

Article

Solvent-Driven Structural Modulation of Co-Ni₃S₂ and Impact on Electrochemical Water Splitting

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Abstract

Understanding the role of synthesis parameters in tailoring catalyst morphology is crucial for enhancing performance in electrochemical water splitting. This research systematically explores how different solvent environments affect the structural evolution and morphology of cobalt-doped nickel sulfide (Co-Ni₃S₂) nanomaterials. By systematically modifying the solvent environment using ethylene glycol and glycerol, distinct morphologies of Co-Ni₃S₂ were obtained, leading to variations in their electrocatalytic water-splitting performance. The fabricated compounds were thoroughly tested for their catalytic performance in facilitating hydrogen and oxygen evolution processes. Notably, the use of ethylene glycol as a synthesis medium led to the formation of a unique interconnected petal-like structure, significantly improving electrocatalytic activity, as evidenced by low overpotentials of 190.7 mV for HER at 10 mA cm⁻² and 414 mV for OER at 30 mA cm⁻². In contrast, when glycerol was employed as the solvent, the resulting Co-Ni₃S₂ material displayed overpotentials of 223.8 mV and 535 mV for HER and OER, respectively. Eventually, Co-doping was found to enhance the electrocatalytic performance, as pure Ni₃S₂ synthesized under the same solvent conditions exhibited higher overpotentials for both HER and OER. These findings underscore the crucial role of solvent selection in tailoring the structural and functional properties of materials for high-performance electrochemical applications.

Keywords: Co-Ni₃S₂; solvent variation; structural modulation; electrocatalytic water splitting



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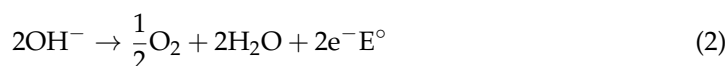
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1. Introduction

The worldwide transition to environmentally friendly and renewable energy solutions has intensified interest in electrochemical water splitting as a viable method for generating hydrogen fuel. A key focus within this approach is the creation of high-performance electrocatalysts that can efficiently facilitate both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), while requiring the least possible energy input [1–4].

In general, the hydrogen evolution reaction (HER) typically occurs at the cathode while the oxygen evolution reaction takes place at the anode, and its overall process in alkaline electrolyte can be expressed by the following equations [5];



Traditionally, noble metals such as platinum (Pt) for hydrogen evolution reactions and ruthenium dioxide (RuO_2) or iridium dioxide (IrO_2) for oxygen evolution reactions have been regarded as benchmark electrocatalysts due to their exceptional activity and stability. However, their widespread application is hindered by several drawbacks, primarily the limited availability and prohibitive cost of these precious elements. This has spurred intensive research into the development of earth-abundant, cost-effective alternatives that can deliver comparable performance in water-splitting processes [6–8]. Recent advancements have led to comprehensive research into a wide array of materials, including transition metal-based oxides, hydroxides, sulfides, phosphides, nitrides, and carbides, which have emerged as efficient bifunctional electrocatalysts capable of driving both hydrogen evolution and oxygen evolution reactions in integrated water-splitting systems [3,9,10]. These materials have garnered considerable attention due to their intrinsic catalytic activity, structural versatility, and favorable electronic configurations, which collectively contribute to their efficiency in driving the dual electrochemical processes required for sustainable hydrogen production. Among the transition metal compound family, transition metal sulfides (TMS) are considered promising alternatives to precious metal catalysts due to their superior electrical conductivity and catalytic activity [11,12].

In transition metal sulfides, nickel-based sulfides (Ni_xS_y), such as Ni_3S_2 , NiS , and NiS_2 , feature an extended Ni–Ni bonding network within their crystal structure, which imparts distinct metallic characteristics and enhances electrical conductivity [13,14]. Nonetheless, the electrocatalytic efficiency of nickel sulfides is still hindered by their sparse active site distribution and suboptimal electrical conductivity. Addressing these challenges necessitates continued refinement and engineering of this non-precious metal material to achieve improved catalytic performance. The catalytic efficiency of any material is fundamentally governed by several interrelated parameters: rapid electron transport ensures swift charge transfer during reactions; low energy barriers facilitate favorable reaction kinetics, and a high density of active sites enhances overall reactivity by offering more locations for catalytic events to occur [15]. These intrinsic properties can be systematically optimized through surface and interface engineering techniques. For instance, defect engineering, such as the introduction of vacancies, dislocations, and grain boundaries via plasma treatment, can disrupt lattice symmetry and create localized electronic states that serve as new catalytic centers [16,17]. Compositional doping modifies the electronic structure and conductivity of the catalyst, often introducing new energy levels or shifting the Fermi level to boost charge mobility and adsorption properties [18,19]. Additionally, the construction of heterogeneous structures enables the formation of high-energy interfaces that promote synergistic interactions between different phases, facilitating improved adsorption, electron transfer, and intermediate stabilization [20]. Together, these strategies offer a multi-faceted approach to enhancing catalytic performance at the atomic and nanoscale levels.

In this context, Cui et al. [21] synthesized a bifunctional electrocatalyst based on Mo-doped Ni_3S_2 by adjusting the reaction temperature during the hydrothermal process to obtain different structural morphologies. Among the three resulting structures, the porous nanorod configuration exhibited the most efficient performance for overall water splitting. When integrated with nickel foam as a substrate, the Mo- Ni_3S_2 electrode exhibited low

overpotentials, specifically 180 mV for oxygen evolution and 278 mV for hydrogen evolution when tested at a current density of 100 mA cm^{-2} . Kong et al. [22] used interface engineering to develop an N-doped $\text{Ni}_3\text{S}_2/\text{CoS}_2$ heterostructure catalyst that was directly fabricated on nickel foam through electrochemical deposition and low-temperature vulcanization, forming a highly conductive and interface-rich material. This catalyst demonstrated outstanding bifunctional performance for water splitting, achieving 10 mA cm^{-2} at low overpotentials for both HER (100 mV) and OER (245 mV), and requiring only 1.56 V for overall water electrolysis in alkaline media. MoS_2 was employed as a surface modifier to enhance the water-splitting capabilities of Ni_3S_2 nanosheets deposited on nickel foam, as demonstrated by Song et al. [2]. The disordered amorphous MoS_2 (a- MoS_2) interacted synergistically with the conductive Ni_3S_2 substrate, leading to outstanding bifunctional electrocatalytic activity. Under alkaline conditions, this setup demonstrated highly efficient overall water splitting, operating at a cell voltage of just 1.54 V. It exhibited minimal overpotentials, only 81 mV for the hydrogen evolution reaction (HER) at 10 mA cm^{-2} and 150 mV for the oxygen evolution reaction (OER) at 100 mA cm^{-2} . Yu et al. [6] introduced a method for synthesizing Co and Ce co-doped Ni_3S_2 nanosheets directly on nickel foam ($\text{CoCe-Ni}_3\text{S}_2/\text{NF}$), aiming to develop a high-performance catalyst for overall water splitting. The dual doping of cobalt and cerium enhances electronic interactions within the material, increasing active site availability and promoting efficient electron transport. The catalyst's ultrathin 2D nanosheet architecture ($\sim 10 \text{ nm}$ thick) improves electrolyte penetration and facilitates effective gas evolution. The catalyst exhibits remarkable electrocatalytic performance, achieving overpotentials as low as 285 mV for the oxygen evolution reaction (OER) and 193 mV for the hydrogen evolution reaction (HER) at a current density of 50 mA cm^{-2} in 1.0 M KOH. It also maintains stable performance over 100 h and reaches 1.68 V at 20 mA cm^{-2} during overall water splitting. In addition to these studies, numerous efforts have focused on enhancing the bifunctional electrocatalytic activity of Ni_3S_2 by employing strategies such as structural modification, interface engineering, cation doping, and tuning of synthesis conditions. However, the influence of solvent variation as a route for structural modification remains largely unexplored, particularly in the context of bifunctional water-splitting applications of doped and undoped Ni_3S_2 . The choice of solvent plays an active role in influencing nucleation dynamics, controlling growth kinetics, and directing phase formation, thereby significantly affecting the physicochemical properties of the synthesized materials. In particular, solvents such as ethylene glycol and glycerol offer complementary physicochemical properties that are highly relevant for nanostructure engineering. Ethylene glycol, with its moderate polarity and reducing ability, promotes uniform nucleation and assists in tuning the electronic structure of the active phase. In contrast, glycerol, owing to its higher viscosity and stronger intermolecular interactions, slows down ion diffusion and crystal growth, thereby enabling better control over particle size, morphology, and surface orientation. Moreover, the abundant hydroxyl groups in both solvents interact with precursor ions and crystal facets, influencing surface energies and stabilizing anisotropic growth. The combined effects of polarity, viscosity, and coordinating ability directly dictate the structural, morphological, and compositional characteristics of the resulting materials, which in turn impact their electrochemical activity and stability in water-splitting applications [23,24].

Building upon the above discussion, this study explores the solvent-driven structural modulation of $\text{Co-Ni}_3\text{S}_2$ synthesized under two distinct solvent environments and examines how these structural variations influence electrochemical performance in water-splitting reactions. A two-step solvothermal–hydrothermal synthesis strategy was employed, wherein ethylene glycol and glycerol served as solvents in the first step to facilitate the formation of the Co-Ni hydroxide framework. This intermediate was subsequently subjected to a

sulfurization process in the second step to yield the final Co-Ni₃S₂ structure. By elucidating the role of different solvents in tailoring the structural and physicochemical properties of Co-doped Ni-sulfide, this work aims to provide a rational basis for optimizing their catalytic activity in water-splitting applications.

2. Results and Discussion

To investigate the crystallinity of the samples, X-ray diffraction (XRD) analysis was conducted on Co-Ni₃S₂ structures grown on Ni foam. The corresponding diffraction patterns are shown in Figure 1 for Co-doped Ni₃S₂ and Figure S1 (Supplementary Information) for pure Ni₃S₂. The synthesis involved constructing Co-Ni hydroxide frameworks within two separate solvent media: ethylene glycol and glycerol. Following the sulfurization step, the products were categorized as CNS-E.G. and CNS-Glycerol for the Co-doped Ni₃S₂ catalysts, while the corresponding undoped Ni₃S₂ samples were labeled NS-E.G. and NS-Glycerol, respectively. While the diffraction signals from the Ni foam substrate are predominant, distinct and relatively intense peaks attributed to Ni₃S₂ can still be identified, indicating the presence and crystalline nature of the active material. The sharp and prominent diffraction peaks of Ni-foam are observed at 44.9°, 52.3°, and 76.7°, corresponding to the crystallographic planes indexed according to JCPDS card No. 04-0850 [3,7]. The XRD peaks of the material deposited on Ni-foam, identified as Ni₃S₂, were observed at 2θ values of 22.3°, 31.65°, 38.4°, 38.7°, 44.7°, 50.2°, 50.4°, 55.4°, 55.5°, 55.8°, 78.02°, 78.20°, and 78.55°. These diffraction peaks correspond to the (101), (110), (021), (003), (202), (211), (113), (300), (122), (104), (401), (223), and (205) crystal planes of Ni₃S₂, respectively, and are consistent with the standard reference pattern JCPDS card No. 01-085-0775 or 00-044-1418 [9,10,15]. This confirms the formation of Ni₃S₂ with a rhombohedral crystal structure. Successful doping of Co ions was confirmed in CNS-E.G. and CNS-Glycerol samples, as no cobalt sulfide phases were detected in the XRD analysis. However, a closer examination of the diffraction patterns reveals a shift in the Co-Ni₃S₂ reflection, synthesized using ethylene glycol, towards a higher 2θ angle, which was also noted for the pure Ni₃S₂ sample (Figure S1). This shift indicates lattice expansion, typically associated with the solvent variation and incorporation of dopant ions with larger ionic radii, suggesting a higher degree of Co incorporation in the CNS-E.G. sample [7,25]. The increased Co incorporation in the ethylene glycol-synthesized sample, indicated by lattice expansion, is expected to enhance water splitting performance by improving charge transfer and increasing active sites.

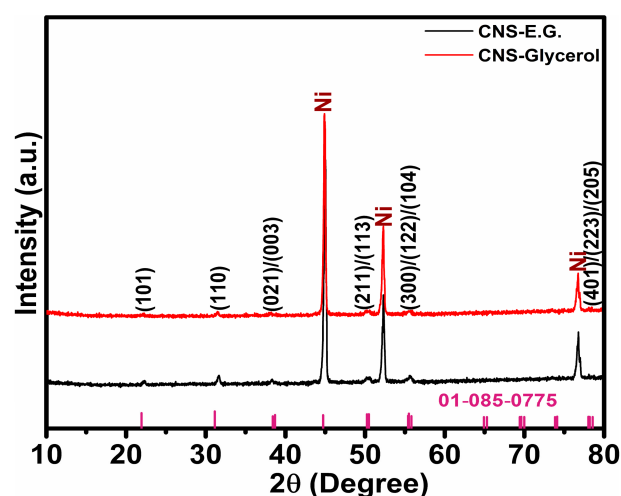


Figure 1. Diffraction patterns of Co-Ni₃S₂ on Ni-foam synthesized using two different solvents (CNS-E.G. and CNS-Glycerol).

Understanding the surface properties of catalysts is vital for improving electrochemical water splitting, since both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are surface-dependent phenomena. To explore these surface-related features, X-ray photoelectron spectroscopy (XPS) was employed to analyze the chemical states and elemental distributions present on the surfaces of the samples. Survey XPS spectra of the CNS-E.G. and CNS-Glycerol samples are illustrated in Figure 2a, indicating the presence of Ni, Co, and S elements in the samples. Figure 2b,c present the deconvoluted Ni 2p spectra for the CNS-E.G. and CNS-glycerol samples, respectively. Although the overall spectral profiles remain similar between the two, noticeable distinctions are evident in the binding energy positions and elusive variations within the peak structures. Both spectra prominently feature the Ni 2p_{3/2} and Ni 2p_{1/2} spin-orbit components, each accompanied by distinct satellite peaks, signifying the presence of nickel species. The spectral fitting indicates contributions from two oxidation states of nickel: Ni²⁺ and Ni³⁺ [7,14]. Detailed analysis reveals that each spin-orbit component (2p_{3/2} and 2p_{1/2}) contains two major contributions with the presence of the Ni-metallic peak (Ni⁰) shown in the orange color in Figure 2b,c, respectively. The peaks rendered in cyan and olive correspond to Ni²⁺ species, while those in dark yellow and violet are attributed to Ni³⁺, confirming the coexistence of multiple valence states of nickel in both samples. Additionally, satellite features were identified: the satellite peak associated with the 2p_{3/2} level is highlighted in magenta, while the satellite peak related to the 2p_{1/2} level appears in navy blue. The binding energies corresponding to the nickel oxidation states were analyzed for both CNS-E.G. and CNS-Glycerol samples. Ni⁰ peak was noted at 853 eV for CNS-E.G., and it was at 852.6 eV for the CNS-Glycerol sample. For the Ni²⁺ oxidation state, the CNS-E.G. sample exhibited characteristic peaks at 854.7 eV and 872.8 eV, which are attributed to the Ni 2p_{3/2} and Ni 2p_{1/2} core levels, respectively. In the case of the CNS-Glycerol sample, these Ni²⁺ peaks were observed at slightly lower energies of 854.5 eV and 872.5 eV for the same core orbitals. Regarding the Ni³⁺ state, the CNS-E.G. sample showed peaks at 855.8 eV (2p_{3/2}) and 874.9 eV (2p_{1/2}), whereas the CNS-Glycerol counterpart presented these peaks at 855.8 eV and 874.7 eV, indicating a minor shift. Furthermore, satellite peaks corresponding to the Ni 2p_{3/2} and 2p_{1/2} levels appeared at 860.7 eV and 878.9 eV for the CNS-E.G. sample. In comparison, the CNS-Glycerol sample's satellites were found at slightly lower energies of 860.4 eV and 878.7 eV, respectively [26,27].

As shown in Figure 2d,e, the Co 2p spectra for the CNS-E.G. and CNS-Glycerol samples display two distinct core-level signals, corresponding to 2p_{3/2} and 2p_{1/2}, respectively. Upon deconvolution, the CNS-E.G. spectrum reveals spin-orbit doublets in both core levels (Figure 2d), signifying the presence of both Co³⁺ and Co²⁺ oxidation states along with their associated satellite features. In contrast, the 2p_{3/2} core level of the CNS-Glycerol sample exhibits a spin-orbit doublet, as shown in Figure 2e, whereas no such feature is observed in the 2p_{1/2} level. This suggests that the integration of cobalt is incomplete when glycerol is used as the solvent, a conclusion that is consistent with observations from the XRD analysis. In the Co 2p XPS analysis, the Co³⁺ species is characterized by distinct peaks appearing in the 2p_{3/2} and 2p_{1/2} regions, highlighted, respectively, by cyan and gold colors. In contrast, the Co²⁺ state is marked by peaks shown in magenta for the 2p_{3/2} level and navy blue for the 2p_{1/2} level, which are uniquely observed in the CNS-E.G. sample spectrum. Satellite features related to these core levels are also present, with the 2p_{3/2} satellite illustrated in pink and the 2p_{1/2} satellite in green. For the CNS-E.G. specimen, the Co³⁺ peaks were found at binding energies of 780.4 eV (2p_{3/2}) and 795.5 eV (2p_{1/2}), while Co²⁺ peaks appeared at 782.6 eV and 796.3 eV for the same respective levels. The corresponding satellite peaks were located at 785.7 eV (2p_{3/2}) and 802.7 eV (2p_{1/2}). Meanwhile, in the CNS-glycerol sample, Co³⁺ was detected with peaks at 780.8 eV for 2p_{3/2} and 796.7 eV for 2p_{1/2}. The Co²⁺ peak

for the $2p_{3/2}$ level was found at 784.8 eV, coinciding with a satellite peak centered at the same position. An additional satellite peak corresponding to the $2p_{1/2}$ level was observed at 800.1 eV [3,17,19,22,28].

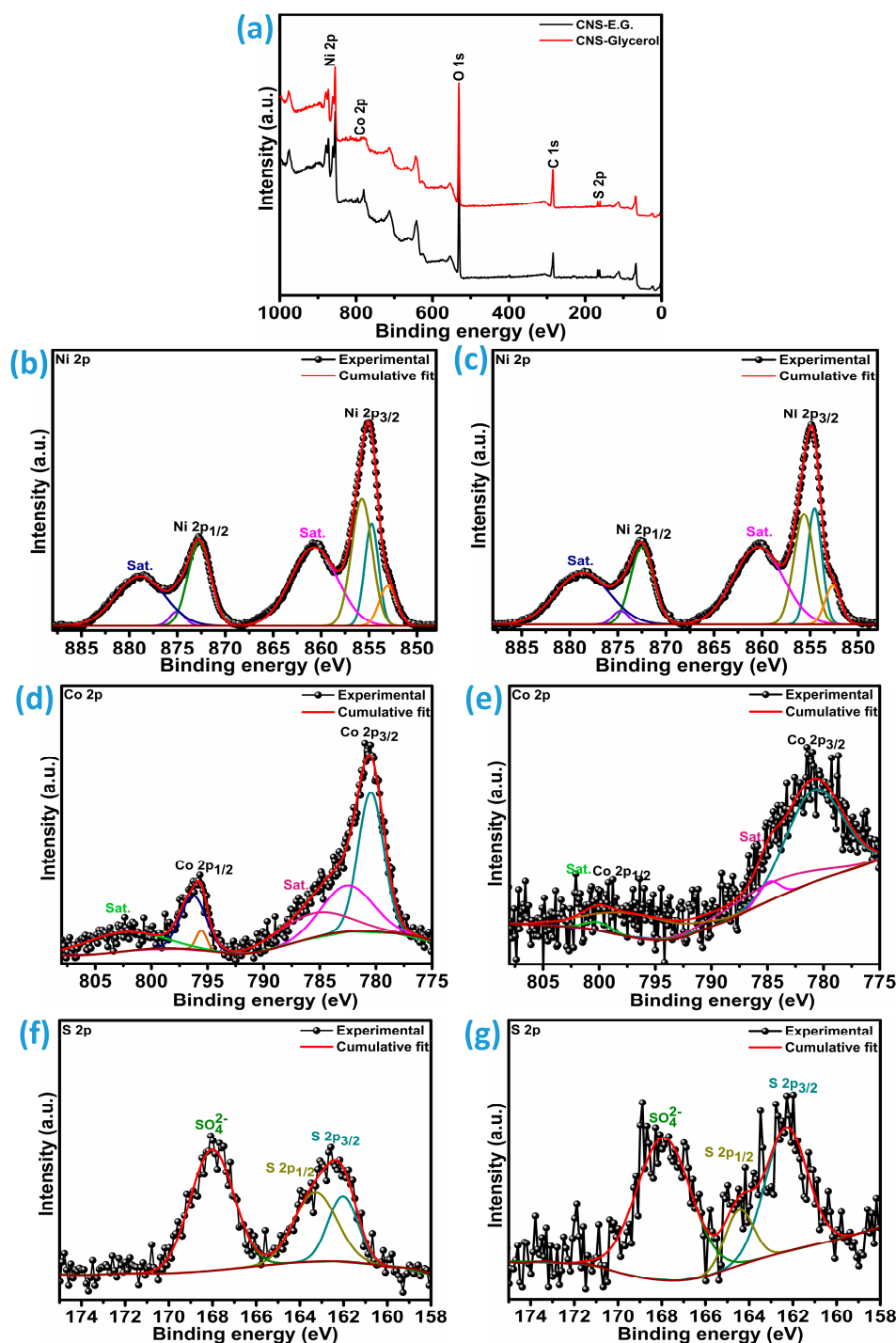


Figure 2. XPS analysis of Co-Ni₃S₂ catalyst fabricated using two different catalysts, (a) survey XPS spectrum of CNS-E.G. and CNS-Glycerol samples, (b,c) Ni-2p spectrum of CNS-E.G. and CNS-Glycerol, respectively, (d,e) Co-2p spectrum of CNS-E.G. and CNS-Glycerol, respectively, and (f,g) S-2p spectrum of CNS-E.G. and CNS-Glycerol, respectively.

The sulfur (S 2p) core-level spectra for CNS-E.G. (Figure 2f) and CNS-Glycerol (Figure 2g) display three prominent binding energy peaks, each corresponding to distinct sulfur chemical states. In the CNS-E.G. spectrum, peaks located at 162.0 eV and 163.3 eV, and in the CNS-Glycerol spectrum at 162.3 eV and 164.4 eV, represent the spin-orbit split

doublets S 2p_{3/2} and S 2p_{1/2}, respectively. These features are typically linked to sulfur in reduced forms, such as metal sulfides or elemental sulfur [1,2,7]. Additionally, both samples exhibit a peak near 168.0 eV, characteristic of oxidized sulfur species, particularly sulfate ions (SO₄^{2−}) [7,9]. The occurrence of this higher energy peak implies possible surface oxidation or residual contamination from sulfur-containing precursors. Overall, this spectral interpretation sheds light on the sulfur speciation and surface chemical characteristics of the materials under investigation.

Figure 3a–f presents FE-SEM micrographs of Co-Ni₃S₂ structures synthesized on Ni-foam substrates under two different solvent conditions, examined at varying magnifications. In the case of the sample synthesized using ethylene glycol (CNS-E.G.), shown in Figure 3a–c, the surface morphology reveals the formation of ultrathin, curled nanosheets, or “nanopetals”. These nanostructures exhibit a high degree of interconnectivity, extending uniformly across the entire Ni-foam surface. The resultant architecture resembles a compact, honeycomb-like network, which is advantageous for maximizing surface area and promoting efficient electron and ion transport pathways. In contrast, the sample prepared using glycerol as the solvent (CNS-Glycerol), depicted in Figure 3d–f, displays a distinctly different morphological profile. Here, the Ni-foam substrate is covered with a densely packed layer of irregularly shaped particles. These particles lack a defined geometry and vary in size, yet they are evenly distributed across the substrate. Over time, their aggregation leads to the development of a slab-like or sheet-like morphology, indicating a different nucleation and growth mechanism compared to the CNS-E.G. sample. These contrasting surface features highlight the significant influence of solvent type on the microstructural evolution of Co-Ni₃S₂ during synthesis, potentially affecting the material’s electrochemical properties and overall performance in device applications. This structural variation is also noted for the pure Ni₃S₂ samples fabricated with ethylene glycol and glycerol, as noted in Figure S2a–f, respectively. Comparing the morphology of pure Ni₃S₂ and Co-doped Ni₃S₂, it is evident that Co-doping induces significant structural transformations. In ethylene glycol, pure Ni₃S₂ shows only the initiation of nanosheet growth, whereas Co-doped Ni₃S₂ develops into highly interconnected and uniformly distributed nanosheet networks. In glycerol, pure Ni₃S₂ primarily forms agglomerated nanoparticles, while Co-doping drives the evolution of more organized sheet-like assemblies. The EDS spectra of CNS-E.G. and CNS-Glycerol are presented in Figure 3g,h, respectively, while the corresponding spectra for NS-E.G. and NS-Glycerol are shown in Figure S2g,h. Subsequently, elemental mapping was performed for the CNS-E.G. and CNS-Glycerol samples, as shown in Figure 4a–d and Figure 5a–d, respectively. EDS spectra (Figure S2g,h) of Ni₃S₂ confirm the constitution of Ni and S elements. Furthermore, EDS with elemental mapping of Co-doped Ni₃S₂ samples confirms the presence of Ni, Co, and S elements. This indicates the successful formation of the target materials Ni₃S₂ and Co-doped Ni₃S₂.

Transmission electron microscopy (TEM) was carried out to gain deeper insight into the nanoscale structure of the CNS-E.G. sample, complementing the surface-level observations obtained from FE-SEM. As presented in Figure 6a–d, the TEM micrographs confirm the formation of extremely thin structures that adopt a curled or petal-like morphology. These petals extend laterally over several hundred nanometers, but due to their ultrathin nature, they appear highly transparent to the electron beam. The curled and wrinkled edges, clearly visible in Figure 6a,b, demonstrate the intrinsic flexibility of the nanopetals, a feature that is advantageous for creating a large electrochemically accessible surface area. Such wrinkling not only prevents dense stacking but also exposes a greater number of edge sites, which can act as highly active regions for ion adsorption and charge transfer. Closer examination at higher magnifications (Figure 6c,d) reveals the presence of nanoscale pores distributed across the surface of the petals. The coexistence of ultrathin dimensions

with internal porosity provides a hierarchical architecture: the thin sheets shorten electron and ion transport distances, while the pores facilitate electrolyte penetration and enhance accessibility of the internal active regions. This unique combination of curling, porosity, and ultrathin sheet morphology indicates a highly open and accessible network that is expected to significantly improve electrochemical kinetics.

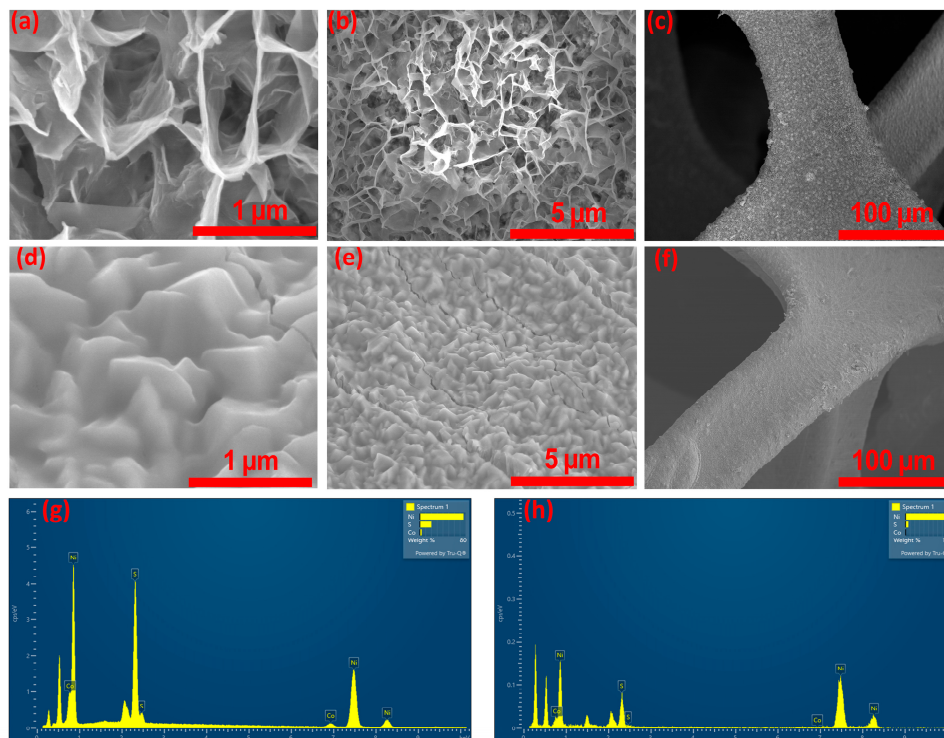


Figure 3. FE-SEM and EDS analysis of Co-Ni₃S₂ catalyst fabricated using two different catalysts, (a–c) FE-SEM images of CNS-E.G. at different magnifications, (d–f) FE-SEM images of CNS-Glycerol at different magnifications, (g,h) EDS spectrum of CNS-E.G. and CNS-Glycerol, respectively.

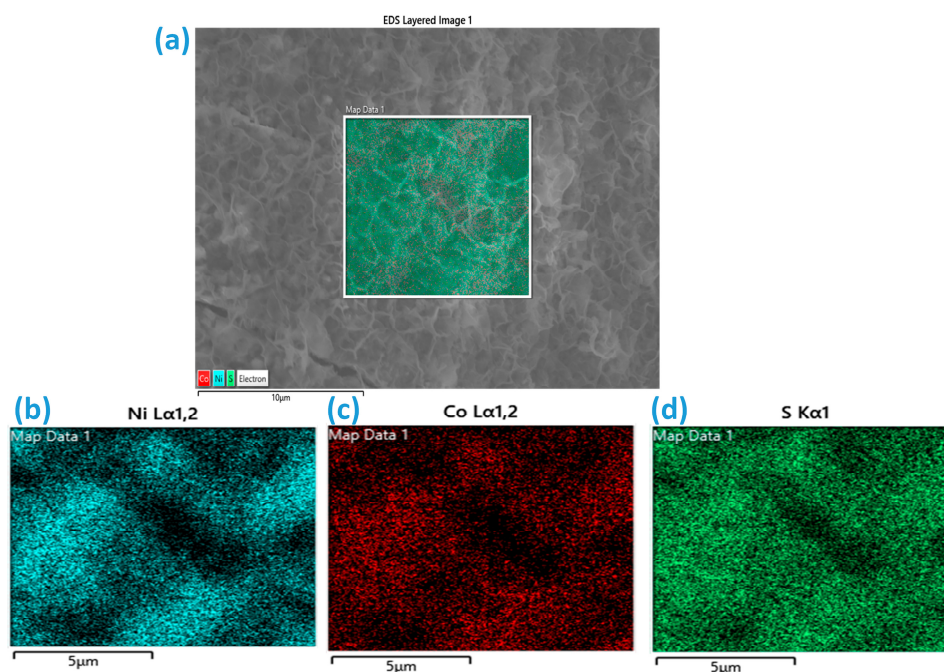


Figure 4. Elemental mapping of CNS-E.G. catalyst, (a) overall mapping, (b) Ni-element, (c) Co-element, and (d) S-element.

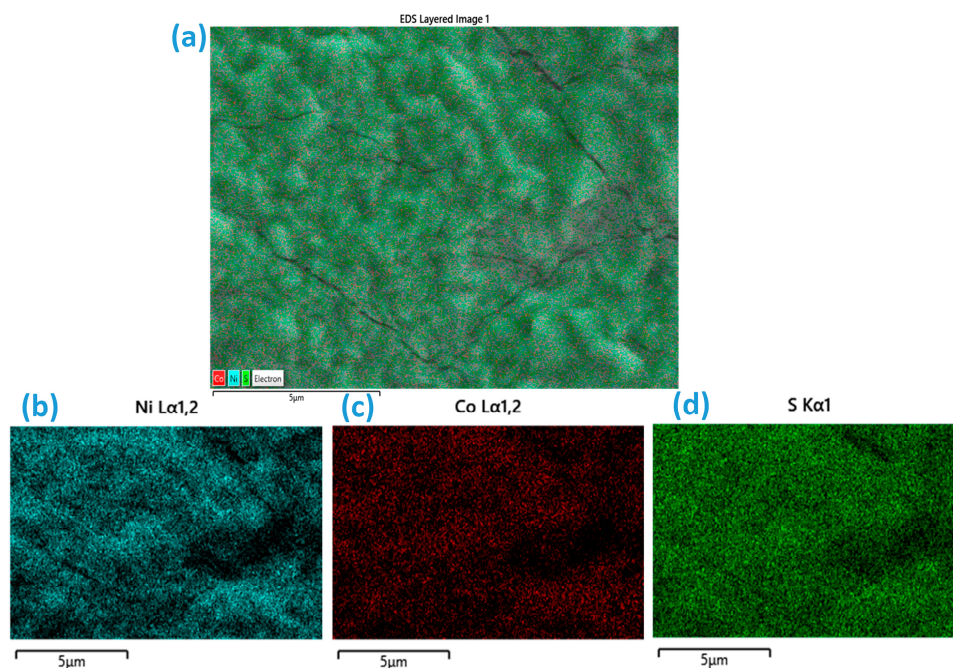


Figure 5. Elemental mapping of CNS-Glycerol catalyst, (a) overall mapping, (b) Ni-element, (c) Co-element, and (d) S-element.

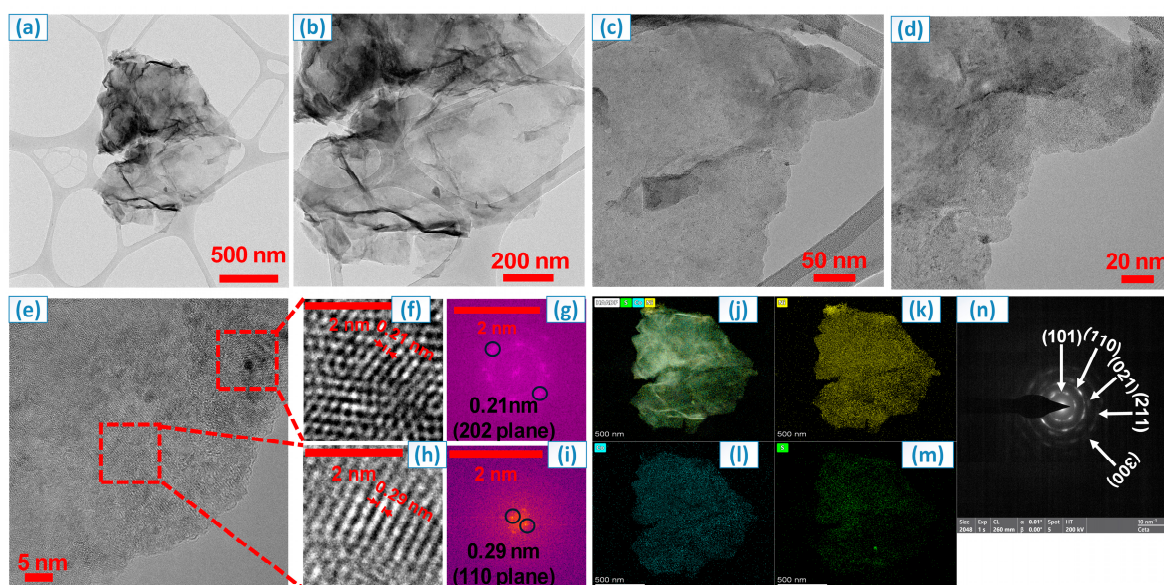


Figure 6. TEM analysis of CNS-E.G. sample, (a–d) TEM images of CNS-E.G. at different magnifications, (e) HRTEM image.

High-resolution TEM (HRTEM) image, as illustrated in Figure 6e, provides more definitive insights into the crystallinity of the nanosheets. Well-resolved lattice fringes are visible, with an interplanar spacing consistent with the (202) and (110) planes of the Co-doped Ni_3S_2 phase, which are represented in Figure 6f,h, respectively, whereas the FFT patterns of both planes were illustrated in Figure 6g,i. This confirms the successful incorporation of Co into the Ni_3S_2 lattice. The presence of coherent lattice fringes throughout large regions suggests high crystallinity, which is favorable for efficient charge transport. The elemental mapping results obtained from TEM, shown in Figure 6j–m, clearly verify that the nanopetals structures are uniformly composed of nickel (Ni), cobalt (Co), and sulfur (S). This elemental distribution is consistent with the findings from other physicochemical characterization techniques, further confirming the successful formation of the intended

Co-doped Ni_3S_2 composition. Selected-area electron diffraction (SAED) pattern represented in Figure 6n collected from the nanosheets displays a set of well-defined diffraction rings/spots corresponding to the characteristic planes of Co- Ni_3S_2 , in good agreement with XRD analysis. The polycrystalline nature, as indicated by the diffraction rings, further supports the nanosheet growth mechanism, in which interconnected crystalline domains are assembled into extended networks.

The hydrogen evolution reaction (HER) activities of the Ni_3S_2 and Co-doped Ni_3S_2 catalysts, NS-E.G., NS-Glycerol, CNS-E.G., and CNS-Glycerol, were evaluated through analysis of their polarization curves. To confirm the involvement of the Ni-foam current collector in the overall process, the polarization curve was obtained using the same experimental procedure and compared accordingly. Electrochemical measurements were performed using a conventional three-electrode configuration immersed in a 1.0 M KOH solution. From the linear sweep voltammetry (LSV) results depicted in Figure 7a, the CNS-E.G. catalyst demonstrated a notably lower onset potential at 149.5 mV, whereas the CNS-Glycerol counterpart showed a higher onset potential of 182.1 mV. For the undoped Ni_3S_2 samples, the onset potential values are comparatively higher than those observed for the Co-incorporated counterparts. Specifically, the sample synthesized in ethylene glycol (NS-E.G.) exhibits an onset potential of 243.7 mV, while the sample prepared in glycerol (NS-Glycerol) shows an onset potential of 269.2 mV. This decrease in onset potential for CNS-E.G. is attributed to the ethylene glycol solvent, which enhances cobalt incorporation and fosters the development of a porous honeycomb-like architecture, thereby boosting catalytic efficiency for HER. The overpotentials corresponding to current densities of 10, 30, and 50 mA cm^{-2} were also determined to compare the catalysts' performance under different operating conditions, as presented in Figure 7b. At these current densities, CNS-E.G. required overpotentials of 190.7, 245.6, and 276.8 mV, respectively. In contrast, CNS-Glycerol exhibited higher overpotentials of 223.8, 307.8, and 348.9 mV at the same current levels. For the pristine NS-E.G. sample, the recorded overpotentials are 267.7, 341.7, and 373.4 mV at the corresponding current densities. In contrast, the NS-Glycerol variant exhibits the largest overpotentials among all tested samples, reaching 291.9, 373.1, and 401.8 mV under the same conditions. For the pure Ni-foam current collector, the measured overpotentials are 329.2 mV at a current density of 10 mA cm^{-2} and 525.7 mV at 30 mA cm^{-2} . However, when the current density is increased to 50 mA cm^{-2} , the overpotential exceeds the measurable range, indicating significant polarization and reduced electrochemical performance. These variations in overpotential with increasing current density clearly illustrate the inherent limitations of bare Ni-foam in sustaining high-rate electrochemical reactions, as depicted in Figure 7a. These findings highlight that increasing the current density during HER leads to a pronounced increase in overpotential for all catalysts, with CNS-E.G. consistently outperforming CNS-Glycerol and two pure samples, NS-E.G. and NS-Glycerol. Specifically, the CNS-Glycerol sample shows an increase in overpotential by approximately 55.9%, whereas the CNS-Ethylene Glycol (CNS-E.G.) sample displays a comparatively lower increase of about 45.2% with an increase in current density from 10 to 50 mA cm^{-2} . NS-E.G. has the lowest change among all samples, with 39.5% and NS-glycerol exhibits a change of 40.5%. This suggests a stronger dependence of the CNS-Glycerol sample on the applied current density, potentially reflecting differences in intrinsic conductivity, active surface area, or catalytic efficiency between the two samples under high reaction rates.

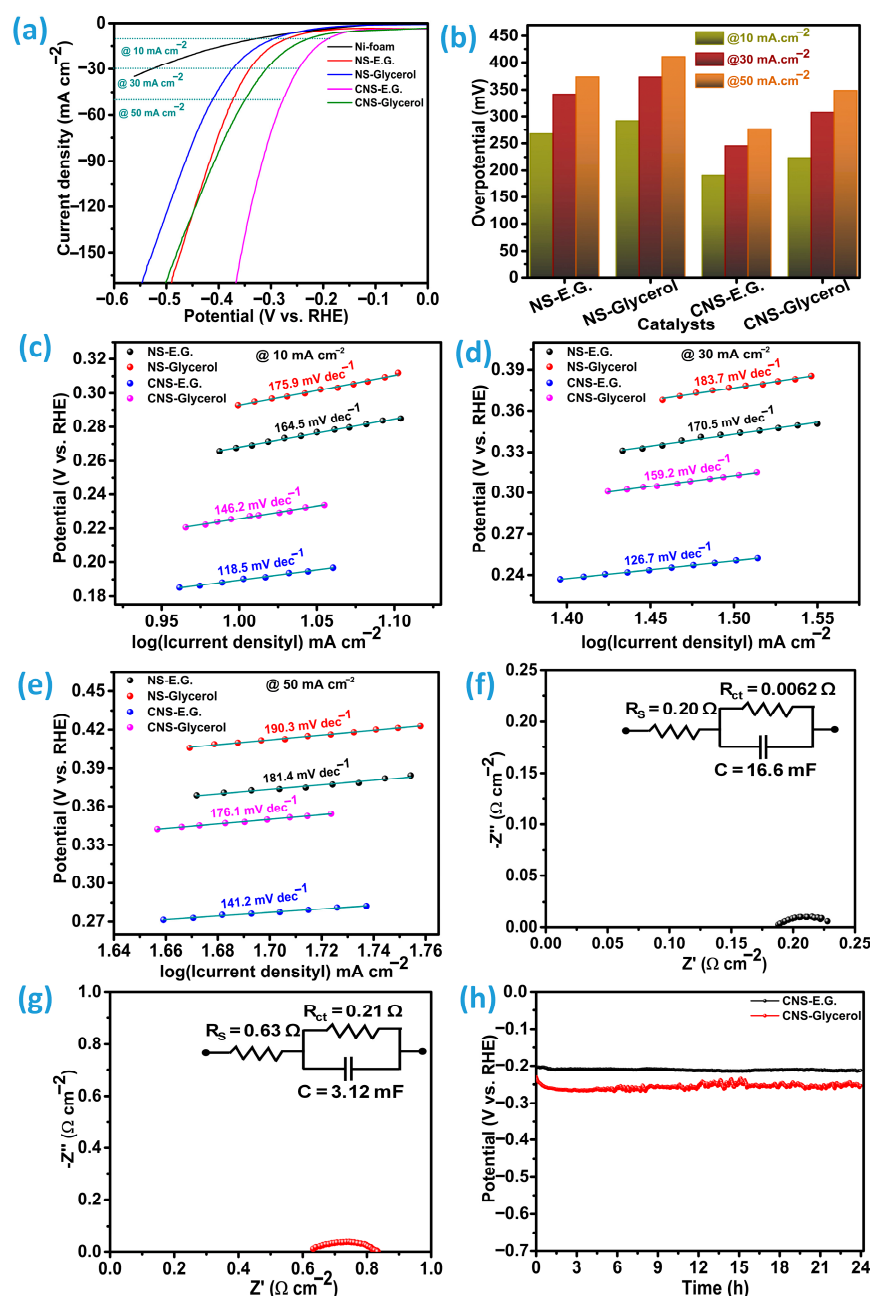


Figure 7. HER activity performance of the Co-Ni₃S₂ catalyst fabricated using two different solvents, (a) LSV curve measured at 5 mV s⁻¹, (b) estimated overpotential at different current densities, (c–e) Tafel slopes at 10, 30, and 50 mA cm⁻², respectively, (f,g) Nyquist plots of CNS-E.G. and CNS-Glycerol, respectively, with equivalent circuit inset, (h) HER stability at 10 mA cm⁻² of CNS-E.G. and CNS-Glycerol.

To thoroughly understand the catalytic reaction kinetics, Tafel slope measurements were conducted at three separate current densities, 10, 30, and 50 mA cm⁻², as depicted in Figure 7c–e. The Tafel slope serves as a vital indicator of the electrochemical reaction rate at the electrode surface, where lower values correspond to enhanced reaction efficiency and quicker electron transfer. In this investigation, the CNS-E.G. catalyst consistently exhibited reduced Tafel slope values compared to the CNS-Glycerol, NS-E.G., and NS-Glycerol catalysts across all tested current densities, highlighting its improved kinetic behavior. The CNS-E.G. catalyst exhibited Tafel slopes of 118.5, 126.7, and 141.2 mV dec⁻¹ at current densities of 10, 30, and 50 mA cm⁻², respectively. In contrast, the CNS-Glycerol variant demonstrated comparatively higher values of 146.2, 159.2, and 176.1 mV dec⁻¹ under the same

testing conditions. Under identical operating parameters, the NS-E.G. sample recorded slopes of 164.5, 170.5, and 181.4 mV dec⁻¹, whereas the NS-Glycerol catalyst yielded the steepest slopes overall, with values of 175.9, 183.7, and 190.3 mV dec⁻¹. Lower Tafel slopes indicate faster reaction kinetics and more efficient charge-transfer at the electrode. The measured slopes follow the order (best → worst): CNS-E.G. (118.5–141.2 mV dec⁻¹) < CNS-Glycerol (146.2–176.1 mV dec⁻¹) < NS-E.G. (164.5–181.4 mV dec⁻¹) < NS-Glycerol (175.9–190.3 mV dec⁻¹). These findings suggest that the hydrogen evolution reaction (HER) on CNS-E.G. proceeds more efficiently via the Volmer–Heyrovsky pathway in alkaline medium [2,3,18]. The noticeable difference in Tafel slopes between the two catalysts highlights the enhanced charge transfer efficiency and lower energy barrier for the electrochemical reaction in the CNS-E.G. system [3]. This suggests that the structural and compositional features imparted by the ethylene glycol treatment contribute positively to its electrocatalytic performance, particularly under increasing current densities.

Electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency spectrum ranging between 100 Hz and 100 kHz. The excitation voltage applied matched the overpotential recorded at a current density of 10 mA cm⁻². The resulting Nyquist plots for the CNS-E.G. and CNS-Glycerol catalysts are presented in Figure 7f,g and Figure S3a,b for NS-E.G. and NS-Glycerol, respectively, all catalysts exhibiting characteristic semicircular profiles. For quantitative analysis, the impedance spectra were modeled using an equivalent circuit, which is displayed as an inset within each Nyquist plot. In such representations, the diameter of the semicircle is directly correlated with the charge transfer resistance (R_{ct}), a critical descriptor of how readily electrons are transported across the catalyst/electrolyte interface. A reduction in R_{ct} corresponds to an accelerated interfacial electron exchange, thereby indicating superior catalytic kinetics. Since R_{ct} is a rate-determining factor for electrochemical reactions, a lower value is indicative of faster charge transfer dynamics and more efficient catalytic activity. Among the catalysts investigated, CNS-E.G. exhibits the lowest R_{ct} of 0.006 $\Omega \cdot \text{cm}^2$, highlighting its superior interfacial conductivity and catalytic efficiency. In contrast, CNS-Glycerol presents a substantially larger R_{ct} of 0.21 $\Omega \cdot \text{cm}^2$, while the non-doped variants NS-E.G. and NS-Glycerol display intermediate values of 0.13 and 0.15 $\Omega \cdot \text{cm}^2$, respectively. This marked reduction in R_{ct} for CNS-E.G. highlights the beneficial role of cobalt incorporation and the ethylene glycol-assisted synthesis route in facilitating charge transfer during the hydrogen evolution reaction (HER). In addition to R_{ct} , the series resistance (R_s) was extracted from the high-frequency intercept of the Nyquist plots. This parameter reflects the combined ohmic contributions from the electrolyte, electrode material, and contact resistance. The R_s values determined were 0.68 $\Omega \cdot \text{cm}^2$ for NS-E.G., 0.92 $\Omega \cdot \text{cm}^2$ for NS-Glycerol, 0.20 $\Omega \cdot \text{cm}^2$ for CNS-E.G., and 0.63 $\Omega \cdot \text{cm}^2$ for CNS-Glycerol. The markedly reduced R_s of CNS-E.G. further supports the superior ionic and electronic transport pathways within this catalyst system. Taken together, the concurrent minimization of both R_{ct} and R_s in CNS-E.G., coupled with its reduced Tafel slope, provides compelling evidence for its enhanced catalytic efficiency in the hydrogen evolution reaction.

Furthermore, the long-term durability of the catalysts was a key parameter in evaluating their overall catalytic efficiency. To examine this, both catalysts were subjected to a continuous stability test over 24 h under a fixed current density of 10 mA cm⁻², as depicted in Figure 7h. Despite showing comparable trends in stability, the CNS-Glycerol catalyst experienced a more pronounced decline, retaining only 90.7% of its initial HER activity. In contrast, the CNS-E.G. catalyst demonstrated better durability, maintaining approximately 95.58% of its original performance over the same period. The structural and morphological features of the CNS-E.G. and CNS-Glycerol catalysts were examined following their assessment for hydrogen evolution reaction (HER) performance. X-ray diffraction (XRD)

analysis and field-emission scanning electron microscopy (FE-SEM) were employed for this purpose. As depicted in Figure 8a, the XRD profiles reveal the diffraction characteristics of both catalyst types. Corresponding surface morphologies captured through FE-SEM are shown in Figure 8b,c for CNS-E.G. and CNS-Glycerol, respectively. While the fundamental crystalline architecture remained stable, a minor decline in peak intensities was noted. This attenuation is likely due to enhanced exposure of the underlying nickel foam, possibly caused by ongoing electrochemical cycling.

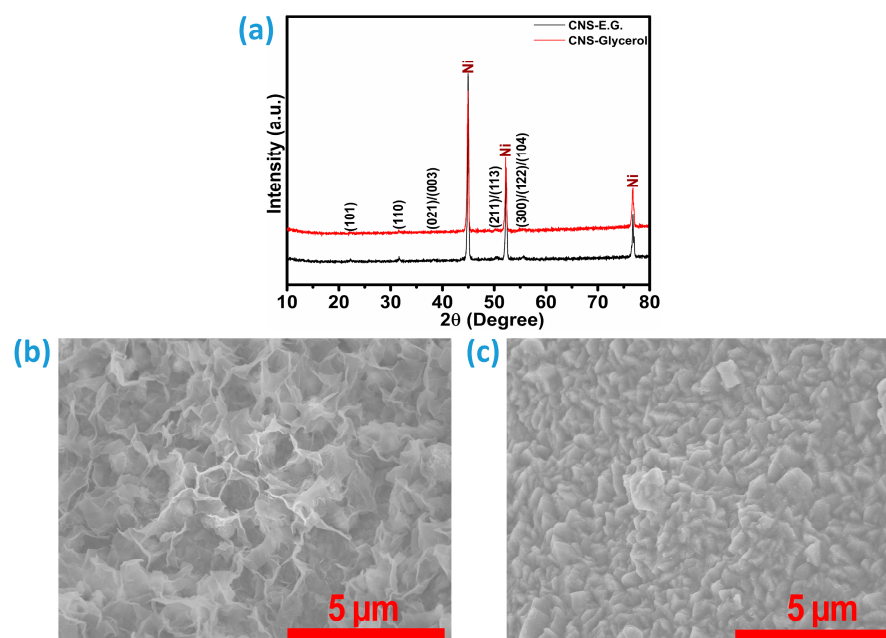


Figure 8. Phase and structure changes after HER stability, (a) diffraction patterns after HER activity, (b,c) FE-SEM images of CNS-E.G. and CNS-Glycerol after HER stability.

Among the reactions that constitute water splitting, the oxygen evolution reaction (OER) is notably the most demanding. This complexity arises from a multi-step mechanism that includes four coupled proton-electron transfers, alongside the slow kinetics associated with forming the O-O bond. Enhancing the catalytic activity for OER is crucial to reducing the overpotential, thereby boosting the overall efficiency of electrochemical water-splitting devices [9]. To evaluate the catalysts' effectiveness in driving OER, polarization measurements were performed using a three-electrode setup at a controlled scan rate of 5 mV per second. Figure 9a presents the comparative results for the NS-E.G., NS-Glycerol, CNS-E.G., and CNS-Glycerol samples. Consistent with the observations from the hydrogen evolution reaction (HER), CNS-E.G. exhibits superior OER activity, displaying a lower overpotential than the CNS-Glycerol and other pure catalysts, NS-E.G., and NS-glycerol. Figure 9b summarizes the overpotential values measured at current densities of 30 and 50 mA·cm^{−2}. The Co-doped Ni₃S₂ synthesized using ethylene glycol as a solvent (CNS-E.G.) demonstrates relatively low overpotentials of 414 mV and 466 mV at 30 and 50 mA·cm^{−2}, respectively. In comparison, the catalyst prepared from glycerol under similar conditions (CNS-Glycerol) exhibits significantly larger overpotentials of 535 mV and 643 mV at the same current densities. In the absence of Co incorporation, the ethylene glycol-derived Ni₃S₂ (NS-E.G.) records overpotentials of 468 mV and 547 mV at 30 and 50 mA·cm^{−2}. These values are slightly higher than those obtained for CNS-E.G., confirming the beneficial role of Co-doping, yet remain lower than the glycerol-derived samples. For the oxygen evolution reaction (OER) performance, only the Ni-foam substrate exhibits measurable catalytic activity. At a current density of 30 mA cm^{−2}, the system demonstrates an overpotential of approximately 810 mV. When the applied current density is increased to 50 mA cm^{−2}, the required overpotential

correspondingly rises to around 890 mV. This progressive increase indicates the intrinsic limitations of the Ni-foam surface in facilitating efficient oxygen evolution at higher reaction rates. The elevated overpotential at larger current densities suggests sluggish charge-transfer kinetics and a higher energy barrier for OER, emphasizing the need for surface modification or catalyst incorporation to enhance the electrochemical activity and lower the energy losses associated with the reaction. Among all catalysts studied, the non-Co-doped glycerol-derived Ni_3S_2 (NS-Glycerol) displays the poorest activity, with overpotentials reaching 580 mV and 683 mV at 30 and 50 mA cm^{-2} , respectively.

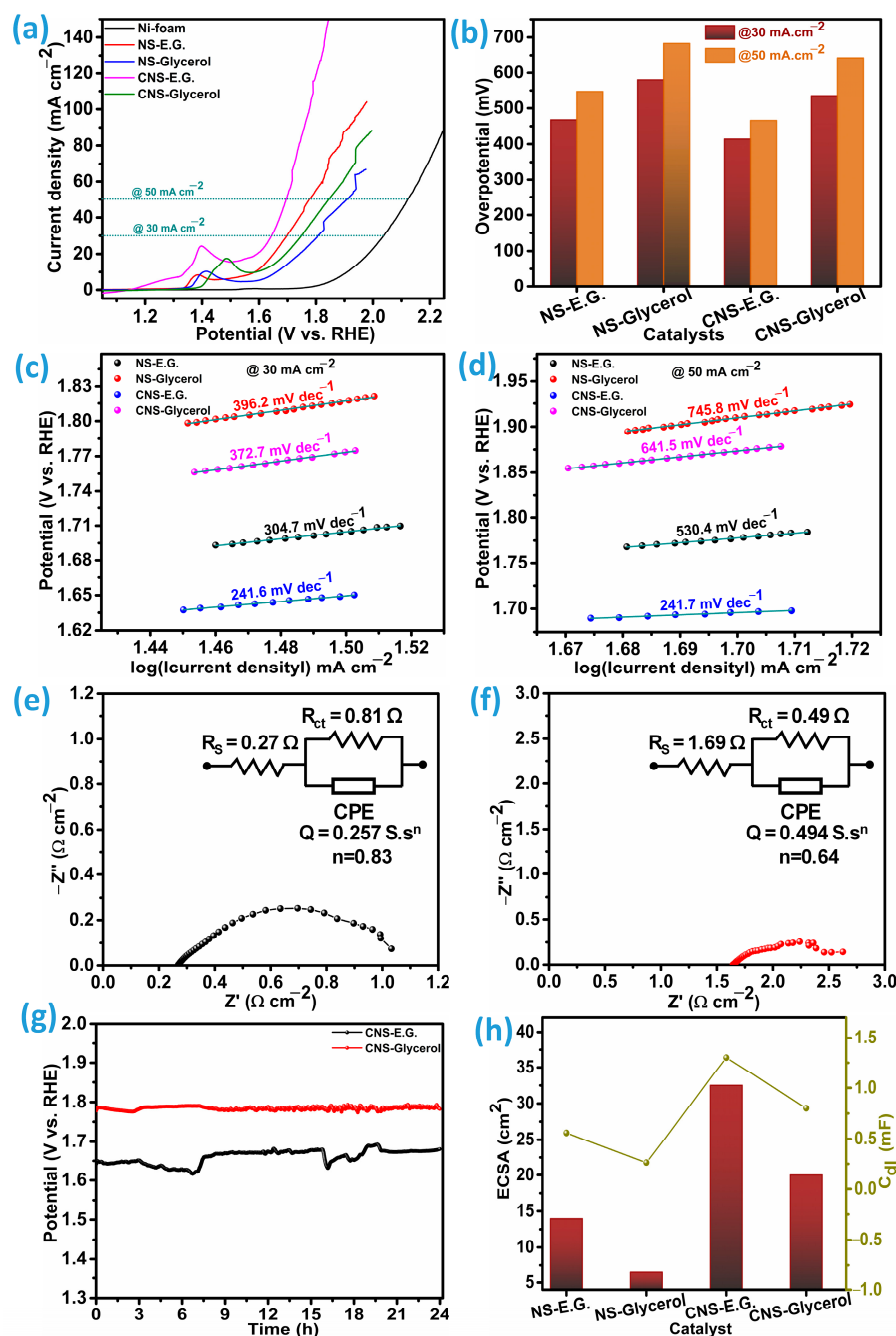


Figure 9. OER activity performance of the Ni_3S_2 and Co- Ni_3S_2 catalyst fabricated using two different solvents, (a) LSV curve measured at 5 mV s^{-1} , (b) estimated overpotential at different current densities, (c,d) Tafel slopes at 30 and 50 mA cm^{-2} , respectively, (e,f) Nyquist plots of CNS-E.G. and CNS-Glycerol, respectively, with equivalent circuit inset, (g) OER stability at 30 mA cm^{-2} of CNS-E.G. and CNS-Glycerol, and (h) electrochemical surface area and double layer capacitance of each electrocatalyst.

These results clearly indicate that (i) Co incorporation significantly lowers the overpotential, enhancing the catalytic activity, and (ii) the ethylene glycol-derived materials outperform the glycerol-derived ones, regardless of Co-doping, suggesting a favorable structural or electronic contribution from the ethylene glycol-based synthesis route. The enhanced OER activity of the CNS-E.G. catalysts is attributed to the effective incorporation of Co atoms and the strong bonding between these metal cations and the electronegative S atoms, which promotes improved electron delocalization. This modification altered the binding characteristics with the OH^* intermediate, leading to enhanced oxygen evolution reaction (OER) activity [2]. Moreover, in the case of the CNS-E.G. catalyst, there is no significant increase in overpotential when the current density is raised from 30 mA cm^{-2} to 50 mA cm^{-2} . This behavior suggests that, with appropriate structural and compositional modifications, such catalysts can be optimized for commercial electrocatalytic applications, where minimal overpotential at higher current densities is a key requirement [6].

The reaction kinetics of the oxygen evolution reaction (OER) can be systematically evaluated through Tafel slope analysis across varying current densities, as depicted in Figure 9c,d. A comparative evaluation of the catalysts demonstrates that CNS-E.G. consistently achieves smaller Tafel slopes than CNS-Glycerol, NS-E.G., and NS-Glycerol across all investigated current densities, signifying more favorable reaction kinetics. At 30 and 50 mA cm^{-2} , the Tafel slopes for CNS-E.G. were measured at 241.6 and $241.7 \text{ mV dec}^{-1}$, respectively. In contrast, CNS-Glycerol showed a pronounced rise in slope values at the same current densities, reaching 372.7 and $641.5 \text{ mV dec}^{-1}$. The NS-E.G. catalyst also performed better than CNS-Glycerol, recording 304.7 and $530.4 \text{ mV dec}^{-1}$ under 30 and 50 mA cm^{-2} , whereas NS-Glycerol exhibited the poorest performance, with the highest slopes of 396.2 and $745.8 \text{ mV dec}^{-1}$. This significant disparity underscores the enhanced oxygen evolution reaction (OER) kinetics provided by CNS-E.G. Notably, the Tafel slope for CNS-E.G. remains nearly constant between the tested current densities, unlike CNS-Glycerol, NS-E.G., and NS-Glycerol catalysts, which display a sharp increase. The stability of the slope in CNS-E.G. indicates that its electrochemical reaction pathway is relatively unaffected by variations in current density. This implies a stable rate-determining step and unaltered surface reaction conditions, which are critical for robust and efficient catalyst performance under varying operational conditions [17]. Moreover, the dramatic increase in Tafel slope for CNS-Glycerol, NS-E.G., and NS-Glycerol at higher current densities may indicate a shift in the rate-determining step or degradation of active surface sites, both of which could compromise catalytic efficiency. In contrast, the electrochemical stability of CNS-E.G. underscores its potential as a more reliable and durable catalyst for practical OER applications.

Electrochemical Impedance Spectroscopy (EIS) was employed to analyze the charge transfer resistance (R_{ct}) associated with the catalysts. The electrochemical impedance spectroscopy (EIS) profiles for the cobalt-doped Ni_3S_2 (CNS) and pristine Ni_3S_2 (NS) electrodes synthesized with ethylene glycol (E.G.) and glycerol as precursors are presented in Figure 9e,f for CNS, and in Figure S3c,d for NS. These Nyquist plots provide a direct comparison of their interfacial charge-transport properties. For the CNS-E.G. electrode, the fitted equivalent circuit analysis revealed a charge-transfer resistance (R_{ct}) of $0.81 \Omega \cdot \text{cm}^{-2}$ along with a series resistance (R_s) of $0.27 \Omega \cdot \text{cm}^{-2}$. The relatively small semicircle diameter and low R_s value reflect highly favorable charge-transfer dynamics at the electrode-electrolyte boundary, suggesting efficient electronic conduction and ion diffusion. On the other hand, the CNS-Glycerol electrode displayed a lower R_{ct} of $0.49 \Omega \cdot \text{cm}^{-2}$ but a substantially larger R_s of $1.69 \Omega \cdot \text{cm}^{-2}$. Although the decreased R_{ct} indicates improved electron-transfer kinetics relative to CNS-E.G., the higher ohmic resistance points to inferior intrinsic conductivity or weaker electrolyte penetration, which counteracts the kinetic benefit. For comparison,

the undoped Ni_3S_2 electrodes show poorer transport characteristics overall. The NS-E.G. electrode exhibited R_{ct} and R_s values of 0.56 and $1.40 \Omega \text{ cm}^{-2}$, respectively, while the NS-Glycerol electrode yielded even higher resistances of 2.20 and $2.10 \Omega \text{ cm}^{-2}$. These results confirm that cobalt incorporation markedly enhances both interfacial kinetics and bulk conductivity compared with the pristine sulfide. The superior performance of CNS-E.G. can be rationalized by considering its physicochemical attributes. The ethylene glycol-assisted synthesis may promote the formation of a more conductive surface network, optimized crystallinity, or favorable electronic states, which collectively reduce interfacial resistance. In contrast, the glycerol-based route seems to introduce structural or morphological features that increase series resistance despite enabling faster charge transfer.

The durability of the Co-incorporated catalysts under oxygen evolution reaction (OER) operation was systematically examined by conducting a continuous electrolysis test for 24 h at a constant current density of 30 mA cm^{-2} , as presented in Figure 9g. Both catalytic systems retained their activity with minimal degradation, indicating strong electrochemical stability during prolonged OER operation. Quantitatively, the CNS-E.G. catalyst displayed a slight reduction of 2.31% in its initial catalytic performance after the 24 h test, corresponding to a retained activity of 97.69%. In contrast, the CNS-Glycerol catalyst showed an even lower performance decay of only 0.24%, maintaining 99.76% of its original activity. To further investigate structural resilience after long-term operation, post-stability characterization was performed using X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM). The diffraction profiles (Figure 10a) confirmed that the crystalline framework of both catalysts remained largely preserved, with only negligible variations in peak intensity or position, suggesting limited structural reorganization during operation. Complementary FE-SEM micrographs of CNS-E.G. (Figure 10b) and CNS-Glycerol (Figure 10c) corroborated this observation, showing that the surface morphology and nanoscale architecture were largely retained, with only minor textural modifications.

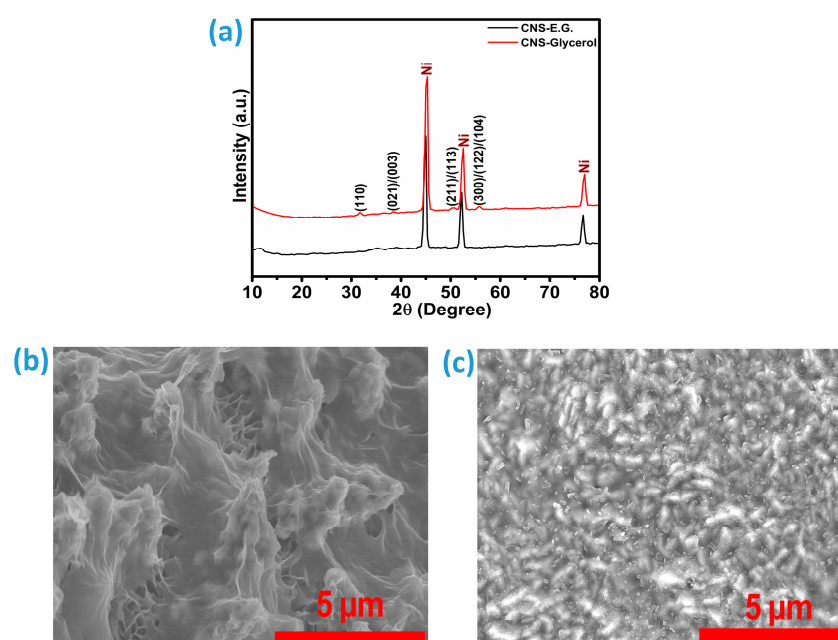


Figure 10. Phase and structure changes after OER stability, (a) diffraction patterns after OER activity, (b,c) FE-SEM images of CNS-E.G. and CNS-Glycerol after OER stability.

The catalytic efficiency of an electrocatalyst is predominantly dictated by the fraction of its surface that actively engages in electrochemical transformations. Importantly, this is not equivalent to the total geometric or physical surface area of the material. Instead, the

critical parameter is the electrochemically accessible and catalytically active portion of the surface, which is generally expressed as the Electrochemical Surface Area (ECSA) [7,11]. This parameter provides a direct measure of the number of surface-active sites available for charge transfer and reaction kinetics during operation. To evaluate the ECSA of the prepared catalysts, NS-E.G., NS-Glycerol, CNS-E.G., and CNS-Glycerol cyclic voltammetry (CV) experiments were conducted, with the corresponding profiles presented in Figure S4a–d. From these CV curves, the double-layer capacitance (C_{dl}) values were determined, as depicted in Figure S5a–d. Since C_{dl} arises from the non-faradaic charging of the electrode-electrolyte interface, it scales proportionally with the accessible surface area. Therefore, C_{dl} values are widely used as a proxy for quantifying the ECSA of nanostructured catalysts. The extracted C_{dl} and ECSA values are summarized in Figure 9h. Among all tested samples, the CNS-E.G. catalyst demonstrated the highest double-layer capacitance (1.3 mF) and the largest electrochemical surface area (32.5 cm²), indicating a superior density of electrochemically active sites. The performance sequence, based on both C_{dl} and ECSA, follows the order: CNS-E.G. (1.3 mF, 32.5 cm²) > CNS-Glycerol (0.8 mF, 20.01 cm²) > NS-E.G. (0.56 mF, 13.96 cm²) > NS-Glycerol (0.26 mF, 6.54 cm²). This trend highlights the significant role of Co-doping and the solvent environment (ethylene glycol vs. glycerol) in enhancing the effective surface exposure of active sites, thereby improving the catalytic behavior.

Following individual evaluations of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) activities, a dual-electrode configuration was constructed to examine the overall water-splitting capabilities of each catalyst. Linear sweep voltammetry (LSV) was conducted at a scan rate of 5 mV s^{−1} for both the CNS-E.G./CNS-E.G. and CNS-Glycerol/CNS-Glycerol cell systems, with the corresponding performance curves depicted in Figure 11a. These LSV profiles were utilized to determine the bifunctional catalytic efficiency, primarily through analysis of overpotentials. The electrolyzer incorporating CNS-E.G. electrodes displayed superior performance by requiring a lower voltage to sustain a current density of 10 mA cm^{−2}, reaching this benchmark at 1.537 V. Conversely, the CNS-Glycerol-based system demanded a higher potential of 1.674 V to achieve the same current density, indicating an approximate 8% increase. As shown in Figure 11b, both systems exhibit a trend of increasing overpotential with rising current density. For instance, the CNS-E.G.-configured electrolyzer reached 30 mA cm^{−2} at 1.717 V and 50 mA cm^{−2} at 1.866 V. Under identical conditions, the CNS-Glycerol system required 1.837 V and 1.994 V to reach 30 and 50 mA cm^{−2}, respectively, underscoring its relatively higher energy demand. Collectively, the Co-doped Ni₃S₂ catalyst demonstrates excellent bifunctional electrocatalytic performance, often surpassing or matching the effectiveness of other Ni₃S₂-based catalysts previously documented. A detailed comparison of performance metrics is summarized in Table 1. From the comparative evaluation, it becomes evident that the Co-doped Ni₃S₂ (CNS-E.G.) catalyst synthesized using ethylene glycol as solvent in this study demonstrates relatively modest activity toward the oxygen evolution reaction (OER) when benchmarked against pristine Ni₃S₂-based systems and state-of-the-art noble metal catalysts such as Pt/C (20 wt.% %) [29] and RuO₂ [30]. Despite this limitation on the anodic side, the catalyst exhibits highly competitive hydrogen evolution reaction (HER) performance. In fact, the HER activity of the CNS material is on par with, or in several cases superior to, previously reported electrocatalysts such as Ni₃S₂-CoMoS_x/NF [9], Co-Ni₃S₂/NF [11], Mo-Ni₃S₂ [13], and Ni₃S₂/NF [15]. Moreover, when implemented in a two-electrode configuration for overall water splitting, the CNS-E.G. electrolyzer surpasses the efficiency of a number of reported Ni₃S₂-based electrolytic systems. Specifically, its performance exceeds that of N-Ni₃S₂/VS₂/N-Ni₃S₂/VS₂ [1], Ni₃S₂/NF/Ni₃S₂/NF [8], Cd-Ni₃S₂/NF/Cd-Ni₃S₂/NF [12], Mo-Ni₃S₂/Mo-Ni₃S₂ [13], Fe-Mo-Ni₃S₂/Fe-Mo-Ni₃S₂ [18], and N-Ni₃S₂/CoS₂/NF/N-Ni₃S₂/CoS₂/NF [22]. This

outcome underscores the favorable synergistic effects introduced by cobalt incorporation and the use of ethylene glycol solvent, which promotes enhanced HER activity and improved bifunctionality, ultimately translating into superior water-splitting efficiency compared to many analogous Ni_3S_2 -based architectures. Chronopotentiometric tests of the CNS-E.G./CNS-E.G. and CNS-Glycerol/CNS-Glycerol electrolyzers were done as illustrated in Figure 11c. In both electrolyzers, the curve initially reaches the overpotential and then continues to increase steadily over time. The CNS-E.G. electrocatalyzer exhibited a 2.5% performance loss, indicating 97.5% stability. In comparison, the CNS-Glycerol electrocatalyzer showed a higher performance loss of 10.3%, corresponding to 89.7% stability relative to its original performance after 24 h. The catalyst prepared in an ethylene glycol medium (designated as CNS-E.G.) exhibits significantly enhanced electrocatalytic efficiency in various applications, namely, the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and comprehensive bifunctional catalysis when evaluated against the version synthesized using glycerol (CNS-Glycerol). This enhanced activity is likely attributable to differences in physicochemical properties as noted through various characterizations.

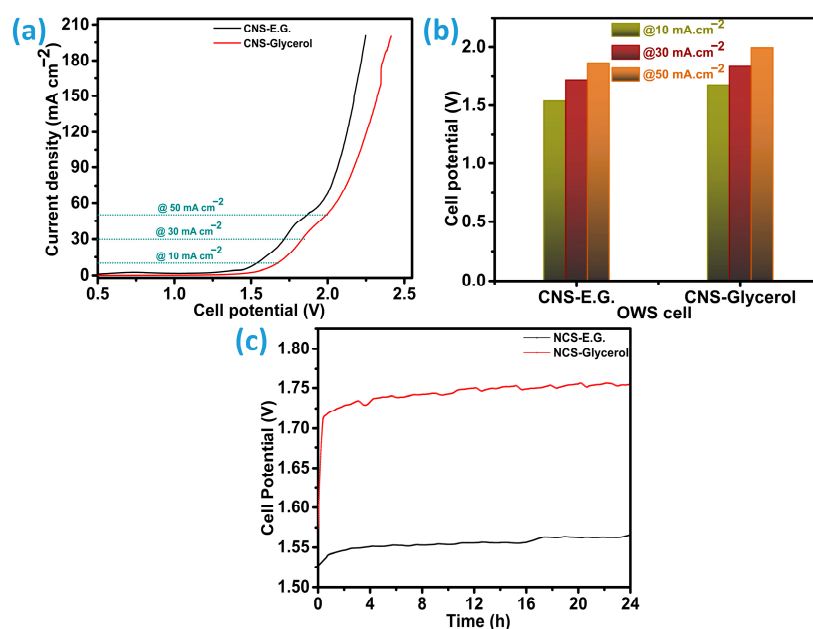


Figure 11. Overall water splitting performance of the Co- Ni_3S_2 catalyst fabricated using two different solvents, (a) LSV curve of CNS-E.G./CNS-E.G. and CNS-Glycerol/CNS-Glycerol electrolyzer at 5 mV s^{-1} , (b) cell potential of electrolyzer at different current densities, (c) stability curves of CNS-E.G./CNS-E.G. and CNS-Glycerol/CNS-Glycerol electrolyzer at 10 mA cm^{-2} .

Table 1. Comparative analysis of electrocatalytic performance of Ni_3S_2 -based catalysts.

Catalyst	HER Overpotential (mV)	OER Overpotential (mV)	Cell Voltage (V)	Reference
N- Ni_3S_2 /VS ₂	151@10 mA	227@10 mA	1.648@10 mA	[1]
MoS ₂ - Ni_3S_2 /NF	81@10 mA	150@100 mA	1.54@100 mA	[2]
3D Ni_3S_2 /Cu-NiCo LDH	156@10 mA and 304@100 mA	119@10 mA and 218@100 mA	1.75@100 mA	[3]
CoCe- Ni_3S_2 /NF	193@50 mA	285@50 mA	1.68@20 mA	[7]
Ni_3S_2 /NF	89@10 mA	242@10 mA	1.577@10 mA	[8]
Ni_3S_2 -CoMoS _x /NF	234@10 mA	90@10 mA	1.52@10 mA	[9]

Table 1. Cont.

Catalyst	HER Overpotential (mV)	OER Overpotential (mV)	Cell Voltage (V)	Reference
Co-Ni ₃ S ₂ /NF	240@10 mA	120@10 mA	1.69@ 50 mA	[11]
Cd-Ni ₃ S ₂ /NF	140@10 mA	197@10 mA	1.54@10 mA	[12]
Mo-Ni ₃ S ₂	212@10 mA	260@10 mA	1.67@10 mA	[13]
Co-N-Ni ₃ S ₂ /NF	215@50 mA	285@50 mA	1.5@10 mA	[14]
Ni ₃ S ₂ /NF	223@10 mA	260@10 mA	--	[15]
Co-doped Ni ₃ S ₂	62@10 mA	297@20 mA	1.52@10 mA	[17]
Fe-Mo-Ni ₃ S ₂	74@10 mA	80@10 mA	1.60@10 mA	[18]
Mo-doped Ni ₃ S ₂	278@100 mA	180@100 mA	1.53@10 mA	[21]
N-Ni ₃ S ₂ /CoS ₂ /NF	100@10 mA	245@10 mA	1.56@10 mA	[22]
Mo-S-Ni	78@10 mA	260@10 mA	1.53@10 mA	[27]
Pt/C (20 wt.%)	43@10 mA	--	--	[29]
RuO ₂	--	199@10 mA	--	[30]
Co-Ni ₃ S ₂	190.7@10 mA	414@ 30 mA	1.537@10 mA	This work

3. Experimental Section

3.1. Materials

All chemical reagents used in this study including nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), sodium sulfide nonahydrate (Na₂S·9H₂O), ethylene glycol (C₂H₆O₂), glycerol (C₃H₈O₃), urea (CH₄N₂O), and ammonium fluoride (NH₄F) were obtained from Sigma-Aldrich, based in Seoul, South Korea. All chemicals had a purity greater than 99% and were used without further purification.

3.2. Fabrication of Co-Ni₃S₂ Electrocatalyst

A two-stage synthetic route combining solvothermal and hydrothermal techniques was employed to fabricate Co-Ni₃S₂ films directly on nickel foam substrates. Prior to the deposition process, the Ni foam was thoroughly cleaned by sequential ultrasonication in hydrochloric acid, ethanol, and deionized (DI) water for 10 min each to eliminate surface contaminants. In the initial solvothermal phase, a precursor solution was prepared using 60 mL of either ethylene glycol or glycerol as the solvent. Initially, 2 mmol of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and 1 mmol of cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O) were introduced into a reaction vessel under constant agitation. Following this, 4 mmol of urea (CH₄N₂O) along with 6 mmol of ammonium fluoride (NH₄F) were added to the solution, which was further stirred for 15 min to ensure homogeneity. This precursor mixture was then sealed in a stainless-steel autoclave lined with Teflon and subjected to hydrothermal conditions at 100 °C for 12 h to facilitate the growth of a cobalt-nickel hydroxide framework. Upon completion of the reaction and natural cooling to room temperature, the solid material was isolated, thoroughly washed with deionized water and ethanol, and subsequently dried. For the sulfidation step, a separate solution was prepared by dissolving 8 mmol of sodium sulfide nonahydrate (Na₂S·9H₂O) in 60 mL of deionized water with 15 min of stirring. The dried Co-Ni hydroxide material from the previous step was immersed in this sulfide-containing solution. The mixture was then transferred into a clean Teflon-lined autoclave, sealed, and placed in an oven at 160 °C for 6 h to complete the sulfidation process. Following the reaction, the resultant Co-Ni₃S₂ films were extracted,

thoroughly rinsed with ethanol and DI water to eliminate residual impurities, and dried for further characterization. For the fabrication of pure Ni_3S_2 on Ni-foam, similar steps were utilized without the addition of Co.

3.3. Physicochemical Characterization

The electrocatalysts prepared using various solvent systems were thoroughly examined to assess their physicochemical characteristics through multiple analytical techniques. Crystalline phase composition was determined via X-ray diffraction (XRD) utilizing an X'Pert Pro instrument (Malvern Panalytical, Worcestershire, UK). To explore the elemental oxidation states and surface composition, X-ray photoelectron spectroscopy (XPS) was conducted using a K-Alpha analyzer (Thermo Fisher Scientific, Seoul, South Korea). Morphological and microstructural features were characterized using field-emission scanning electron microscopy (FE-SEM, model S-4800; Hitachi, Tokyo, Japan), which also facilitated energy-dispersive X-ray spectroscopy (EDS) and spatial distribution mapping of elements.

3.4. Electrocatalytic Measurements

The electrocatalytic characteristics of both catalyst samples were thoroughly analyzed using a VersaSTAT3 electrochemical workstation. Their activity in facilitating the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) was studied using a standard three-electrode configuration. In this setup, a nickel foam electrode with an exposed surface area of 1 cm^2 , coated with the catalyst material, was used as the working electrode. A graphite sheet acted as the counter electrode, and an Ag/AgCl electrode served as the reference. To evaluate the bifunctional electrocatalytic capability, symmetric full-cell assemblies were constructed using two identical catalyst-coated electrodes (e.g., CNS-E.G. paired with CNS-E.G.). All electrochemical assessments were conducted in a 1 mol L^{-1} potassium hydroxide (KOH) alkaline solution. Linear sweep voltammetry (LSV) was employed to probe catalytic activity, with measurements taken at a scan rate of 5 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was performed at the overpotential required to sustain a current density of 10 mA cm^{-2} . To examine durability and long-term functionality, chronopotentiometric measurements were carried out under constant current operation at 30 mA cm^{-2} for OER, 10 mA cm^{-2} for HER, and complete water splitting.

4. Conclusions

This study highlights the pivotal influence of solvent environment on the morphological engineering and electrochemical performance of nickel sulfide (Ni_3S_2) and cobalt-doped nickel sulfide ($\text{Co-Ni}_3\text{S}_2$) nanostructures for water splitting applications. By employing ethylene glycol and glycerol as solvent systems, we successfully tailored the nanostructure of Ni_3S_2 and $\text{Co-Ni}_3\text{S}_2$ to yield morphologies with distinct catalytic behaviors. A distinct petal-shaped network was synthesized using ethylene glycol as the medium, leading to enhanced electrocatalytic efficiency. This structure exhibited notably low overpotentials, measuring 190.7 mV for the hydrogen evolution reaction (HER) and 1.537 V for overall water splitting. In contrast, the glycerol-derived material, while still active, showed comparatively higher overpotentials. These findings establish a clear link between solvent-driven morphology modulation and catalytic efficiency, emphasizing the strategic importance of solvent selection in catalyst design. This study enhances insight into how structural features influence the properties of transition metal sulfides and provides a strategic approach for designing efficient electrocatalysts aimed at sustainable hydrogen generation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics13110359/s1>.

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