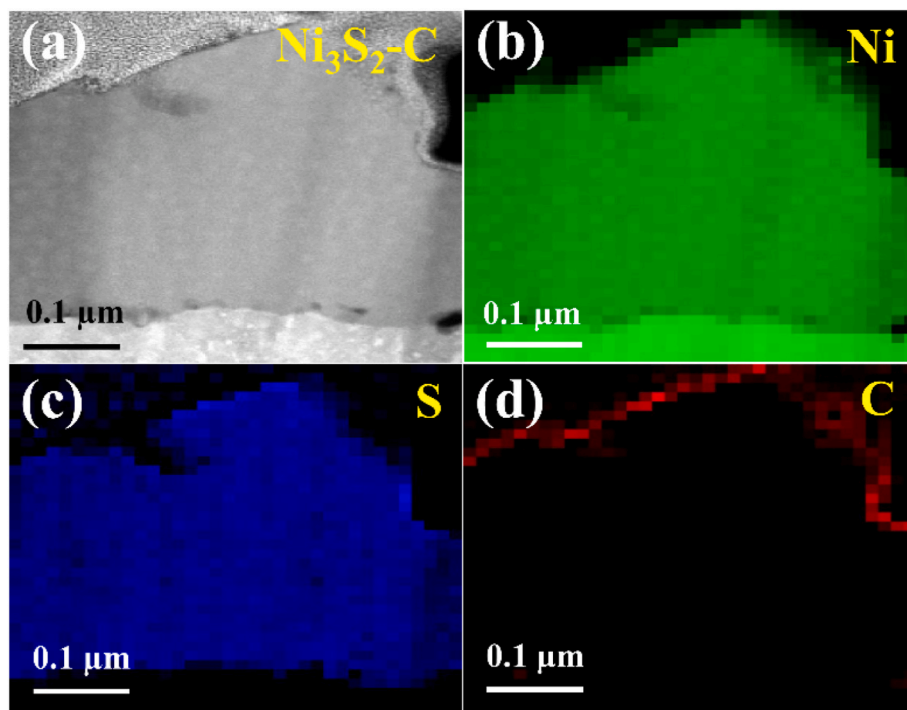


Fig. 3. (a) The cross-sectional TEM images of $\text{Ni}_3\text{S}_2\text{-C}$, and (b–d) EELS analysis of Ni, S, and C elements, respectively.

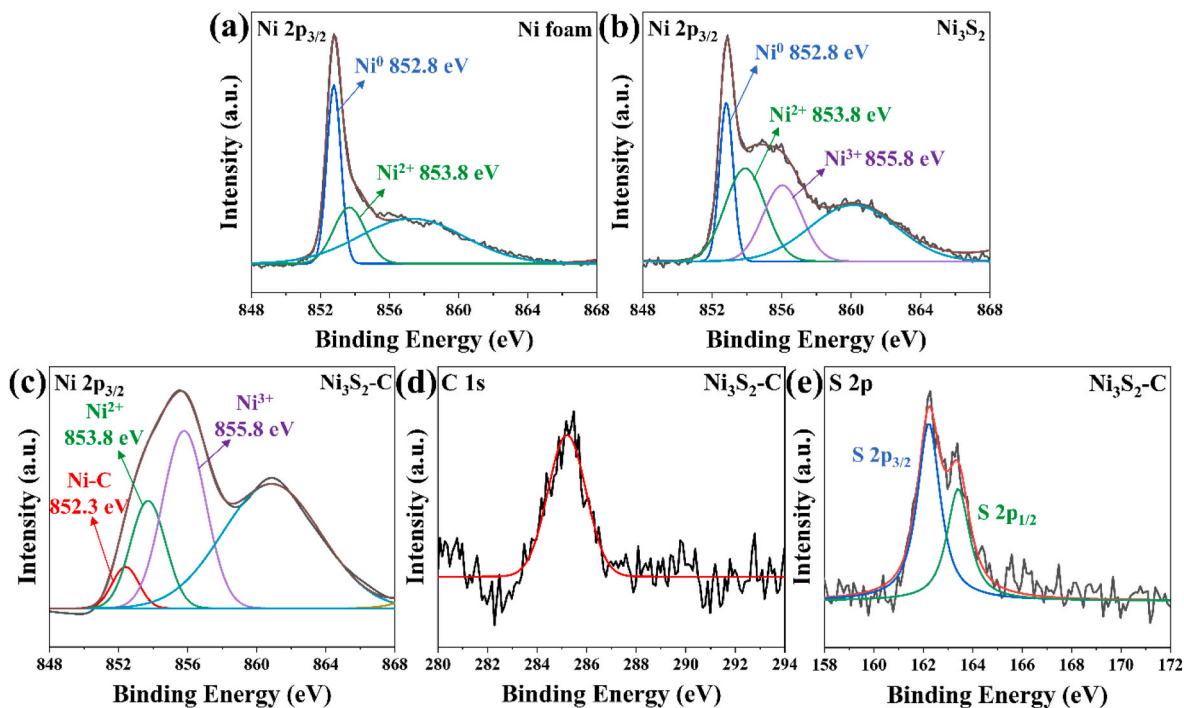


Fig. 4. XPS spectra showing the Ni 2p peak for (a) Ni, (b) Ni_3S_2 , and (c) $\text{Ni}_3\text{S}_2\text{-C}$, as well as (d) the C 1s and (e) S 2p peak of $\text{Ni}_3\text{S}_2\text{-C}$ electrocatalyst.

generated by ion-beam bombardment during sample preparation. STEM-EELS mapping of $\text{Ni}_3\text{S}_2\text{-C}$ clearly reflects the uniform distribution of the elemental Ni (Fig. 3(b)), S (Fig. 3(c)) and C (Fig. 3(d)), respectively. Note that carbon is distributed along the edge of $\text{Ni}_3\text{S}_2\text{-C}$ surface with the thickness of approximately 11 nm. This indicates that carbon permeated into the surface of Ni_3S_2 and substituted the S, thus the foam was transformed to $\text{Ni}_3\text{S}_2\text{-x-C}_x$. HAADF TEM image with EDX elemental mapping also supports the integration of carbon atoms into the Ni_3S_2

lattice, showing a homogeneous distribution of carbon within the Ni_3S_2 (Fig. A.6). Therefore, the cross-sectional view of STEM analysis and XRD prove the formation of $\text{Ni}_3\text{S}_2\text{-C}$ on Ni foam through self-complex formation mechanism with highly porous grass-like morphologies.

X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical structure of Ni, Ni_3S_2 , and $\text{Ni}_3\text{S}_2\text{-C}$ electrocatalysts. In the case of bare Ni foam, the Ni 2p_{3/2} peaks were located at 852.8 eV (Ni^0) and 853.8 eV (Ni^{2+}). The chemical state of Ni^{2+} is attributed to the native

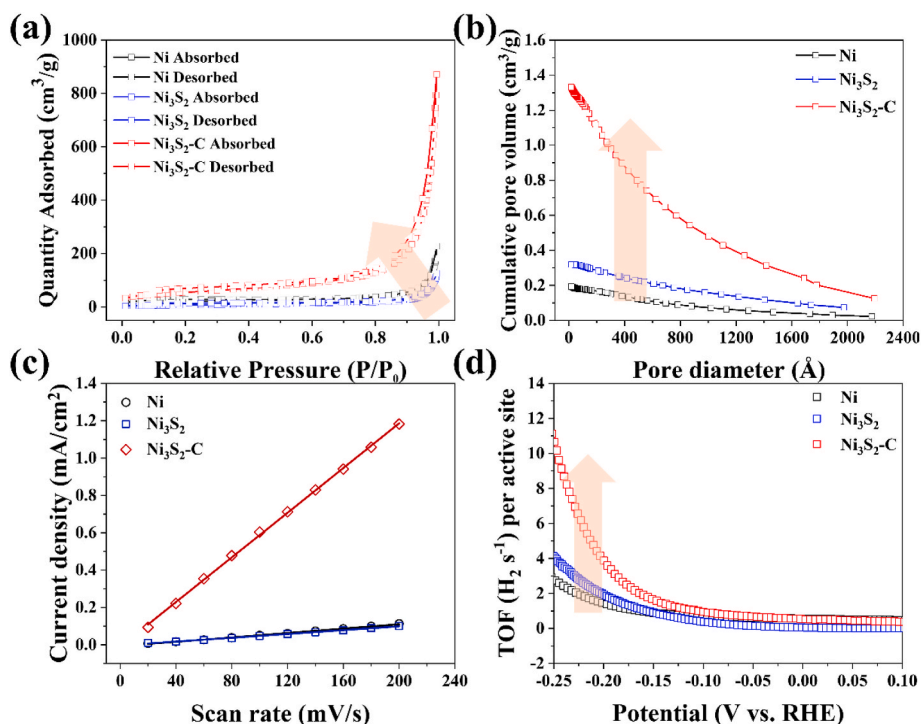


Fig. 5. (a) Nitrogen gas adsorption-desorption isotherms and (b) Cumulative pore volumes of Ni, Ni₃S₂ and Ni₃S₂-C electrocatalysts, respectively. (c) The linear slope, equivalent to twice the double-layer capacitance, C_{dl} , was used to represent the ECSA. (d) TOF value of Ni, Ni₃S₂ and Ni₃S₂-C electrocatalysts, respectively. Measured capacitive currents plotted of Ni, Ni₃S₂, and Ni₃S₂-C electrocatalysts as a function of scan rate between 20 mV/s to 200 mV/s.

oxygen on the surface of Ni foam in Fig. 4(a). The sulfurized Ni₃S₂ electrocatalyst contained the 855.8 eV peak of Ni³⁺ as shown in Fig. 4 (b), which corresponds to the inherent defect sites of nickel, as reported in a previous work [52]. Moreover, Fig. A.7 and Fig. 4(e) exhibit two main characteristic peaks at 162.2 and 163.2 eV, corresponding to the S 2p_{3/2} and S 2p_{1/2}, respectively, confirming successful sulfurization. For the Ni₃S₂-C electrocatalyst, the metallic Ni signal, Ni⁰, at 852.8 eV was not observed after the annealing reaction, while a peak at 852.3 eV associated with the Ni-C chemical state [17] and a C 1s peak newly appeared, indicating that carbon was chemically bonded with the Ni₃S₂ phase (Fig. 4(c) and (d)). Furthermore, the increase of ratio of Ni³⁺ states including Ni vacancies was observed in Ni₃S₂-C which has been reported to promote highly active sites owing to the lack of a d-electron configuration [16].

The surface area and pore volume of the as-prepared Ni, Ni₃S₂, and Ni₃S₂-C electrocatalysts were determined by nitrogen ab- and desorption measurements at 77 K (Fig. 5(a) and (b)). The synthesized electrocatalysts show the typical type-IV isotherm of nitrogen. As-prepared Ni₃S₂-C displays the highest BET surface area of 196.68 m²/g, compared

with 26.41 m²/g for Ni and 35.28 m²/g for Ni₃S₂. This a 7.4-fold increase relative to Ni is most likely due to changes in the porous, grass-like nanostructure. Moreover, the pore volumes between Ni, Ni₃S₂, and Ni₃S₂-C are compared, wherein Ni₃S₂-C exhibits a nanopore volume up to 5 times greater than that of Ni, which indicates that the nickel oxalate complex leads to increased nanopore size on the Ni₃S₂-C electrocatalysts (Fig. 5(b)). We further determined the electrochemically active surface area (ECSA) of all the electrocatalysts for better understanding of the results. As shown in Fig. A.8, the non-Faradaic capacitive current associated with electrochemical double-layer charging was measured upon repeated potential cycles between 20 and 200 mV/s. The capacitive charging behavior was plotted as a function of the scan rate of the measured capacitive current. The ECSA was calculated using the following equation:

$$A_{ECSA} = \frac{\text{Specific capacitance } (C_{dl})}{40 \mu\text{F} \cdot \text{cm}^{-2} \text{ per cm}^2_{ECSA}} \quad (3)$$

where 40 μF/cm² is the specific capacitance, based on a previous report [53]. In Fig. 5(c), the result of the double layer capacitance (C_{dl}) was

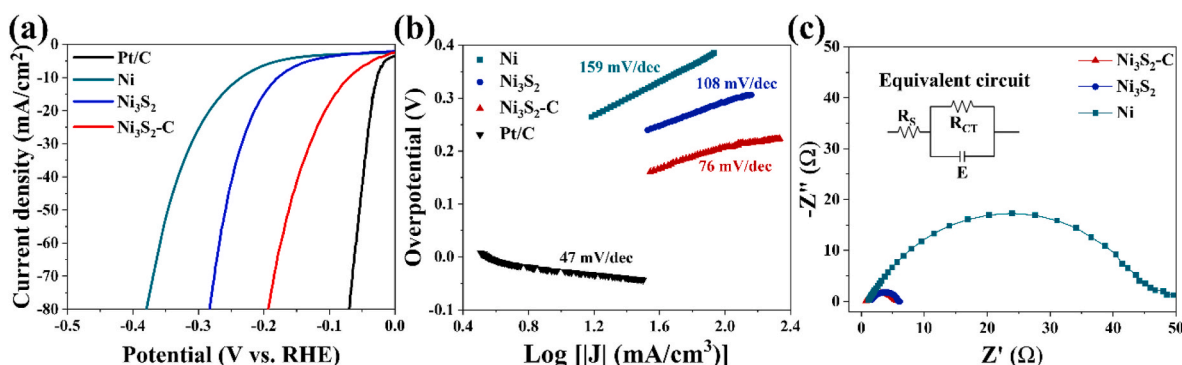


Fig. 6. (a) Polarization curves, (b) Tafel plots and (c) Nyquist plot of Ni, Ni₃S₂, and Ni₃S₂-C electrocatalysts comparing to Pt/C.

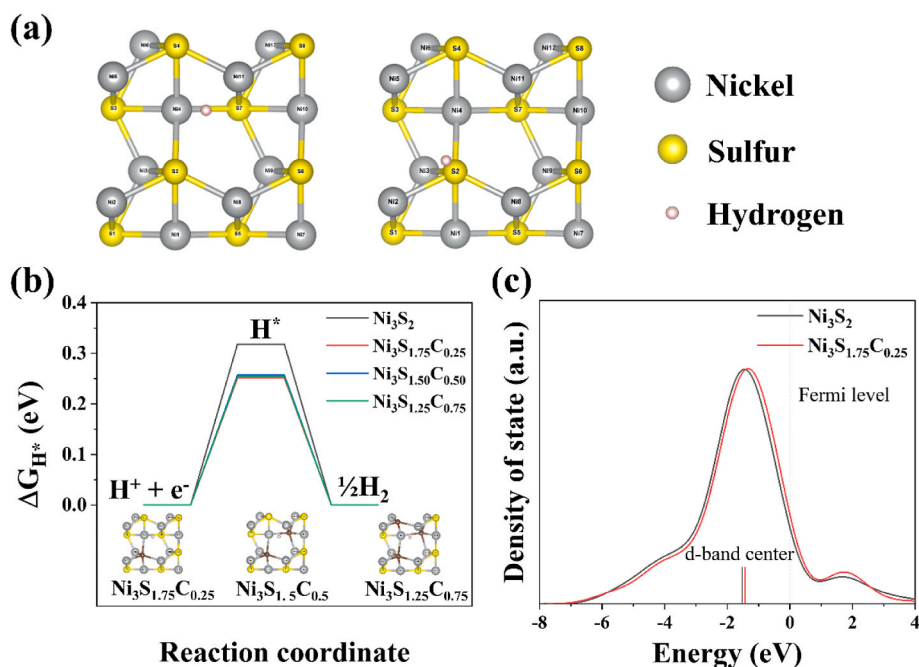


Fig. 7. (a) DFT optimized geometry of hydrogen adsorption on nickel site (left) and sulfur site (right). (b) Calculated free-energy diagram of HER over Ni₃S₂ and carbon-doped Ni₃S₂-C with various ratio of carbon. (c) Projected DOS of d-band for Ni atoms of the Ni₃S₂ and carbon-doped Ni₃S₂-C (Ni₃S_{1.75}C_{0.25}).

calculated from the slope of the linear fit to plots of current density as a function of scan rate. The Ni₃S₂-C electrocatalyst displayed the highest C_{dl} , i.e., 5.98 mF/cm², an increase of up to 10 times greater than that of Ni₃S₂ (0.51 mF/cm²) and Ni (0.58 mF/cm²). Moreover, the obtained ECSA value for the Ni₃S₂-C (149.5 cm²) was significantly larger than that of Ni₃S₂ (12.7 cm²) and Ni (14.5 cm²). This implies that Ni₃S₂-C improved the current density for the electrochemical reaction. The turnover frequency (TOF) was also determined to investigate the intrinsic activity of the electrocatalysts for hydrogen evolution per second, which plays a critical role in determining the HER activity. The detailed calculation method is shown in the supporting information. In Fig. 5(d), the TOF value of Ni₃S₂-C electrocatalyst for HER is calculated to be 4.14/s at an overpotential of 200 mV, which is higher than those of Ni₃S₂ (2.13/s) and Ni (1.45/s). These results indicate that the Ni₃S₂-C electrocatalyst shows higher intrinsic HER activity because the large nanopore surface and carbon composite can create more exposed active sites, which contributes to improving the HER catalytic performance.

We also evaluated the electrocatalytic activities of the Ni₃S₂-C electrocatalysts toward the HER, and the polarization curves were obtained in 1 M KOH with a Pt/C catalyst for comparison. The commercial Ni foam displays an appropriate performance as shown in Fig. 6(a–c), with an onset potential of −126 mV and an overpotential of −234 mV at 10 mA/cm². In contrast, the Ni₃S₂ electrocatalysts show enhanced HER activity, with a decreased onset potential of −80 mV and an overpotential of −178 mV. This improvement indicates that the Ni₃S₂ structure enhance the hydrogen ab- and desorption performance due to an increased number of active site and lower Gibbs free energy on their surface. As expected, the Ni₃S₂-C electrocatalysts exhibited a low onset potential of −14 mV and an overpotential of −70 mV, demonstrating excellent HER performance. To better understand the HER mechanism, the Tafel slopes were determined from the equation $\eta = b \log(j) + a$, which is the rate-determining step. The Tafel slope for the Ni₃S₂-C electrocatalyst was 76 mV/dec, which is much lower than the values for Ni₃S₂ (108 mV/dec) and Ni (159 mV/dec), implying that the Ni₃S₂-C electrocatalyst follows the Volmer-Heyrovsky mechanism in the range of 40–120 mV/dec (Fig. 6(b)). Moreover, EIS analysis was performed to evaluate the charge transfer resistance of the Ni₃S₂-C electrocatalysts. As shown in Fig. 6(c), regarding the Nyquist plots with an equivalent

circuit for the electrodes at −0.2 V, the Ni₃S₂ and Ni₃S₂-C electrodes show smaller semicircles of charge transfer resistance (R_{ct}) than the Ni electrode, indicating fast charge-transfer properties between the electrode and electrolyte. Moreover, the series (electrolyte) resistance (R_s) of Ni₃S₂-C (0.78 Ω/cm²) is lower than that of Ni₃S₂ (1.6 Ω/cm²), implying that C-doping on Ni₃S₂ allows for more efficient conductive electrode for the HER electrode. Thus, the best performance of the Ni₃S₂-C electrocatalyst suggests faster electrocatalytic kinetics and a higher hydrogen evolution rate during the HER process compared with the other catalysts. Considering the comprehensive results of the electrochemical analysis, the Ni₃S₂-C electrocatalyst demonstrates exceptional catalytic performance as a result of several contributing factors. The lower charge transfer resistance identified through EIS analysis suggests more efficient electron transfer, which is crucial for enhancing the HER kinetics. The significant capacitive contribution observed at higher scan rates in the CV analysis indicates that the surface of Ni₃S₂-C is well-optimized for rapid charge storage and release, which is essential for high-TOF HER operations. The calculated ECSA, along with the detailed understanding of the charge storage mechanisms, highlights the critical role of both the increased number of active sites and the optimized surface electronic structure in driving the enhanced HER activity of Ni₃S₂-C. Consequently, the comprehensive understanding of the electrochemical properties suggests that the observed improvements in HER activity are due to the synergistic effects of enhanced charge transfer, increased porosity, and enhanced electronic interactions, which are expected to result from carbon doping in Ni₃S₂.

To better understand the catalytic activity of high contents of carbon elements doped Ni₃S₂, DFT calculations were performed using theoretical models (Fig. 7(a–c)). It is well known that the HER activity over an electrocatalyst can be described by the adsorption free energy of hydrogen (ΔG_{H^*}) [42,43]. The closer the ΔG_{H^*} value is to zero, the more important factor it become in determining the HER activity as hydrogen evolution rate of corresponding surface [54]. The nickel site is found to have a smaller ΔG_{H^*} value (0.318 eV) than sulfur site (0.410 eV), indicating the nickel is catalytically more active (Fig. 7(a)). When a sulfur atom is substituted by a carbon atom to demonstrate the carbon doping, the ΔG_{H^*} value is reduced from 0.318 eV at Ni₃S₂ to 0.253 eV at Ni₃S_{1.75}C_{0.25} (Fig. 7(b)). In addition, the d-band center of Ni₃S₂ and

Table 1

Summary of HER activity of Ni₃S₂ based electrocatalysts. “-X” means X doped Ni₃S₂.

Electro-catalysts	C _{dl} (mF/cm ²)	Tafel slope (mV/dec)	Overpotential @10 mA/cm ² (mV)	References
Ni	0.58	159	234	This work
Ni ₃ S ₂	0.51	108	178	This work
Ni₃S₂-C	5.98	76	70	This work
Ni ₃ S ₂ -Cu	31.4	86.2	121	[21]
Ni ₃ S ₂ -Zn	104.2	78	78	[22]
Ni ₃ S ₂ -Fe	7.2	252	111	[23]
Ni ₃ S ₂ -V	69.6	82.5	85	[24]
Ni ₃ S ₂ -P	30.3	75	141	[26]
Ni ₃ S ₂ -N	36.88	95	100	[28]

Ni₃S_{1.75}C_{0.25} (Ni₃S₂-C) relative to Fermi level were calculated to be −1.520 eV and −1.433 eV, respectively, through the d-orbital projected density of states (DOS) of nickel atom (Fig. 7(c)). According to the d-band theory, the positive shift of d-band center results in the increase of binding interaction between active metal and adsorbate, which is ascribed to reduced filling of antibonding states [55,56]. Therefore, the adsorption energy of hydrogen atom on carbon-doped Ni₃S₂-C should be stronger than that on Ni₃S₂. Considering the hydrogen adsorption on the Ni₃S₂ is too weak, the increase of adsorption strength could be beneficial to the HER kinetics [57]. Moreover, in Fig. A.9, the carbon doping of Ni₃S_{1.75}C_{0.25} (0.253 eV), Ni₃S_{1.5}C_{0.5} (0.257 eV), Ni₃S_{1.25}C_{0.75} (0.254 eV) and Ni₃SC (0.212 eV) shows toward lower ΔG_{H*} than Ni₃S₂ (0.318 eV) with number of carbon atoms in Ni₃S₂ crystal structure. In addition, the ΔG_{H*} of Ni₃S_{0.5}C_{1.5} (0.161 eV) electrocatalyst exhibits two times smaller value than Ni₃S₂, indicating the stronger interaction of H* between Ni and carbon. In-depth analysis of DFT simulation on the HER kinetics reveals that carbon doping in Ni₃S₂ significantly enhances catalytic activity by optimizing ΔG_{H*} and modifying the electronic structure. DFT calculations indicate a substantial reduction in ΔG_{H*} from Ni₃S₂ to Ni₃S₂-C, which balances hydrogen adsorption and desorption, thereby accelerating the Volmer and Heyrovsky steps of the HER mechanism, which partially result in lower Tafel slope (76 mV/dec) and reduced overpotential (−70 mV at 10 mA/cm²) compared to bare Ni₃S₂. The shift in the d-band center towards the Fermi level further enhances the bonding interaction with hydrogen, promoting more efficient charge transfer and faster reaction rates. Therefore, carbon doping effectively modulates the electronic and catalytic properties of Ni₃S₂, combined with improvement of Ni₃S₂ in surface area and charge transfer from our synthesis process, leading to a significant improvement in HER kinetics and overall electrocatalytic performance.

The obtained specific performance value of hydrogen evolution including overpotential and Tafel slope is compared with the recently

reported Ni based electrocatalysts (Table 1). The long-term stability and durability were also evaluated in alkaline solution using chronoamperometry at −0.1 V, which is another critical issue for the application of a promising electrocatalyst. As a result, Ni₃S₂-C displayed a stable current density for 77 h, implying outstanding long-term stability (Fig. 8(a) and (b)). In addition, the durability was also evaluated through continuous cyclic voltammetry for 1000 cycles at a scan rate of 50 mV/s. The chronoamperometric result for the Ni₃S₂-C electrocatalyst showed only minimal variation throughout 77 h of the durability test, with a slight increase in overpotential at current density above 50 mA/cm² due to the change of grass-like structure (Fig. A.10), while the intrinsic activity remained stable within the range of 0 to −0.15 V before and after the cycling. The XPS surveys in Fig. A.11 also confirm a minimal change after the stability test, excepting a bit of increase in O1s peak which may be incurred from Volmer-Heyrovsky reaction. Through the proof of the analysis above, the enduring HER stability provides Ni₃S₂-C great feasibility for hydrogen production.

4. Conclusion

In summary, we demonstrated the HER performance of Ni₃S₂-C is strengthened through carbon doping which was achieved using a simple one-pot hydrothermal method. The resulting materials displays a grass-like highly porous structure with a higher proportion of chemical active site, Ni³⁺. Moreover, the Ni₃S₂-C exhibits high TOF value and significantly low overpotential which indicates the enhanced electron transfer with optimized electronic surface structure. DFT calculations also reveal that the carbon doped Ni₃S₂-C has a synergistic property for HER, low Gibbs free energy of hydrogen adsorption and desorption. As a result, the Ni₃S₂-C exhibits the low overpotential of 70 mV, Tafel slope of 76 mV/dec and long-term stability at alkaline solution, similar catalytic properties to noble metal catalyst as Pt/C. This study presents a promising strategy for enhancing HER performance through carbon doping in transition metal compounds, nickel sulfide, offering a scalable and cost-effective alternative to noble metal catalysts. We believe this approach holds potential for application in other energy storage and conversion systems, paving the way for broader advancements in sustainable energy technologies.

CRediT authorship contribution statement

Sungjin Kim: Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Yongheum Choi:** Investigation, Formal analysis, Data curation. **Hyun-Jong Kim:** Writing – original draft, Software, Methodology, Investigation. **Tae Joo Park:** Validation, Investigation, Formal analysis. **Young Min Park:** Writing – review & editing, Supervision, Investigation, Formal analysis, Conceptualization.

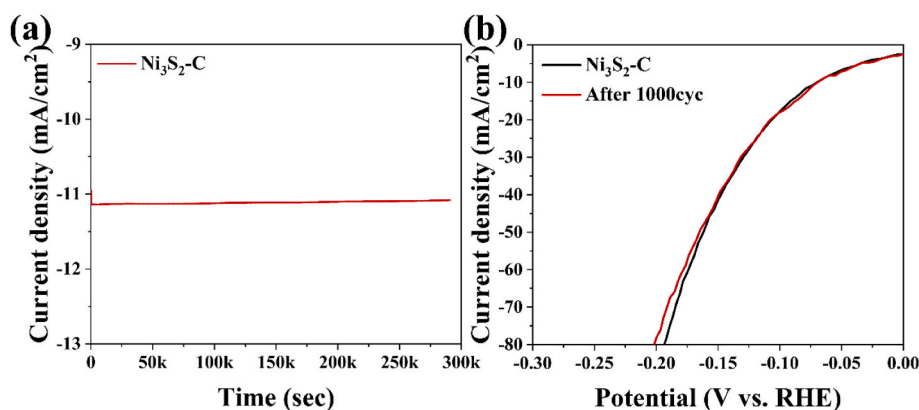


Fig. 8. (a) Chronoamperometric result of Ni₃S₂-C at −10mV (in 1 M KOH) for 77 h. (b) Polarization curves for the HER recorded on of Ni₃S₂-C before and after 1000 cycles.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was funded by Korea Institute of Industrial Technology as “Development of core technology for smart sensing and digital medical process to support medical surgical field diagnosis” (KITECH EH-24-0005).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2024.12.480>.

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