Interfacial Interaction in NiFe LDH/NiS$_2$/VS$_2$ for Enhanced Electrocatalytic Water Splitting

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Abstract: A bifunctional electrocatalyst with high efficiency and low costs for overall water splitting is critical to achieving a green hydrogen economy and coping with the energy crisis. However, developing robust electrocatalysts still faces huge challenges, owing to unsatisfactory electron transfer and inherent activity. Herein, NiFe LDH/NiS$_2$/VS$_2$ heterojunctions have been designed as freestanding bifunctional electrocatalysts to split water, exhibiting enhanced electron transfer and abundant catalytic sites. The optimum NiFe LDH/NiS$_2$/VS$_2$ electrocatalyst exhibits a small overpotential of 380 mV at 10 mA cm$^{-2}$ for overall water splitting and superior electrocatalytic performance in both hydrogen and oxygen evolution reactions (HER/OER). Specifically, the electrocatalyst requires overpotentials of 76 and 286 mV at 10 mA cm$^{-2}$ for HER and OER, respectively, in alkaline electrolytes, which originate from the synergistic interaction among the facilitated electron transfer and increasingly exposed active sites due to the modulation of interfaces and construction of heterojunctions.

Keywords: vanadium disulfide; nickel disulfide; layered double hydroxide; interfacial regulation; electrocatalytic overall water splitting; hydrogen/oxygen evolution reaction

1. Introduction

Electrocatalytic overall water splitting, as a promising green hydrogen (ideal zero-carbon energy carrier)-producing strategy, has attracted more attention for developing carbon-neutral alternatives [1–3]. However, electrocatalytic water-splitting activity is severely limited, owing to the sluggish catalytic kinetics for OER and HER [4–7]. Electrocatalysts of excellent efficiency are essential to reducing the overpotential by lowering the activation energy of water splitting [8,9]. At present, although IrO$_2$, RuO$_2$ and Pt-based materials have been employed as highly effective electrocatalysts for OER and HER, respectively, their scarcity and high price have hampered their industrialized application on a large scale [10,11]. The preparation of cost-effective bifunctional electrocatalysts with superior activity for OER and HER is crucial to promoting the practical applications and industrialized development of overall electrocatalytic water splitting.

Non-noble transition metal sulfides (TMSs) have presented themselves as appealing catalysts for both HER and OER on the basis of their favorable electrocatalytic activity and electrical conductivity [12,13]. Recently, vanadium disulfide (VS$_2$) has attracted considerable attention as a candidate electrocatalyst, owing to its intrinsic catalytic properties, which exhibit weak van der Waals interlayer interactions and an interlayer spacing of 5.76 Å [14]. In particular, benefiting from its metallic conductivity and electrocatalytic active sites both on the surface and at the active edge, the 1T phase VS$_2$ has been widely employed as an electrocatalyst for HER and OER [15]. Nevertheless, previous research reveals that individual TMSs exhibit insufficient active sites due to their strong van der Waals forces [16]. Massive efforts have been directed at constructing multi-component nanomaterial, which has been expected to improve its electrocatalytic activity by providing an abundance of active sites [17,18]. Ru cluster-modified VS$_2$ can achieve a current density...
of 50 mA cm$^{-2}$ at an overpotential of 245 mV, and this can be attributed to the optimization of intermediate adsorption/desorption through the interactions between Ru and VS$_2$ and the sufficient catalytic sites afforded by electro-oxidized of Ru species [19]. Benefiting from induced-layer electron transfer between NiCo$_2$S$_4$ and ReS$_2$ interfaces, the NiCo$_2$S$_4$/ReS$_2$ nanocomposite showed excellent HER properties in both acidic and alkaline conditions [20]. The CoS$_2$-ReS$_2$ heterojunction exhibited improved electrocatalytic activity for HER and OER, which can be accounted for by the rich catalytic sites on the edge and the optimized catalytic kinetics of the interfacial modulation of ReS$_2$ via modifying CoS$_2$ [21]. Therefore, constructing binary transition metal sulfide-based electrocatalysts is beneficial to creating abundant catalytic active sites.

Interfacial regulation has been regarded as a powerful method to adjust electronic structure and catalytic kinetics to significantly enhance electrocatalysis [22–26]. NiFe layered double hydroxides (LDHs) have been widely investigated for OER because they can convert into $\gamma$-NiOOH by surface reconstruction, which has been proven to be the actual active sites [27,28]. Nevertheless, NiFe LDH exhibits limited electrocatalytic activity for OER due to weak conductivity and insufficient active sites [29]. Constructing heterostructures has been employed to improve its intrinsic catalytic activity by facilitating electron transfer kinetics and promoting the conversion of NiFe LDH into $\gamma$-NiOOH active species [30]. Urchin-like Co$_9$S$_8@$NiFe layered double-hydroxide heterostructured hollow spheres have been designed to enhance the electrocatalytic OER process by improving electrical conductivity and reducing the reaction energy barrier, requiring a smaller overpotential of 220 mV at 10 mA cm$^{-2}$ [31]. By virtue of the abundant Ni$_3$S$_2$-NiFe LDH interfaces, this catalyst is regarded as one of the most productive non-precious metal-based OER catalysts [32]. Furthermore, the in-situ growth of heterogeneous structure electrocatalysts using a binder-free method can provide intimate contact between multi-components and electrodes, which can induce facilitated electron transfer [33,34]. Electrodeposition is a useful technique to rapidly fabricate multi-component nanomaterials through an in-situ growth process [35,36].

Inspired by the above-mentioned facts, a heterogeneous structure-based binary metal sulfide-modified carbon cloth (NiS$_2$/VS$_2$) has been constructed via a one-step hydrothermal process. Subsequently, an active OER electrocatalyst, NiFe LDH, was integrated into the surface of NiS$_2$/VS$_2$ (NiFe LDH/NiS$_2$/VS$_2$) using a facile electrochemical deposition method, which was simultaneously exploited as a bifunctional electrocatalyst for both HER and OER. This designed heterostructure of NiFe LDH/NiS$_2$/VS$_2$ nanosheets exhibits interfacial charge transfer from NiS$_2$ to VS$_2$ and promotes electron transfer during the electrocatalytic process. Moreover, the formed porous nanoflower-like structure is favorable for exposing more active sites and facilitating bubble releasing, all of which can promote the electrocatalytic performance for overall water splitting. As a bifunctional electrocatalyst, the obtained NiFe LDH/NiS$_2$/VS$_2$ can deliver a current density of 10 mA cm$^{-2}$ at an overpotential of 76 and 286 mV severally for HER and OER, together with excellent electrocatalytic stability. Furthermore, the solar-driven electrocatalytic overall splitting system constructed by NiFe LDH/NiS$_2$/VS$_2$ demonstrated that it has good potential for practical applications.

2. Results and Discussion

2.1. Characterization of Samples

The synthetic pathway of NiFe LDH/NiS$_2$/VS$_2$ is schematically illustrated in Scheme 1, in which VS$_2$ was in-situ deposited on the surface of carbon cloth (decorated as VS$_2$/CC) by a facile hydrothermal method. Similarly, the NiS$_2$/VS$_2$ decorated CC was constructed by the above-mentioned method with the addition of NiSO$_4$·6H$_2$O. Subsequently, the NiFe LDH was modified onto the surface of NiS$_2$/VS$_2$ via a simple electrodeposition method, resulting in NiFe LDH/NiS$_2$/VS$_2$. 
The phase and composition of pure VS$_2$, NiS$_2$/VS$_2$ and NiFe LDH/NiS$_2$/VS$_2$ were measured by XRD. As shown in Figure S1a, the diffraction peaks located at 2θ values of 15.2, 35.64, 45.07, 47.06 and 57.02° can be ascribed to the (001), (011), (012), (003) and (110) lattice planes of VS$_2$ (JCPDS No. 89-1640) [37,38]. The additional peaks at 31.58, 38.76, 53.43, 58.50 and 60.91° appeared when NiS$_2$ was modified on the surface of VS$_2$, which can be indexed to the (200), (211), (311), (230) and (321) plane of NiS$_2$ (JCPDS No. 11-0099), respectively [39–41]. Compared with the XRD pattern of NiS$_2$/VS$_2$, the characteristic diffraction peaks at 11.26 and 35.28° appeared after the electrodeposition of NiFe LDH, which can be assigned to the (003) and (006) planes of NiFe LDH species (JCPDS No. 51-0463) [42,43]. The above-mentioned results suggest the co-existence of VS$_2$, NiS$_2$ and NiFe LDH in NiFe LDH/NiS$_2$/VS$_2$.

The morphology of the electrocatalysts was studied using SEM and TEM. As shown in Figure 1a, the pure VS$_2$ exhibits a nanoflower-like structure, which is distinguished from the NiS$_2$/VS$_2$ by a nanosheet morphology (Figure 1b). By contrast, the NiFe LDH/NiS$_2$/VS$_2$ has a thin nanosheets structure (Figure 1c), which was beneficial for exposing more active sites. Furthermore, the TEM image (Figure 1d) reveals that NiFe LDH/NiS$_2$/VS$_2$ exhibits a nanosheet structure. An interplanar spacing of 2.0, 2.3 and 1.9 Å is shown in the HRTEM image (Figure 1e) and can be identified as the (012) plane of VS$_2$, (220) plane of NiS$_2$ and (018) plane of NiFe LDH, respectively [44–46]. As illustrated in Figure 1f, the selected area electron diffraction (SAED) reveals that the (012) plane of NiFe LDH, (012) plane of VS$_2$ and (321) plane of NiS$_2$ appeared in the NiFe LDH/NiS$_2$/VS$_2$ sample, suggesting the successful construction of the NiFe LDH/NiS$_2$/VS$_2$ electrode [44,47,48]. The EDS-mapping measurement (Figure 2) was employed to investigate the element distribution of NiFe LDH/NiS$_2$/VS$_2$, revealing an evenly distribution of V, S, Ni, Fe and O elements in the NiFe LDH/NiS$_2$/VS$_2$.

To investigate the superficial element composition and the chemical state of the respective elements of the as-prepared electrocatalysts, X-ray photoelectron spectroscopy (XPS) characterization was utilized for the VS$_2$, NiS$_2$/VS$_2$ and NiFe LDH/NiS$_2$/VS$_2$. Compared with the XPS survey spectra of the VS$_2$ (Figure S1b), an obvious signal of the Ni element appears in the survey spectra of the NiS$_2$/VS$_2$ and NiFe LDH/NiS$_2$/VS$_2$ samples. The XPS survey of NiFe LDH/NiS$_2$/VS$_2$ reveals the co-existence of Ni, Fe, V, O and S elements, which corresponds to the result of the EDS-mapping images. As revealed in Figure 3a, the high-resolution XPS spectrum of V for VS$_2$ contains typical characteristic peaks at 514.12 and 521.62 eV, which can be related to the V$^{2+}$ 2P$_{3/2}$ and V$^{2+}$ 2P$_{1/2}$, respectively [49,50]. Additionally, there are two dominant peaks at 516.87 and 524.10 eV that can be indexed to the V$^{4+}$ 2P$_{3/2}$ and V$^{4+}$ 2P$_{1/2}$, respectively [49–51]. By contrast, the V$^{4+}$ 2P$_{3/2}$ peak around
517.49 eV and V$^{4+}$ 2p$_{1/2}$ around 524.72 eV of NiS$_2$/VS$_2$ display a positive shift, demonstrating the electronic interaction between NiS$_2$ and VS$_2$. Similarly, the V 2p XPS pattern of NiFe LDH/NiS$_2$/VS$_2$ exhibits the two characteristic peaks at 517.61 and 524.86 eV, which can be ascribed to the V$^{4+}$ 2p$_{3/2}$ and V$^{4+}$ 2p$_{1/2}$, respectively [49–51]. Consequently, this indicates that the valence state of V does not change after the electrodeposition of NiFe LDH, while an obvious positive shift occurs for V$^{4+}$ 2p$_{3/2}$ and V$^{4+}$ 2p$_{1/2}$ in NiFe LDH/NiS$_2$/VS$_2$ compared with NiS$_2$/VS$_2$ and VS$_2$. In the S 2p XPS survey of VS$_2$, NiS$_2$/VS$_2$ and NiFe LDH/NiS$_2$/VS$_2$ (Figure 3b), the peaks at 162.2 and 163.4 eV can be fitted to the S$^{2-}$ 2p$_{3/2}$ and S$^{2-}$ 2p$_{1/2}$, respectively [50,52]. Moreover, the peak at 168.5 eV in the S 2p XPS of NiFe LDH/NiS$_2$/VS$_2$ can be attributed to the S-O bond, owing to slight oxidization [38].

Figure 1. SEM images of (a) VS$_2$, (b) 1:5 NiS$_2$/VS$_2$, and (c) 350 s NiFe LDH/NiS$_2$/VS$_2$. (d) TEM, (e) HRTEM image and (f) SAED pattern of 350 s NiFe LDH/NiS$_2$/VS$_2$.

Figure 2. (a) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of NiFe LDH/NiS$_2$/VS$_2$ and the corresponding elemental mapping of (b) V, (c) S, (d) Ni, (e) Fe and (f) O in NiFe LDH/NiS$_2$/VS$_2$. 
Figure 3. (a) High-resolution XPS spectra of (a) V 2p, (b) S 2p, (c) Ni 2p and (d) Fe 2p of the prepared VS$_2$, NiS$_2$/VS$_2$ and NiFe LDH/NiS$_2$/VS$_2$.

As revealed in Figure 3c, the high-resolution Ni 2p XPS survey of NiS$_2$/VS$_2$ reveals a negative shift compared with NiS$_2$, further suggesting the strong interfacial electronic interaction of NiS$_2$ and VS$_2$. In detail, the Ni 2p XPS of NiS$_2$ displays a peak at 857.23 eV with a satellite peak of 862.45 eV and a peak at 874.44 eV with a satellite peak of 881.11 eV, belonging to the Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ of Ni$^{2+}$, respectively [53–55]. In comparison, the characteristic peaks of Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ of NiS$_2$/VS$_2$ shift to 856.83 and 874.30 eV, respectively. For further exploring the potential effects of the introduction of NiFe LDH, the high-resolution Fe 2p XPS of NiFe LDH and NiFe LDH/NiS$_2$/VS$_2$ was measured. As revealed in Figure 3d, the peaks of Fe$^{3+}$ 2p$_{3/2}$ and Fe$^{3+}$ 2p$_{1/2}$ in the NiFe LDH/NiS$_2$/VS$_2$ are separately located at 712.33 and 725.84 eV, which reveals a negative shift of Fe 2p XPS compared with the peaks of Fe$^{3+}$ 2p$_{3/2}$ (713.10 eV) and Fe$^{3+}$ 2p$_{1/2}$ (726.5 eV) in the NiFe LDH [55–57].

2.2. Electrocatalytic Oxygen Evolution Reaction Performance

The electrocatalytic OER performance of the prepared products (VS$_2$, NiS$_2$/VS$_2$, NiFe LDH and NiFe LDH/NiS$_2$/VS$_2$) was evaluated in 1.0 M KOH with a typical three-electrode system. As shown in Figure 4a,b, the VS$_2$ shows poor electrocatalytic performance for OER, which exhibits a high overpotential of 540 mV to reach a current density of 10 mA cm$^{-2}$, suggesting that the VS$_2$ is inactive for electrocatalytic OER. Obviously, the NiS$_2$/VS$_2$ heterogeneous structure exhibits enhanced electrocatalytic activity for OER, revealing that
the formed multi-phase interface is a key factor in boosting the electrocatalytic activity of OER. Figure S2a shows the electrocatalytic OER activity of the VS$_2$-based electrocatalysts with different additive ratios of NiSO$_4$, in which the 1:5 NiS$_2$/VS$_2$ (denoted as NiS$_2$/VS$_2$) exhibits an optimal electrocatalytic activity with an overpotential of 386 mV at 10 mA cm$^{-2}$. Additionally, the electrodeposition time of NiFe LDH was optimized, ranging from 0 to 400 s. Figure S2b reveals that the 350 s NiFe LDH/NiS$_2$/VS$_2$ exhibits superior electrocatalytic activity when the electrodeposition time of NiFe LDH is 350 s, which has been denoted as NiFe LDH/NiS$_2$/VS$_2$. The NiFe LDH/NiS$_2$/VS$_2$ exhibits better electrocatalytic performance for OER compared with VS$_2$, NiS$_2$/VS$_2$ and NiFe LDH, which provides a lower overpotential of 286 mV to deliver a current density of 10 mA cm$^{-2}$. Additionally, the LSV curves of NiFe LDH/NiS$_2$/VS$_2$ and NiFe LDH show small peaks around 1.35 V, which can be interpreted as the redox reactions of the Ni species. These results imply that the formed heterogeneous structure and NiFe LDH decoration are beneficial to improving the electrocatalytic performance of OER.

Figure 4. Electrochemical OER performance of the as-prepared VS$_2$, NiS$_2$/VS$_2$, NiFe LDH and NiFe LDH/NiS$_2$/VS$_2$ samples: (a) polarization curves, (b) the corresponding overpotential to deliver a current density of 10 and 50 mA cm$^{-2}$ in 1.0 M KOH, (c) the Tafel plots and (d) the EIS spectra.

Moreover, the electrocatalytic kinetics of as-prepared catalysts were evaluated by measuring Tafel plots. As shown in Figure 4c, the NiFe LDH/NiS$_2$/VS$_2$ exhibits a smaller Tafel slope of 99 mV dec$^{-1}$ than NiFe LDH (167 mV dec$^{-1}$), NiS$_2$/VS$_2$ (221 mV dec$^{-1}$) and VS$_2$ (442 mV dec$^{-1}$), suggesting the facilitated catalytic kinetics of NiFe LDH/NiS$_2$/VS$_2$ for OER. The electrochemical impedance spectroscopy (EIS) measurement was utilized to evaluate the charge transfer properties. As Figure 4d depicts, the NiFe LDH/NiS$_2$/VS$_2$ exhibits the smallest charge transfer resistance ($R_{ct}$) among the as-prepared electrocatalysts,
indicating that the lower resistance and accelerated electron transfer can be achieved by constructing a heterogeneous structure and decorating NiFe LDH.

The electrochemically active surface area (ECSA) of the as-prepared electrocatalysts was evaluated by calculating the $C_{dl}$ according to the CV curves at various scan rates. As displayed in Figure 5a, the NiFe LDH/NiS$_2$/VS$_2$ exhibits a much larger $C_{dl}$ of 3.38 mF cm$^{-2}$ than NiFe LDH (2.55 mF cm$^{-2}$), NiS$_2$/VS$_2$ (1.41 mF cm$^{-2}$) and VS$_2$ (0.43 mF cm$^{-2}$), which can be attributed to the formed heterogeneous structure and the NiFe LDH decoration. Accordingly, the NiFe LDH/NiS$_2$/VS$_2$ exhibits an ECSA of 84.80 cm$^2$, which is higher than that of NiFe LDH (63.75 cm$^2$), NiS$_2$/VS$_2$ (35.25 cm$^2$) and VS$_2$ (10.75 cm$^2$) (Figure S5a). The current density was normalized by the ECSA to evaluate the specific activity. As observed in Figure S5b and Figure 5c, the NiFe LDH/NiS$_2$/VS$_2$ exhibits intrinsic activity compared to the others, suggesting that the formed heterogeneous structure and modulated electronic structure are favorable to enhancing electrocatalytic activity. Additionally, the electrocatalytic stability of NiFe LDH/NiS$_2$/VS$_2$ was evaluated by i–t curves in 1.0 M KOH. In Figure 5b, we can observe that the NiFe LDH/NiS$_2$/VS$_2$ can maintain its superior electrocatalytic activity over 24 h, demonstrating that the prepared NiFe LDH/NiS$_2$/VS$_2$ can sustain long-term electrolysis without obvious attenuation. Furthermore, an XPS measurement of the NiFe LDH/NiS$_2$/VS$_2$ was employed after the stability test to investigate the structural stability. As observed in Figure S6, the NiFe LDH/NiS$_2$/VS$_2$ can maintain its initial chemical composition and chemical state after a long-term stability test. The thin nanosheet structure also can be observed (Figure S7) after long-term stability, demonstrating the structural stability of NiFe LDH/NiS$_2$/VS$_2$.

![Figure 5](image_url)

**Figure 5.** (a) The $C_{dl}$ of the as-prepared VS$_2$, NiS$_2$/VS$_2$, NiFe LDH and NiFe LDH/NiS$_2$/VS$_2$ samples and (b) the long-term stability of NiFe LDH/NiS$_2$/VS$_2$ under the potential of 0.5 V (vs. SCE).

### 2.3. Electrocatalytic Hydrogen Evolution Reaction and Overall Water-Splitting Performance

To investigate its potential for efficient overall water splitting, the electrocatalytic performance of the NiFe LDH/NiS$_2$/VS$_2$ for HER was evaluated in 1.0 M KOH. Figure 6a,b shows that the NiFe LDH/NiS$_2$/VS$_2$ electrocatalyst exhibits excellent electrocatalytic activity, acquiring a smaller overpotential of 76 mV to deliver a current density of 10 mA cm$^{-2}$, which is greatly superior to that of the VS$_2$ (546 mV), NiS$_2$/VS$_2$ (270 mV) and NiFe LDH (122 mV). The corresponding Tafel plots are illustrated in Figure 6c. The NiFe LDH/NiS$_2$/VS$_2$ has a smaller Tafel slope of 79 mV dec$^{-1}$ than VS$_2$ (202 mV dec$^{-1}$), NiS$_2$/VS$_2$ (175 mV dec$^{-1}$) and NiFe LDH (145 mV dec$^{-1}$). Moreover, the NiFe LDH/NiS$_2$/VS$_2$ exhibits remarkable stability during 24 h electrochemical measurement and maintains its electrocatalytic activity for HER (Figure 6d).

Electrocatalytic overall water splitting was measured by a two-electrode system composed of NiFe LDH/NiS$_2$/VS$_2$ in 1.0 M KOH. As shown in Figure 7a, the constructed overall water-splitting system is able to deliver a current density of 10 mA cm$^{-2}$ at 1.61 V, confirming its potential to drive the overall water splitting. Furthermore, a commercial
solar cell under 2.0 V was employed to explore its solar-drive overall water-splitting performance. As shown in Figure 7b, a number of microbubbles of H$_2$ and O$_2$ gas at the cathode and anode, respectively, evolved, which clearly demonstrates the superior electrocatalytic activity of the NiFe LDH/NiS$_2$/VS$_2$. Furthermore, the corresponding Video S1 recorded this dynamic state.

**Figure 6.** Electrochemical HER performance of the as-prepared VS$_2$, NiS$_2$/VS$_2$, NiFe LDH and NiFe LDH/NiS$_2$/VS$_2$ samples: (a) polarization curves, (b) the corresponding overpotential to deliver a current density of 10 and 50 mA cm$^{-2}$ in 1.0 M KOH, (c) the Tafel plots and (d) the long-term stability text of NiFe LDH/NiS$_2$/VS$_2$ under the potential of −1.2 V (vs. SCE).

**Figure 7.** (a) The LSV curves of LDH/NiS$_2$/VS$_2$ (+, −) device for overall water splitting. (b) image of the solar-driven water-splitting system in 1.0 M KOH electrolyte.
3. Experimental Section

3.1. Materials

Ammonium metavanadate (NH₄VO₃, AR, Tianjin Damao Chemical Reagent Factory, Tianjin, China), thioacetamide (CH₃CSNH₂, Aladdin Industrial Corporation, Shanghai, China), nickel sulfate hexahydrate (NiSO₄·6H₂O, AR, Zhongxin Fine Chemical Co., Ltd., Jinan, China), (FeSO₄·7H₂O, AR, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) ammonium hydroxide (NH₄OH, AR, Tianjin Fuyu Fine Chemical Co., Ltd., Tianjin, China), and carbon cloth (CC, SCI Materials Hub, Taiwan, China) were employed as substrates for the in-situ formation of VS₂ and NiS₂/VS₂ on its surface via hydrothermal synthesis. Potassium hydroxide (KOH, Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China), nitric acid (HNO₃, AR, Chengdu Kelong Chemical, Chengdu, China), and ethyl alcohol (C₂H₅OH, AR, Tianjin Fuyu Fine Chemical Co., Ltd., Tianjin, China) were obtained to pretreat CC. Deionized water was prepared in our laboratory. All chemicals mentioned were utilized as received without further purification.

3.2. Pretreatment of Carbon Cloth (CC) Substrate

Carbon cloth (CC) with a geometric area of 2 × 4 cm² was sonicated in an ultrasonic bath with deionized water and ethanol (C₂H₅OH) severally for 15 min to clean its surface thoroughly. Then, the hydrophilic surface was obtained via pretreatment in concentrated HNO₃ at 100 °C for 2 h. Finally, the CC surface was fully rinsed with deionized water to remove residual HNO₃, and the pretreated CC was obtained.

3.3. Preparation of 1:5 NiS₂/VS₂

A typical procedure to synthesize 1:5 NiS₂/VS₂ was performed as follows: 1 mmol NH₄VO₃ was added to a weak alkaline solution produced by 25 mL deionized water and 2 mL NH₄OH while stirring constantly. At the same time, 10 mmol CH₃CSNH₂ and 0.2 mmol NiSO₄·6H₂O were dispersed in 10 mL deionized water with stirring. The above two solutions were blended and stirred vigorously at room temperature for 1 h. The mixture solution and prepared CC (2 × 4 cm²) were sealed and maintained at 160 °C for 24 h in a 50 mL Teflon-lined autoclave. The sample was cooled to an ambient temperature naturally after the reaction. Then, the prepared sample was rinsed several times with absolute ethanol and deionized water, respectively. Finally, it was dried at 60 °C for 6 h, and the 1:5 NiS₂/VS₂ was obtained.

For investigating the effect of NiS₂ on electrocatalytic HER and OER activities, VS₂, 1:10 NiS₂/VS₂, 1:7.5 NiS₂/VS₂, and 1:2 NiS₂/VS₂ were synthesized by a similar method with 1:5 NiS₂/VS₂ in terms of finely varying the additive amount of NiSO₄·6H₂O. More specifically, 0 mmol, 0.1 mmol, 0.133 mmol, and 0.5 mmol NiSO₄·6H₂O were added into the precursor solution for preparing VS₂, 1:10 NiS₂/VS₂, 1:7.5 NiS₂/VS₂, and 1:2 NiS₂/VS₂, individually.

3.4. Preparation of 350 s NiFe LDH/NiS₂/VS₂

The hydrothermal synthetic method for 1:5 NiS₂/VS is based on the above-mentioned method. NiFe LDH was grown through an electrodeposition method on the surface of 1:5 NiS₂/VS₂. Then, 0.025 M NiSO₄ and 0.0125 M FeSO₄ solutions were homogeneously mixed in a three-electrode system with saturated calomel electrode (SCE), NiS₂/VS₂, and Pt plate as the reference, working, and counter electrode, respectively. The electrodeposition process was operated at a constant voltage of -1.0 V (vs. SCE) at room temperature with different electrodeposition times (250 s, 300 s, 350 s and 400 s), and the corresponding samples were denoted 250 s NiFe LDH/NiS₂/VS₂, 300 s NiFe LDH/NiS₂/VS₂, 350 s NiFe LDH/NiS₂/VS₂, and 400 s NiFe LDH/NiS₂/VS₂, respectively. Finally, these as-obtained catalytic electrodes were gently washed several times using deionized water and then dried naturally.

As a reference, NiFe LDH was grown on pretreated CC using the same electrodeposition synthetic process for 350 s with the absence of 1:5 NiS₂/VS₂.
3.5. Structural Characterization

The phase composition was determined on an XRD-7000 s device (Shimadzu, Kyoto, Japan) with Cu Kα radiation (λ = 1.5418 Å) in a 2 Theta scanning range from 10 to 80° at a current of 40 mA and a voltage of 40 kV. The morphology of the electrocatalysts was measured by means of a scanning electron microscope (SEM, Sigma 300, ZEISS, Oberkochen, Germany), and the energy dispersive spectrum (EDS) was recorded on Oxford Xplore. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were determined using a TEM instrument (Talos F200×, FEI, Hillsboro, OR, USA) with a field-emission gun operated at 200 kV, and the EDS was recorded. Surface chemical analysis was performed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific, K-Alpha Nexsa, Waltham, MA, USA) using monochromatic Al Kα radiation (1486.6 eV).

3.6. Electrochemical Measurements

The electrocatalytic performances for both HER and OER were carried out on a CHI660E electrochemical workstation using a traditional three-electrode system and an H-type electrochemical cell in an electrolyte of 1.0 M KOH. The as-prepared electrode with a geometric area of 1.0 cm², the saturated calomel electrode (SCE), and the Pt plate were individually employed as working, reference and counter electrodes. The working electrode and SCE reference electrode were placed in the same chamber, and the Pt plate was placed in the others. All potentials in the present work were measured compared to reversible hydrogen evolution (RHE) in accordance with the following formula (ERHE = ESCE + 0.0591pH + EθSCE) [58,59]. Before testing, the working electrode was stabilized and the surface was cleaned using a cyclic voltammetry (CV) method. The catalytic activity of each electrocatalyst for HER and OER was estimated through linear sweep voltammetry (LSV) at a scanning rate of 5 mV s⁻¹. According to the formula (ECSA = Cdl/Cs), the electrochemical active area (ECSA) was determined by calculating the double-layer capacitance (Cdl) values, where Cdl can be calculated by CV measurements in the non-Faradaic region with variable scan rates, and Cs represents the specific capacitance [60,61]. The Tafel plots were measured in the same testing system for unraveling the electrocatalytic kinetics of the as-prepared samples. To probe the electron transfer, the electrochemical impedance spectroscopy (EIS) was measured by application of an alternating voltage of 10 mV amplitude with a frequency ranging from 0.1 Hz to 100 kHz. The electrocatalytic stability was evaluated by current–time curves (i–t). Moreover, the potentials related to OER and HER were set as 0.5 V (vs. SCE) and −1.2 V (vs. SCE), respectively. The electrocatalytic overall water-splitting activity of the as-prepared electrocatalyst was measured by a two-electrode configuration, in which the NiFe LDH/NiS₂/VS₂ was employed as an electrocatalyst for the HER cathode and the OER anode in 1.0 M KOH.

4. Conclusions

In conclusion, NiFe LDH/NiS₂/VS₂ heterostructured electrocatalysts have been designed as bifunctional high-efficiency electrocatalysts to split water using a simple method, in which VS₂ with metallic properties and the heterostructured construction endow enhanced electron conductivity and smaller charge transfer resistance to the NiFe LDH/NiS₂/VS₂ electrocatalyst. Furthermore, the formation of a nanoflower structure through decorating NiFe LDH on the surface of NiS₂/VS₂ via a facile electrodeposited method realizes more exposed active sites. The interfacial electron interaction between NiS₂/VS₂ and NiFe LDH was expected to enhance its electrocatalytic activity for overall water splitting. Remarkably, the NiFe LDH/NiS₂/VS₂ exhibits superior electrocatalytic activity compared to VS₂, NiS₂/VS₂ and NiFe LDH; it can achieve a current density of 10 mA cm⁻² at an overpotential of 76 and 286 mV for HER and OER, respectively. At the same time, the corresponding Tafel plots also decreased significantly. Furthermore, the two-electrode system for overall water splitting was constructed by employing the NiFe LDH/NiS₂/VS₂ as a bifunctional electrocatalyst, which requires an overpotential of 380 mV to achieve a current density of 10 mA cm⁻². This study presents a tactic base
regarding the interfacial regulation of NiFe LDH, NiS$_2$ and VS$_2$ to enhance electrocatalytic OER and HER activity, which is helpful for developing highly efficient electrocatalysts to split water.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules29050951/s1, Figure S1. (a) XRD patterns and (b) XPS survey spectra of the prepared VS$_2$, NiS$_2$/VS$_2$ and NiFe LDH/NiS$_2$/VS$_2$. Figure S2. Electrocatalytic OER activity of (a) the VS$_2$ and NiS$_2$/VS$_2$ with different addition ratios of nickel source and (b) the NiFe LDH/NiS$_2$/VS$_2$ with different electrodeposition times. Figure S3. Cyclic voltammetry curves of the (a) VS$_2$, (b) NiS$_2$/VS$_2$, (c) 250 s NiFe LDH/NiS$_2$/VS$_2$, (d) 300 s NiFe LDH/NiS$_2$/VS$_2$, (e) 350 s NiFe LDH/NiS$_2$/VS$_2$, (f) 400 s NiFe LDH/NiS$_2$/VS$_2$ and (g) 350 s NiFe LDH in the non-faradaic region with different scan rates. (b) The C$_0$ value of the corresponding samples. Figure S4. Electrocatalytic HER activity of (a) the VS$_2$ and NiS$_2$/VS$_2$ with different addition ratios of nickel source and (b) the NiFe LDH/NiS$_2$/VS$_2$ with different electrodeposition times. Figure S5. (a) ECSA and the electrocatalytic activity normalized by ECSA for (b) OER and (c) HER of the as-prepared VS$_2$, NiS$_2$/VS$_2$, NiFe LDH and NiFe LDH/NiS$_2$/VS$_2$. Figure S6. High-resolution XPS survey of the NiFe LDH/NiS$_2$/VS$_2$ before and after stability test; (a) V 2p, (b) S 2p, (c) Ni 2p and (d) Fe 2p. Table S1. Comparisons of HER and OER activity of NiFe LDH/NiS$_2$/VS$_2$ with other electrocatalysts in 1.0 M KOH. Figure S7. SEM of NiFe LDH/NiS$_2$/VS$_2$ after stability test. Video S1: The dynamic state of the constructed overall water-splitting system. Refs [62–74] are cited in the Supplementary Materials.

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