

Article

Regulation of Electrochemical Activity via Controlled Integration of NiS₂ over Co₃O₄ Nanomaterials for Hydrogen Evolution Reaction

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Abstract

Electrochemical water splitting represents a sustainable approach for hydrogen production, yet efficient hydrogen evolution reaction (HER) catalysts operating in alkaline environments remain critically needed. Herein, we report the fabrication of Co₃O₄–NiS₂ nanocomposites synthesized through a facile coprecipitation and subsequent thermal treatment method. Detailed characterization via physicochemical techniques confirmed the successful formation of a hybrid Co₃O₄–NiS₂ heterostructure with tunable compositional and morphological characteristics. Among the synthesized catalysts (Co–Ni–1, Co–Ni–2, and Co–Ni–3), the Co–Ni–2 sample demonstrated optimal structural integration, displaying interconnected nanosheet morphologies and balanced elemental distribution. Remarkably, Co–Ni–2 achieved exceptional HER performance in 1 M KOH electrolyte, requiring an ultralow overpotential of only 84 mV at 10 mA cm^{−2} and exhibiting a favorable Tafel slope of 67.5 mV dec^{−1}. Electrochemical impedance spectroscopy and electrochemical surface area measurements further substantiated the superior electrocatalytic kinetics, rapid charge transport, and abundant active site accessibility in the optimized Co–Ni–2 composite. Additionally, Co–Ni–2 demonstrated outstanding durability with negligible activity decay over 5000 cycles. This study not only highlights the strategic synthesis of Co₃O₄–NiS₂ nanostructures but also provides valuable insights for designing advanced, stable, and efficient non-noble electrocatalysts for sustainable hydrogen generation.

Keywords: hydrogen evolution reaction; Co₃O₄–NiS₂ nanocomposites; alkaline electrocatalysis; synergistic interface



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1. Introduction

Hydrogen has emerged as a highly promising alternative energy carrier owing to its exceptionally high gravimetric energy density and environmentally benign nature, as its utilization produces only water as a by-product, resulting in zero carbon emissions [1–3]. Among the various hydrogen generation methods, electrochemical water splitting stands out as a clean and efficient route, particularly when powered by renewable energy sources such as solar, wind, or hydropower [4,5]. This process involves two half-reactions: the oxygen evolution reaction (OER) at the anode and the hydrogen evolution reaction (HER) at the cathode. The overall water-splitting reaction requires a minimum thermodynamic potential of 1.23 V, but due to kinetic barriers, practical operation often demands higher voltages, mainly attributed to the sluggish multi-electron transfer process

of the OER [1,6–8]. The HER, in contrast, is a two-electron process and generally proceeds more rapidly. However, in alkaline media, where hydroxide ions are involved instead of protons, the HER is comparatively slower than in acidic environments due to additional water dissociation steps [6,9]. Therefore, the development of highly active, stable, and low-cost HER catalysts is essential to promote efficient hydrogen evolution in alkaline water electrolysis. Traditionally, noble metals such as platinum (Pt) for the HER and ruthenium/iridium oxides (Ru, Ir) for the OER have been recognized as the benchmark electrocatalysts due to their outstanding catalytic activity and low overpotentials. However, their high cost, scarcity, and poor long-term stability in alkaline environments hinder their large-scale deployment in commercial electrolyzers. This has stimulated considerable research interest in the development of earth-abundant, low-cost, and stable transition metal-based alternatives [9–11].

Transition metals such as cobalt (Co), nickel (Ni), iron (Fe), and their respective compounds (oxides, sulfides, phosphides, and carbides) have emerged as promising non-precious metal catalysts for electrochemical water splitting. These materials exhibit multiple valence states, high intrinsic redox activity, and structural tunability, which are advantageous for tailoring their catalytic performance. In particular, the synergistic combination of different transition metal phases has been shown to enhance electronic conductivity, promote charge transfer, and increase the density of active sites [11–13]. Cobalt oxide (Co_3O_4), a typical spinel-type oxide, has demonstrated promising activity for both the HER and the OER due to its favorable electronic structure, thermal stability, and corrosion resistance [1,14]. It contains both Co^{2+} and Co^{3+} ions within its crystal lattice, which facilitates redox reactions through reversible valence changes. The Co^{2+} ions with three unpaired d-electrons and Co^{3+} ions with all paired electrons create a mixed valence system that promotes fast electron transfer and intermediate adsorption/desorption during electrocatalysis [11]. Recently, a Co_3O_4 @CDs nanocomposite was synthesized via a hydrothermal method, yielding an overpotential of 165 mV at a current density of 10 mA cm^{-2} in alkaline electrolyte [15]. Similarly, a $\text{Co}_3\text{O}_4/\text{MoS}_2$ p–p type heterojunction electrocatalyst featuring a nanoparticle/nanoflower hierarchical architecture was developed to exploit the synergistic interactions between the two semiconductors. When evaluated in 1 M KOH solution, the heterostructure exhibited an overpotential of 156 mV to drive a current density of 10 mA cm^{-2} , reflecting its superior electrocatalytic efficiency and interfacial charge transfer characteristics [16].

Nickel disulfide (NiS_2), a typical transition metal dichalcogenide (TMD), has recently attracted growing attention for HER applications due to its high electrical conductivity, favorable metal–sulfur bonding, and abundant edge-active sites [6]. NiS_2 exhibits excellent electron transport properties, which help to alleviate the inherent limitations of sluggish HER kinetics in alkaline conditions. Nanostructured NiS_2 has garnered considerable attention due to its intrinsic catalytic activity and ability to be engineered into high-surface-area architectures that enhance electrolyte accessibility and charge transport [3]. A noteworthy development in this field is the fabrication of nitrogen-doped NiS_2 nanosheets grown directly on carbon fiber cloth (denoted by N- NiS_2 /CF), forming an integrated electrode. The resulting N- NiS_2 /CF electrode demonstrates excellent HER activity, requiring an overpotential of only 96 mV to achieve a current density of 10 mA cm^{-2} in 1.0 M KOH electrolyte [17]. In another study, a hybrid nanowire architecture was constructed by integrating Cu-doped MoS_2 nanosheets onto NiS_2 nanowires through a multi-step strategy involving electrospinning, sulfuration, and hydrothermal treatment. The heterostructured nanowires exhibit significantly enhanced HER performance with a low overpotential of 105 mV at 10 mA cm^{-2} in alkaline medium [18]. Moreover, a unique heterostructure was engineered by introducing early transition metal vanadium (V) species into a NiS/NiS_2

hybrid matrix. The resultant V-NiS/NiS₂ electrocatalyst exhibited remarkable catalytic behavior with an overpotential of only 94 mV at 10 mA cm⁻² in 1 M KOH solution [19].

However, despite these advancements, many of the reported electrocatalysts still face inherent limitations such as relatively high overpotentials (typically >90 mV at 10 mA cm⁻²), insufficient long-term stability, or complex multi-step synthesis routes that hinder large-scale applicability. In this regard, there remains a critical need for rationally designed, compositionally tunable hybrid materials that offer both high catalytic activity and operational robustness in alkaline HER environments. To overcome these limitations, the current study reports the successful synthesis of a Co₃O₄-NiS₂ (Co-Ni) nanocomposite through a straightforward coprecipitation strategy. The resulting hybrid material was systematically evaluated as a highly active electrocatalyst for the hydrogen evolution reaction (HER) in alkaline environments. To address these challenges, the present study introduces a Co₃O₄-NiS₂ (Co-Ni) nanocomposite successfully synthesized via a facile coprecipitation method and investigated as an efficient electrocatalyst for the HER in alkaline media. Comprehensive spectroscopic and structural analyses confirmed the successful formation of the heterostructured composite, with nanosheet-like features presumably derived from sheet-structured NiS₂ uniformly integrated with the Co₃O₄ matrix. Among the series of fabricated samples, the Co-Ni-2 electrocatalyst exhibited superior HER activity, delivering a low overpotential of 84 mV at a current density of 10 mA cm⁻², along with a favorable Tafel slope of 67.5 mV dec⁻¹, as evaluated in a three-electrode configuration. Furthermore, the electrochemical durability of the optimized electrocatalyst was rigorously assessed through extended cyclic voltammetry (CV) tests, demonstrating remarkable structural and catalytic stability under prolonged alkaline operation. These superior electrocatalytic properties are attributed to the synergistic interaction between Co₃O₄ and NiS₂, which enhances charge transport, increases the electrochemically active surface area, and facilitates rapid hydrogen evolution kinetics. This work provides valuable insights into the development of high-performance electrocatalysts for sustainable hydrogen production.

2. Experimental Section

2.1. Chemicals

Cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, ≥98%), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 99.9%), Thiourea (CH₄N₂S, ≥99.0%), polyvinylidene fluoride (PVDF), and N-methyl-2-pyrrolidone (NMP, ≥99%) were obtained from Sigma-Aldrich, St. Louis, MO, USA. Potassium hydroxide (KOH, >85%) was provided by Daejung Chemicals & Metals, Gyeonggi-do, Republic of Korea. Acetylene black (99.9+%) was attained from Thermo Scientific, Seoul, Republic of Korea. The nickel foam utilized in this study was acquired from NARA Cell-Tech Corporation, Seoul, Republic of Korea. No extra purification was performed on any of the compounds utilized in this study. The experiments were conducted with deionized (DI) water.

2.2. Synthesis of Co₃O₄-NiS₂ Composite

The Co₃O₄-NiS₂ composite electrocatalysts were synthesized via a coprecipitation strategy, designed to explore the influence of compositional variation on structural and electrocatalytic performance. Initially, 0.03 mol of Co(NO₃)₂·6H₂O was dissolved in 25 mL of ethanol and sonicated for 10 min to achieve complete dissolution and homogeneity of the precursor solution. Subsequently, Ni(NO₃)₂·6H₂O and CH₄N₂S were introduced into the solution at varying concentrations, specifically, Ni(NO₃)₂·6H₂O at 0.001, 0.003, and 0.005 mol and CH₄N₂S at 0.01, 0.02, and 0.03 mol. The resulting mixtures were subjected to an additional 10 min of ultrasonication to ensure uniform dispersion of the metal and sulfur sources. The precursor solutions were then vigorously stirred at

110 °C for 2 h to the formation of intermediate complexes. Following this, the mixtures were dried at 110 °C for 1 h in an oven to remove residual solvents. The dried powders were then subjected to thermal treatment in a muffle furnace at 350 °C for 6 h to induce phase transformation, crystallization, and the formation of the desired Co₃O₄-NiS₂ composite. Finally, the annealed materials were finely ground using an agate mortar and pestle to obtain homogeneous powders. The synthesized samples were denoted by Co-Ni-1, Co-Ni-2, and Co-Ni-3 corresponding to increasing Ni and S precursor concentrations in order to systematically investigate the effect of compositional tuning on their physicochemical properties and HER electrocatalytic performance.

2.3. Material Characterization

The phase composition and structural characteristics of the synthesized nanomaterials were thoroughly assessed by employing X-ray diffraction (XRD) analysis, conducted using an X'Pert Pro diffractometer equipped with Cu K α radiation as the X-ray source. Furthermore, the surface chemical composition was comprehensively evaluated through X-ray photoelectron spectroscopy (XPS), performed with a Thermo Scientific K- α spectrometer, providing detailed insights into the elemental states and bonding environments. Lastly, scanning electron microscopy (SEM), coupled with energy-dispersive X-ray spectroscopy (EDX), was conducted using a HITACHI S-4800 microscope to investigate the morphological features, elemental distribution, and compositional homogeneity within the synthesized composites.

2.4. Electrochemical Analysis

Electrochemical measurements were systematically conducted using a Biologic Instrument (WBCS3000 battery cycler). A standard three-electrode configuration was adopted to perform a detailed electrochemical analysis. Before electrode preparation, nickel foam (NF) substrates underwent thorough pretreatment procedures involving sequential ultrasonication in DI water, acetone, and ethanol, each step lasting for 20 min. Following ultrasonication, the substrates were dried overnight at 60 °C to eliminate residual solvents and moisture. The electrocatalyst slurry was meticulously prepared by combining the active material, polyvinylidene fluoride (PVDF), and acetylene black in an optimized weight ratio of 80:10:10. N-methyl-2-pyrrolidone (NMP) was employed as the dispersing agent to ensure a homogeneous distribution. Subsequently, the well-prepared slurry was uniformly coated onto the pretreated NF substrate (dimensions: 1 $\times$ 1 cm²), and the coated substrates were dried at 60 °C overnight, ensuring robust adhesion of the electrocatalyst to the NF surface. For electrochemical characterizations, the coated NF served as the working electrode, with platinum plate and Hg/HgO electrodes utilized as counter and reference electrodes, respectively. The electrochemical experiments were executed in a nitrogen-saturated 1 M KOH electrolyte solution to ensure an inert environment, preventing undesired redox interference. Cyclic voltammetry (CV) measurements were conducted within a strictly controlled non-Faradaic potential window from 0.1 to 0.2 V at multiple scan rates (5, 10, 15, 20, and 25 mV s⁻¹). From these CV profiles, the electrochemically active surface area (ECSA) of the electrocatalyst was quantitatively determined using the following established equation [20,21]:

$$\text{ECSA} = \frac{C_{\text{dl}}}{C_s} \quad (1)$$

Here, C_{dl} is the electrochemical double-layer capacitance, while C_s is the specific capacitance of a planar surface in a 1 M KOH electrolyte, typically reported as 0.040 mF cm⁻². Electrochemical impedance spectroscopy (EIS) was systematically performed on all prepared samples within a frequency range from 100 kHz to 0.1 Hz, employ-

ing an amplitude of 10 mV, to comprehensively investigate the charge transfer resistance and interfacial properties. To precisely evaluate the electrocatalyst's activity for the HER, linear sweep voltammetry (LSV) was performed at a constant scan rate of 5 mV s^{-1} over a potential window ranging from 0 to 1 V. To precisely evaluate the electrocatalyst's activity for the HER, linear sweep voltammetry (LSV) was carried out at a constant scan rate of 5 mV s^{-1} across a potential window ranging from 0 to 1 V. The corresponding Tafel slopes were subsequently derived by fitting the linear regions of the obtained Tafel plots, providing valuable insights into the kinetics of the electrochemical reaction. Additionally, the stability and durability of the optimized electrocatalysts were critically assessed through LSV measurements performed before and after 5000 CV cycles.

3. Results and Discussion

The crystalline phases and structural integrity of the synthesized Co-Ni composites were investigated using XRD, as shown in Figure 1a. The diffraction patterns clearly confirm the coexistence of both Co_3O_4 and NiS_2 phases within the composite system. Distinct reflections of Co_3O_4 are observed at 2θ of 36.46° , 45.2° , 54.8° , and 59.02° , which are indexed to the (311), (400), (422), and (511) planes, respectively, of the cubic spinel phase (JCPDS No. 01-080-1540). The presence of these well-defined peaks indicates the successful formation of phase-pure Co_3O_4 with high crystallinity. Simultaneously, additional prominent peaks appearing at 2θ of 27.71° , 32.3° , 35.9° , 39.5° , and 54.1° correspond to the (111), (200), (210), (211), and (311) planes of cubic NiS_2 (JCPDS No. 01-080-0376), confirming the incorporation of the NiS_2 phase. The concurrent appearance of both sets of diffraction peaks without any extraneous signals affirms the formation of a clean binary composite with no secondary or impurity phases. Importantly, no observable peak shifting was detected, suggesting that both Co_3O_4 and NiS_2 maintain their individual crystal structures without significant lattice distortion or interdiffusion. With increasing NiS_2 content, a progressive enhancement in the intensity of NiS_2 -related peaks is noted. This trend highlights the increasing contribution of NiS_2 in the composite and confirms its effective integration within the Co_3O_4 matrix.

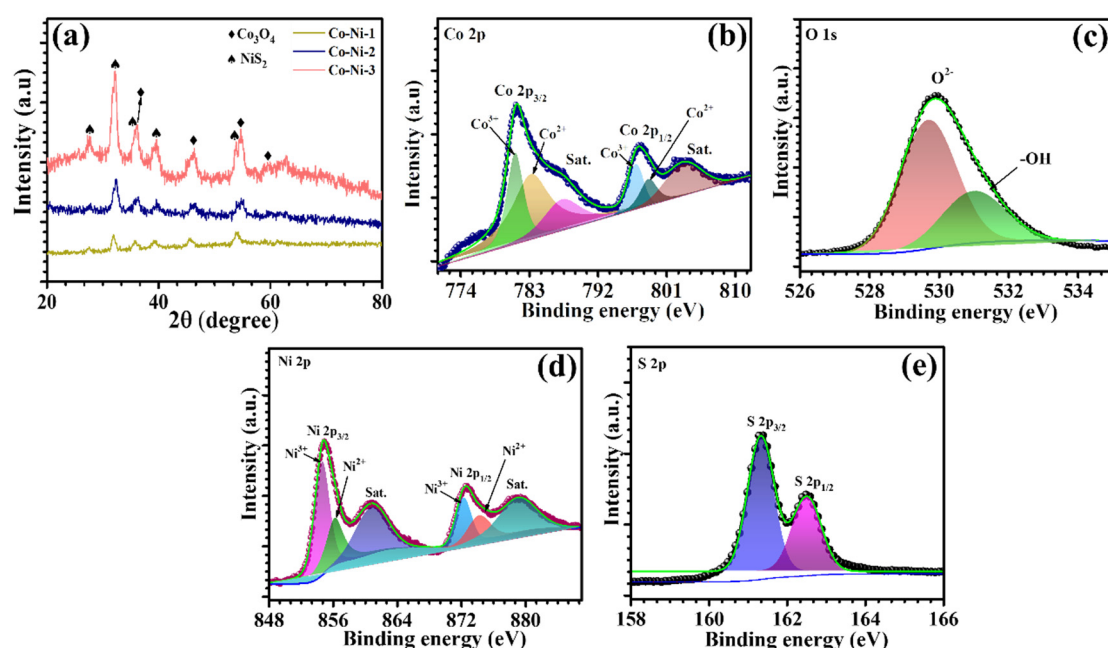


Figure 1. (a) XRD patterns of Co-Ni composites; (b–e) high-resolution XPS spectra of Co 2p, O 1s, Ni 2p, and S 2p.

XPS was carried out to investigate the surface chemical states and electronic interactions within the Co-Ni-2 composite. The high-resolution Co 2p spectrum (Figure 1b) reveals two prominent peaks at 781.16 eV and 796.9 eV, corresponding to Co 2p_{3/2} and Co 2p_{1/2}, respectively. These peaks exist along with the deconvoluted peaks at 783.41 eV and 798.7 eV. The deconvoluted peaks confirm the coexistence of Co²⁺ and Co³⁺ oxidation states, with satellite features near 787.6 eV and 803.3 eV characteristic of the spinel Co₃O₄ phase. This mixed-valence state is critical for promoting reversible redox reactions during electrocatalytic water splitting. The O 1s spectrum (Figure 1c) further supports this framework, with a strong peak at 529.71 eV assigned to lattice oxygen (M–O) and additional peaks at 531.08 eV corresponding to surface hydroxyl groups. These surface oxygenated species are known to enhance catalytic activity by facilitating intermediate adsorption [22]. The high-resolution Ni 2p spectrum (Figure 1d) reveals a well-defined set of spin–orbit doublets accompanied by shake-up satellite features, indicative of the coexistence of Ni²⁺ and Ni³⁺ oxidation states. As illustrated in Figure 1d, the deconvoluted peaks located at binding energies of 854.7 eV and 872.26 eV correspond to Ni³⁺ (2p_{3/2} and 2p_{1/2}), while those at 856.36 eV and 874.35 eV are attributed to Ni²⁺ species. The observed satellite peaks further confirm the presence of divalent nickel, a common feature in sulfide-based materials. This dual-valence configuration reflects the redox flexibility of nickel within the NiS₂ matrix and is anticipated to play a crucial role in enhancing electrochemical kinetics. The high-resolution S 2p spectrum, presented in Figure 1e, exhibits two well-defined peaks centered at binding energies of 161.34 eV and 162.56 eV, which are assigned to the S 2p_{3/2} and S 2p_{1/2} spin–orbit components, respectively. The observed spin–orbit splitting of approximately 1.22 eV is consistent with the typical signature of sulfide (S^{2−}) anions in nickel-sulfur frameworks such as NiS₂. The symmetrical and sharp nature of these peaks confirms the dominance of S^{2−} species without detectable contributions from oxidized sulfur states, indicating that the sulfur environment remains chemically intact during synthesis [23]. These results strongly validate the formation of stoichiometric NiS₂.

FESEM was employed to investigate the surface morphology and microstructural evolution of the Co-Ni composites with varying NiS₂ content, as depicted in Figure 2. The images provide insights into the impact of compositional tuning on the particle distribution, agglomeration behavior, and surface texturing, all of which are critical for optimizing electrochemical activity in water-splitting applications. In the case of Co-Ni-1 (Figure 2(a₁–a₃)), which corresponds to the lowest NiS₂ loading, the surface is dominated by densely packed, cauliflower-like nanoclusters. These agglomerates are composed of interconnected nanoscale subunits, resulting in a moderately porous structure. The relatively uniform distribution and moderate texturing suggest limited NiS₂ integration at this stage, with Co₃O₄ features largely preserved. With the intermediate NiS₂ content in Co-Ni-2 (Figure 2(b₁–b₃)), the surface morphology undergoes a significant transformation. Nanosheet-like layers, presumably originating from exfoliated or sheet-structured NiS₂, become prominently integrated with the underlying Co₃O₄ matrix. These wrinkled and interlaced sheets impart a higher degree of surface roughness and hierarchical porosity. The partial embedding of small Co₃O₄ particles within the sheet matrix creates abundant interfacial contact, which is beneficial for facilitating electron transport and ion diffusion. This sample exhibits the most balanced morphology, combining structural integrity, surface area, and interconnectivity, suggesting it as the optimized configuration for catalytic applications. In contrast, Co-Ni-3 (Figure 2(c₁–c₃)), which contains the highest NiS₂ content, shows a marked departure from the earlier architectures. The surface appears densely populated with aggregated spherical particles, leading to the formation of a granular and highly compact structure. While the increased presence of NiS₂ is evident, the excessive particle crowding results in reduced porosity and less-defined surface features. This morphology

may hinder electrolyte accessibility and limit active site exposure, ultimately negatively affecting catalytic performance when compared to Co-Ni-2. Overall, the progressive incorporation of NiS_2 distinctly alters the microstructure of the Co_3O_4 -based composites. Co-Ni-2 demonstrates the most favorable morphology, characterized by a well-integrated Co_3O_4 - NiS_2 hybrid framework with high surface accessibility and interfacial connectivity. Such hierarchical texturing and synergistic nano-architectures are essential for enhancing electrochemical kinetics in redox-based catalytic systems.

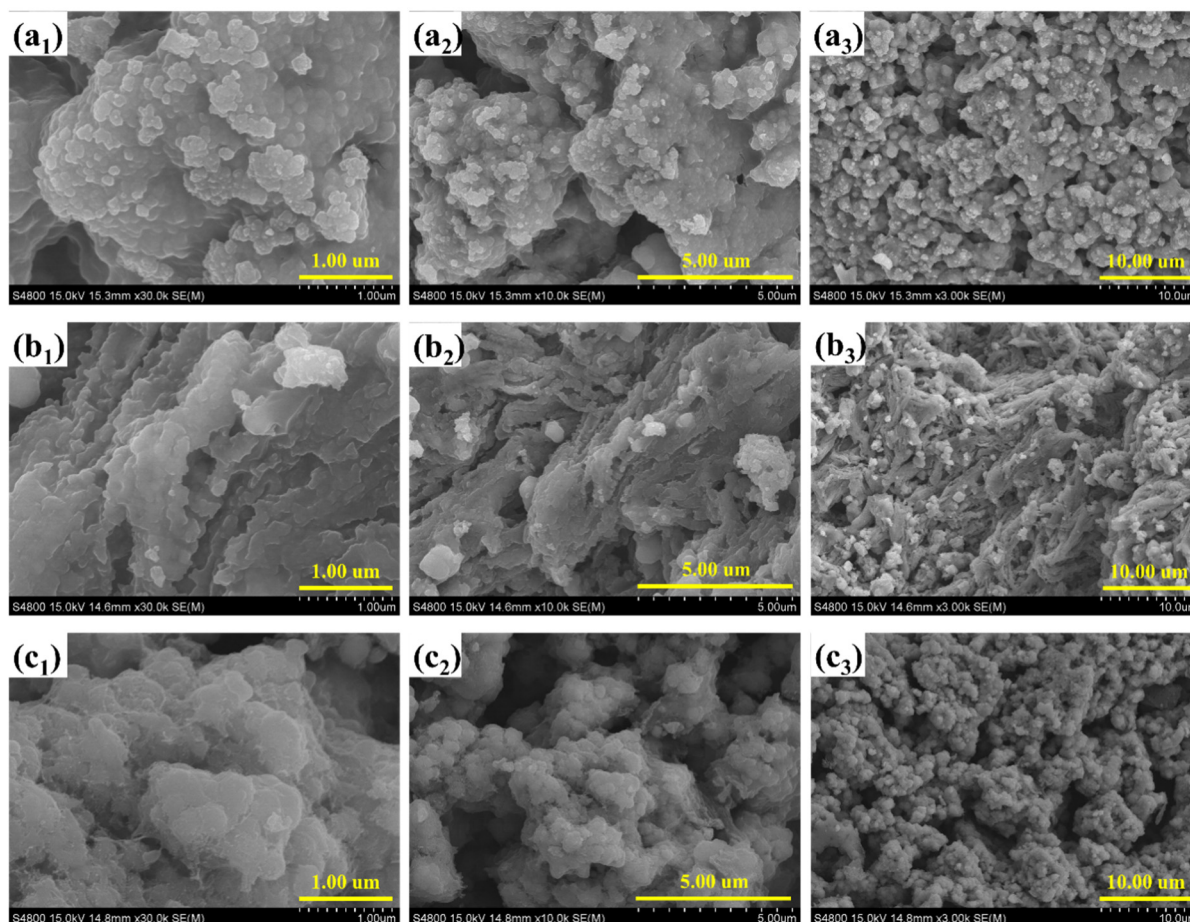


Figure 2. FESEM images of Co-Ni composites: (a₁–a₃) Co-Ni-1, (b₁–b₃) Co-Ni-2, and (c₁–c₃) Co-Ni-3 at increasing magnifications.

EDS and elemental mapping analyses were carried out to examine the elemental composition and spatial distribution of Co, Ni, S, and O in the Co_3O_4 - NiS_2 composites. All samples exhibit the expected elements without any impurity signals, confirming the successful formation of the intended heterostructure. In Co-Ni-1 (Figure 3(a₁–a₆)), Co dominates the composition, with relatively lower amounts of Ni and S, indicating a Co_3O_4 -rich phase. In contrast, Co-Ni-3 (Figure 3(c₁–c₆)) shows a significant increase in Ni and S contents with a considerable reduction in Co, suggesting excessive NiS_2 loading that may suppress the redox-active oxide phase. Co-Ni-2 (Figure 3(b₁–b₆)) exhibits a well-balanced elemental ratio with uniform and dense distributions of all elements across the surface, as evident from the mapping images. This compositional synchronization and homogeneous dispersion are expected to enhance interfacial charge transfer, structural stability, and electrochemical activity.

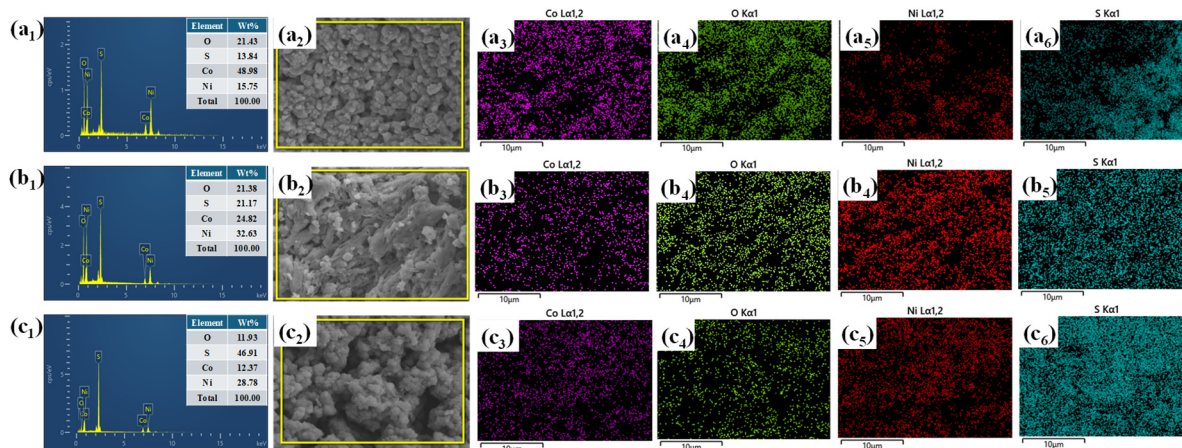
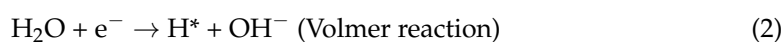


Figure 3. EDS spectra of (a₁) Co-Ni-1, (b₁) Co-Ni-2, and (c₁) Co-Ni-3 samples; FESEM images and corresponding mapping images (a₂–a₆, b₂–b₆, c₂–c₆) for Co-Ni-1, Co-Ni-2, and o-i-3, respectively, show uniform spatial distributions of elements.

The electrocatalytic activity of the synthesized Co-Ni-based materials toward the HER was systematically evaluated using a standard three-electrode configuration in 1 M KOH aqueous electrolyte. LSV spectra were obtained to compare the HER performance of the Co-Ni-1, Co-Ni-2, and Co-Ni-3 electrocatalysts, and the corresponding polarization curves are presented in Figure 4a. Among the tested samples, Co-Ni-2 exhibited the most promising HER activity, requiring a minimal overpotential of 84 mV to achieve a benchmark current density of 10 mA cm^{−2}. In comparison, Co-Ni-1 and Co-Ni-3 required overpotentials of 151 mV and 99 mV, respectively, to reach the same current density, as shown in Figure 4a,c. This marked reduction in overpotential for Co-Ni-2 indicates its superior intrinsic catalytic activity, which can be attributed to its optimized composition, enhanced active surface exposure, and favorable electronic configuration that promotes efficient proton adsorption and subsequent hydrogen evolution. To gain deeper insights into the HER kinetics, Tafel plots were constructed from the LSV data, as shown in Figure 4b,c. The Tafel slope of Co-Ni-2 was determined to be 67.5 mV dec^{−1}, which is substantially lower than those of Co-Ni-1 (105.2 mV dec^{−1}) and Co-Ni-3 (98.4 mV dec^{−1}). A smaller Tafel slope indicates more favorable reaction kinetics, implying that the hydrogen evolution reaction (HER) proceeds through a more efficient electron transfer pathway. A lower Tafel slope signifies faster kinetics and suggests that the HER proceeds. The improved reaction kinetics further support the superior catalytic behavior of the Co-Ni-2 catalyst. A detailed analysis of the Tafel slope offers valuable insights into the underlying HER mechanism. Generally, a Tafel slope in the range of 30–40 mV dec^{−1} is indicative of a Volmer–Tafel pathway, wherein the recombination of surface-adsorbed hydrogen atoms (H*) constitutes the rate-limiting step. In contrast, Tafel slopes between 40 and 120 mV dec^{−1} are typically associated with the Volmer–Heyrovsky mechanism, characterized by the electrochemical desorption of H* as the rate-determining step [24]. For the Co-Ni-2 electrocatalyst, a measured Tafel slope of 67.5 mV dec^{−1} suggests that the HER proceeds predominantly via the Volmer–Heyrovsky route. This mechanism involves an initial discharge step where water molecules are reduced to generate adsorbed hydrogen species (H*) [25,26]:



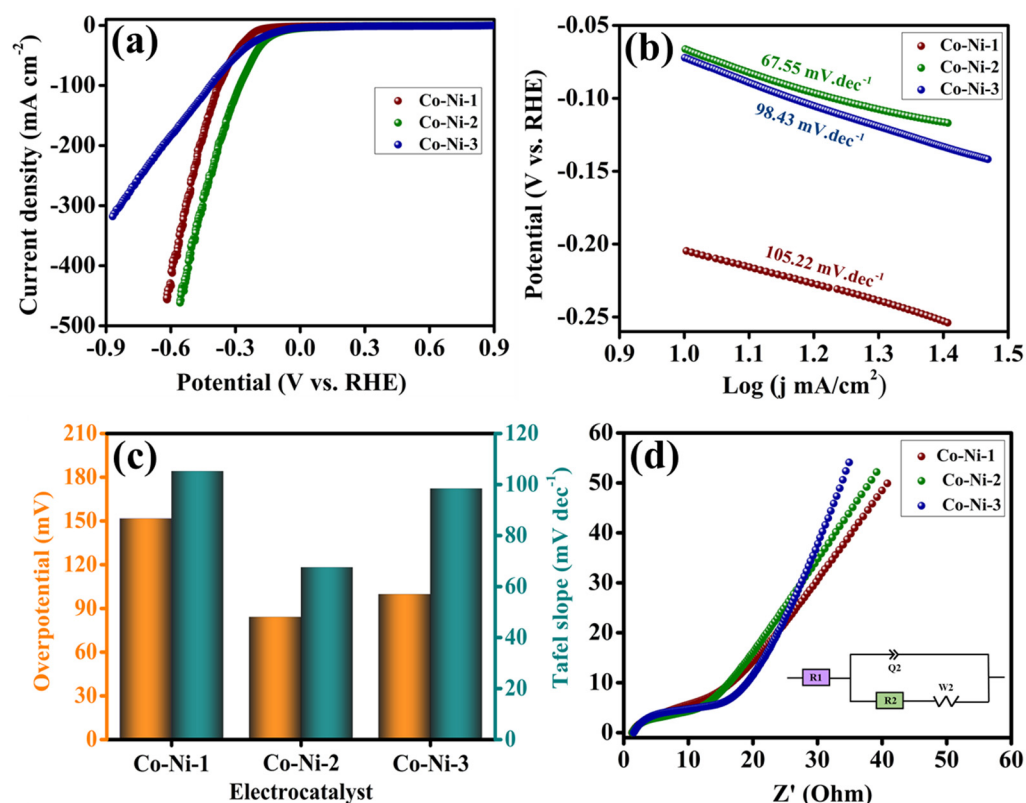


Figure 4. Electrochemical characterizations of electrocatalyst HER performance: (a) LSV curves at 5 mV/s scan rate, (b) equivalent Tafel slopes, (c) assessment of HER performance concerning overpotential at 10 mA cm^{-2} Tafel slope, and (d) EIS spectra of all electrocatalysts.

This is followed by the electrochemical desorption of H^* to produce molecular hydrogen:



Consequently, targeted optimization aimed at enhancing H^* desorption efficiency is critical for achieving substantial improvements in HER kinetics for this electrocatalytic system. Electrochemical impedance spectroscopy (EIS) was conducted to evaluate the interfacial charge transfer resistance (R_{ct}) and probe the conductivity characteristics of the electrode–electrolyte interface. The Nyquist plots displayed in Figure 4d, along with the equivalent circuit model shown in the inset, allowed for measurable extraction of R_{ct} values. The Co-Ni-2 electrocatalyst exhibited the smallest semicircle diameter, reflecting the lowest R_{ct} value of $7.7 \, \Omega$ compared to the other tested samples, Co-Ni-1 ($12.5 \, \Omega$) and Co-Ni-3 ($10.6 \, \Omega$). This lower R_{ct} is indicative of rapid electron transport and efficient interfacial charge transfer, which plays a critical role in enhancing HER kinetics. The improved conductivity and reduced resistance observed for Co-Ni-2 are in line with its superior HER performance, strengthening the synergetic effect between cobalt and nickel in optimizing the electronic structure and accelerating reaction dynamics.

A comparative analysis of the overpotential values for Co-Ni-2 and previously reported electrocatalysts is presented in Figure 5a and Table 1. The data clearly indicate that the electrocatalytic performance of Co-Ni-2 is highly competitive, demonstrating similar or superior HER activity relative to other benchmark materials. This enhanced performance can be attributed to the synergistic integration of Co_3O_4 and NiS_2 phases within the composite, which collectively contribute to optimized electronic conductivity, increased active site density, and improved reaction kinetics. Beyond activity, long-term electrochemical stability is a critical principle in evaluating the practical applicability of electrocatalysts. To assess the stability of Co-Ni-2, continuous CV measurements were performed over

5000 cycles in alkaline media. The CV profiles recorded throughout the cycling test are illustrated in Figure 5b. Additionally, the corresponding polarization curves before and after the 5000 CV cycles are shown in Figure 5c. Remarkably, the Co-Ni-2 electrode maintained an overpotential of 84.11 mV at 10 mA cm^{-2} even after prolonged cycling, showing negligible deviation from its initial performance. This negligible change in HER overpotential after extensive electrochemical cycling indicates excellent structural integrity, chemical robustness, and long-term operational stability of the Co-Ni-2 electrocatalyst under harsh alkaline conditions. These results establish Co-Ni-2 as a durable and high-performance candidate for sustained hydrogen evolution applications.

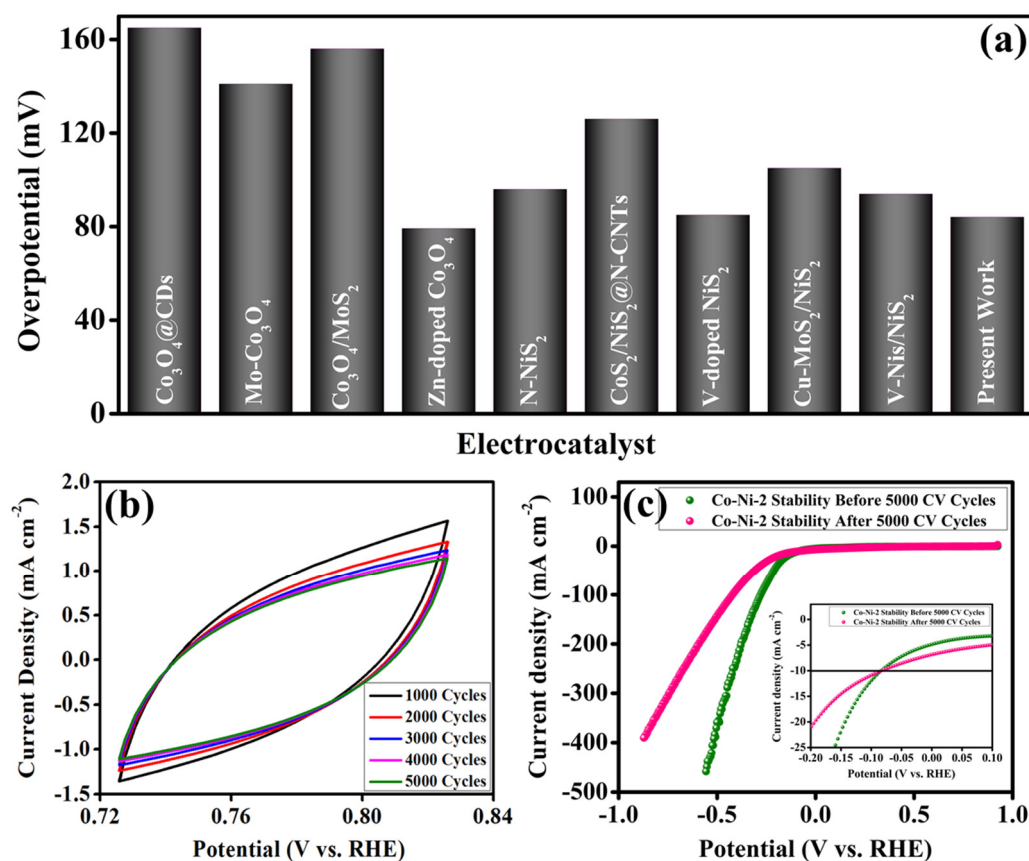


Figure 5. (a) Comparative overpotential of Co-Ni-2 with reported electrocatalysts, (b) CV stability of Co-Ni-2 over 5000 cycles (1000, 2000, 3000, 4000, and 5000 cycles), and (c) LSV curves of Co-Ni-2 before and after 5000 CV cycles (inset: overpotential at 10 mA cm^{-2}).

Table 1. Comparison of present electrocatalyst's HER performance with that of other reported electrocatalysts in 1.0 M KOH electrolyte.

Electrocatalyst	Overpotential @ 10 mA cm^{-2} (mV)	Ref.
$\text{Co}_3\text{O}_4@\text{CDs}$	165	[15]
$\text{Mo-Co}_3\text{O}_4$	141	[11]
$\text{Co}_3\text{O}_4/\text{MoS}_2$	156	[16]
Zn-doped Co_3O_4	79.2	[27]
N- NiS_2	96	[17]
$\text{CoS}_2/\text{NiS}_2@\text{N-CNTs}$	126	[28]
V-doped NiS_2	85	[29]
Cu- $\text{MoS}_2/\text{NiS}_2$	105	[18]
V- $\text{NiS}_2/\text{NiS}_2$	94	[19]
$\text{Co}_3\text{O}_4\text{-NiS}_2$	84	[Present work]

Figure 6 comprehensively illustrates the CV profiles of Co-Ni electrocatalysts with varying metal ratios recorded at different scan rates alongside the corresponding plots of current density versus potential. Specifically, the CV curves of Co-Ni-1 (Figure 6a), Co-Ni-2 (Figure 6b), and Co-Ni-3 (Figure 6c) reveal a progressive increase in current density with increasing scan rate. This behavior highlights a strong scan rate dependence, suggesting rapid redox kinetics within the electrical double-layer region. To elucidate the relationship between electrochemical activity and the availability of catalytically active sites, the ECSA was estimated by evaluating $2C_{dl}$ and C_{dl} , which were derived from the non-Faradaic current response at different scan rates. The linear fitting of current density differences against the scan rate yielded the respective C_{dl} values for each sample, as shown in Figure 6d,e. The C_{dl} values obtained for Co-Ni-1, Co-Ni-2, and Co-Ni-3 were 38.0, 73.4, and 58.8 mF cm⁻², respectively. The estimated ECSA values for Co-Ni-1, Co-Ni-2, and Co-Ni-3 were calculated to be 950.0, 1836.2, and 1471.2 cm², respectively, as presented in Figure 6f. Among the studied compositions, Co-Ni-2 exhibits the highest ECSA, suggesting a substantial increase in electrochemically available active sites as a result of optimized nickel incorporation. The enhanced surface area not only promotes improved charge carrier accessibility but also facilitates a greater number of active centers for catalytic interaction during the HER.

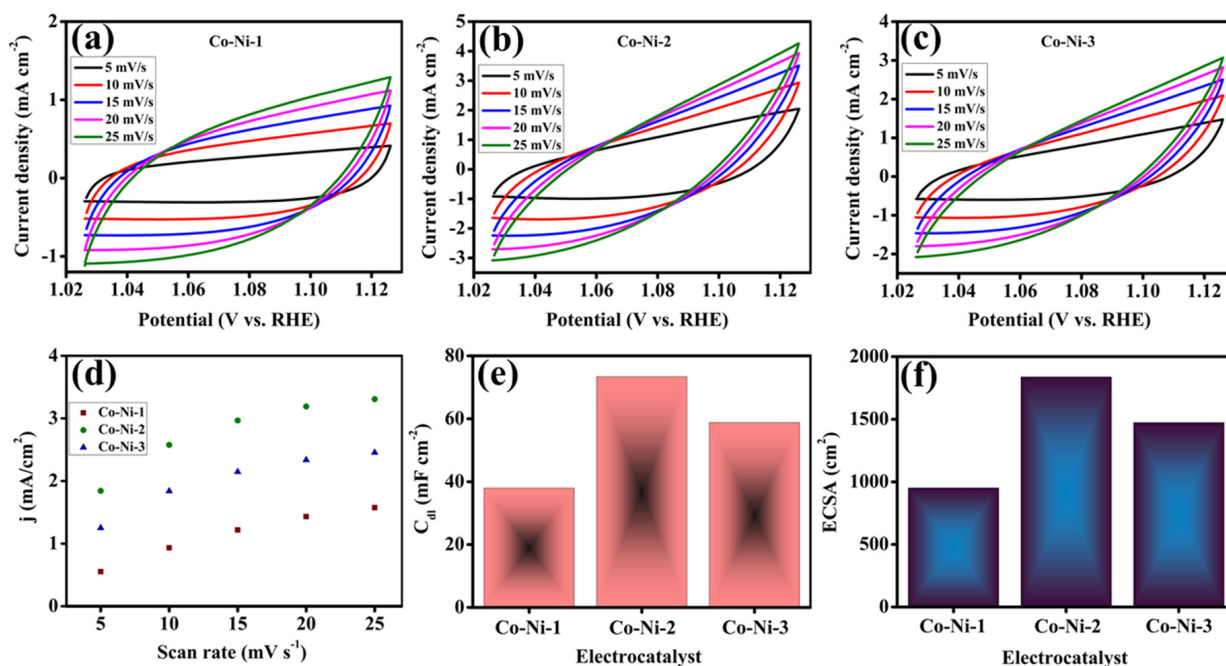


Figure 6. CV analysis of (a) Co-Ni-1 (b) Co-Ni-2, and (c) Co-Ni-3 electrocatalysts at different scan rates of 5, 10, 15, 20 and 25 mV s⁻¹; (d) $2C_{dl}$, (e) C_{dl} and (f) ECSA results for all the electrocatalysts.

4. Conclusions

In summary, we successfully developed Co₃O₄-NiS₂ composite electrocatalysts via a simple coprecipitation approach followed by controlled thermal treatment, systematically exploring the effect of compositional tuning on their structural features and electrocatalytic HER activity. Comprehensive characterization confirmed the coexistence of crystalline Co₃O₄ and NiS₂ phases, a favorable heterostructured interface, and the presence of multiple oxidation states, essential for rapid electron transfer and catalytic enhancement. Among all samples, Co-Ni-2 exhibited superior electrocatalytic performance, achieving a low overpotential of 84 mV at 10 mA cm⁻² with a notably reduced Tafel slope (67.5 mV dec⁻¹), indicating significantly improved HER kinetics in alkaline media. This remarkable performance is attributed to its balanced elemental composition, hierarchical

nanosheet architecture, increased electrochemically active surface area (1836.2 cm²), and optimal charge transfer properties. Stability testing underscored the robustness and durability of Co–Ni–2, demonstrating negligible performance degradation after 5000 CV cycles. Collectively, these findings underline the significant potential of Co₃O₄–NiS₂ composites as cost-effective and efficient alternatives to noble-metal catalysts, paving the way for large-scale implementation in sustainable hydrogen production systems.

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