Ni₃S₂/Ball-milled silicon flour as a bi-functional electrocatalyst for hydrogen and oxygen evolution reactions

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Abstract

Elaborate design of highly efficient and durable electrocatalysts from earth-abundant elements is a milestone in the field of electrochemistry. In this study, heazlewoodite (Ni₃S₂) was successfully grafted on the silicon flour (Ni₃S₂@SiF) and ball-milled silicon flour (Ni₃S₂@B–SiF) through a simple hydrothermal process. The products were then etched using the HF solution to prepare the modified porous silicon (PSi) compounds of Ni₃S₂@PSi and Ni₃S₂@B–PSiF. Electrochemical studies showed that Ni₃S₂@B–SiF and Ni₃S₂@B–PSiF were not only durable but also exhibited electrocatalytic activity toward both alkaline and acidic hydrogen evolution reactions (HER) with appropriate Tafel slopes of 74 and 52 mV dec⁻¹, respectively. Moreover, they recorded an electrocatalytic activity for the oxygen evolution reaction (OER) with an overpotential of 164 mV dec⁻¹. Based on the electrocatalytic studies, the Ni₃S₂@B–PSiF electrocatalyst was found to have the best electrocatalytic behavior toward HER and OER. The isolated island architecture of the bi-functional (i.e., HER and OER) electrocatalyst could act as promising electrode materials for water splitting using electrochemical methods.

Keywords: Heazlewoodite bi-functional electrocatalyst; Ball-milled silicon; Hydrothermal method; Hydrogen evolution reaction; Oxygen evolution reaction.

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1. Introduction	25
Electrolysis of water to produce oxygen and hydrogen (i.e., $\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2$)	26
provides a favorable route for the large-scale storage of energy from the sun or other	27
renewable resources. Over the past several decades, electrochemical water splitting has	28
attracted a lot of attention as a critical process in hydrogen production from electricity	29
[1–3]. In this regard, the development of inexpensive, highly active, and durable	30
electrocatalysts for water splitting plays a pivotal role in the commercialization of the	31
so-called hydrogen economy that involves the use of hydrogen as an energy storage	32
system rather than a fossil fuel [4,5].	33
The electrocatalytic water splitting process involves two independent half-redox	34
reactions: an oxygen evolution reaction (OER) on the anode site, and a hydrogen	35
evolution reaction (HER) on the cathode site [6]. Even though noble metal-based	36
catalysts are known to catalyze HER efficiently regardless of the pH level of the	37
medium, their prevalent use has been severely limited by their high cost and low earth-	38
abundance. Hence, the search for inexpensive catalysts remains a grave challenge for	39
the successful achievement of OER and HER [7,8]. Substantial efforts have been	40
devoted to the investigation of more efficient electrocatalysts for OER as it is	41
kinetically slow in both acidic and basic media. The relationships between catalyst	42
architecture and activity are also critical for the development of highly efficient	43
electrocatalysts.	44
The electrochemical water splitting process requires voltages higher than the	45
thermodynamic potential corresponding to the activation barriers inherent to both HER	46
and OER. In other words, a fundamental aspect of making water-splitting reaction less	47
energy-intensive is to reduce the overpotentials for both by using HER and/or OER	48
electrocatalysts. It is, however, too difficult to find effective HER and OER catalysts	49

that can be coupled for good operation under similar pH levels to make the overall water splitting reaction more energy-efficient [7,9,10].

Despite these limitations, Trasatti introduced IrO₂ and RuO₂ as the best active OER electrocatalysts [3,11]. In recent years, transition metal sulfides, particularly nickel sulfide, have been extensively investigated as the electrocatalysts for different purposes. The nickel sulfide system contains several phases such as NiS, NiS₂, Ni₃S₂, Ni₃S₄, Ni₇S₆, and Ni₉S₈, among others [12]. Among all the different kinds of nickel sulfide, Ni₃S₂ is the most critical one with broad applications in catalysis [13], photology [14], magnetism [15], and electrochemistry [16,17]. Surendranath et al. [18] used Ni₃S₂ for oxygen reduction. Wang et al. [19] employed the hierarchically porous Ni₃S₂ nanorod for HER and OER while Zou [17] used Ni₃S₂ nanosheet arrays for water splitting. Moreover, Zhang et al. [20] used the Ni₃S₂ nanorods@Ni foam composite for OER. Ni₃S₂ has its own advantages and disadvantages; for one thing, it is cheap because heazlewoodite is abundant in nature. However, Ni₃S₂ is characterized by poor conductivity even though it is expected to be an advanced material in OER and HER [21,22]. Hence, certain modifications on heazlewoodite seem inevitable to make it more efficient for different applications.

This article introduces an original method using etched silicon flour (Ni₃S₂@PSi and Ni₃S₂@B-PSiF) for fabricating Ni₃S₂ at the silicon flour (Ni₃S₂@SiF), ball-milled silicon flour (Ni₃S₂@B-SiF), porous silicon (Ni₃S₂@PSiF), and ball-milled porous silicon. In this strategy, Ni₃S₂ nanoparticles are fabricated in-situ and grown on the surface of SiF and/or B-SiF. Fig. 1 shows the schematic diagram of the method. To prepare the Ni₃S₂ hybrid material, a novel strategy was developed which provides several key advantages. First, it is a simple one-step reaction that neither creates harsh conditions nor requires any special instruments. Second, Ni₃S₂ nanoparticles can

catalyze the in-situ formation of $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ on their surfaces. As a result, the aggregation of Ni_3S_2 nanoparticles can be prevented. Finally, B-SiF provides a highway for electron transfer due to its excellent conductivity.

The $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ electrocatalyst has a bi-functional catalytic activity which was investigated at a current density of 10 mA cm^{-2} for both alkaline HER and OER. The results of our study revealed the low overpotentials of the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ in both acidic and alkaline HER with a proportionately acceptable overpotential for OER. Moreover, the electrochemical results proved the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ alkaline/acidic HER and OER catalyst as the best electrocatalyst among the non-noble metal electrocatalysts reported in the literature.

2. Experimental

2.1. Reagents and apparatus

HNO_3 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, H_2SO_4 , and HF were purchased from Merck. Glucose, silicon (99.99%, 325 mesh), and thiourea were purchased from Sigma-Aldrich. All the other chemicals needed were of analytical grade purchased from Merck. To prepare solutions, de-ionized water (DI) was used throughout.

A Philips CM120 Transmission electron microscope (TEM) was used to obtain TEM images of the nanoparticles synthesized. X-ray photoelectron spectroscopy (XPS) was performed using an ultra-high vacuum (UHV) setup equipped with a concentric hemispherical analyzer. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area of the nanostructures. Distributions of the pore sizes and volumes were derived from the adsorption branches of the relevant isotherms using the Barrett–Joyner–Halenda (BJH) model while total pore volumes (V_t) were estimated from the adsorbed amounts at a relative pressure, P/P_0 , of 0.989. All the

electrochemical measurements were performed in a solution of 1.0 mol L⁻¹ KOH and/or 0.5 mol L⁻¹ H₂SO₄ at room temperature (RT) using an Autolab electrochemical analyzer, Model PGSTAT 30 potentiostat/galvanostat (Eco-Chemie, The Netherlands). The data were acquired and processed (background correction) using GPSE and FRA computrace software 4.9.007. A standard three-electrode cell containing a platinum wire was used as the auxiliary electrode, a saturated Ag/AgCl as the reference electrode, and modified silicon nanostructures at the surface of a glassy carbon electrode (Ni₃S₂@SiF, Ni₃S₂@B-SiF, Ni₃S₂@PSi, and Ni₃S₂@B-PSiF) as the working electrodes.

2.2. *Synthesis of the ball-milled silicon flour*

Ball-milled SiF (B-SiF) was prepared according to the procedure described in Ref. [23]. Briefly, commercial micrometric SiF was used as a starting material. The Si flour was introduced along with three stainless-steel balls (one 14.5 mm and two 11 mm in diameter), at a ball-to-flour mass ratio of 5:1, into a stainless steel vial (50 cm³). High-energy ball milling was carried out at room temperature for 20 h under the nitrogen atmosphere.

2.3. *Synthesis of Ni₃S₂ at SiF or B-SiF and chemical etching*

To synthesize Ni₃S₂ at SiF or B-SiF, 200 mg of SiF or B-SiF and 2.39 g of glucose were added to 45 mL of ethanol/water (35/10 v/v). The mixture was sonicated for 20 min before 1.27 g of nickel chloride, 0.331 g of thiourea, and 26.6 mL of ammonium hydroxide (28% w/v) were added to the B-SiF dispersion. The mixture was then transferred into a 70-mL stainless-steel autoclave and sealed before autoclave temperature was raised to 200 °C at which the mixture was stored for 15 h followed by

cooling to room temperature. Finally, the precipitate was filtered, washed with distilled water three times, and dried in the air.

Chemical etching was used to prepare Ni_3S_2 at the porous silicon flour ($\text{Ni}_3\text{S}_2@\text{PSiF}$) and/or at the ball-milled porous silicon flour ($\text{Ni}_3\text{S}_2@\text{B-PSiF}$). For this purpose, $\text{Ni}_3\text{S}_2@\text{B-SiF}$ and/or $\text{Ni}_3\text{S}_2@\text{SiF}$ were dispersed in 10 mL of HF (20% w/w) for 30 min. The mixture was then centrifuged, separated, rinsed several times with water, and dried at room temperature for 24 h to form $\text{Ni}_3\text{S}_2@\text{PSiF}$ and/or $\text{Ni}_3\text{S}_2@\text{B-PSiF}$.

2.4. Modified electrode preparation and electrochemical measurements

A quantity of 2.5 mg of the electrocatalyst (i.e., $\text{Ni}_3\text{S}_2@\text{SiF}$, $\text{Ni}_3\text{S}_2@\text{B-SiF}$, $\text{Ni}_3\text{S}_2@\text{PSiF}$, and/or $\text{Ni}_3\text{S}_2@\text{B-PSiF}$) was dispersed in 1.0 mL of H_2O under ultrasonic agitation to form an electrocatalyst ink. Then, 10 μL of the ink was dropped on the surface of a glassy carbon electrode (GCE) and dried at room temperature. Finally, 10 μL of Nafion (2.0% w/v) was dropped on the surface of the glassy carbon electrode modified with the silicon nanostructures to fabricate $\text{Ni}_3\text{S}_2@\text{B-SiF/GCE}$ or $\text{Ni}_3\text{S}_2@\text{B-PSiF/GCE}$ and dried at room temperature.

The geometric surface area of the as-prepared electrodes was used to normalize the current densities. All the reported potentials were referenced to the reversible hydrogen electrode (RHE).

3. Results and discussion

The highly active and durable catalysts made from earth-abundant elements offer a great potential for creating new materials that can replace the noble metal-based catalysts commonly used in (electro)-chemical processes [24]. In this study, a novel

strategy is proposed for the first time for the fabrication and in situ growth of Ni_3S_2 at the surface of B-SiF or B-PSiF synthesized by ball-milling and chemical etching, respectively. The morphologies and structures of the $\text{Ni}_3\text{S}_2@\text{B-SiF}$ and $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ thus prepared are characterized by different methods such as X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET), and Fourier transform infrared spectroscopy (FT-IR). Finally, the electrochemical properties of these electrocatalysts used for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are investigated in alkaline and acidic media.

3.1. *Physical and chemical characterization of the B-SiF, $\text{Ni}_3\text{S}_2@\text{B-SiF}$ and $\text{Ni}_3\text{S}_2@\text{B-PSiF}$*

The TEM image of the B-SiF confirms the presence of plates and/or nanoparticles of silicon with an average size of around 20–100 nm (Fig. 1A). Also, the image reveals the presence of many dislocations and defects in the B-SiF. Fig. 1-B presents three different magnifications of the TEM images of Ni_3S_2 nanoparticles at the surface of SiF and PSiF. Before the silicon surface was subjected to etching, hierarchical structures formed due to the assembly of nanoparticles, nanoplates, and holes several nanometers in diameter. Clearly, the presence of Ni_3S_2 nanoparticles influenced the arrangement and structure of silicon nanoplates or nanoparticles (Fig. 1B). On the other hand, the hierarchical structures disappeared after the B-SiF was etched with HF (20% w/w), as shown in Fig. 1C. The TEM images of the etched silicon demonstrated that agglomeration and hierarchical spherical shape morphology of nanoplates and/or nanoparticles dramatically decreased around the nanosized Ni_3S_2 particles. Finally, the blocked spaces near the Ni_3S_2 nanoparticles decreased due to the

etching process. The TEM images confirmed that Ni_3S_2 materials are composed of random holes and plate-like particles with spatially separated nanoparticles.

Fig. 1. A): TEM images of B-SiF; B): Ni_3S_2 @B-SiF; and C): Ni_3S_2 @B-PSiF.

N_2 adsorption-desorption isotherms and BHJ results were used to characterize the SiF and B-SiF before and after chemical etching for designing and fabricating high-performance electrocatalysts (i.e., Ni_3S_2 @SiF, Ni_3S_2 @B-SiF, Ni_3S_2 @PSiF, and Ni_3S_2 @B-PSiF) for OER and HER. For this purpose, surface analysis data were collected before and after the ball-milling and etching processes (Table 1). According to the results, the surface areas of the SiF increased after ball-milling and etching.

These changes in the surface characteristics clearly confirm the increasing porosity of the silicon surface and Ni_3S_2 nanoparticles after ball milling and etching. The Langmuir adsorption/desorption properties of the $\text{Ni}_3\text{S}_2@\text{B-SiF}$ and $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ are shown in Fig. 2.

Fig. 2. A): Langmuir adsorption/desorption of A): $\text{Ni}_2\text{S}_3@\text{B-SiF}$; and B): $\text{Ni}_2\text{S}_3@\text{B-PSiF}$.

Table 1. Surface area and the porosity of the porous synthesized catalysts.

Sample	Surface area ($\text{m}^2 \text{g}^{-1}$)			Pore volume ($\text{cm}^3 \text{g}^{-1}$)		Pore diameter (nm)	
	BET_{ads}	BET_{des}	BJH	BJH_{ads}	BJH_{des}	BET_{ads}	BET_{des}
$\text{Ni}_3\text{S}_2@\text{B-PSiF}$	34.3	35.2	45.8	0.11	0.10	11.8	11.5
$\text{Ni}_3\text{S}_2@\text{B-SiF}$	19.9	21	26.5	0.086	0.09	15.7	14.9
$\text{Ni}_3\text{S}_2@\text{PSiF}$	14.1	15	19	0.15	0.14	10.2	12.3
$\text{Ni}_3\text{S}_2@\text{SiF}$	9.3	10.8	13.2	0.13	0.13	14.8	14.1

The chemical compositions of $\text{Ni}_3\text{S}_2@\text{B-SiF}$ before and after adding HF (20% w/w for 30 min) was investigated by X-ray photoelectron spectroscopy (XPS) in the region of 0–1200 eV (Fig. 3). The relevant Si 2p core level spectra are displayed in Fig. 3 (d and e) and the peak deconvolution was performed Fig. 3 shows the Si 2p spectra for the silicon surface before (Fig.3d) and after (Fig.3 e) chemical etching. The spectrum of B-SiF is divided into two components. The doublet (103.0 to 103.5 eV) is ascribed to the silicon oxide associated with the native SiO_2 layer present on the surface of the Si particles while the other doublet located at 99 eV is assigned to the bulk silicon [25-27]. However, the intensity ratio of the bulk silicon and surface silicon (e.g. SiO_2) is too high, confirming that the amount of SiO_2 on the surface dramatically increased during the milling of SiF [23]. On the other hand, SiO_2 and Si peaks disappeared in the spectrum of the etched silicon surface, confirming the removal of the silicon surface by HF during the etching process. Furthermore, real chemical shifts are observed for all the peaks of the ball-milled silicon because chemical shifts (towards higher energies) occur due to increasing distances between the SiO_2 layers [28,29].

XPS was also used to analyze the atomic peaks of S (Fig. 3c) and Ni in both $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ and $\text{Ni}_3\text{S}_2@\text{PSiF}$ (Fig.3 e and f) . The two strong peaks observed at 855.2 and 872.7 eV may be assigned to Ni $2p_{3/2}$ and Ni $2p_{1/2}$, respectively (Fig. 3f). The peak at 852.7 eV is characteristic of Ni_3S_2 . The associated excited final state satellite near 860 and 879 eV indicates the presence of nickel-sulfur species on the surface of Ni_3S_2 . The S (2p) spectrum in (Fig. 3c) consists of a major doublet at 162.2 eV, with components asymmetrically broadened on the high binding energy side. This pair is assigned to Ni_3S_2 . Every nickel atom in the heazlewoodite network not only occupies a

pseudo-tetrahedral site in a nearly body-centered cubic sulfur lattice but is also linked 219
to the four sulfur atoms (there are four nickel atoms at ~ 0.25 nm) [30]. These very 220
short metal-metal distances are indicative of intermetallic links; indeed, heazlewoodite 221
has metallic electrical properties. Consequently, a photoelectron peak is expected to 222
show asymmetry as a consequence of the screening response of the conduction 223
electrons to the sudden creation of the core hole [31-33]. Moreover, no peaks of any 224
elements, other than O, Ni, C, S and O, are observed in the broad XPS spectrum. This 225
is further evidence of the formation of Ni_3S_2 , where the binding energy for Ni_3S_2 is in 226
agreement with those reported by Xie et. al [34] and Marcus et. al [35]. 227

Fig. 3. Survey of XPS data for (a): $\text{Ni}_2\text{S}_3@B\text{-SiF}$ and (b) $\text{Ni}_2\text{S}_3@B\text{-PSiF}$. (c): High- 229
resolution XPS for S element in $\text{Ni}_2\text{S}_3@B\text{-SiF}$. (d): High-resolution XPS for Si element 230
in $\text{Ni}_2\text{S}_3@B\text{-SiF}$. (e): High-resolution XPS for Si element in $\text{Ni}_2\text{S}_3@B\text{-PSiF}$; and (f): 231
High-resolution XPS for Ni element in $\text{Ni}_2\text{S}_3@B\text{-PSiF}$ spectra and those fitting curve. 232

The FT-IR spectra of a typical $\text{Ni}_3\text{S}_2@\text{B-SiF}$ before and after etching revealed the following dominant surface groups identified in the spectrum as Si-H, Si-H₂, and Si-H₃. These bands increased in intensity after etching. This is because of the Si-O-Si present on the surface of the ball-milled SiF before etching but the presence of Si-H_x after chemical etching. Si-H bending (625 cm⁻¹) and Si-H₂ wagging (662 cm⁻¹) vibration modes are observed for these different groups in the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ and $\text{Ni}_3\text{S}_2@\text{B-SiF}$.

Stretching modes (equal to 2050 cm⁻¹ and 2285 cm⁻¹ for x = 2 and 3, respectively) are also observed for the Si-H_x bonds. A feature related to the Si-O-Si asymmetric stretching mode (1272 cm⁻¹) caused by the surface oxidation of $\text{Ni}_3\text{S}_2@\text{B-SiF}$ in air can also be clearly seen in the spectra shown in Fig. 4A.

Fig. 4. A): FT-IR spectra of $\text{Ni}_2\text{S}_3@\text{B-SiF}$; before and after of HF treatment. B): Cyclic voltammetry of $\text{Ni}_2\text{S}_3@\text{B-SiF}$; before (b) and after (a) of HF treatment in 1.0 mol L⁻¹ KOH solution.

3.2. Electrochemical characterization

The electrochemical properties of the $\text{Ni}_3\text{S}_2@\text{B-SiF}$ were investigated before and after etching the electrode surface by recording cyclic voltammograms of the modified electrodes in an alkaline solution (KOH, 1.0 mol L⁻¹). The cyclic voltammograms (Fig.

4B) revealed identical peak potentials before and after etching, whereas the current density of the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ was higher than that of the $\text{Ni}_3\text{S}_2@\text{B-SiF}$ because of the higher surface area of the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ than that of the $\text{Ni}_3\text{S}_2@\text{B-SiF}$ (based on the BET results).

3.3. Electrocatalytic activities of the silicon nanostructures for hydrogen evolution

Linear sweep voltammetry (LSV) was used for HER using $\text{Ni}_3\text{S}_2@\text{SiF}$, $\text{Ni}_3\text{S}_2@\text{PSiF}$, $\text{Ni}_3\text{S}_2@\text{B-SiF}$, and/or $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ as the electrocatalysts. Initially, the electrocatalytic activities of the products formed during the step-by-step synthesis of the $\text{Ni}_3\text{S}_2@\text{SiF}$ were studied. For this purpose, the behavior of the electrocatalyst toward HER was studied for the two cases of thiourea and/or glucose present and absent in its synthesis. Results showed that the electrocatalyst synthesized in the presence of glucose and thiourea has the highest electrocatalytic activity for HER, as shown in Fig.

4. Then, the synergistic effects of Ni_3S_2 on SiF and/or B-SiF for HER were investigated using LSV. For this purpose, the hydrogen generation activity of the commercial SiF, B-SiF, and Ni_3S_2 decorated on SiF and B-SiF were studied under identical conditions. Based on the results obtained, the commercial SiF showed very poor HER performance with overpotentials greater than ~ 820 mV and with a current density of 2 Ma cm^{-2} (Fig. 5B-a) whereas B-SiF showed better properties with overpotentials higher than ~ 700 mV and a current density of 2 Ma cm^{-2} (Fig. 5B-b). In contrast, the $\text{Ni}_3\text{S}_2@\text{SiF}$ (as an electrocatalyst for HER) exhibited a much lower onset overpotential of ~ 540 mV and a higher current density of 10 mA cm^{-2} (Fig. 5B-c). After Ni_3S_2 had been decorated on the surface of the B-SiF (to produce $\text{Ni}_3\text{S}_2@\text{B-SiF}$), the electrocatalyst's behavior showed an overpotential of ~ 300 mV and a current density of 10 mA cm^{-2} (Fig. 5B-d). The superior HER activity of the $\text{Ni}_3\text{S}_2@\text{B-SiF}$ may be attributed to the following underlying causes. First, the 3D $\text{Ni}_3\text{S}_2@\text{B-SiF}$ structures cause the Ni_3S_2 to get

involved with the reactant. Moreover, the ball milled silicon provides conductive highway networks for the easy charge diffusion and mass transfer. Last but not least, the active sites of the ball milled silicon and those of the heazlewoodite get more integrated compared to their single participation in the HER.

To design and develop catalytic materials, it is critical to identify their most active site(s). In this third part of our HER study, the etching of the $\text{Ni}_3\text{S}_2@\text{B-SiF}$ and/or $\text{Ni}_3\text{S}_2@\text{SiF}$ was conducted as an efficient strategy for designing the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ and/or $\text{Ni}_3\text{S}_2@\text{PSiF}$. For this purpose, the electrocatalytic activity of the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$

Fig. 5. A): Linear sweep voltammogram of: (a) Ni_3S_2 in the absence of thiourea; (b): Ni_3S_2 in the absence of glucose; and (c): Ni_3S_2 in the presence of thiourea and glucose at the surface of GCE. (B): Linear sweep voltammogram of a) SiF; b) B-SiF; c)

$\text{Ni}_3\text{S}_2@\text{SiF}$; and d) $\text{Ni}_3\text{S}_2@\text{B-SiF}$ at the surface of GCE. (C): Linear sweep
 voltammogram of a) $\text{Ni}_3\text{S}_2@\text{SiF}$; b) $\text{Ni}_3\text{S}_2@\text{B-SiF}$; c) $\text{Ni}_3\text{S}_2@\text{PSiF}$; and d) $\text{Ni}_3\text{S}_2@\text{B-PSiF}$
 at the surface of GCE. and D): Linear sweep voltammogram of a) $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ and
 Pt/C at the surface of GCE, in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution with a scan rate of 10 mV s^{-1} .

and $\text{Ni}_3\text{S}_2@\text{PSiF}$ were evaluated using LSV in a solution of $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. Results
 showed that the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ (Fig. 5C-d) and $\text{Ni}_3\text{S}_2@\text{PSiF}$ (Fig. 5C-c) exhibited
 more satisfactory current densities and onset potentials (for HER) than did the
 $\text{Ni}_3\text{S}_2@\text{B-SiF}$ (Fig. 5C-b) and $\text{Ni}_3\text{S}_2@\text{SiF}$ (Fig. 5C-a). The differences observed
 between the hydrogen generation activities of the $\text{Ni}_3\text{S}_2@\text{B-SiF}$ and $\text{Ni}_3\text{S}_2@\text{B-PSiF}$
 may be explained by reference to differences in their morphologies (as shown in the
 relevant TEM images), functional groups (the related XPS results), and hydrogen
 generation active sites. After the etching process, however, the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ showed
 far more active sites and less hindered sites (e.g., nano-holes) than did the $\text{Ni}_3\text{S}_2@\text{B-SiF}$
 as indicated by the morphological and surface analyses; the Ni_3S_2 particles in the B-
 PSiF have fewer aggregates than the B-SiF, which is desirable for easy transfer of
 electrons to the active sites. In this regard, the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ showed a more random
 distribution of nano-holes which creates far more active edges to lead to the highest
 HER activity. Finally, the HER activities of the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ and commercial Pt/C
 were compared. Results showed that the activity of the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ was nearly
 similar to that of Pt/C (Fig 5-D).

The Tafel slope provides additional insight into the HER mechanisms. It is
 associated with the rate-limiting step of the hydrogen generation derived from the Tafel
 plots. Tafel slope is determined by fitting the linear part of the Tafel plot using the
 following Tafel equation:

$$\eta = a + b \cdot \log |j| \quad 317$$

where, η represents overpotential, b is the Tafel slope, and j is the current density. 318
 Generally, there exist three HER mechanisms with different Tafel slopes: Volmer 319
 reaction (120 mV dec^{-1}), Heyrovsky reaction (40 mV dec^{-1}), and Tafel reaction (30 mV 320
 dec^{-1}) [36,37]. The Tafel slopes for the $\text{Ni}_3\text{S}_2@\text{B-SiF}$ and $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ were 321
 determined to be 74 and 52 mV dec^{-1} , respectively. The corresponding Tafel plots 322
 suggest that both electrodes are mainly promoted by the Heyrovsky reaction in the 323
 catalytic process. One possible explanation for the different Tafel slopes (observed 324
 between $\text{Ni}_3\text{S}_2@\text{B-SiF}$ and $\text{Ni}_3\text{S}_2@\text{B-PSiF}$) is the fewer number of aggregates 325
 hindering Ni_3S_2 during the synthesis of the porous surface. 326

In addition to the stringent requirement of perfect activity, an important 327
 criterion in the selection of an electrocatalyst is its stability. To assess the 328
 electrocatalysts ($\text{Ni}_3\text{S}_2@\text{B-SiF}$ and $\text{Ni}_3\text{S}_2@\text{B-PSiF}$) with respect to their stability for 329
 HER, long-term successive potential cycling was used in a solution of 0.5 mol L^{-1} 330
 H_2SO_4 for 1000 cycles at room temperature at a scan rate of 10 mV s^{-1} . As shown in 331
 Fig. 6 for the $\text{Ni}_3\text{S}_2@\text{B-SiF}$, not only was no slight losses observed in the cathodic 332
 current after the last cycle, but current density also rose, the overpotential declined, and 333
 the catalyst exhibited a good durability in acidic media. A likely reason for this 334
 behavior is the porosity of the synthesized surface, as also reported in our pervious 335
 article [39]. The $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ showed (Fig. 6B) a very stable electrocatalytic activity 336
 with no significant changes in the current density or onset potential. The stability study 337
 of the $\text{Ni}_3\text{S}_2@\text{B-SiF}$ for HER revealed an increased current density but a reduced onset 338
 potential of the $\text{Ni}_3\text{S}_2@\text{B-SiF}$ as a result of successive cycles. This is because after the 339
 $\text{Ni}_3\text{S}_2@\text{B-SiF}$ has remained in the acidic medium for several hours, some of the 340
 nanoparticles of the silicon nanostructure that have weak interactions with the surface 341

and that play no key and effective role in HER are removed from the surface of the electrocatalyst due to the dissolution of the electrocatalyst in the acid and peeling off of the electrode. Thus, surface porosity increases to enhance current density and reduce the onset potential of the $\text{Ni}_3\text{S}_2@\text{B-SiF}$ after successive cycles.

In continuation of our study of the HER activities of silicon nanostructures, the HER activities of the electrocatalysts were investigated in alkaline solutions. Hydrogen generation reaction is one of the two significant half reactions in current chloralkali electrolyzers in water-alkali media. The successful achievement of this energy-efficient reaction requires highly active and stable catalytic materials to be developed for use in alkaline media [40]. A few noble metal-free HER catalysts working in alkaline media² have been reported in the literature. However, all are reportedly quite inferior to the noble metal Pt despite their superior catalytic activity compared to the metallic nickel.

Fig. 6. Linear sweep voltammograms for electrochemical H_2 generation in 0.5 mol L^{-1} H_2SO_4 at (A): $\text{Ni}_3\text{S}_2@\text{B-SiF}$ at the surface of GCE after every 200 successive cyclic voltamogram from 0 to 1000 cyclic. B): $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ at the surface of GCE after every 200 successive cyclic voltamogram from 0 to 1000 cyclic with a scan rate of 10 mV s^{-1} .

The slow development of HER catalysts performing in alkaline environments, compared to HER catalysts working in acidic media, is mainly attributed to the intrinsically slower HER reaction kinetics and to the presently scant knowledge of the HER mechanism in alkaline environments¹. Based on our literature review and the above considerations, the Ni₃S₂@B-SiF and Ni₃S₂@B-PSiF were selected to investigate their alkaline HER activity. For this purpose, LSV was conducted in a solution of 0.5 mol L⁻¹ KOH at a scan rate of 10 mV s⁻¹. The synergistic effects of the etching process of the ball-milled silicon surface toward the alkaline HER were investigated and compared with the behavior of the synthesized electrocatalysts, ball-milled silicon, Ni₃S₂@B-SiF, and Ni₃S₂@B-PSiF under identical conditions. As expected, the Ni₃S₂@B-SiF and Ni₃S₂@B-PSiF exhibited the best alkaline HER activity with a current density of 10 mA cm⁻² and low overpotentials of 450 and 270 mV, respectively. In contrast, the free B-SiF showed a very poor alkaline HER activity, whereas the Ni₃S₂@B-SiF and Ni₃S₂@B-PSiF proved to be suitable electrocatalysts for alkaline HER performance. More specifically, it was the Ni₃S₂@B-PSiF that showed the highest alkaline HER performance. Electrocatalytic performance for HER is suggested to be related to adsorption strength. This suggestion is in line the Sabatier principle which states that the optimal catalytic performance may be obtained by optimizing the strength of the interaction between the adsorbate and the catalyst [41]. Thus, if hydrogen or water is strongly bound to the catalyst, the desorption in the intermediate step should be rate limiting [41]. It must be noted that the Tafel slopes of Ni₃S₂@B-SiF and Ni₃S₂@B-PSiF matched the Volmer step as evidenced by the values of 140 and 125 mV dec⁻¹, respectively, obtained for the Tafel slopes of the Ni₃S₂@B-SiF and Ni₃S₂@B-PSiF.

Stability is a pivotal parameter in the development of electrocatalysts. To assess the $\text{Ni}_3\text{S}_2@\text{B-SiF}$ and $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ with respect to their stability, the alkaline HER was allowed to proceed with $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ for 1000 successive cycles in 0.50 mol L^{-1} KOH at a scan rate of 10 mV s^{-1} . Similar to the case with an acidic medium, electrochemical investigations in the case of an alkaline medium indicated perfect durability throughout the long-term operation of the electrocatalysts. However, current density was observed to reduce with increasing cycles in the case of the $\text{Ni}_3\text{S}_2@\text{B-SiF}$. This is due to the instability of silicon in alkaline media and the dissolution of the electrocatalyst in the KOH solution (results not shown).

3.5. Electrocatalytic activities of the silicon nanostructures for oxygen evolution

Even though oxygen evolution reaction (OER) may be accompanied by some significant cathodic processes, the challenge in the electrocatalytic water splitting process lies in the anodic multi-electron OER with its extremely sluggish surface kinetics [42,43]. On a Pt electrode, for example, the OER proceeds [44,45] about 10 times [10] more slowly than does the HER one. The OER catalysis is a great impediment to the conversion of sunlight or electricity into storable fuels [46]. The $\text{Ni}_3\text{S}_2@\text{B-SiF}$ and $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ were designed and developed in this study for the successful achievement of OER based on all the merits and demerits mentioned above. To investigate the electrocatalytic activities of the nanoparticles towards oxygen evolution reaction, the as-synthesized electrocatalysts were used in a three-electrode setup cell at a scan rate of 5 mV s^{-1} . Fig. 7 shows the linear sweep voltammograms of the synthesized Ni_3S_2 in different conditions (Fig. 7A), commercial SiF, ball-milled silicon, synergic effects of silicon and Ni_3S_2 ($\text{Ni}_3\text{S}_2@\text{SiF}$ and $\text{Ni}_3\text{S}_2@\text{B-SiF}$) (Fig. 7B), and the effects of chemical etching (Fig. 7C) with an anodic potential window between

0.00 to 1.20 V vs. Ag/AgCl. Fig. 7A shows the OER activity of Ni₃S₂ in 1.0 mol L⁻¹ KOH under different conditions of synthesis. The results indicate that the presence of both glucose and thiourea in the synthesis pathway affected OER reactivity, as was the case with the HER activity. The behavior of commercial SiF and ball-milled silicon as well as the synergic effects of silicon and Ni₃S₂ (Ni₃S₂@SiF and Ni₃S₂@B-SiF) were also investigated to find that the electrochemical activity of the ball-milled silicon was superior to that of the commercial silicon, whereas the hybrid Ni₃S₂ and SiF showed a high electrochemical activity for OER. Moreover, subjecting the commercial silicon to the ball milling process before Ni₃S₂ was decorated on the silicon surface was observed to affect the OER activity of the electrocatalyst. Clearly, then, Ni₃S₂@B-SiF exhibited a superior OER activity to those observed with the other nanoparticles synthesized (Fig. 7B). This finding is consistent with what was observed in both acidic and alkaline HERs. The unique nanosized holes of the porous structure in the Ni₃S₂@B-SiF enhanced its electrocatalytic activity for OER. In the case of the Ni₃S₂@B-SiF, however, the enhanced charge was due to its high surface area and porosity.

In the final stage of the present study, the effects of chemical etching were studied on the OER activity of the electrocatalyst. Results showed that current density increased but overpotential decreased with increasing porosity after etching the Ni₃S₂@B-SiF to Ni₃S₂@B-PSiF. The linear sweep voltammograms in Fig. 7 show catalytic currents of around 0.75 V and 1.10 V for the Ni₃S₂@B-SiF and Ni₃S₂@B-PSiF, respectively, along with the vigorous evolution of oxygen bubbles. The Ni₃S₂@B-PSiF electrocatalyst showed a small overpotential of ~0.21 V with a current density of 15 mA cm⁻² (compared to the standard potential), which is comparable with those reported for the best OER catalysts such as Co₃O₄-RGO (0.31 V)¹², Co₃O₄ (0.29 V) [23], or Co(PO₃)₂ [37] (0.31 V).

The relevant Tafel plots were derived from the LSVs. As can be seen, mild
Tafel slopes of as low as 187 and 164 mV per decade were observed for the $\text{Ni}_3\text{S}_2@\text{B-SiF}$
and $\text{Ni}_3\text{S}_2@\text{B-PSiF}$, respectively. The value obtained for the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ clearly
indicates its superior electrocatalytic activity for OER. Moreover, the low Tafel slope

Fig. 7. A): Linear sweep voltammogram of a) Ni_3S_2 in absence of thiourea; b) Ni_3S_2 in
the absence of glucose and c) Ni_3S_2 in the presence of thiourea and glucose at the
surface of GCE, (B): Linear sweeps voltammogram of a) SiF; b) B-SiF; c) $\text{Ni}_3\text{S}_2@\text{SiF}$;
and d) $\text{Ni}_3\text{S}_2@\text{B-SiF}$ at the surface of GCE. (C): Linear sweep voltammogram of a)
 $\text{Ni}_3\text{S}_2@\text{B-PSiF}$; b) $\text{Ni}_3\text{S}_2@\text{B-SiF}$ at the surface of GCE, in $1.0 \text{ mol L}^{-1} \text{ KOH}$ solution
with a scan rate of 5 mV s^{-1} .

of ~164 mV per decade obtained for the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ is comparable to that (159.3 mV per decade) previously reported in the literature for highly active OER catalysts [12,23,37].

To investigate the durability of the catalysts for OER, the silicon nanostructure modified glassy carbon electrode was used under long-term operation conditions. Also, its long-term stability was evaluated by implementing successive CV cycles. OER CVs were obtained at the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ in the potential range of 0.00 and 1.20 V vs. Ag/AgCl at a sweep rate of 5 mV s^{-1} for 1000 cycles. The LSV, after every 200 cycles, was recorded at a scan rate of 5 mV s^{-1} . Results indicate the lower stability of the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ compared to the $\text{Ni}_3\text{S}_2@\text{B-SiF}$, whereas both electrocatalysts exhibited a higher stability in an alkaline solution (Fig. 8) than the OER catalysts reported in the literature [12,23,37]. Undoubtedly, a rapid decay was observed in the current density, generally as a result of the blockage of the active sites on the surface of GCE due to the gradual accumulation of the O_2 bubbles evolving. This is evidenced by the images of the electrode taken at 10, 20, and 60 min during the test, which clearly display that O_2 bubbles gradually accumulated on the surface of the electrode. Another possible explanation for the declining activity is the peeling off of the electrocatalyst off the glassy carbon electrode because of the vigorous evolution of oxygen bubbles on the surface of the glassy carbon electrode; this was also observed during the experiments.

4. Electrochemical impedance spectroscopy studies

All the above results of LSV and CV indicate the superior electrocatalytic activity of the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ for OER, alkaline HER, and acidic HER as compared to those of B-SiF, $\text{Ni}_3\text{S}_2@\text{SiF}$, $\text{Ni}_3\text{S}_2@\text{PSiF}$, and $\text{Ni}_3\text{S}_2@\text{B-SiF}$.

Fig. 8. Linear sweep voltammograms for electrochemical H₂ generation in 1.0 mol L⁻¹ KOH at (A): Ni₃S₂@B-SiF at the surface of GCE after every 200 successive cyclic voltamogram from 0 to 1000 cyclic. B): Ni₃S₂@B-PSiF at the surface of GCE after every 200 successive cyclic voltamogram from 0 to 1000 cyclic with a scan rate of 5 mV s⁻¹.

Electrochemical impedance spectroscopy (EIS) measurements were conducted to study the kinetics of the electrochemical OER, alkaline HER, and acidic HER; results confirmed those obtained from the LSV and CV. The Ni₃S₂@B-PSiF, Ni₃S₂@B-SiF, Ni₃S₂@SiF, and Ni₃S₂@PSiF were subjected to EIS by applying an AC voltage of 5 mV with a frequency range of 100,000 to 0.01 Hz and recorded at different potentials vs. Ag/AgCl in 1.0 mol L⁻¹ KOH for OER, in 0.5 mol L⁻¹ H₂SO₄ solutions for acidic HER, and in 0.5 mol L⁻¹ KOH for basic HER. In the EIS spectra, the diameter of the arc (R_{ct}) is related to the charge transfer reaction kinetics during the OER or HER process at the surface of the electrode. The results of our study showed a significant decrease in R_{ct} for the Ni₃S₂@B-PSiF in OER and HER, indicating a reduction in the reaction resistance. A significant reduction in the R_{ct} values for the Ni₃S₂@B-PSiF in OER and HER showed a smaller reaction resistance but a higher

catalytic activity for OER and HER at the surface of the other nanocatalysts (SiF, B-SiF, Ni₃S₂@ SiF, Ni₃S₂@B-SiF).

Conclusion

A porous Ni₃S₂ nanorod hole on the ball-milled silicon was successfully prepared through a facile hydrothermal process and used as an efficient electrocatalyst for both acidic/alkaline HER and OER. It was demonstrated that the successful preparation of the desired structure and morphology relies on the etching of the ball-milled silicon with HF. The as-prepared porous Ni₃S₂ nanoscale hole on the ball-milled silicon exhibited excellent electrocatalytic activity towards acidic/alkaline HER and OER with appropriate Tafel slopes in acidic/alkaline HER and OER. Results showed Tafel slopes of 74 and 52 mV dec⁻¹ for the Ni₃S₂@B-SiF and Ni₃S₂@B-PSiF, respectively, in the acidic HER. A possible explanation for the differences observed in the Tafel slopes (of Ni₃S₂@B-SiF and Ni₃S₂@B-PSiF) may be the fewer aggregates and the less Ni₃S₂ hindrance in the synthesized porous surface. Also, the Ni₃S₂@B-SiF and Ni₃S₂@B-PSiF exhibited the best alkaline HER activity with a current density of 10 mA cm⁻² and the low overpotentials of 450 and 270 mV, respectively. This is while the current density for the Ni₃S₂@B-PSiF was higher than that of the Ni₃S₂@B-SiF because of the greater surface area of the Ni₃S₂@B-PSiF. The Tafel slopes of the Ni₃S₂@B-SiF and Ni₃S₂@B-PSiF in the alkaline HER were recorded to be 140 and 125 mV dec⁻¹, respectively, indicating a Volmer step. Moreover, the current densities and the onset potentials of the Ni₃S₂@B-PSiF and Ni₃S₂@PSiF, for both acidic and alkaline HER, were more satisfactory than those recorded for the Ni₃S₂@B-SiF and Ni₃S₂@SiF. Small Tafel slopes of as low as 187 and 164 mV per decade were observed for the Ni₃S₂@B-SiF and Ni₃S₂@B-PSiF, respectively. The OER activity of the Ni₃S₂@B-SiF

with a small overpotential of ~ 0.21 V and a current density of 15 mA cm^{-2} was found to be superior to those of the other nanoparticles synthesized. The results obtained for the electrodes developed in this study are far better than those for the non-noble metal electrocatalysts reported in the literature. Three explanations were claimed in this study for the outstanding catalytic activity of the $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ towards acidic/alkaline HER and OER. Firstly, the nanoscale hole structure provided fast channels for the mass transport and electron transfer. Secondly, the ball-milled silicon with its unique hierarchically porous structure (as a result of etching that offers a large electrochemical surface area) possibly exposed more active sites for electrocatalysis in acidic/alkaline HER and OER. Thirdly, the direct growth of the Ni_3S_2 nanoholes due to the etching of the silicon provided a strong interaction between the Ni_3S_2 and the porous silicon, which possibly enhanced the long-term stability of the electrocatalyst for acidic/alkaline HER and OER. The $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ may, therefore, be recommended as a promising, low-cost, and highly-efficient electrocatalyst for both acidic/alkaline HER and OER.

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Legends for the figures

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Fig. 1. A) TEM images of B-SiF, B) $\text{Ni}_2\text{S}_3@\text{B-SiF}$, and C) $\text{Ni}_2\text{S}_3@\text{B-PSiF}$.

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Fig. 2. Langmuir adsorption/desorption of a) $\text{Ni}_2\text{S}_3@\text{B-SiF}$ and B) $\text{Ni}_2\text{S}_3@\text{B-PSiF}$.

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Fig. 3. Survey of XPS data for a) $\text{Ni}_2\text{S}_3@\text{B-SiF}$, and b) $\text{Ni}_2\text{S}_3@\text{B-PSiF}$, c) High-resolution XPS for S in the $\text{Ni}_2\text{S}_3@\text{B-SiF}$. d) High-resolution XPS for Si in the $\text{Ni}_2\text{S}_3@\text{B-SiF}$, e) High-resolution XPS for Si in the $\text{Ni}_2\text{S}_3@\text{B-PSiF}$, and f) High-resolution XPS for Ni in the $\text{Ni}_2\text{S}_3@\text{B-PSiF}$ spectra and the fitting curves.

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Fig. 4. A) FT-IR spectra of the $\text{Ni}_2\text{S}_3@\text{B-SiF}$ before and after HF treatment; B) Cyclic voltammetry of $\text{Ni}_2\text{S}_3@\text{B-SiF}$ before b) and after a) HF treatment in 1.0 mol L⁻¹ KOH solution.

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Fig. 5. A): Linear sweep voltammograms of a) Ni_3S_2 in the absence of thiourea, b) Ni_3S_2 in the absence of glucose, and c) Ni_3S_2 in the presence of thiourea and glucose at the surface of GCE; B): Linear sweep voltammograms of a) SiF, b) B-SiF, c) $\text{Ni}_3\text{S}_2@\text{SiF}$, and d) $\text{Ni}_3\text{S}_2@\text{B-SiF}$ at the surface of GCE; C) Linear sweep voltammograms of a) $\text{Ni}_3\text{S}_2@\text{SiF}$, b) $\text{Ni}_3\text{S}_2@\text{B-SiF}$, c) $\text{Ni}_3\text{S}_2@\text{PSiF}$, and d) $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ at the surface of GCE; and D): Linear sweep voltammograms of a) $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ and Pt/C at the surface of the GCE in 0.5 mol L⁻¹ H₂SO₄ solution at a scan rate of 10 mV s⁻¹.

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Fig. 6. Liner sweep voltammograms for electrochemical H₂ generation in 0.5 mol L⁻¹ H₂SO₄ at (A): $\text{Ni}_3\text{S}_2@\text{B-SiF}$ at the surface of GCE after every 200 successive cyclic voltamogram from 0 to 1000 cyclic. B): $\text{Ni}_3\text{S}_2@\text{B-PSiF}$ at the surface

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of GCE after every 200 successive cyclic voltamogram from 0 to 1000 cyclic 712
with a scan rate of 10 mV s⁻¹. 713

Fig. 7. A) Linear sweep voltammograms of a) Ni₃S₂ in the absence of thiourea, b) 714
Ni₃S₂ in the absence of glucose, and c) Ni₃S₂ in the presence of thiourea and 715
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of GCE in 1.0 mol L⁻¹ KOH solution at a scan rate of 5 mV s⁻¹. 719

Fig. 8. Liner sweep voltammograms for electrochemical H₂ generation in 1.0 mol L⁻¹ 720
KOH at (A): Ni₃S₂@B-SiF at the surface of GCE after every 200 successive 721
cyclic voltamogram from 0 to 1000 cyclic. B): Ni₃S₂@B-PSiF at the surface 722
of GCE after every 200 successive cyclic voltamogram from 0 to 1000 cyclic 723
with a scan rate of 5 mV s⁻¹. 724

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Graphical Abstract

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