Electrochemical Performance of $\beta$-Nis@Ni(OH)$_2$ Nanocomposite for Water Splitting Applications

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ABSTRACT: Investigation on the formation mechanism of the $\beta$-Nis@Ni(OH)$_2$ nanocomposite electrode for electrochemical water splitting application was attempted with the use of the hydrothermal processing technique. Formation of single-phase $\beta$-Nis, Ni(OH)$_2$ and composite-phase $\beta$-Nis@Ni(OH)$_2$ has been thoroughly analyzed by X-ray diffractometer (XRD) spectra. Three different kinds of morphologies such as rock-like agglomerated nanoparticles, uniformly stacked nanogills, and uniform nanoplates for $\beta$-Nis, Ni(OH)$_2$, and $\beta$-Nis@Ni(OH)$_2$ materials, respectively, were confirmed by SEM images. The characteristic vibration modes of $\beta$-Nis, Ni(OH)$_2$, and $\beta$-Nis@Ni(OH)$_2$ nanocomposites were confirmed from Raman and Fourier transform infrared spectra. Near band edge emission and intrinsic vacancies present in the nanocomposites were retrieved by photoluminescence spectra. The optical band gaps of the synthesized nanocomposites were calculated as 2.1, 2.5, and 2.2 eV for $\beta$-Nis, Ni(OH)$_2$, and $\beta$-Nis@Ni(OH)$_2$ products, respectively. The high-performance electrochemical water splitting was achieved for the $\beta$-Nis@Ni(OH)$_2$ nanocomposite as 240 mA/g at 10 mV/s from a linear sweep voltammogram study. The faster charge mobile mechanism of the same electrode was confirmed by electrochemical impedance spectra and a Tafel slope value of 53 mV/dec. The 18 h of stability was achieved with 95% retention, which was also reported for the NiS@Ni(OH)$_2$ nanocomposite for continuous electrochemical water splitting applications.

1. INTRODUCTION

For sustainable energy production, the electrochemical water splitting approach played a vital role for the past few years of energy research. This approach produces clean energy by two half-reactions, namely, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), thereby reducing the usage of fossil fuels merely for energy. The electrochemical water splitting approach generally converts the abundant hydrogen and oxygen through redox reactions. Among other hydroxide nanomaterials, nickel hydroxide is one of the best efficient nanomaterials for potential application and is believed to enhance the overall electrochemical kinetics of the electrode under an electrode/electrolyte interface. Further, property wise, we can easily tune the structure, morphology, and physicochemical properties, which will definitely satisfy the requirements such as high theoretical capacitance and high electrochemical stability in an alkaline medium over a long duration of electrochemical energy production and storage applications. With this, suitable strategies are also available to boost the material’s electrochemical performance such as combinational linkages of different kinds of nanostructures and diverse morphology achievement. A number of current collectors are used by researchers for potential applications such as nickel foam, graphite sheet, titanium plate, and aluminum foil. Usually, nickel foam has been adapted as an efficient collector for such applications, and also, there was almost zero adhesion problem found in the nickel foam substrate for long-time electro-
The novelty of the present work is exclusively focused on the electrocatalysts for electrochemical water splitting applications. The availability at the interface due to the composite nature of the nanocomposites has also been reported in fully explored, and also, the novel electrochemical mechanism of NiS@Ni(OH)2 nanocomposites has been preferred to stimulate the reaction rate and conductivity. (c) Usually, NiS@Ni(OH)2 nanocomposites were synthesized by adapting a two-step hydrothermal route; nevertheless, we tuned the hydrothermal parameters and optimized the growth condition to obtain NiS@Ni(OH)2 nanocomposite particle growth toward getting nanoplate morphology for electrochemical water splitting applications. (d) A number of active sites and conductivity of the nanocomposites for electrochemical water splitting applications highly depend on the material morphology. Hence, in order to achieve uniform nanoplate morphology of the synthesized nanocomposites, we have followed the hydrothermal route.

Many of the research activities have been explored for nickel-based materials for potential applications. Recently, Zhang and his co-workers controlled the synthesis method to produce diverse morphological transition hydroxide nanomaterials for hybrid supercapacitor applications. Lee and his team investigated a detailed analysis on the phase change mechanism and conversion of nickel sulfide to the hydroxide phase in an electrochemical water oxidation reaction. Liang and his group revealed the enhancement of specific capacitance of Ni hydroxide nanostructure by morphology tailoring. From these attempts, due to the versatile role of Ni sulfide and Ni hydroxide nanostructures, in the present study, we have been focused to synthesize β-NiS@Ni(OH)2 nanocomposite electrocatalysts for electrochemical water splitting applications. The novelty of the present work is exclusively focused on the synergic effect of the number of the oxidative species availability at the interface due to the composite nature of the electrode by addressing the material morphology and composite nature of NiS and Ni(OH)2 in the aspect of improving electrochemical stability and conductivity and has been fully explored from this work systematically. The compact nanoplate morphology of the nanocomposites and the combined effect of NiS and Ni(OH)2 at the interface have been preferred to stimulate the reaction rate and conductivity. The combination of sulfur and hydroxyl derivatives of Ni electrocatalysts via a one-step hydrothermal route has been fully explored, and also, the novel electrochemical mechanism of NiS@Ni(OH)2 nanocomposites has also been reported in the present study. Hence, good quality β-NiS@Ni(OH)2 nanocomposite electrocatalysts were synthesized and characterized by XRD, Raman, PL, and UV studies. The diverse morphologies obtained for β-NiS, Ni(OH)2, and β-NiS@Ni(OH)2 nanostructures have been revealed by SEM images. The electrochemical performance of the fabricated β-NiS@Ni(OH)2 nanocomposite electrodes was systematically revealed by cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and chronoamperometry (CA) studies, and the enhancement of the OER active mechanism of the electrode has been proposed.

2. RESULTS AND DISCUSSION

Structural optimization of β-NiS, Ni(OH)2, and β-NiS@Ni(OH)2 nanocomposite synthesis via the hydrothermal route has been attempted in this work. The formation mechanism of the β-NiS@Ni(OH)2 nanocomposite consisted of three steps of controlled growth kinetics. (a) At first, the strong chemical reaction between the sulfur source and one-third of nickel nitrate precursor might initiate the nucleation reaction that thereby produced the β phase NiS nanostuctures. (b) In a later reaction time, the excess amount of nickel nitrate precursors may not interact with the sulfur group of thiourea due to the nonstoichiometric ratio of the precursors, which might lead to the formation of hydroxide nanostructures. (c) At the end of the reaction, ethylene glycol might act as a linking agent between the formed β-NiS and Ni(OH)2 nanostructures and may favor the strong chemical coupling that resulted in the formation of β-NiS@Ni(OH)2 nanocomposites for electrochemical water splitting applications. The structures of obtained nanostructures have been confirmed by XRD spectra as shown in Figure 1. From XRD spectra, the formation of rhombohedral β-NiS, hexagonal Ni(OH)2, and the mixed phase of rhombohedral and hexagonal β-NiS@Ni(OH)2 nanocomposites is confirmed. Figure 1a represents the typical rhombohedral phase of β-NiS without any additional phase formation by the concerned 2θ values of 30.3, 32.2, 35.7, 40.4, 48.8, 50.1, 52.6, 56.2, 57.3, and 59.1° for the oriented planes of (101), (300), (021), (211), (131), (410), (401), (321), (330), and (012), respectively. Those crystal planes are correlated to the crystal plane of rhombohedral β-NiS of JCPDS card number #86-2281. Figure 1b demonstrates the formation of pure-phase hexagonal Ni(OH)2 from the diffraction peaks at 19.2, 33.1, 38.6, 52.1, 59.3, 62.9, 70.3, and 73.0° for the crystal planes (001), (100), (002), (012), (110), (111), (103), and (201), respectively, which are matched to the diffraction peaks of hexagonal Ni(OH)2 nanostructures of JCPDS card number #73-1520. Figure 1c clearly represents the composite-phase formation of β-NiS@Ni(OH)2 nanostuctures. Thus, the stabilized optimization and suitable condition for nano-composite formation of Ni-based sulfide and hydroxide phases.
were strongly suggested by XRD spectra, and also, no other secondary impurities were present in the sample as well, showing very good quality of the crystalline nature of the materials performed in this work.

SEM images of the synthesized nanostructures have been verified by Figure 2 in detail. Figure 2a displays the agglomerated rock-like nanostructures of $\beta$-NiS, which represented the rigid surface morphology with a less dispersive nature. It may not facilitate the smoother pathway of the electrochemical reaction due to the clumsy nature of its surface. Figure 2b displays the stacked nanogill-like nanostructures of Ni(OH)$_2$ consisting of highly functionalized, monodispersed nanogills that strongly facilitate the electron transport pathway to enhance the water oxidation reaction. Figure 2c demonstrates the surface morphology of $\beta$-NiS@Ni(OH)$_2$ nanocomposites. There is a uniform nanoplate morphology of $\beta$-NiS@Ni(OH)$_2$ nanocomposite with clear compact nanoplate edges in an approximate particle size range of 50–70 nm plates. This kind of clear edge surface morphology with compact particle size may provide higher electron mobility and a more number of active sites for the electrochemical reaction, which has been discussed in electrochemical studies in detail. Hence, three different kinds of surface morphology of $\beta$-NiS, Ni(OH)$_2$, and $\beta$-NiS@Ni(OH)$_2$ nanostructures has been confirmed by SEM images.

Raman spectra of the prepared nanocomposites have been provided in Figure 3. The characteristic Raman active vibrations of Ni-based sulfide and hydroxide nanostructures have been confirmed by noticeable strong phonon vibration modes. Figure 3a clearly reveals the characteristic peaks of rhombohedral $\beta$-NiS nanostructures through the phonon vibration peaks around 236 and 347 cm$^{-1}$. These are the characteristic vibration peaks of $\beta$-NiS. The absence of some other Raman active vibrations may be due to the agglomeration of nanosized particles with combined nanostructure formation, which may affect the vibrations of the crystal lattice. Figure 3b displays the strong characteristic vibration modes of hexagonal-phase Ni(OH)$_2$ nanostructures around 390, 440, and 580 cm$^{-1}$ that are attributed to the characteristic vibrations of Ni hydroxide phase nanostructures. The peak 390 cm$^{-1}$ could be attributed to the $E_g$ vibration mode of Ni–OH lattice, and the other two peaks were assigned to the stretching vibration mode of Ni–O nanostructures. Figure 3c displays the composite formation of $\beta$-NiS and Ni(OH)$_2$ nanostructures by the strong Ni–S and Ni–OH phonon vibrations observed around 347, 398, and 472 cm$^{-1}$. Nevertheless, there is an intensity decrement observed

![Figure 2. SEM images of (a) $\beta$-NiS, (b) Ni(OH)$_2$, and (c) $\beta$-NiS@Ni(OH)$_2$ nanocomposites in the 200 nm scale range.](image-url)
may strongly support the formation of hydroxide derivatives of Ni that may be due to exciton recombination by an exciton–exciton collision during excitation.\(^{21}\) Figure 4c shows the moderate NBE emission and also the other oxygen vacancies present in the composite nanostructures by the peaks at 485 and 496 nm due to the charge transfer between Ni\(^{2+}\) to Ni\(^{3+}\) of Ni-based derivatives. From the observed results, it may be derived that, even though the emissive nature of the samples strongly depended on excitation wavelength, the intensity of the emission peaks revealed the information about recombination nature and interstitial vacancies present in the samples.

Figure 5 displays the FTIR spectra of the prepared Ni-based sulfide and hydroxide derivative and its composite in the range of 400 to 4000 cm\(^{-1}\). Figure 5a displays the typical FTIR spectra of NiS nanostructures. The band around 640 cm\(^{-1}\) was caused by strong Ni\(^{2+}\)-S stretching vibration mode of $\beta$-NiS.\(^{22}\) Figure 5b displays the strong vibration band around 498 cm\(^{-1}\) caused by Ni–O stretching vibration modes.\(^{23}\) Figure 5c displays the combined vibration modes of Ni–S and Ni–O stretching of the $\beta$-NiS@Ni(OH)\(_2\) nanocomposite. The other vibration bands of C–O stretching, C–H bending, OH bending, and OH stretching appear around 1097, 1378, 1641, and 3400–3600 cm\(^{-1}\), respectively.\(^{24,25}\) Hence, FTIR spectra evidenced the formation of Ni-based sulfide and hydroxide and its composite derivatives in this study.

The optical band gap of the prepared nanocomposites has been analyzed by UV–visible spectra shown in Figure 6A,B. The UV spectra of the three different samples show three different profiles that may suggest the appreciable band gap variations possessed by the samples. From UV data, the Tauc plot has been drawn to calculate the band gap values of the prepared materials. The Tauc plot follows the equation $\alpha h \nu = A(\nu - E_g)^n$, where $\alpha$, $h$, $\nu$, and $E_g$ are the coefficient of absorption, Planck’s constant, energy of incident photon, and optical band gap, respectively. As per Tauc plot, the estimated band gap values of $\beta$-NiS, Ni(OH)\(_2\), and $\beta$-NiS@Ni(OH)\(_2\) nanocomposites are 2.1, 2.5, and 2.2 eV, respectively. The appreciable band gap variations observed for the three prepared samples may be due to the various morphological and particle nature of the samples in addition to the metal sulfide and metal hydroxide band structures. The obtained
results are matched well with those in the literature. These three band structures are favorable to OER activity of the electrode for electrochemical water splitting applications. Among these three, 2.2 eV was highly recommendable for efficient oxidation of water due to its optimum gap between the valence band and Fermi level for the electrochemical OER reaction to proceed. Hence, UV-visible spectra and Tauc plot results strongly provide the information about the optical properties and band gap of the synthesized nanocomposites.

Electrochemical activities of all the three samples have been thoroughly investigated by an electrochemical workstation at room temperature in a 1 M KOH alkaline electrolyte medium. The stability of the fabricated electrodes is also reported in a strong alkaline medium. Figure 7A–C represents the CV graphs of β-NiS, Ni(OH)₂, and β-NiS@Ni(OH)₂ nanocomposites for five different scan rates of 10, 30, 50, 80, and 100 mV/s. CV graphs evidently proved the distinctive oxidation and reduction peaks of the pseudocapacitive nature...
of the electrodes. During the electrochemical process, \( \beta \)-NiS may undergo some complexities in diffusion with electrolyte ions due to its bulky surface nature, whereas Figure 7B represents the larger area CV curve, thereby supporting the higher storage mechanism of Ni-based hydroxides. At the same time, the \( \beta \)-NiS@Ni(OH)\(_2\) nanocomposite provided the same kind of CV curve as that of \( \beta \)-NiS excluding the combination effect shown in higher current density obtained in CV. The specific capacitances calculated for \( \beta \)-NiS, Ni(OH)\(_2\), and \( \beta \)-NiS@Ni(OH)\(_2\) nanocomposite electrodes are 216, 230, and 428 F/g at 10 mV/s, respectively. This result clearly evidenced that the novel combination of \( \beta \)-NiS and Ni(OH)\(_2\) shows higher storage capacity barely twice than that of individual electrode performance, which may be due to the origin of the faradaic reaction initiated by Ni–O/Ni–O–OH and its interaction with electrolyte OH\(^{-}\) ions.\(^{28}\) This kind of nanoplate morphology further facilitated the efficient charge separation and transportation. Moreover, there is an appreciable peak shift observed in CV curves of NiS, Ni(OH)\(_2\), and \( \beta \)-NiS@Ni(OH)\(_2\) nanocomposites during the redox couple reaction. It may be due to the different onset potentials of the corresponding electrodes during oxidation as 0.44, 0.42, and 0.43 V, respectively, at 10 mV/s. Generally, Ni (Ni\(^{3+}\)) oxidized into its higher valence species (Ni\(^{2+}\) or Ni\(^{1+}\)) around 0.4 V.\(^{29}\) At this juncture, the composite exhibited an onset oxidation potential of 0.43 V, which lies in between the oxidation of NiS and Ni(OH)\(_2\) nanostructures during oxidation. Hence, it is suggested that the \( \beta \)-NiS@Ni(OH)\(_2\) nanocomposite electrode may be adapted as an efficient electrode for supercapacitor application, and also, the CV result suggested that the high-performance electrode may possess good OER activity toward electrochemical water splitting, which has been discussed in LSV.

Figure 7D represents the EIS spectra of the fabricated electrodes in the frequency range of 100 mHz to 100 kHz. This result further made the strong notation on the CV graph. As per CV study, the highly commendable \( \beta \)-NiS@Ni(OH)\(_2\) nanocomposite electrode illustrated higher electronic conductivity than the other two electrodes with a very low charge transfer resistance of 118 \( \Omega \). Further, the conducting spike region of the \( \beta \)-NiS@Ni(OH)\(_2\) nanocomposite revealed the maximized conducting nature compared to the other two electrodes. It may also suggest that the synergistic role of \( \beta \)-NiS and Ni(OH)\(_2\) nanocomposites provided easy interaction of electrolyte ions and electrode species. These kinds of combinations are undoubtedly supported by a more number of electron transportation from the working electrode that obviously enhanced the current density. Hence, the expected \( \beta \)-NiS@Ni(OH)\(_2\) nanocomposite electrode performed well in OER during the electrochemical water splitting reaction.
LSV graphs explored the OER activity of the fabricated electrodes at a 10 mV/s scan rate as shown in Figure 8A. The maximum current densities achieved for β-NiS, Ni(OH)2, and β-NiS@Ni(OH)2 electrodes are 132, 204, and 240 mA/g, respectively. Interestingly, as an individual performance, both β-NiS and Ni(OH)2 possessed low current densities, but the combination of the same two phases performed higher OER activity.31 It strongly suggested that the individual phase of β-NiS and Ni(OH)2 involved in the electrolysis reaction via the following electrochemical mechanism: 

\[ \text{NiS} + \text{H}_2\text{O} + 1/2 \text{O}_2 \rightarrow \text{Ni(OH)}_2 + \text{S} \]

During the synergistic role of both the sulfide and hydroxide derivatives of the Ni electrode, there is a more possibility of the OER reaction to proceed by reaction species. Furthermore, the NiS@Ni(OH)2 electrode, there is a more possibility of the OER reaction to proceed by reaction species. The Tafel slopes of the NiS, Ni(OH)2, and NiS@Ni(OH)2 nanocomposites are 111, 76, and 53 mV/dec, respectively. Interestingly, as an individual performance, both β-NiS and Ni(OH)2 nanocomposites exhibited dominant performance compared to the other two electrodes. The three samples almost retained its activity as 100% after 1 h of stability test. The highly active NiS@Ni(OH)2 nanocomposite electrode was further subjected to 18 h of stability test to evaluate its long-time electrochemical OER activity. As a result of 18 h OER activity of the electrode, it retained 95% of the electrochemical oxygen evolution reaction in a three-cell electrochemical setup.

To evaluate the OER performance after 18 h of long-time stability test, LSV and EIS have been run again for the NiS@Ni(OH)2 nanocomposite electrode as shown in Figure 8A. LSV graphs predicted the reduction in its performance after 18 h of stability. There was some noticeable decay in the current density value that may be due to the continuous electrochemical water oxidation performance of the electrode for 18 h, which may increase the surface rigidity of the electrode, which may block the easy electron transfer evidenced by EIS spectra by the increment in charge transfer resistance. Hence, a high-quality and strongly coupled β-NiS@Ni(OH)2 nanocomposite electrode has been fabricated by a typical optimized procedure, and the water splitting ability of the electrode has been explored with very high efficiency. The synergistic effect of different phase nanocomposites, sharp edge nanoplate morphology, and good electronic conductivity adhered by the β-NiS@Ni(OH)2 nanocomposite electrode strongly suggested as a resourceful electrode for electrochemical water splitting application and other potential applications such as supercapacitors.

### Table 1. Comparison of OER Activity of the Fabricated β-NiS@Ni(OH)2 Electrode with Recent Literature Reports

| electrocatalysts | electrolyte medium | obtained OER current density (mA/g) | Tafel slope value (mV/dec) | ref |
|------------------|--------------------|------------------------------------|---------------------------|-----|
| NiS/NiP         | 1 M KOH            | 190 mA/g at 1.9 V vs RHE           | 76                        | 32  |
| NiS             | 1 M KOH            | 140 mA/g at 1.8 V vs RHE           | 93                        | 33  |
| Ni(OH)2@NiS2    | 1 M KOH            | 138 mA/g at 1.8 V vs RHE           | 152                       | 34  |
| β-Ni(OH)2        | 1 M KOH            | 60 mA/g at 1.52 V vs RHE           | 66                        | 35  |
| β-NiS@Ni(OH)2   | 1 M KOH            | 240 mA/g at 1.6 V vs RHE           | 53                        | present work |

The Tafel slope has been drawn from LSV data of the fabricated electrodes shown in Figure 8B. Calculated Tafel slope values of β-NiS, Ni(OH)2, and β-NiS@Ni(OH)2 nanocomposites are 111, 76, and 53 mV/dec, respectively. The Tafel slope directly correlated the electron transport mechanism of fabricated electrodes. The lower Tafel slope value dominantly resulted in higher OER performance. Hence, the smaller Tafel slope value of 53 mV/dec possibly evidenced the first electron rate limiting step of the electrode, which solidly arose due to the large number of active sites participated in the electrochemical reaction of the β-NiS@Ni(OH)2 nanocomposite electrode. This may also suggest that very good electrical coupling of β-NiS and Ni(OH)2 nanostructures may be one of the causes for higher OER activity.

### 3. CONCLUSIONS

Efficient combination of β-NiS and Ni(OH)2 to obtain β-NiS@Ni(OH)2 nanocomposites has been a success in this work. The formation mechanism of strongly coupled β-NiS@Ni(OH)2 nanocomposites has been proposed in this work. The Ni-based sulfide and hydroxide derivative nanocomposite electrodes were fabricated and investigated for electrochemical water splitting application. Higher OER activity of the electrode was revealed by a higher current density of 240 mA/g at a 10 mV/s scan rate, and also, the electrode withstood the 18 h stability test with 95% of electrochemical performance to adapt as a device quality electrode for electrochemical water splitting applications.

### 4. MATERIALS AND METHODS

For the synthesis of the β-NiS rocky texture nanostucture, 0.1 M nickel acetate (C6H5NiO2) and 0.3 M thiourea CS(NH2)2 were dissolved in 80 mL of deionized water separately. The above mixtures were mixed together for a successful chemical reaction and then placed to a 250 mL autoclave, which was stabilized at 180 °C for 24 h. The final product was cleaned.
and dried for characterization, which was named NS1. For the synthesis of Ni(OH)2 stacked nanogill-like nanostructures, 0.1 M nickel acetate (C12H11NiO4) and 0.3 M urea CH2N2O were dissolved in 80 mL of deionized water separately. The same treatment time and temperature were stabilized to obtain NS2 nanopowder. For the synthesis of β-NiS@Ni(OH)2 nanoplates, 0.3 M nickel acetate (C12H11NiO4) and 0.3 M thiourea (CS(NH2)2) were dissolved in 80 mL of deionized water separately, and then they were mixed together with 5 mL of ethylene glycol added to the mixed solution. The same treatment time and temperature were also followed to get β-NiS@Ni(OH)2 nanoplates, named NS3. The obtained products’ material characterization was reported in our previous literature. The coating procedure of the active material on Ni foam has been mentioned as follows: initially, 80% NS1 active material, 18% activated carbon, and 2% polyvinylidone hexafluoropropylene (PVDF) binder were ground with the help of 20 drops of N-methyl pyrrolidone (NMP) solution. The homogeneous slurry was then coated on Ni foam with the help of a micropipette. The active-material-coated Ni foam was then dried and used for further electrochemical characterization. Similarly, the other two NS2 and NS3 samples were fabricated as electrodes on Ni foam. The entire electrochemical measurement was done in a Biologic SP 150 workstation at room temperature in a typical three-electrode cell setup in which the working electrode bears the active-material-coated Ni foam, counter electrode bears platinum wire, and the reference electrode bears Ag/AgCl electrodes.

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