



Article MoS₂/NiSe₂/rGO Multiple-Interfaced Sandwich-like Nanostructures as Efficient Electrocatalysts for Overall Water Splitting

Xiaoyan Bai^{1,†}, Tianqi Cao^{1,†}, Tianyu Xia^{1,*}, Chenxiao Wu¹, Menglin Feng¹, Xinru Li¹, Ziqing Mei¹, Han Gao¹, Dongyu Huo¹, Xiaoyan Ren¹, Shunfang Li¹, Haizhong Guo^{1,*} and Rongming Wang^{2,*}

- Key Laboratory of Materials Physics, School of Physics and Microelectronics, Zhengzhou University, Ministry of Education, Zhengzhou 450052, China
- ² Beijing Advanced Innovation Center for Materials Genome Engineering,
 Beijing Key Laboratory for Magneto-Photoelectrical Composite and Interface Science,
 School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, China
- Correspondence: tyxia@zzu.edu.cn (T.X.); hguo@zzu.edu.cn (H.G.); rmwang@ustb.edu.cn (R.W.)
- + These authors contributed equally to this work.

Abstract: Constructing a heterogeneous interface using different components is one of the effective measures to achieve the bifunctionality of nanocatalysts, while synergistic interactions between multiple interfaces can further optimize the performance of single-interface nanocatalysts. The non-precious metal nanocatalysts $MoS_2/NiSe_2/reduced$ graphene oxide (rGO) bilayer sandwich-like nanostructure with multiple well-defined interfaces is prepared by a simple hydrothermal method. MoS_2 and rGO are layered nanostructures with clear boundaries, and the NiSe₂ nanoparticles with uniform size are sandwiched between both layered nanostructures. This multiple-interfaced sandwich-like nanostructure is prominent in catalytic water splitting with low overpotential for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) and almost no degradation in performance after a 20 h long-term reaction. In order to simulate the actual overall water splitting process, the prepared nanostructures are assembled into $MoS_2/NiSe_2/rGO | |MoS_2/NiSe_2/rGO modified two-electrode system, whose overpotential is only 1.52 mV, even exceeded that of noble metal nanocatalyst (Pt/C | RuO_2~1.63 mV). This work provides a feasible idea for constructing multi-interface bifunctional electrocatalysts using nanoparticle-doped bilayer-like nanostructures.$

Keywords: nanoparticle-doped bilayer-like nanostructures; multiple interfaces; overall water splitting; dual function; non-precious metal catalysis

1. Introduction

Since limited fossil energy is massively consumed and the resulting environmental pollution is becoming increasingly serious, the development of renewable and clean energy is a proven method and has become the future development trend [1–4]. The high-quality H₂ produced in the hydrogen evolution reaction (HER) at the cathode of a water splitting device can be used as a green energy source, but the oxygen evolution reaction (OER) at the anode faces problems such as multiple reaction steps and slow kinetics [5–7]. Many efforts have been made to explore efficient electrocatalysts that can reduce the overpotential of both HER and OER to improve their reaction efficiency. However, the optimal catalysts for OER [8–11]. When completely different catalyst materials are used for the cathode and anode of a given water splitting device, the inconsistency of the two electrodes will lead to inefficiencies [12–14]. Accordingly, employing different components of nanocatalysts to construct heterogeneous interfaces is the most effective measure to alleviate the above problems, but it still faces a technical bottleneck to further improve the catalytic performance. In addition to searching for bifunctional catalysts that can catalyze both HER and



Citation: Bai, X.; Cao, T.; Xia, T.; Wu, C.; Feng, M.; Li, X.; Mei, Z.; Gao, H.; Huo, D.; Ren, X.; et al. MoS₂/NiSe₂/rGO Multiple-Interfaced Sandwich-like Nanostructures as Efficient Electrocatalysts for Overall Water Splitting. *Nanomaterials* **2023**, *13*, 752. https://doi.org/10.3390/nano13040752

Academic Editor: Justo Lobato

Received: 19 January 2023 Revised: 10 February 2023 Accepted: 13 February 2023 Published: 16 February 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). OER in industrial applications, it is also crucial to find inexpensive materials to replace the high-cost Pt-, Ir-, and Ru-based electrocatalysts [15,16].

With the advantages of low cost, abundant reserves, and suitable d-electron configuration, transition metal-based catalysts have attracted much attention and are considered promising candidate materials for electrocatalysis [10,11,17]. Transition metal dichalcogenides (TMDs), represented by layered MoS₂, are clearly the star players among them [18–20]. Early in 2005, Nørskov's group explored the HER mechanism of different catalysts through density functional theory (DFT) calculations and found that the free energy of binding hydrogen atoms to MoS₂ is similar to that of binding hydrogen atoms to Pt in HER, predicting that MoS_2 is a promising non-noble metal catalyst [21]. However, the poor conductivity and inert planes of MoS₂ lead to its suboptimal performance in electrocatalysis [22]. Graphene seems to compensate for the above-mentioned defects of MoS₂ due to its ultra-thin nanostructure, large specific surface, and high electrical conductivity [23,24]. The combination of the two-layered nanostructures can expose abundant edge sites and provide favorable HER catalytic performance [25,26]. However, OER requires a higher overpotential than HER due to the involvement of a four-electron transfer process. Therefore, it is necessary to prepare an excellent electrocatalyst to accelerate the kinetics and reduce the overpotential in the OER process for obtaining the dual function of water splitting.

The selenides featuring the $4s^2p^4$ electronic structure and vacant 3d orbitals can form strong metal bonds with transition metals, and this is very profitable for the multi-electron transport of OER [27]. Due to the narrow band gap ($\approx 2.0 \text{ eV}$) of NiSe₂ and the good corrosion resistance of Ni in alkaline solvents, NiSe₂ has been identified as a very important non-precious metal OER catalyst in alkaline media [28]. Park et al. compared the catalytic performance of NiSe₂ and CoSe₂ for OER and found that the former was superior to the latter due to the oxide layer in NiSe₂ as the actual active site was more active than that in CoSe₂ [29]. Xu et al. proposed a strategy of heteroatom-doped composite phase engineering to further modulate the electronic conductivity and active sites of NiSe₂ to obtain more excellent OER properties [30]. With this understanding, the introduction of nanoparticles (NiSe₂) in bilayer nanomaterials (MoS₂/reduced graphene oxide (rGO)) to build the multi-heterogeneous interfaces and create the bifunctional catalysts seems to offer an exciting approach for catalytic water splitting.

Based on the above issues, a MoS₂/NiSe₂/rGO multiple interfaced sandwich-like nanostructure was synthesized by a simple hydrothermal method, where MoS₂ and rGO are layered nanostructures with clear boundaries and NiSe₂ are nanoparticles with a diameter of about 20 nm. The obtained MoS₂/NiSe₂/rGO nanostructures exhibited extremely high electrochemical activity for both OER and HER in alkaline electrolytes by taking advantage of the synergistic effect of the three interfaces (MoS₂/NiSe₂/rGO, and MoS₂/rGO). This approach of doping TMD nanoparticles in the middle of bilayer-like nanostructures to obtain multiple interfaces can provide a new strategy for obtaining efficient bifunctional catalysts.

2. Materials and Methods

2.1. Materials

 $NiCl_2 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and polytetrafluoroethylene (PTFE, 10%) are purchased from Aladdin Ltd. (Shanghai, China). NaBH₄ and L-cysteine are purchased from Kermel (Tianjin, China). Se powder (99.9%) is purchased from Xiya Reagent (Linyi, China). KOH and Ruthenium Dioxide (RuO₂) are purchased from Macklin (Shanghai, China). JM 40% Pt/C catalyst is purchased from Hesen (Shanghai, China). Ni foam is purchased from Changde Liyuan New Materials Co. Ltd. (Changde, China). Ethanol and acetone are purchased from Hengxing (Tianjin, China). All reagents are purchased ready for use without further processing.

2.2. Synthesis of NiSe₂/rGO

Graphene oxide (GO) is prepared from pristine graphite flakes using an improved Hummers' method [31]. NiSe₂/rGO is prepared by an improved facile hydrothermal process [32]. First, 10 mmol NaBH₄ and 8 mmol Se powder are dispersed in 50 mL deionized water with vigorous magnetic stirring for 1 h at room temperature. At the same time, 25 mg GO is dispersed in 20 mL deionized water by ultrasonic treatment for 30 min, and then 4 mmol NiCl₂·6H₂O is added, and the ultrasonic treatment is continued for 30 min. Subsequently, the Se-containing solution and GO-containing suspension are mixed and stirred for 1 h. After that, the mixture is transferred into a 100 mL Teflon-lined autoclave for hydrothermal treatment at 160 °C for 12 h. The resulting product (NiSe₂/rGO) is collected by filtration, washed with deionized water and ethanol several times, and then dried at 60 °C. For comparison, bare NiSe₂ catalyst is prepared in a similar procedure without adding GO.

2.3. Preparation of MoS₂/NiSe₂/rGO

The MoS₂/NiSe₂/rGO composite is prepared by the second hydrothermal process by improving the reported MoS₂ preparation method [33]. Total amounts of 130 mg NiSe₂/rGO, 100 mg (NH₄)₆Mo₇O₂₄·4H₂O, and 290 mg L-cysteine are dispersed in 30 mL deionized water with vigorous magnetic stirring at room temperature for 30 min. Then, the mixture is transferred into a 50 mL Teflon-lined autoclave for hydrothermal treatment at 220 °C for 24 h. The resulting product (MoS₂/NiSe₂/rGO) is collected by filtration, washed with deionized water and ethanol several times, and then dried at 60 °C. For comparison, the mass of (NH₄)₆Mo₇O₂₄·4H₂O is changed to 50 and 150 mg, and other preparation conditions are kept constant to obtain MoS₂/NiSe₂/rGO-1 and MoS₂/NiSe₂/rGO-2, respectively. Similarly, other comparison samples are obtained: MoS₂, MoS₂/NiSe₂, MoS₂/NiSe₂-1, and MoS₂/NiSe₂-2.

2.4. Morphological and Structural Characterization

The morphology of MoS₂/NiSe₂/rGO is obtained using a focused ion beam scanning electron microscopy (SEM; JCM-6000PLUS, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM; JEM-2100, JEOL, Tokyo, Japan). The structure of MoS₂/NiSe₂/rGO is analyzed using a powder X-ray diffractometer (XRD; Smart Lab SE, Rigaku, Osaka, Japan). The phase composition and the electronic structures of the elements are investigated via Raman spectroscopy (Raman; Renishaw inVia, Renishaw, New Mills, UK) and X-ray photoelectron spectroscopy (XPS; AXIS Supra, Kratos, Manchester, UK).

2.5. Electrocatalysis Measurements

An amount of 20.0 mg of $MoS_2/NiSe_2/rGO$ material is dispersed in a 1.0 mL mixed solution of ethanol/deionized water/10% PTFE (1:1:1), ultrasonically treated for 10 min to form a uniform suspension, and then dropped onto clean Ni foam (NF), followed by drying under vacuum at 60 °C. The final mass load of $MoS_2/NiSe_2/rGO$ material is calculated to be 4.0 mg cm⁻².

The electrochemical measurements of OER and HER are measured using a threeelectrode workstation (CHI660E, Shanghai Chenhua Instruments, Shanghai, China) at room temperature. The counter, reference, and working electrodes are graphite rods, Ag/AgCl electrodes, and Ni foam electrodes, respectively. The tested potentials are calibrated to reversible hydrogen electrode (RHE) by the Nernst equation: $E_{vs.RHE} = E_{vs.Ag/AgCl} + 0.059$ pH + 0.197, all linear sweep voltammetry (LSV) curves are corrected with IR compensation (LSV-IR) derived from the electrochemical impedance spectroscopy (EIS) measurements under open circuit voltage [34]. The electrochemical double layer capacitance (C_{dl}) of the catalyst can be obtained from the linear slope between the current density difference at the cathode and anode and the scan rate [27]. The overall water splitting measurements are measured using a two-electrode system in 1.0 M KOH solution.

3. Results

The improved Hummers' method is used to prepare rGO with good quality, exhibiting a flat surface and the expected ductility, as shown in Figure S1. Then, the NiSe₂ nanoparticles and MoS₂ layered nanostructures with different ratios are sequentially grown on rGO by a simple hydrothermal method to obtain a series of MoS₂/NiSe₂/rGO composites. A schematic diagram of the MoS₂/NiSe₂/rGO fabrication process is shown in Figure 1a. Figure S2 shows the SEM images of NiSe₂ and NiSe₂/rGO, respectively, and it can be seen that the uniformly sized NiSe₂ nanoparticles do not change their size before and after being anchored on rGO. According to the designed plan, MoS₂ is deposited on NiSe₂/rGO in order to obtain the MoS₂/NiSe₂/rGO bilayer-like sandwich nanostructures. It can be seen from Figures 1b and S3 that after loading MoS₂, both MoS₂ and NiSe₂ maintain their previous morphology. Notably, the MoS₂ layered nanostructure becomes more and more dense as the amount of MoS₂ increases by keeping NiSe₂ invariant, as shown in S4b–d. However, after they are loaded on rGO (Figures 1b and S4e,f), this denseness decreases, and the dispersibility increases, indicating that rGO can be used as a good dispersion substrate.



Figure 1. Structural characterizations of $MoS_2/NiSe_2/rGO$. (a) Schematic illustration of the $MoS_2/NiSe_2/rGO$ formation process. (b) SEM, (c) TEM, (d) HRTEM, and (e) HADDF-STEM images and the corresponding element mapping of $MoS_2/NiSe_2/rGO$. (d-1,d-2,d-3) are the local enlargements of (d), respectively.

The structure of MoS₂/NiSe₂/rGO is characterized more finely by TEM, and it is clearly seen in Figure 1c that MoS₂ and rGO have a high-quality layered structure with NiSe₂ nanoparticles uniformly sandwiched between both, forming a well-defined bilayerlike sandwich nanostructure. Figure 1d shows a typical local structure at the boundary, and Figure 1(d-1,d-2,d-3) are enlarged views of the boxes therein, respectively. Clear lattice stripes with spacings of 0.62, 0.29, and 0.26 nm are visible in these three enlarged images, corresponding to the (002) plane of MoS₂ and the (200) and (210) planes of NiSe₂, respectively [18,35]. The STEM-energy dispersive spectrometer (EDS) elemental mapping of $MoS_2/NiSe_2/rGO$ in Figure 1e confirms the presence of element C and shows its uniform distribution in the layered sandwich-like nanostructure. It is also noted that the distributions of Mo, S, Ni, and Se elements are almost identical, indicating not only that MoS_2 and $NiSe_2$ are uniformly distributed on rGO but also that the $NiSe_2$ nanoparticles are covered in the MoS_2 layered nanostructure.

Subsequently, the structural characteristics, phase composition, and element analysis of the prepared samples are analyzed by XRD, Raman, and XPS spectra, respectively. Figures S1b and S5a,b exhibit the XRD spectra of rGO, NiSe₂, and MoS₂, respectively. As shown in Figure 2a, distinct diffraction peaks appear at 29.67°, 33.61°, 36.95°, 50.79°, 55.58°, and 57.82° in MoS₂/NiSe₂/rGO, MoS₂/NiSe₂, and NiSe₂/rGO, corresponding to the (200), (210), (211), (311), (023), and (321) crystal plane of NiSe₂, respectively, which are well consistent with the standard crystal of NiSe₂ (PDF No. 65-5016), indicating that NiSe₂ exhibits excellent crystallinity in all three samples [35]. In contrast, none of the diffraction peaks of MoS₂ appear, which is due to the poor crystallinity of MoS₂ obtained by the hydrothermal method [36]. Raman spectroscopy is used to further determine the composition of $MoS_2/NiSe_2/rGO$. As shown in Figures 2b and S6, the Raman characteristic peaks of the $MoS_2/NiSe_2/rGO$ and pure MoS_2 samples at 375 and 401 cm⁻¹ belong to the E_{2g}^{1} and A_{1g} modes of the semiconductor phase (2H) MoS₂, representing the in-plane Mo–S bond and the out-of-plane S atom vibration mode, respectively [37,38]. In addition, the characteristic peaks of NiSe₂ are also displayed at 148, 208, and 235 cm⁻¹, while the peaks at 1358 and 1588 cm^{-1} correspond to the D band and G band of rGO, respectively [39,40]. The Raman results confirm that the 2H-phase-dominated MoS₂ nanosheets are on the NiSe₂/rGO surfaces.



Figure 2. Chemical analysis of the $MoS_2/NiSe_2/rGO$. (a) XRD patterns of $MoS_2/NiSe_2/rGO$, $MoS_2/NiSe_2$, and $NiSe_2/rGO$. (b) Raman spectra of $MoS_2/NiSe_2/rGO$. XPS spectra of (c) Mo 3d and (d) S 2p for MoS_2 and $MoS_2/NiSe_2/rGO$.

XPS is used to examine the molecular structure and atomic valence states of the materials [41]. The presence of Mo, S, Ni, and Se in the MoS₂/NiSe₂/rGO material is confirmed from the full XPS spectrum (Figure S7a), but the Ni content on the surface of the sample is relatively low (Figure S7b). Figure 2c,d present the high-resolution XPS

spectra of Mo 3d and S 2p in pure MoS₂ and MoS₂/NiSe₂/rGO, respectively. As shown in Figure 2c, the fitting peaks of the pure MoS₂ at 232.2, 229, and 226.1 eV correspond to Mo⁴⁺ $3d_{3/2}$, Mo⁴⁺ $3d_{5/2}$, and S 2s, respectively, while the high binding energy peak of the Mo 3d (235.5 eV) corresponds to the MoO₃, which may result from the oxidation of the sample in the air [42]. Compared with pure MoS₂, both the peaks of Mo⁴⁺ $3d_{3/2}$ and Mo⁴⁺ $3d_{5/2}$ in MoS₂/NiSe₂/rGO are slightly shifted to lower binding energies (~0.35 eV), which indicates that there is a significant electron transfer between NiSe₂ and MoS₂. In addition, the peak at 232.8 eV is attributed to Mo-Se, which also indicates the formation of a heterogeneous interface between MoS₂ and NiSe₂, where some of the Se atoms replace the S atoms [43].

As shown in the XPS spectrum of S 2p (Figure 2d), pure MoS₂ has only two typical peaks corresponding to S $2p_{1/2}$ and S $2p_{3/2}$. In contrast, the S_{Mo-S} $2p_{1/2}$ and S_{Mo-S} $2p_{3/2}$ of the MoS₂/NiSe₂/rGO have a negative offset, implying the occurrence of electron transfer. At the same time, two peaks are separated at 161.6 and 162.8 eV, corresponding to S_{Ni-S} $2p_{1/2}$ and S_{Ni-S} $2p_{3/2}$, respectively. Compared with pure MoS₂, the formation of heterostructure caused a slight negative shift in the energy band position of S (~0.16 eV), which is due to the synergistic effect between NiSe₂ and molybdenum disulfide [44]. In addition, the positive displacement of Se 3d in Figure S7c fully proves this point. The XPS results confirmed the strong interfacial electronic interactions in the heterostructure and the electrons transfer from NiSe₂ to MoS₂, which would optimize the electronic structure of NiSe₂ and MoS₂ and thus enhance the activity of OER and HER.

The OER electrocatalytic performance of $MoS_2/NiSe_2/rGO$ in an alkaline solution (1 M KOH) is first investigated (Figure 3). To better demonstrate the effect of multiple interfaces on performance, three heterogeneous interfaces ($MoS_2/NiSe_2$, $NiSe_2/rGO$, and MoS_2/rGO) consisting of three constituent units are used as the samples to be tested under the same conditions. Meanwhile, the properties are tested for NiSe₂, NF, and RuO₂, and different precursor ratios of MoS₂/NiSe₂-1, MoS₂/NiSe₂-2, MoS₂/NiSe₂/rGO-1, and MoS₂/NiSe₂/rGO-2 are investigated, as shown in Figure S8. From the iR-compensated LSV curves (Figure 3a), it is obvious that $MoS_2/NiSe_2/rGO$ has the optimum performance among the four electrocatalysts. When the current density is 20 mA cm^{-2} , the overpotential of MoS₂/NiSe₂/rGO is only 277 mV, which is 22, 51, and 113 mV lower than that of $MoS_2/NiSe_2$, $NiSe_2/rGO$, and MoS_2/rGO , respectively. For a comprehensive comparison of the LSV performance of the four catalysts, whose overpotentials at two additional current densities are also identified. As shown in Figure 3b, although the overpotentials of the four catalysts increase gradually with the current density, the overpotential of MoS₂/NiSe₂/rGO is consistently the lowest among them. The overpotential of $MoS_2/NiSe_2/rGO$ is surprisingly 123 mV lower than that of MoS_2/rGO when the current density is 100 mA cm⁻², and the relevant values are shown in Table S2. The results fully demonstrate that the $NiSe_2$ nanoparticles sandwiched between the two layered structures can effectively optimize the overpotential of MoS_2/rGO . Furthermore, multiple interfacial nanostructures can greatly improve the contribution of a single interface to performance, and this new multi-interfacial nanostructure constructed by the three composites acting together can facilitate the OER performance [44,45].

The enhanced OER kinetics of $MoS_2/NiSe_2/rGO$ is confirmed by the smaller Tafel slope (107 mV dec⁻¹) compared to those of $MoS_2/NiSe_2$ (157 mV dec⁻¹), $NiSe_2/rGO$ (110 mV dec⁻¹), and MoS_2/rGO (126 mV dec⁻¹), as shown in Figure 3c. To further validate the electron transfer dynamics of OER, EIS are also performed on four electrocatalysts. From the corresponding Nyquist plots in Figure 3d, it can be seen that $MoS_2/NiSe_2/rGO$ exhibits significantly lower charge transfer resistance compared to $NiSe_2/rGO$, $MoS_2/NiSe_2$, and MoS_2/rGO , indicating faster electron transfer on $MoS_2/NiSe_2/rGO$, and also suggesting that the multiple interfaced sandwich-like nanostructure can significantly improve the conductivity of the electrocatalyst. The C_{dl} values are proportional to the electrochemical active surface area (ECSA) and can be estimated by performing cyclic voltammetry (CV) curves at different scan rates in a non-faradic potential range, which is usually used to further evaluate the OER catalytic activity [11]. As shown in Figure 3e, the C_{dl} values of

the four electrocatalysts are calculated from the slopes of the linear fits of the CV curves (Figure S9), in which $MoS_2/NiSe_2/rGO$ has the largest electrical double-layer capacitance value, denoting a larger electrochemically active surface area. Durability is also an important indicator to assess the performance of the electrocatalyst. The chronopotential measurement curve of $MoS_2/NiSe_2/rGO$ at a constant current density of 10 mA cm⁻² is obtained for continuous 20 h (Figure 3f). Compared to the initial potential of 1.46 V, there is only a slight elevation of 30 mV in the potential after 20 h of continuous oxygen generation. This indicates that the as-prepared $MoS_2/NiSe_2/rGO$ not only has excellent catalytic activity, but also has outstanding catalytic durability.



Figure 3. The OER performance of $MoS_2/NiSe_2/rGO$, $MoS_2/NiSe_2$, $NiSe_2/rGO$, and MoS_2/rGO in 1.0 M KOH solution. (**a**) Polarization curves (iR-corrected) at a scan rate of 2 mV s⁻¹. (**b**) Overpotential required at a current density of 20, 50, and 100 mA cm⁻². (**c**) Tafel plots. (**d**) Nyquist plots at an overpotential of 300 mV and fitted lines for an equivalent circuit. (**e**) The C_{dl} values can be estimated from the linear slopes between Δj (= $j_{anodic} - j_{cathodic}$) and scan rates. (**f**) Chronopotentiometry curve of $MoS_2/NiSe_2/rGO$ with a constant current density of 10 mA cm⁻².

The HER performance of the samples is evaluated in the same electrolyte (1.0 M KOH) at a scan rate of 5 mV s⁻¹ (Figures 4 and S10). Figure 4a shows the LSV curves of $MoS_2/NiSe_2/rGO$, $MoS_2/NiSe_2$, $NiSe_2/rGO$, and MoS_2/rGO with iR-compensation, and it can be seen that the curves are smooth with a uniform trend, which proves that all four catalysts have HER activity. However, the overpotential of the four catalysts differed greatly at the same current density, as marked in the purple line in Figure 4a at a current density of 10 mA cm⁻², and $MoS_2/NiSe_2/rGO$ has the lowest overpotential among the four catalysts, indicating that it has the favorable HER activity. For a more comprehensive assessment of the intrinsic reaction kinetics of the catalysts, the overpotentials at different current densities are visualized in Figure 4b as histograms. It can be seen that $MoS_2/NiSe_2/rGO$ exhibits the lowest overpotential regardless of the determined current density and is the best among four samples in HER. Even at a high current density of 100 mA cm⁻², 301 mV of $NiSe_2/rGO$, and 374 mV of MoS_2/rGO .



Figure 4. HER performance of the MoS₂/NiSe₂/rGO, MoS₂/NiSe₂, NiSe₂/rGO, and MoS₂/rGO in 1.0 M KOH solution. (a) Polarization curves (iR-corrected) at a scan rate of 5 mV s⁻¹. (b) Overpotential required at a current density of 10, 50, and 100 mA cm⁻². (c) Tafel plots. (d) Nyquist plots at an overpotential of 120 mV. (e) The C_{dl} values can be estimated from the linear slopes between Δj (= $j_{anodic} - j_{cathodic}$) and scan rates. (f) Chronopotentiometry curve of MoS₂/NiSe₂/rGO with a constant current density of 10 mA cm⁻².

The calculated Tafel slopes of the four catalysts are calculated to be 73, 79, 105, and 149 mV dec $^{-1}$, respectively, as shown in Figure 4c. The lower Tafel slopes of MoS₂/NiSe₂/rGO and MoS₂/NiSe₂ prove that the combination of MoS₂ and NiSe₂ helps to improve the reaction rate and kinetics [46]. The corresponding Nyquist plots shown in Figure 4d are similar to the OER test results. Compared with MoS₂/NiSe₂, NiSe₂/rGO, and MoS₂/rGO, MoS₂/NiSe₂/rGO exhibits lower charge transfer resistance, indicating that MoS₂/NiSe₂/rGO has superior electron transport capability. In addition, the C_{dl} is again used to assess the HER catalytic activity of the catalysts. Figure 4e and Figure S11 reveal that the fitted line slopes of 38.13, 21.11, 23.76, and 5.25 mF cm⁻² for MoS₂/NiSe₂/rGO, MoS₂/NiSe₂, NiSe₂/rGO, and MoS₂/rGO, respectively, suggesting that the multiple interfaced sandwichlike nanostructure provides more effective active sites than the other three catalysts [47]. Of these, more active sites might be due to the effect of the unique heterogeneous interface of MoS₂/NiSe₂/rGO. Furthermore, the HER electrochemical stability of MoS₂/NiSe₂/rGO is also evaluated by the chronopotentiometry measurement curve (Figure 4f). After 20 h of continuous testing, the overpotential increases by only 15 mV at a constant current density of 10 mA cm⁻². Moreover, MoS₂/NiSe₂/rGO shows negligible catalytic degradation, confirming its excellent electrochemical stability.

In view of the excellent OER and HER catalytic behaviors of the MoS₂/NiSe₂/rGO catalyst discussed above, it is further served as a bifunctional catalyst and assembled into a two-electrode test system to investigate its overall water splitting performance in 1.0 M KOH electrolyte. The schematic diagram of all-water electrolysis in the double-electrode test system is shown in Figure 5a. At the cathode, the electrons transferred to the electrolyte combine with water to produce H₂ gas, while the generated hydroxide ions are transferred to the anode and oxidized to release O₂ gas. Polarized electrons are released at the anode so that the hydroxide is oxidized in the solution to release O₂ gas. The two-electrode test device is shown in Figure 5b. In the LSV curves with a scan rate of 5 mV s⁻¹ shown

in Figure 5c, MoS₂/NiSe₂/rGO | MoS₂/NiSe₂/rGO exhibits excellent catalytic activity, affording a current density of 10 mA cm⁻² at 1.52 V, while Pt/C | |RuO₂ requires the same current density at 1.63 V. The inset is a photograph of the experimental device, clearly showing the high density of bubbles on the surface of both electrodes. The H_2 and O_2 generated from the MoS₂/NiSe₂/rGO catalyzed overall water-splitting are collected quantitatively by the drainage method. As shown in Figure 5d, the volume ratio of collected H_2 to O_2 is 2.05:1, close to the theoretical value of 2:1. Taking into account that the airtightness of the equipment produces errors, it can be seen that the Faraday efficiency of the overall water splitting is almost 100% [48]. The stability test results of MoS₂/NiSe₂/rGO at a constant current density of 10 mA cm⁻² are shown in Figure 5e. It can be seen from the chronopotential curve that MoS₂/NiSe₂/rGO | MoS₂/NiSe₂/rGO features extremely outstanding stability, which maintains the output voltage almost constant at 1.65 V throughout the continuous 25 h of the overall water splitting performance. In general, MoS₂/NiSe₂/rGO is proven to trigger the overall water splitting with favorable efficiency and stability. Compared with the recently reported advanced electrocatalysts, MoS₂/NiSe₂/rGO demonstrates outstanding performance (Table S1), indicating that the prepared sandwich nanostructure is an excellent overall water splitting bifunctional electrocatalyst [16,49–53].



Figure 5. Overall water splitting performance of $MoS_2/NiSe_2/rGO$ in 1.0 M KOH solution. (a) Schematic diagram of overall water splitting. (b) Double-electrode device for overall water splitting. (c) LSV curves of the $MoS_2/NiSe_2/rGO \mid MoS_2/NiSe_2/rGO$ and $Pt/C \mid RuO_2$ catalysts. Inset: A photo of the overall water splitting cell. (d) The production of H_2 and O_2 as a function of time. (e) Time-dependent current density curve of $MoS_2/NiSe_2/rGO \mid MoS_2/NiSe_2/rGO \mid MoS_2/NiSe_2/rGO \mid S_2/NiSe_2/rGO \mid S_2/NiSe_2$

The outstanding OER, HER, and overall water splitting performance of $MoS_2/NiSe_2/rGO$, where OER and overall water splitting even surpasses those of noble metals (Figures 5 and S8),

are mainly attributed to the highly advantageous multiple interfaced sandwich-like nanostructure of the NiSe₂ nanoparticles sandwiched between two different layered structures (MoS₂ and rGO). The DFT calculations confirm this point of view (Figure S12). Due to the smaller size of the intercalated NiSe₂ nanoparticles, this unique nanostructure can simultaneously construct three different interfacial relationships: $MoS_2/NiSe_2$, NiSe₂/rGO, and MoS_2/rGO , and the synergistic effect of the three interfaces can dramatically facilitate the rapid and smooth electrocatalytic reaction. Moreover, the NiSe₂ nanoparticles are sandwiched between both layers, making them less tightly packed and contributing to the rapid transport of the gases generated by the reaction, enhancing the reaction dynamics, as evidenced by the Tafel curves. In addition, compared with the ordinary nanoparticles, both layered nanostructures that supported nanoparticles are more helpful in maintaining a robust nanostructure for excellent stability. This design approach can offer new ideas for obtaining efficient catalysts with structural stability.

4. Conclusions

In summary, $MoS_2/NiSe_2/rGO$ with multiple interfaced sandwich-like nanostructures consisting of NiSe₂ nanoparticles sandwiched between layered MoS₂ and rGO are successfully prepared by a simple and convenient two-step hydrothermal method. Compared with similar catalysts, $MoS_2/NiSe_2/rGO$ has better electrocatalytic performance, even OER and overall water splitting surpass those of the noble metals, which are attributed to the efficient interfacial relationship between $MoS_2/NiSe_2/rGO$, and MoS_2/rGO . The overpotential of $MoS_2/NiSe_2/rGO \mid MoS_2/NiSe_2/rGO$ in overall water splitting is only 1.52 mV, which is much lower than that of the noble metal electrocatalyst $Pt/C \mid RuO_2$ (1.63 mV). Additionally, there is almost no loss of performance in the long-term stability test, implying its good stability. This multi-interface idea can open new avenues for the design of efficient bifunctional overall water catalysts.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/nano13040752/s1, Figure S1. (a) SEM image and (b) XRD pattern of the graphene oxide (GO); Figure S2. SEM images of (a) NiSe2 and (b) NiSe2/rGO; Figure S3. SEM image of the pure MoS₂; Figure S4. SEM images of (a) NiSe₂, (b) MoS₂/NiSe₂-1, (c) MoS₂/NiSe₂, (d) MoS2/NiSe₂-2, (e) MoS₂/NiSe₂/rGO-1, and (f) MoS₂/NiSe₂/rGO-2; Figure S5. XRD patterns of (a) NiSe₂, MoS₂/NiSe₂, MoS₂/NiSe₂-1, MoS₂/NiSe₂-2, MoS₂/NiSe₂/rGO, MoS₂/NiSe₂/rGO-1, MoS₂/NiSe₂/rGO-2 and (b) the pure MoS₂; Figure S6. Raman spectra of NiSe₂, NiSe₂/rGO, MoS₂/NiSe₂, MoS₂/NiSe₂/rGO and MoS₂; Figure S7. (a) XPS survey spectra. (b) Ni 2p and (c) Se 3d high resolution spectrum of $MoS_2/NiSe_2/rGO$, respectively; Figure S8. (a) Polarization curves (iR-corrected) at a scan rate of 2 mV s⁻¹ of NiSe₂, MoS₂/NiSe₂, MoS₂/NiSe₂-1, MoS₂/NiSe₂-2, MoS₂/NiSe₂/rGO, MoS₂/NiSe₂/rGO-1, MoS₂/NiSe₂/rGO-2, RuO₂ and Ni foam, respectively. (The overall thickness, porosity, thread thickness, and pore density of Ni foam is 0.3 mm, 96%, 40–100 μm, and 110 PPI, respectively.) (b) Tafel plots of a series of samples. (c) Nyquist plots at an overpotential of 300 mV; Figure S9. CV curves for (a) MoS₂/NiSe₂/rGO, (b) MoS₂/NiSe₂, (c) NiSe₂/rGO, (d) MoS_2/rGO with various scan rates (20, 50, 80, 100, 120, 150 mV s⁻¹); Figure S10. (a) Polarization curves (iR-corrected) at a scan rate of 5 mV s⁻¹ of NiSe₂, MoS₂/NiSe₂, MoS₂/NiSe₂-1, MoS₂/NiSe₂-2, MoS₂/NiSe₂/rGO, MoS₂/NiSe₂/rGO-1, MoS₂/NiSe₂/rGO-2, Pt/C and Ni foam, respectively. (b) Tafel plots of a series of samples. (c) Nyquist plots at an overpotential of 120 mV; Figure S11. CV curves for (a) MoS₂/NiSe₂/rGO, (b) MoS₂/NiSe₂, (c) NiSe₂/rGO, (d) MoS₂/rGO with various scan rates (20, 50, 80, 100, 120, 150 mV s⁻¹); Figure S12. Optimized structural representations for hydrogen adsorption at (a) MoS₂, (b) MoS₂/rGO, (c) MoS₂/NiSe₂/rGO. Calculated free energy diagrams of the HER on MoS₂, MoS₂/rGO, NiSe₂/rGO, and MoS₂/NiSe₂/rGO, respectively; Table S1. Comparison of electrocatalytic performance of different catalysts in 1 M KOH electrolyte; Table S2. Comparison of the electrocatalytic activity of MoS₂/NiSe₂/rGO with MoS₂/rGO, NiSe₂/rGO in 1 M KOH electrolyte. References [16,49–57] are cited in the Supplementary Materials.

Author Contributions: Data Curation, X.B. and T.C.; Funding Acquisition, T.X., H.G. (Haizhong Guo) and R.W.; Investigation, C.W., M.F. and H.G. (Han Gao); Methodology, D.H., X.R. and S.L.; Resources, X.L. and Z.M.; Supervision, T.X., H.G. (Haizhong Guo) and R.W.; Writing—Original Draft Preparation, X.B. and T.C.; Writing—Review and Editing, T.X., H.G. (Haizhong Guo) and R.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key Research and Development Program of China (Grant Nos. 2021YFA1400204 and 2021YFA0718700), the National Natural Science Foundation of China (Grant Nos. 52171051, 12034002, 51971025, and 12174347), and the Natural Science Foundation of Henan province (Grant Nos. 202300410356 and 222300420086) and Beijing Natural Science Foundation (Grant No. 2212034).

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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

References

- Kittner, N.; Lill, F.; Kammen, D. Energy storage deployment and innovation for the clean energy transition. *Nat. Energy* 2017, 2, 17125. [CrossRef]
- 2. Wang, R. The dynamics of the peel. Nat. Catal. 2020, 3, 333–334. [CrossRef]
- Xia, T.; Zhao, K.; Zhu, Y.; Bai, X.; Gao, H.; Wang, Z.; Gong, Y.; Feng, M.; Li, S.; Zheng, Q.; et al. Mixed-dimensional Pt-Ni alloy polyhedral nanochains as bifunctional electrocatalysts for direct methanol fuel cell. *Adv. Mater.* 2022, 35, 2206508. [CrossRef] [PubMed]
- Zhang, Q.; Xia, T.; Huang, H.; Liu, J.; Zhu, M.; Yu, H.; Xu, W.; Huo, Y.; He, C.; Shen, S.; et al. Autocatalytic reduction-assisted synthesis of segmented porous PtTe nanochains for enhancing methanol oxidation reaction. *Nano Res. Energy* 2023, *2*, e9120041. [CrossRef]
- 5. Seh, Z.; Kibsgaard, J.; Dickens, C.; Chorkendorff, I.; Norskov, J.; Jaramillo, T. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* **2017**, *355*, aad4998. [CrossRef]
- 6. Liu, T.; Li, A.; Wang, C.; Zhou, W.; Liu, S.; Guo, L. Interfacial electron transfer of Ni₂P–NiP₂ polymorphs inducing enhanced electrochemical properties. *Adv. Mater.* **2018**, *30*, 1803590. [CrossRef]
- 7. Wilhelm, M.; Bastos, A.; Neves, C.; Martins, R.; Tedim, J. Ni-Fe layered double hydroxides for oxygen evolution reaction: Impact of Ni/Fe ratio and crystallinity. *Mater. Des.* **2021**, *212*, 110188. [CrossRef]
- Xiong, Q.; Zhang, X.; Wang, H.; Liu, G.; Wang, G.; Zhang, H.; Zhao, H. One-step synthesis of cobalt-doped MoS₂ nanosheets as bifunctional electrocatalysts for overall water splitting under both acidic and alkaline conditions. *Chem. Commun.* 2018, 54, 3859–3862. [CrossRef]
- 9. Lin, T.; Liu, C.; Dai, C. Ni₃S₂/carbon nanotube nanocomposite as electrode material for hydrogen evolution reaction in alkaline electrolyte and enzyme-free glucose detection. *Appl. Catal. B* **2014**, *154*, 213–220. [CrossRef]
- 10. Shi, H.; Liang, H.; Ming, F.; Wang, Z. Efficient overall water-splitting electrocatalysis using lepidocrocite VOOH hollow nanospheres. *Angew. Chem. Int. Ed. Engl.* 2017, *56*, 573–577. [CrossRef]
- 11. Sun, H.; Lian, Y.; Yang, C.; Xiong, L.; Qi, P.; Mu, Q.; Zhao, X.; Guo, J.; Deng, Z.; Peng, Y. A hierarchical nickel–carbon structure templated by metal–organic frameworks for efficient overall water splitting. *Energy Environ. Sci.* 2018, *11*, 2363–2371. [CrossRef]
- 12. Lee, Y.; Suntivich, J.; May, K.; Perry, E.; Shao-Horn, Y. Synthesis and activities of rutile IrO₂ and RuO₂ nanoparticles for oxygen evolution in acid and alkaline solutions. *J. Phys. Chem. Lett.* **2012**, *3*, 399–404. [CrossRef]
- Wang, P.; Pu, Z.; Li, W.; Zhu, J.; Zhang, C.; Zhao, Y.; Mu, S. Coupling NiSe₂-Ni₂P heterostructure nanowrinkles for highly efficient overall water splitting. J. Catal. 2019, 377, 600–608. [CrossRef]
- 14. Du, Y.; Cheng, G.; Luo, W. NiSe₂/FeSe₂ nanodendrites: A highly efficient electrocatalyst for oxygen evolution reaction. *Catal. Sci. Technol.* **2017**, *7*, 4604–4608. [CrossRef]
- 15. Yan, Y.; Xia, B.; Zhao, B.; Wang, X. A review on noble-metal-free bifunctional heterogeneous catalysts for overall electrochemical water splitting. *J. Mater. Chem. A* 2016, *4*, 17587–17603. [CrossRef]
- Sun, Y.; Xu, K.; Wei, Z.; Li, H.; Zhang, T.; Li, X.; Cai, W.; Ma, J.; Fan, H.; Li, Y. Strong electronic interaction in dual-cationincorporated NiSe₂ nanosheets with lattice distortion for highly efficient overall water splitting. *Adv. Mater.* 2018, *30*, 1802121. [CrossRef]
- 17. Zhang, J.; Wang, T.; Pohl, D.; Rellinghaus, B.; Dong, R.; Liu, S.; Zhuang, X.; Feng, X. Interface engineering of MoS₂/Ni₃S₂ heterostructures for highly enhanced electrochemical overall-water-splitting activity. *Angew. Chem. Int. Ed. Engl.* **2016**, *55*, 6702–6707. [CrossRef]
- 18. Xia, T.; Zhou, L.; Gu, S.; Gao, H.; Ren, X.; Li, S.; Wang, R.; Guo, H. A subtle functional design of hollow CoP@MoS₂ heteronanoframes with excellent hydrogen evolution performance. *Mater. Des.* **2021**, *211*, 110165. [CrossRef]
- 19. Wang, K.; Paulus, B. Cluster formation effect of water on pristine and defective MoS2 monolayers. *Nanomaterials* **2023**, *13*, 229. [CrossRef]

- 20. Zhu, Y.; Sun, Y.; Zhang, H.; He, Y.; Liu, W.; Wang, R. Interface structure and strain controlled Pt nanocrystals grown at side facet of MoS₂ with critical size. *Nano Res.* **2022**, *15*, 8493–8501. [CrossRef]
- 21. Hinnemann, B.; Moses, P.; Bonde, J.; Jørgensen, K.; Nielsen, J.; Horch, S.; Chorkendorff, I.; Nørskov, J. Biomimetic hydrogen evolution: MoS₂ nanoparticles as catalyst for hydrogen evolution. *J. Am. Chem. Soc.* **2005**, *127*, 5308–5309. [CrossRef] [PubMed]
- 22. Cheng, Z.; Xiao, Y.; Wu, W.; Zhang, X.; Fu, Q.; Zhao, Y.; Qu, L. All-pH-tolerant in-plane heterostructures for efficient hydrogen evolution reaction. *ACS Nano* 2021, *15*, 11417–11427. [CrossRef] [PubMed]
- Irzhak, A.; Irzhak, D.; Kononenko, O.; Pundikov, K.; Roshchupkin, D. Changes in the Raman spectrum of monolayer graphene under compression/stretching strain in graphene/piezoelectric crystal structures. *Nanomaterials* 2023, 13, 350. [CrossRef] [PubMed]
- 24. Wang, H.; Feng, H.; Li, J. Graphene and graphene-like layered transition metal dichalcogenides in energy conversion and storage. *Small* **2014**, *10*, 2165–2181. [CrossRef]
- 25. Meng, X.; Yu, L.; Ma, C.; Nan, B.; Si, R.; Tu, Y.; Deng, J.; Deng, D.; Bao, X. Three-dimensionally hierarchical MoS₂/graphene architecture for high-performance hydrogen evolution reaction. *Nano Energy* **2019**, *61*, 611–616. [CrossRef]
- Shan, A.; Teng, X.; Zhang, Y.; Zhang, P.; Xu, Y.; Liu, C.; Li, H.; Ye, H.; Wang, R. Interfacial electronic structure modulation of Pt-MoS₂ heterostructure for enhancing electrocatalytic hydrogen evolution reaction. *Nano Energy* 2022, 94, 106913. [CrossRef]
- Jeghan, S.; Kim, D.; Lee, Y.; Kim, M.; Lee, G. Designing a smart heterojunction coupling of cobalt-iron layered double hydroxide on nickel selenide nanosheets for highly efficient overall water splitting kinetics. *Appl. Catal. B* 2022, 308, 121221. [CrossRef]
- Oyetade, O.; Kriek, R. NiSe-Ni₃Se₂/multiwalled carbon nanotube composites as efficient electrocatalysts for the oxygen evolution reaction in alkaline media. *Electrocatalysis* 2019, 11, 35–45. [CrossRef]
- 29. Kwak, I.; Im, H.; Jang, D.; Kim, Y.; Park, K.; Lim, Y.; Cha, E.; Park, J. CoSe₂ and NiSe₂ nanocrystals as superior bifunctional catalysts for electrochemical and photoelectrochemical water splitting. *ACS Appl. Mater. Interfaces* **2016**, *8*, 5327–5334. [CrossRef]
- Zhou, J.; Yuan, L.; Wang, J.; Song, L.; You, Y.; Zhou, R.; Zhang, J.; Xu, J. Combinational modulations of NiSe₂ nanodendrites by phase engineering and iron-doping towards an efficient oxygen evolution reaction. *J. Mater. Chem. A* 2020, *8*, 8113–8120. [CrossRef]
- 31. Li, F.; Zhang, L.; Li, J.; Lin, X.; Li, X.; Fang, Y.; Huang, J.; Li, W.; Tian, M.; Jin, J.; et al. Synthesis of Cu–MoS₂/rGO hybrid as non-noble metal electrocatalysts for the hydrogen evolution reaction. *J. Power Sources* **2015**, 292, 15–22. [CrossRef]
- Li, Z.; Ma, X.; Wu, L.; Ye, H.; Li, L.; Lin, S.; Zhang, X.; Shao, Z.; Yang, Y.; Gao, H. Synergistic effect of cocatalytic NiSe₂ on stable 1T-MoS₂ for hydrogen evolution. *RSC Adv.* 2021, *11*, 6842–6849. [CrossRef] [PubMed]
- Cui, W.; Ge, C.; Xing, Z.; Asiri, A.; Sun, X. Ni_xS_y-MoS₂ hybrid microspheres: One-pot hydrothermal synthesis and their application as a novel hydrogen evolution reaction electrocatalyst with enhanced activity. *Electrochim. Acta* 2014, 137, 504–510. [CrossRef]
- Nai, J.; Xu, X.; Xie, Q.; Lu, G.; Wang, Y.; Luan, D.; Tao, X.; Lou, X. Construction of Ni(CN)₂/NiSe₂ heterostructures by stepwise topochemical pathways for efficient electrocatalytic oxygen evolution. *Adv. Mater.* 2022, 34, 2104405. [CrossRef] [PubMed]
- Lv, L.; Li, Z.; Xue, K.; Ruan, Y.; Ao, X.; Wan, H.; Miao, X.; Zhang, B.; Jiang, J.; Wang, C.; et al. Tailoring the electrocatalytic activity of bimetallic nickel-iron diselenide hollow nanochains for water oxidation. *Nano Energy* 2018, 47, 275–284. [CrossRef]
- 36. Ding, S.; He, P.; Feng, W.; Li, L.; Zhang, G.; Chen, J.; Dong, F.; He, H. Novel molybdenum disulfide nanosheets–decorated polyaniline: Preparation, characterization and enhanced electrocatalytic activity for hydrogen evolution reaction. *J. Phys. Chem. Solids* **2016**, *91*, 41–47. [CrossRef]
- 37. Sandoval, S.; Yang, D.; Frindt, R.; Irwin, J. Raman study and lattice dynamics of single molecular layers of MoS₂. *Phys. Rev. B Condens. Matter Mater. Phys.* **1991**, 44, 3955–3962. [CrossRef]
- Gao, X.; Qi, J.; Wan, S.; Zhang, W.; Wang, Q.; Cao, R. Conductive molybdenum sulfide for efficient electrocatalytic hydrogen evolution. *Small* 2018, 14, 1803361. [CrossRef]
- 39. Zhai, L.; Lo, T.; Xu, Z.; Potter, J.; Mo, J.; Guo, X.; Tang, C.; Tsang, S.; Lau, S. In situ phase transformation on nickel-based selenides for enhanced hydrogen evolution reaction in alkaline medium. *ACS Energy Lett.* **2020**, *5*, 2483–2491. [CrossRef]
- 40. Yu, J.; Li, Q.; Xu, C.; Chen, N.; Li, Y.; Liu, H.; Zhen, L.; Dravid, V.; Wu, J. NiSe₂ pyramids deposited on N-doped graphene encapsulated Ni foam for high-performance water oxidation. *J. Mater. Chem. A* **2017**, *5*, 3981–3986. [CrossRef]
- Liang, M.; Xia, T.; Gao, H.; Zhao, K.; Cao, T.; Deng, M.; Ren, X.; Li, S.; Guo, H.; Wang, R. Modulating reaction pathways of formic acid oxidation for optimized electrocatalytic performance of PtAu/CoNC. *Nano Res.* 2021, 15, 1221–1229. [CrossRef]
- 42. Guo, Y.; Tang, J.; Qian, H.; Wang, Z.; Yamauchi, Y. One-pot synthesis of zeolitic imidazolate framework 67-derived hollow Co₃S₄@MoS₂ heterostructures as efficient bifunctional catalysts. *Chem. Mater.* **2017**, *29*, 5566–5573. [CrossRef]
- 43. Yin, Y.; Zhang, Y.; Gao, T.; Yao, T.; Zhang, X.; Han, J.; Wang, X.; Zhang, Z.; Xu, P.; Zhang, P.; et al. Synergistic phase and disorder engineering in 1T-MoSe₂ nanosheets for enhanced hydrogen-evolution reaction. *Adv. Mater.* **2017**, *29*, 1700311. [CrossRef]
- 44. Liu, H.; Xie, R.; Luo, Y.; Cui, Z.; Yu, Q.; Gao, Z.; Zhang, Z.; Yang, F.; Kang, X.; Ge, S.; et al. Dual interfacial engineering of a chevrel phase electrode material for stable hydrogen evolution at 2500 mA cm⁻². *Nat. Commun.* **2022**, *13*, 6382. [CrossRef] [PubMed]
- 45. Feng, Y.; Guan, Y.; Zhou, E.; Zhang, X.; Wang, Y. Nanoscale double-heterojunctional electrocatalyst for hydrogen evolution. *Adv. Sci.* **2022**, *9*, 2201339. [CrossRef]
- 46. Sun, Q.; Tong, Y.; Chen, P.; Zhou, B.; Dong, X. Universal strategy of bimetal heterostructures as superior bifunctional catalysts for electrochemical water splitting. ACS Sustain. Chem. Eng. 2021, 9, 4206–4212. [CrossRef]

- Deng, J.; Li, H.; Wang, S.; Ding, D.; Chen, M.; Liu, C.; Tian, Z.; Novoselov, K.; Ma, C.; Deng, D.; et al. Multiscale structural and electronic control of molybdenum disulfide foam for highly efficient hydrogen production. *Nat. Commun.* 2017, *8*, 14430. [CrossRef]
- Zeng, L.; Sun, K.; Wang, X.; Liu, Y.; Pan, Y.; Liu, Z.; Cao, D.; Song, Y.; Liu, S.; Liu, C. Three-dimensional-networked Ni₂P/Ni₃S₂ heteronanoflake arrays for highly enhanced electrochemical overall-water-splitting activity. *Nano Energy* 2018, *51*, 26–36. [CrossRef]
- 49. Hu, E.; Feng, Y.; Nai, J.; Zhao, D.; Hu, Y.; Lou, X. Construction of hierarchical Ni–Co–P hollow nanobricks with oriented nanosheets for efficient overall water splitting. *Energy Environ. Sci.* **2018**, *11*, 872–880. [CrossRef]
- Zhang, J.; Wang, Y.; Zhang, C.; Gao, H.; Lv, L.; Han, L.; Zhang, Z. Self-supported porous NiSe₂ nanowrinkles as efficient bifunctional electrocatalysts for overall water splitting. ACS Sustain. Chem. Eng. 2017, 6, 2231–2239. [CrossRef]
- 51. Li, B.; Li, Z.; Pang, Q.; Zhang, J. Core/shell cable-like Ni₃S₂ nanowires/N-doped graphene-like carbon layers as composite electrocatalyst for overall electrocatalytic water splitting. *Chem. Eng. J.* **2020**, 401, 126045. [CrossRef]
- An, L.; Feng, J.; Zhang, Y.; Wang, R.; Liu, H.; Wang, G.; Cheng, F.; Xi, P. Epitaxial heterogeneous interfaces on N-NiMoO₄/NiS₂ nanowires/nanosheets to boost hydrogen and oxygen production for overall water splitting. *Adv. Funct. Mater.* 2019, 29, 1805298. [CrossRef]
- Zhang, Y.; Xia, X.; Cao, X.; Zhang, B.; Tiep, N.; He, H.; Chen, S.; Huang, Y.; Fan, H. Ultrafine metal nanoparticles/N-doped porous carbon hybrids coated on carbon fibers as flexible and binder-free water splitting catalysts. *Adv. Energy Mater.* 2017, 7, 1700220. [CrossRef]
- 54. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169–11186. [CrossRef] [PubMed]
- 55. Hammer, B.; Hansen, L.; Nørskov, J. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Phys. Rev. B* 1999, *59*, 7413–7421. [CrossRef]
- Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* 2006, 27, 1787–1799. [CrossRef]
- Nørskov, J.; Bligaard, T.; Logadottir, A.; Kitchin, J.; Chen, J.; Pandelov, S.; Stimming, U. Trends in the exchange current for hydrogen evolution. *Phys. Inorg. Chem.* 2005, 152, J23–J26. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.