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Facile Electrodeposition of WS₂/Ni₃S₂ Heterostructure on Nickel Mesh as Binder-Free Electrocatalyst for Enhanced Hydrogen Evolution Reaction

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ABSTRACT: Electrocatalytic hydrogen evolution reaction (HER) underpins the scalable synthesis of renewable green hydrogen, yet conventional catalytic systems are constrained by overreliance on scarce noble metals, sluggish mass transport kinetics, and inefficient intermediate modulation. In this work, an efficient HER electrocatalyst with a WS₂/Ni₃S₂ heterostructure was constructed through an electrodeposition strategy on nickel mesh. The WS₂/Ni₃S₂ electrocatalyst shows an overpotential of 52 mV at a current density of 10 mA·cm⁻², a small Tafel slope of 52.1 mV·dec⁻¹, and a reduced charge transfer resistance (R_{ct} = 22.80 Ω) in 1.0 M KOH electrolyte, as well as excellent stability. The boosted HER performance originates from the strong interfacial electronic coupling at the WS₂/Ni₃S₂ heterojunction, which simultaneously maximizes the density of accessible active sites and triggers interfacial charge redistribution to accelerate water cleavage kinetics. This work develops a feasible synthetic strategy to construct high-performance self-supported HER electrocatalysts for large-scale hydrogen production.

KEYWORDS: WS₂/Ni₃S₂ heterostructure; hydrogen evolution reaction; electrodeposition; electrocatalyst; alkaline media

1 Introduction

Growing global energy demands and escalating climate change risks are driving researchers to pursue sustainable, environmentally benign energy alternatives. Green hydrogen has emerged as a core pillar of carbon-neutral economic systems, benefiting from its ultrahigh gravimetric energy density (~142 MJ·kg⁻¹) and exceptional energy conversion efficiency [1,2]. Electrochemical water splitting for hydrogen generation is universally recognized as one of the most viable technologies for large-scale industrial deployment, featuring zero pollutant emission and full carbon neutrality throughout the process [3,4]. Nevertheless, the hydrogen evolution reaction (HER) inherently suffers from large overpotentials, stemming from sluggish reaction kinetics induced by the high activation energy of the requisite water dissociation step ($\text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^- + \text{H}^*$) [5,6]. While precious metals such as platinum and palladium represent the benchmark catalysts for hydrogen production, their geological rarity and exorbitant costs severely hinder the widespread commercialization of water electrolysis systems [7,8]. Consequently, engineering robust and highly active HER electrocatalysts derived from Earth-abundant materials remains a critical imperative in contemporary energy research.

To date, considerable research effort has focused on earth-abundant transition-metal compounds (including sulfides, nitrides, carbides, and phosphides) as alternative HER electrocatalysts owing to their

favorable d-orbital configurations, high corrosion resistance, and natural abundance [9–11]. Among them, nickel sulfides [12], particularly metallic Ni_3S_2 , are particularly promising for alkaline HER due to their favorable electronic structure for hydrogen adsorption/desorption, cost-effectiveness, and corrosion resistance. This electronic advantage originates from the Ni-S bonding, which elevates the electron density around Ni atoms, strengthens Ni-Ni metallic interactions, and facilitates charge transfer. However, Ni_3S_2 inherently suffers from sluggish charge transport and poor active-site exposure, significantly impeding its HER kinetics [13].

Constructing heterostructures is regarded as an effective strategy for enhancing the HER, because electronic-state regulation at the heterointerface can optimize hydrogen adsorption energetics and accelerate interfacial proton/electron transfer. The synergistic effect originating from the heterointerface can further modulate the electronic environment of active sites, thereby lowering the energy barrier for water dissociation and improving the intrinsic activity of catalysts [14,15]. For example, constructing a $\text{Ni}_7\text{S}_6/\text{Co}_3\text{S}_4$ heterojunction shifts the d-band center away from the Fermi level relative to NiCo-LDHs [16]. This electronic regulation optimizes the adsorption of reactive intermediates and consequently reduces the HER energy barrier. Notably, WS_2 exhibits a Gibbs free energy of hydrogen adsorption (ΔG_{H}) close to that of Pt, and its W 5d electrons are highly active toward hydrogen adsorption [17,18]. Therefore, the rational integration of WS_2 and Ni_3S_2 into a heterostructure is expected to couple the favorable hydrogen adsorption of WS_2 with the efficient water-dissociation capability of Ni_3S_2 at the heterointerface, thereby delivering outstanding electrocatalytic performance for the HER.

Motivated by refined fabricating protocols and deeper mechanistic understanding of nickel-sulfur electrocatalysis, the scientific community has designed numerous material variants with customized morphologies, spatial scales, and chemical profiles. Conventional production pathways for such systems comprise hydrothermal reactions, physical and chemical vapor deposition (PVD/CVD), solvothermal processing, as well as electrodeposition procedures. Among these synthetic avenues, electrodeposition [19,20] offers several compelling advantages for producing HER catalysts. Its inherently mild operating conditions (ambient temperature and pressure) circumvent the high-temperature sintering or phase segregation often encountered in vapor-phase or thermal routes. Moreover, the fine tunability of deposition parameters, such as applied potential, current density, and electrolyte composition, enables precise control over film thickness, elemental stoichiometry, and nanoscale morphology, all of which are critical determinants of catalytic activity and durability. The one-step, solution-based nature of electrochemical fabrication also facilitates uniform coating onto complex substrate geometries and scalable production, making it an economically attractive and industrially relevant route for large-area electrode fabrication.

Based on the aforementioned rationale, we prepared $\text{WS}_2/\text{Ni}_3\text{S}_2$ heterostructure through an efficient single-step electrodeposition technique. The synthesized $\text{WS}_2/\text{Ni}_3\text{S}_2$ heterostructure demonstrates remarkable HER activity under alkaline conditions, attaining $10 \text{ mA}\cdot\text{cm}^{-2}$ at an overpotential of 52 mV, along with a small Tafel slope ($52.1 \text{ mV}\cdot\text{dec}^{-1}$) and robust operational durability. The boosted HER performance originates from the strong interfacial electronic coupling at the $\text{WS}_2/\text{Ni}_3\text{S}_2$ heterojunction, which simultaneously maximizes the density of accessible active sites and triggers interfacial charge redistribution, thereby accelerating water dissociation kinetics. Ultimately, our findings establish a scalable and reliable protocol for fabricating binder-free hydrogen-evolving architectures, holding immense promise for next-generation industrial alkaline electrolyzers.

2 Experimental Details

2.1 Reagents

Thiourea ($\text{CH}_4\text{N}_2\text{S}$), sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), sodium citrate ($\text{C}_6\text{H}_5\text{O}_7\text{Na}_3$), nickel sulfate hydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), sodium chloride (NaCl), 5-sulfosalicylic acid ($\text{C}_7\text{H}_6\text{O}_6\text{S}$), boric acid (H_3BO_3), potassium hydroxide (KOH), saccharin sodium ($\text{C}_7\text{H}_4\text{NNaO}_3\text{S}$), Pt/C catalyst (20 wt% Pt loading), and Nafion (5 wt%) were procured from Aladdin Chemistry Co., Ltd. Every chemical was utilized in its as-received state, bypassing any supplementary refining procedures. Aqueous electrolytes and reaction mixtures were formulated exclusively with deionized water possessing a minimum resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$, which was dispensed by a Millipore purification apparatus (Millipore Corp., USA).

2.2 Synthesis of $\text{WS}_2/\text{Ni}_3\text{S}_2$ Heterostructure

Before electrodeposition, the as-received Ni meshes (dimensions of $10 \times 10 \text{ mm}$ and 40 mesh) experienced progressive ultrasonic washing in ethanol, 3 M HCl, and ultrapure water for 20 min each, effectively eliminating adsorbed impurities and passivation layers. The chemically activated frameworks were subsequently subjected to vacuum desiccation at 60°C overnight, yielding completely dehydrated surfaces for subsequent use.

Electrodeposition was carried out in a two-electrode configuration, where the pre-cleaned Ni mesh substrate was used as the cathode and a $2 \text{ cm} \times 2 \text{ cm}$ graphite plate as the anode. The distance between the two electrodes was 2 cm. Electrodeposition was performed using a DLX-6020APC power supply (Delixi Electric). The electrolyte consists of $140 \text{ g}\cdot\text{L}^{-1}$ $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $40 \text{ g}\cdot\text{L}^{-1}$ $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $100 \text{ g}\cdot\text{L}^{-1}$ thiourea, $70 \text{ g}\cdot\text{L}^{-1}$ $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3$, $30 \text{ g}\cdot\text{L}^{-1}$ NaCl , $40 \text{ g}\cdot\text{L}^{-1}$ H_3BO_3 , $1.5 \text{ g}\cdot\text{L}^{-1}$ $\text{C}_7\text{H}_4\text{NNaO}_3\text{S}$, $5 \text{ g}\cdot\text{L}^{-1}$ $\text{C}_7\text{H}_6\text{O}_6\text{S}$. Titration of the electrolyte to pH 4.0 with 1 M HCl was necessary to suppress Ni_2O_3 formation at higher pH and mitigate competitive hydrogen evolution at lower pH, both of which impede alloy deposition. Electrodeposition proceeded at $30 \text{ mA}\cdot\text{cm}^{-2}$ for 1 h at 40°C . After synthesis, the obtained specimens were washed in sequence with distilled water and ethanol, and then dried at 60°C for 12 h. The exposed geometric area of the 40-mesh Ni mesh substrate was strictly controlled at 1.0 cm^2 . The catalyst loading masses of the self-supported electrodes were determined by weighing the Ni mesh before and after the electrodeposition using a high-precision analytical balance ($\pm 0.01 \text{ mg}$). The average loading mass for the $\text{WS}_2/\text{Ni}_3\text{S}_2$ heterostructure was measured to be $\sim 1.9 \text{ mg}\cdot\text{cm}^{-2}$, while the Ni_3S_2 electrode was $\sim 1.7 \text{ mg}\cdot\text{cm}^{-2}$.

For comparison, Pt/C electrodes were fabricated by mixing 10 mg of commercial 20 wt% Pt/C powder, $40 \text{ }\mu\text{L}$ of 5 wt% Nafion, and $400 \text{ }\mu\text{L}$ of ethanol. Following 30 min of sonication, a $10 \text{ }\mu\text{L}$ drop of this mixture was cast onto a glassy carbon disk, yielding a mass loading of about $3.2 \text{ mg}\cdot\text{cm}^{-2}$, which was then left to dry overnight at 60°C .

2.3 Physicochemical Characterization

Phase identification and crystal structures of the fabricated specimens were evaluated via X-ray diffraction (XRD) measurements, utilizing a Rigaku Smartlab diffractometer equipped with $\text{Cu K}\alpha$ monochromatic radiation ($\lambda = 0.154178 \text{ nm}$). To visualize surface topographies and microstructural features, scanning electron microscopy (SEM) was employed on a Hitachi S-4800 instrument, which was simultaneously coupled with energy-dispersive X-ray spectrometry (EDS, X-Max Oxford Instruments) for elemental mapping. Morphological and structural characterizations were performed utilizing high-resolution transmission electron microscopy (HRTEM) alongside selected-area electron diffraction (SAED). These measurements were executed on an FEI Tecnai G2 F20 apparatus operating at an acceleration potential of 200 kV. To elucidate

the surface chemical environments and elemental oxidation states, X-ray photoelectron spectroscopy (XPS) analyses were conducted. Spectra were collected using a Thermo Scientific Escalab 250Xi spectrometer featuring a monochromatized Al K α excitation source ($h\nu = 1486.6$ eV). For precise energy alignment, all derived binding energies were referenced to the C 1s peak of adventitious hydrocarbon contamination, fixed at 284.8 eV.

2.4 Electrochemical Measurements

All electrochemical tests were performed on a CHI660E workstation (CH Instruments Inc.) in a three-electrode cell, employing the as-synthesized sample as the working electrode, a saturated calomel electrode (SCE, saturated KCl) as the reference, and a graphite plate (2 cm $\times$ 2 cm) as the counter electrode. Prior to each measurement, the electrolyte was degassed for 30 min by purging nitrogen gas to achieve inert atmosphere. All recorded potentials (vs. SCE) were rigorously converted to the reversible hydrogen electrode (RHE) scale using the Nernst equation [21]: $E(\text{RHE}) = E(\text{SCE}) + 0.244 + (0.059 \times \text{pH})$ (at 25°C).

Polarization curves derived from linear sweep voltammetry (LSV) were recorded with a scan rate of 2 mV·s⁻¹, and the presented potentials were strictly calibrated with 95% iR_s correction to exclude ohmic losses. Charge transfer kinetics were further investigated via electrochemical impedance spectroscopy (EIS) by applying a 5 mV sinusoidal signal over frequencies ranging from 100 kHz to 0.01 Hz. Equivalent circuit fitting of the acquired impedance spectra was accomplished employing the ZView analytical program. To examine electrocatalyst stability for HER, cyclic voltammetry (CV) and chronopotentiometry experiments were adopted. During electrochemical characterization, current density values were determined through geometric normalization of measured currents to the surface area of Ni mesh substrate. The Tafel slope was quantified by constructing a polarization plot of overpotential (η) versus the logarithmic scale of current density ($\log j$), where the linear region at low overpotentials was subjected to kinetic analysis via the Tafel equation [22]: $\eta = a + b \log(j)$, where b is Tafel slope and reflects the charge transfer kinetics of HER.

3 Results and Discussion

As illustrated in Fig. 1, the WS₂/Ni₃S₂ heterostructure for HER was fabricated via controlled electrodeposition. Nickel mesh was selected as the conductive substrate for the *in-situ* growth of target electrocatalytic materials in our research, benefiting from its inherent structural and economic merits including remarkable electronic transport capability, strong anti-corrosion performance, reliable mechanical flexibility, as well as desirable functional features that facilitate mass transfer and prevent unwanted interfacial diffusion.

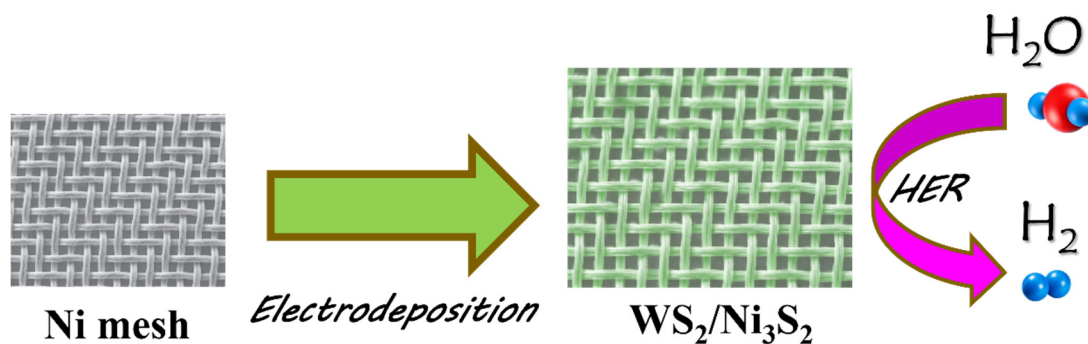


Figure 1: Schematic illustration of the fabrication of WS₂/Ni₃S₂ electrocatalysts on Ni mesh.

To investigate the phase composition of Ni_3S_2 and $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalysts, XRD measurements were conducted. As depicted in Fig. 2, both electrocatalysts present three well-resolved diffraction peaks located near 2θ values of 44.3° , 51.8° , and 76.4° , which can be readily assigned to the (111), (200), and (220) planes of face-centered cubic (fcc) Ni, consistent with the standard PDF card (No. 04-0850). Notably, no distinct diffraction peaks belonging to Ni_3S_2 or WS_2 phases are observed in the macroscopic XRD patterns. This absence is primarily attributed to the relatively thin thickness of the electrodeposited coating and the low crystallinity of the deposited phases, whose weak diffraction signals are inevitably shielded by the strong substrate background. The variations in the intensity and width of the Ni peaks between the two samples cannot demonstrate the crystallinity of the catalyst; rather, they are likely a result of differences in coating loading, thickness, and the degree of substrate exposure during the electrodeposition process. Although macroscopic XRD lacks the resolution to probe these surface configurations, subsequent HRTEM and SAED analyses microscopically authenticate the successful construction of a $\text{WS}_2/\text{Ni}_3\text{S}_2$ heterostructure.

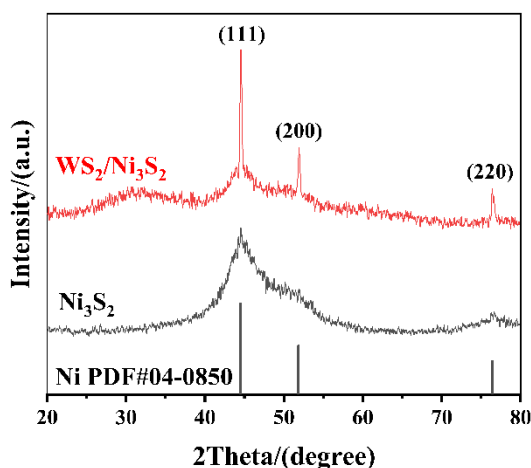


Figure 2: XRD pattern of Ni_3S_2 and $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalysts.

The surface chemistry and chemical states of the $\text{WS}_2/\text{Ni}_3\text{S}_2$ heterostructure were analyzed by XPS. The XPS spectra were analyzed via peak deconvolution using XPSpeak software, with the fitting results presented in Table S1. The survey spectrum (Fig. 3a) confirms the presence of Ni, S, W, O, and C in the $\text{WS}_2/\text{Ni}_3\text{S}_2$ heterostructure. The detection of carbon is attributable to adventitious solvent residuals, while oxygen contamination likely originates from surface oxidation of the freshly prepared electrocatalysts [23]. In the high-resolution Ni 2p spectrum (Fig. 3b), peaks located at 855.25 eV ($\text{Ni } 2p_{3/2}$) and 872.84 eV ($\text{Ni } 2p_{1/2}$) are indicative of Ni^{2+} species [24], whereas signals at 856.41 eV ($\text{Ni } 2p_{3/2}$) and 874.2 eV ($\text{Ni } 2p_{1/2}$) correspond to higher-valence Ni^{3+} configurations [25]. Two distinct satellite features of the Ni 2p orbital were observed at binding energies of 861.5 eV and 879.8 eV. The peak appearing at 852.31 eV corresponds well to metallic nickel. Quantitative analysis based on integrated peak areas reveals that the surface molar fractions of Ni^0 , Ni^{2+} and Ni^{3+} are 7.45%, 48.82% and 43.73%, respectively. The high-resolution spectrum of S 2p (Fig. 3c) reveals a prominent component centered at a binding energy of 168.55 eV, which is assigned to the S-O bond of residual SO_4^{2-} species originating from partial surface oxidation of the underlying metal sulfides in air. Additionally, the high-resolution S 2p spectrum exhibits a prominent doublet emerges at binding energies of 161.64 and 162.80 eV, which are assigned to the S $2p_{3/2}$ and S $2p_{1/2}$ states, respectively. Crucially, the observed energy separation of approximately 1.16 eV, alongside the specific peak locations, identifies these signals as divalent sulfide (S^{2-}) species [26]. Lattice S^{2-} dominates the sulfur species with a proportion of

79.23%, demonstrating the successful formation of nickel sulfide active matrix. The electronegative S²⁻ rearranges the interfacial electron density of adjacent Ni sites to promote the cleavage of O-H bonds, and the ultrathin surface S-O passivation layer can enhance the electrochemical corrosion resistance of the catalyst without hindering electrolyte permeation. Fig. 3d presents the high-resolution W 4f XPS spectrum, depicting two intense peaks at 34.81 eV (W 4f_{7/2}) and 35.29 eV (W 4f_{5/2}), consistent with the literature [27]. Additionally, a minor feature at 37.17 eV is attributable to W 4f_{5/2} in WO₃, indicating surface oxidation upon air exposure.

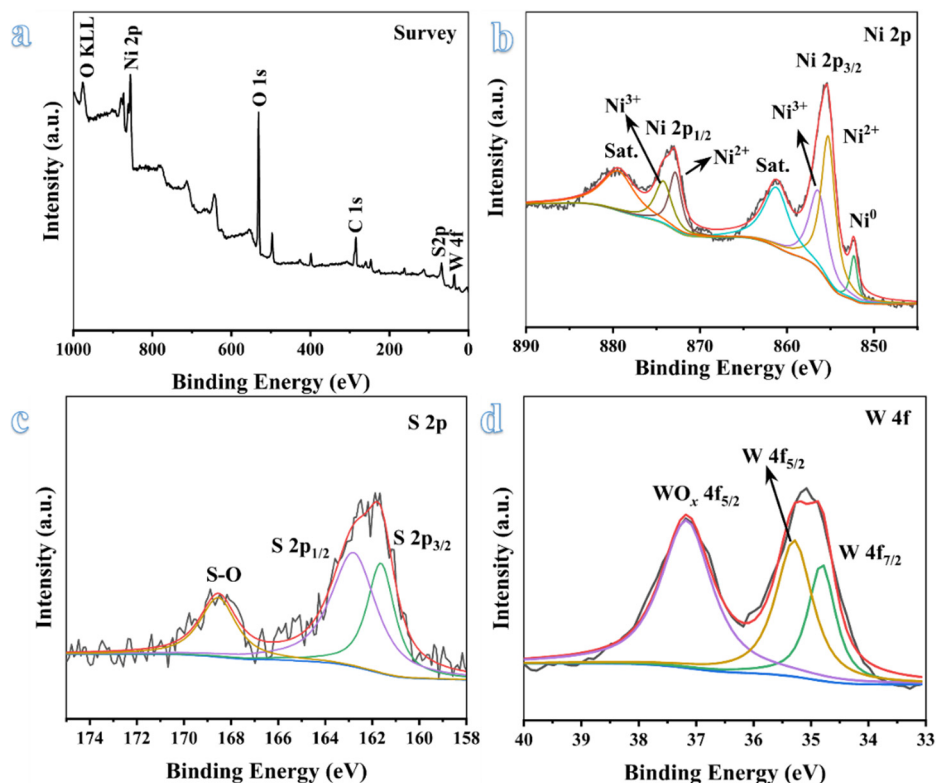


Figure 3: XPS spectra of WS₂/Ni₃S₂ heterostructure. (a) Survey; (b) Ni 2p; (c) S 2p; (d) W 4f.

The surface morphology of Ni₃S₂ and WS₂/Ni₃S₂ electrocatalysts were studied by SEM. As shown in Fig. 4, the Ni₃S₂ electrocatalyst delivers a densely packed thin film constructed by spherical granular aggregates with smooth surfaces, in which sparse narrow cracks emerge to relieve the internal stress accumulated during the sulfidation procedure. Nevertheless, the compact stacking of large spherical grains tends to encapsulate plentiful electrocatalytic active sites and impedes electrolyte infiltration as well as the timely detachment of evolved gaseous products, thereby triggering inferior active site utilization and sluggish mass-transfer kinetics toward electrocatalytic reactions. Upon the construction of the WS₂/Ni₃S₂ heterostructure, prominent morphological reconstruction is observed for the WS₂/Ni₃S₂ electrocatalyst. The initially regular spherical crystallites are remarkably refined and rearranged into irregular wrinkled agglomerates assembled from tiny nanograins, accompanied by the formation of a highly interconnected crack network and drastically improved surface roughness. Benefiting from interfacial coupling-induced grain refinement, abundant undercoordinated edge sites and grain boundaries are exposed, which act as privileged catalytic centers to drive the electrocatalytic process. Meanwhile, the hierarchical interconnected voids and extended crack pathways greatly accelerate electrolyte penetration and facilitate the rapid escape of *in-situ*

generated gas bubbles, efficiently suppressing the masking of active sites and structural pulverization under high current densities. Furthermore, the atomic percentages derived from EDS (Fig. S1 and Table S2) for the $\text{WS}_2/\text{Ni}_3\text{S}_2$ heterostructure are 74.98% Ni, 16.82% S, and 8.20% W, indicating that tungsten is effectively integrated into the nickel-sulfide framework.

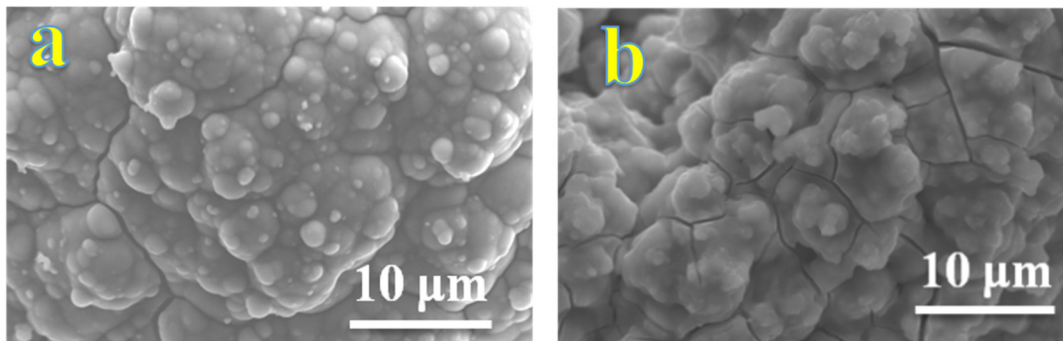


Figure 4: SEM images of (a) Ni_3S_2 and (b) $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalysts.

To probe the intrinsic microstructural properties of the fabricated electrocatalyst, HRTEM was subsequently performed. As illustrated in Fig. 5a, the interplanar spacings of diverse lattice fringes were measured, where a lattice spacing of $d = 0.29$ nm in Fig. 5a matches well with the (110) crystal plane of Ni_3S_2 (PDF No. 44-1418). Another measured spacing of $d = 0.42$ nm is close to the standard interplanar distance ($d = 0.41$ nm) of the (101) plane for Ni_3S_2 (PDF No. 44-1418), which verifies the existence of the Ni_3S_2 phase in the fabricated electrode. Fig. 5b reveals a polycrystalline diffraction pattern characterized by concentric rings formed by the superposition of numerous randomly oriented crystallites. These diffraction rings are precisely indexed to the (103) and (107) planes of WS_2 , alongside the (214) plane of Ni_3S_2 . The coexistence of these specific diffraction signals conclusively verifies the dual-phase $\text{WS}_2/\text{Ni}_3\text{S}_2$ heterostructure of the prepared composite, which is expected to provide abundant heterointerfaces for enhancing electrocatalytic kinetics.

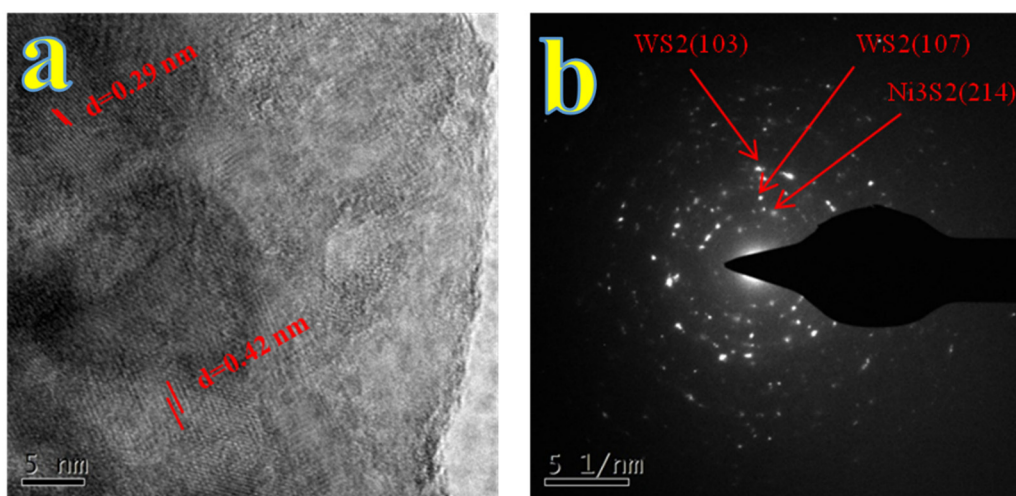


Figure 5: (a) High-resolution TEM images of $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalyst. (b) Selected area electron diffraction patterns of $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalysts.

The HER activity of the synthesized catalysts was initially assessed in 1.0 M KOH. To establish a reliable baseline, a commercial Pt/C reference and a bare nickel mesh substrate were analyzed under identical conditions. The resulting LSV (Fig. 6a) demonstrate that Pt/C exhibited superior HER activity, while the bare nickel mesh showed negligible performance. The HER overpotentials for WS₂/Ni₃S₂ heterostructure and Ni₃S₂ electrocatalysts at 10 mA·cm⁻² were 52 mV and 92 mV, respectively. Beyond this, the alkaline HER overpotential of WS₂/Ni₃S₂ heterostructure is comparable to, or even surpasses, the vast majority of previously documented earth-abundant catalysts (Table S3). These findings highlight that tungsten doping significantly boosts electrocatalytic kinetics for HER in alkaline electrolytes, as evidenced by the reduced overpotential. To exclude the influence of catalyst loading differences, mass-normalized polarization curves were evaluated (Fig. S2). The WS₂/Ni₃S₂ heterostructure consistently exhibits higher mass activity than Ni₃S₂ sample across the tested potential window. This unambiguously confirms that the WS₂/Ni₃S₂ heterointerface intrinsically improves the catalytic activity, rather than merely increasing the catalyst quantity.

To meet the demands of industrial applications, the HER performance of the various electrocatalysts was further evaluated in a 30 wt% KOH solution. Following rigorous 95% ohmic drop correction of the polarization curves in 30 wt% KOH, utilizing the experimentally determined electrolyte resistance, the overpotentials required to drive 10 mA·cm⁻² for the bare Ni mesh, Ni₃S₂, and WS₂/Ni₃S₂ heterostructure electrocatalysts were 504, 310, and 256 mV, respectively (Fig. S3), indicating that heterostructure effectively enhances the HER catalytic activity of the Ni₃S₂ electrocatalysts. Notably, the highly concentrated KOH environment resulted in varying degrees of degradation in the HER activity of all electrodes compared to that in 1.0 M KOH. This decay mainly results from the reduced free water activity in the concentrated alkaline electrolyte, which restricts the water dissociation kinetics of the Volmer step. Meanwhile, the increased electrolyte viscosity impedes mass transport and leads to sluggish bubble detachment, thereby blocking a portion of the active sites. Even under such harsh conditions, the WS₂/Ni₃S₂ heterostructure still exhibits the optimal catalytic performance, highlighting its promising potential for industrial-scale high-current electrolysis.

Serving as a vital kinetic descriptor, the Tafel slope provides critical insights into the rate-determining step (RDS) governing the hydrogen evolution process. Derived from the corresponding polarization curves (Fig. 6b), the WS₂/Ni₃S₂ heterostructure delivers a remarkably low value of 52.1 mV·dec⁻¹, standing in sharp contrast to the 71.9 mV·dec⁻¹ recorded for the Ni₃S₂ electrocatalyst. This dramatic reduction in the Tafel metric dictates that tungsten incorporation fundamentally expedites the reaction kinetics, presumably by optimizing the adsorption energetics of key intermediates and shifting the underlying catalytic pathway. Typically, HER in an alkaline environment is characterized by the following reactions [28,29]:



Kinetic analysis in alkaline media suggests that the HER proceeds via either the Volmer-Heyrovsky or Volmer-Tafel route (Fig. S4), wherein the Tafel slope serves as a diagnostic metric for isolating the RDS. For the WS₂/Ni₃S₂ heterostructure, a Tafel slope of 52.1 mV·dec⁻¹ was recorded. This value indicates a

Volmer-Heyrovsky mechanism, in which the Heyrovsky step governs the alkaline kinetics, thereby acting as the RDS for the HER.

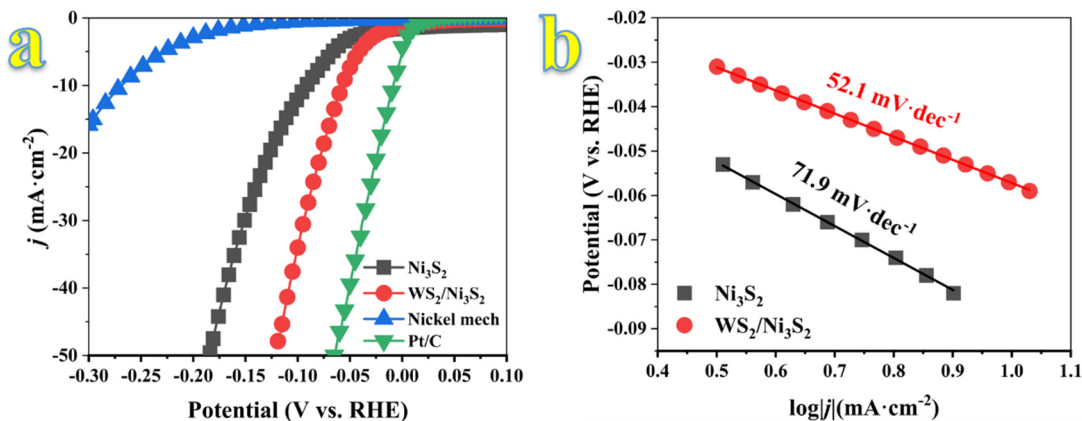


Figure 6: (a) Polarization curves and (b) Tafel plots for HER of Ni₃S₂ and WS₂/Ni₃S₂ heterostructure in 1.0 M KOH electrolyte.

Furthermore, the intrinsic HER kinetics were benchmarked by extracting the exchange current density (j_0), a fundamental descriptor of electrocatalytic activity. As summarized in Table S4, the WS₂/Ni₃S₂ electrocatalyst exhibits a j_0 of 2.96×10^{-2} mA·cm⁻², outperforming that of Ni₃S₂ (2.91×10^{-2} mA·cm⁻²). The higher j_0 of WS₂/Ni₃S₂ electrocatalyst highlights the boosted intrinsic HER activity conferred by heterostructure.

The transfer coefficient (α), serving as a critical parameter defining electrocatalytic intrinsic activity, was determined by employing the following Eq. (4) [30]:

$$\alpha = \frac{2.303RT}{nbF} \quad (4)$$

Here, R represents the universal gas constant ($8.314 \text{ J} \cdot (\text{K} \cdot \text{mol})^{-1}$), F denotes the Faraday constant ($96,485 \text{ C} \cdot \text{mol}^{-1}$), and T corresponds to the absolute temperature (298 K in this study). The α value of 0.57 obtained for the WS₂/Ni₃S₂ electrocatalyst exceeds that of the Ni₃S₂ electrocatalyst (0.41), indicating more favorable reaction kinetics for the WS₂/Ni₃S₂ electrocatalyst. The excellent HER electrocatalytic activity of the WS₂/Ni₃S₂ electrocatalyst originates from the distinctive valence electronic configurations of Ni and W atoms, which are $3d^8 4s^2$ and $5d^4 4s^2$, respectively. Both metals possess unpaired electrons in their d-orbitals. During the HER, a strong synergistic catalytic effect emerges between Ni and W centers, which expedites interfacial electron transfer and thereby boosts the overall HER catalytic efficiency. Furthermore, the incorporation of W reduces the electron density of surrounding S atoms. This weakens the binding strength between S-based active sites and adsorbed atomic hydrogen (H^*), facilitates the desorption of H^* intermediates, and ultimately accelerates the HER kinetics of the electrode.

Turnover frequency (TOF) is widely adopted to assess the intrinsic catalytic activity. Regarding the hydrogen evolution reaction (HER), TOF values were evaluated based on Eq. (5):

$$\text{TOF} = \frac{j}{2nF} \quad (5)$$

In this equation, j refers to the current density obtained from the LSV curves, n is the molar amount of active sites on the electrode, and F corresponds to the Faraday constant ($96,485 \text{ C} \cdot \text{mol}^{-1}$). The variable n was determined via Eq. (6):

$$n = \frac{S}{2\mu F} \quad (6)$$

where μ represents the scan rate ($50 \text{ mV}\cdot\text{s}^{-1}$) and S is the integrated charge area of the CV curve recorded in a pH 7.0 phosphate buffer solution (PBS) at the same scan rate. Fig. S5a displays the CV curves of the Ni_3S_2 and $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalysts in the pH 7.0 PBS. According to Eq. (6), the amounts of active sites for Ni_3S_2 and $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalysts were calculated as 8.651×10^{-8} and 2.238×10^{-7} mol, respectively. Since both electrodes share the same geometric area (1 cm^2), the $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalyst exhibits a higher density of active sites. The TOF plots calculated from Eq. (5) are shown in Fig. S5b. To reach a TOF of 1 s^{-1} , the required overpotentials for Ni_3S_2 and $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalysts are 120 and 103 mV, respectively. This lower overpotential further confirms the enhanced intrinsic activity of the $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalyst.

The electrochemically active surface area (ECSA) holds paramount significance in electrocatalytic HER processes, as it dictates the density of accessible active sites available for interfacial charge transfer. A larger ECSA is intrinsically proportional to an expanded electrocatalytic interface, thereby mitigating mass-transport limitations and substantially augmenting the intrinsic activity toward the HER. The ECSA of the Ni_3S_2 and $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalysts were determined through quantification of electrochemical double-layer capacitance (C_{dl}) values extracted from CV measurements acquired across a range of scan rates within the non-faradaic potential window (Fig. S6). In this region, charge transfer kinetics are negligibly insignificant, ensuring that the measured current exclusively originates from the charging and discharging processes of the electric double layer. The slope coefficient is determined from the linear correlation between current density and scan rate, directly proportionate to twice the C_{dl} . As shown in Fig. 7a, the C_{dl} of Ni_3S_2 and $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalysts are 41.1 and $44.4 \text{ mF}\cdot\text{cm}^{-2}$, with high linear correlation coefficients ($R^2 > 0.99$) confirming the reliability of the measurements, revealing enlarged ECSA upon heterostructure. By applying the relation $\text{ECSA} = C_{\text{dl}}/C_s$ with a conventional specific capacitance ($C_s = 0.040 \text{ mF}\cdot\text{cm}^{-2}$) for metallic electrodes in alkaline environments, the $\text{WS}_2/\text{Ni}_3\text{S}_2$ was determined to possess an active area of approximately 1110 cm^2 , which more than doubles that of the Ni_3S_2 sample (1027.5 cm^2) and thereby verifies the substantial surface enlargement induced by tungsten doping. The surface roughness factor (R_f), defined as the ratio of ECSA to the geometric footprint of the electrode (A_{geo} , 1 cm^2 for the $10 \times 10 \text{ mm}$ Ni mesh), was subsequently calculated. Specifically, the R_f was calculated to be 1110 for $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalyst, about 2.18 times of Ni_3S_2 electrocatalyst ($R_f = 1027.5$). Consequently, the $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalyst possesses a high density of active sites, ensures facile access to these catalytic centers, and enables enhanced HER kinetics.

Electrochemical impedance spectroscopy (EIS) was leveraged to probe the interfacial charge transfer dynamics governing the HER. Fig. 7b displays the Nyquist plots of the electrocatalysts, which were modeled using the equivalent circuit shown therein to extract key kinetic parameters. In this equivalent circuit, R_s signifies the electrolyte resistance; R_{ct} represents the charge-transfer impedance governing the faradaic reaction at the electrode-electrolyte boundary; while CPE constitutes the constant-phase element characterizing frequency-dependent polarization effects. As shown in Fig. 7b and Table S5, $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalyst exhibits a much smaller radius of the semicircle in the low frequency region compared with Ni_3S_2 electrocatalyst, indicating lower R_{ct} of 22.8Ω than that of Ni_3S_2 electrocatalyst (189.5Ω), corresponding to faster HER kinetics and excellent conductivity. The significant reduction in R_{ct} from 189.5Ω (Ni_3S_2) to 22.8Ω ($\text{WS}_2/\text{Ni}_3\text{S}_2$) signifies a markedly lowered HER activation barrier, arising from the synergistic modulation achieved by constructing the $\text{WS}_2/\text{Ni}_3\text{S}_2$ heterojunction. The strong coupling at the

WS₂/Ni₃S₂ heterointerface not only induces grain refinement and interconnected crack networks to expose abundant undercoordinated sites and shorten the charge-transfer distance, but is also anticipated to trigger interfacial charge redistribution. This expected charge redistribution is proposed to optimize the local electron density of adjacent Ni active sites and promote H₂O polarization, collectively lowering the energy barrier of the rate-determining Heyrovsky step and accelerating interfacial electron kinetics. In addition, Fig. S7 shows that the WS₂/Ni₃S₂ electrocatalyst exhibits a substantially lower R_{ct}/ECSA ratio than that of the Ni₃S₂ electrocatalyst, providing further evidence for the enhanced intrinsic catalytic activity conferred by the WS₂/Ni₃S₂ heterostructure.

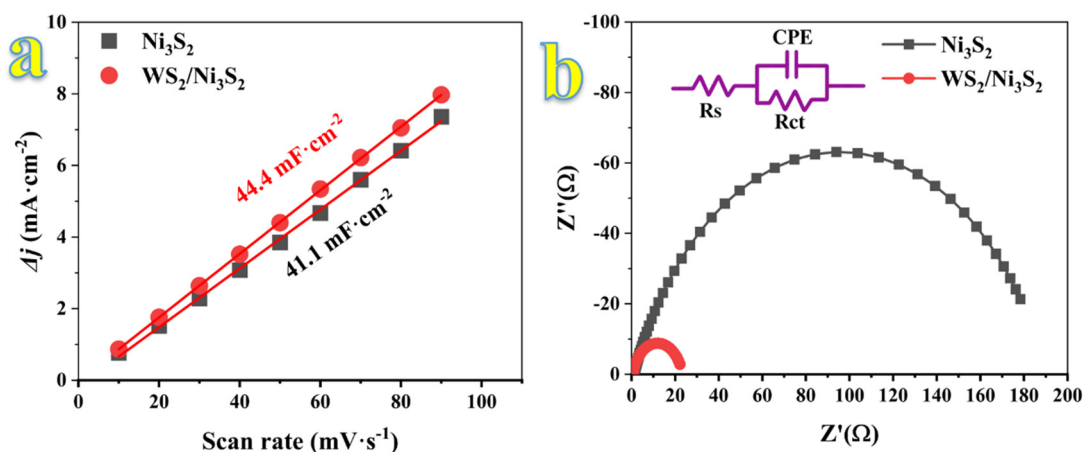


Figure 7: (a) Scan rate dependence of the current densities of Ni₃S₂ and WS₂/Ni₃S₂ electrocatalysts. (b) Nyquist plots of Ni₃S₂ and WS₂/Ni₃S₂ electrocatalysts (inset: equivalent circuit diagram).

In addition to catalytic activity, the stability of the electrocatalyst is another key indicator for assessing the HER behavior. The catalytic stability of WS₂/Ni₃S₂ electrocatalyst was first estimated by chronopotentiometry at 10 mA·cm⁻² in 30 wt% KOH without *i*R_s compensation. As illustrated in Fig. 8a, there is only a slight degradation during the HER stability measurement. Additionally, the LSV curves (Fig. 8b) of the WS₂/Ni₃S₂ electrocatalyst merely undergoes a slight negative shift after 2000 CV cycles from 0 to -200 mV vs. RHE at 100 mV·s⁻¹ in 30 wt% KOH. All of the above results showed that the WS₂/Ni₃S₂ electrocatalyst has good stability for the HER in alkaline media.

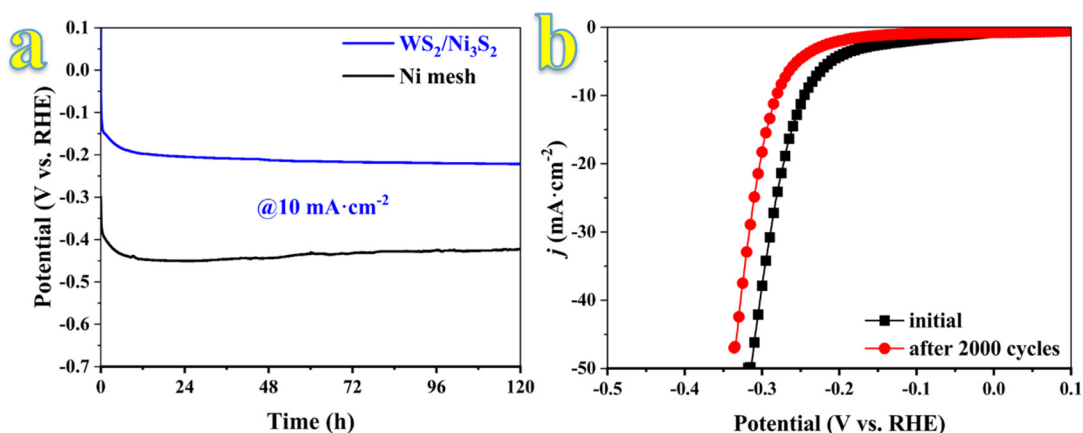


Figure 8: (a) Chronopotentiometry of WS₂/Ni₃S₂ electrocatalysts at 10 mA·cm⁻²; (b) LSV plots of WS₂/Ni₃S₂ electrocatalyst before and after 2000 cycles of CV tests.

4 Conclusion

In summary, the $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalyst was grown *in situ* on Ni mesh using a simple electrodeposition approach, and its electrocatalytic activity was investigated for HER. The $\text{WS}_2/\text{Ni}_3\text{S}_2$ electrocatalyst affords an overpotential of 52 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$, a Tafel slope of $52.1 \text{ mV}\cdot\text{dec}^{-1}$, and a reduced R_{ct} of 22.8Ω in 1.0 M KOH, along with excellent durability. This HER catalytic activity is competitive with the most recently developed Ni-based HER electrocatalysts. The excellent HER performance is mainly ascribed to the increased number of exposed active sites and facilitated electron/mass transfer. Our findings establish a rational design strategy for high-performance transition metal catalysts, simultaneously achieving enhanced intrinsic activity and structural integrity for sustainable alkaline HER applications.

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Conflicts of Interest: The authors declare no conflicts of interest.

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