



# Article The High Electrocatalytic Performance of NiFeSe/CFP for Hydrogen Evolution Reaction Derived from a Prussian Blue Analogue

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**Abstract:** Non-noble-metal-based chalcogenides are promising candidates for hydrogen evolution reaction (HER) by harnessing the architectural design and the synergistic effect between the elements. Herein, a porous bimetallic selenide (NiFeSe) nanocube deposited on carbon fiber paper (NiFeSe/CFP) was synthesized through a facile selenization reaction based on Prussian blue analogues (PBAs) as precursors. The NiFeSe/CFP exhibited excellent HER activity with an overpotential of just 186 mV for a current density of 10 mA cm<sup>-2</sup> in 1.0 M KOH at ambient temperature, similar to most of the state-of-the-art transition metal chalcogenides. The corresponding Tafel slope was calculated to be 52 mV dec<sup>-1</sup>, indicating fast discharge of the proton during the HER. Furthermore, the catalyst could endure long-term catalytic tests and showed remarkable durability. The enhanced electrocatalytic performance of NiFeSe/CFP is attributed to the unique 3D porous configuration inherited from the PBA templates, enhanced charge transfer occurring at the heterogeneous interface due to the synergistic effect between the bimetallic phases, and the high conductivity improved by the formation of amorphous carbon shells during the selenization. These findings prove that the combination of inexpensive metal-organic framework precursors and hybrid metallic compounds is a feasible way to realize the performance enhancement of non-noble-metal-based chalcogenides towards alkaline HER.

**Keywords:** transition metal chalcogenides; hydrogen-evolution reaction; Prussian blue analogue; multi-component hybrid structures

# 1. Introduction

Water splitting powered by intermittent solar and wind energy is widely recognized as a sustainable clean energy storage system because of the depletion of fossil fuels [1–5]. The hydrogen evolution reaction (HER), as an indispensable half-reaction to water splitting, requires highly active electrocatalysts to ensure high energy efficiency [6,7]. Although precious metals, including Pt, Ir, Ru, Pd, and Rh and their alloys, exhibit favorable HER activity, their practical application is hampered owing to their low reserves and high cost [8,9]. The design of earth-abundant and cost-effective catalysts with outstanding performance has received considerable effort.

Currently, transition metal sulfides [7,10], phosphides [6,11], nitride [12–14] and selenides [15,16] are the most investigated catalysts for the HER. Among these, the transition metal chalcogenides (TMCs) have shown great potential as a large-scale applicable catalyst benefiting from their excellent intrinsic activity and stability in both acidic and alkaline solutions [17,18]. However, the state-of-the-art TMC catalysts still required relatively high overpotentials, particularly in a strong basic electrolyte. In previous works, we have found



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**Copyright:** © 2022 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/). that the catalytic performance of NiS<sub>2</sub> and NiSe<sub>2</sub> could be remarkably enhanced by tuning the morphology [19,20]. Apart from this strategy, it has been recently proven that multicomponent hybrid structures exhibited enhanced HER performance compared with their single-component counterparts owing to the beneficial electronic interaction and synergistic effects between the different interfaces [21-23]. For instance, FeNiSe nanosheets developed through a selenization process on vertically oriented layered double hydroxides (LDHs) exhibit better HER activity than Ni<sub>3</sub>Se<sub>2</sub> [16], implying the incorporation of Fe atoms is a feasible method to modify the HER performance. Similarly, Co-doped nickel selenide derived from zeolitic imidazolate framework-67 (ZIF-67) precursor shows higher catalytic activity than the nickel selenide [22]. The synergistic effects of multi-phases, the porous nanostructures stemming from the metal-organic framework (MOF) and the integration of catalysts with conductivity substrates were found to accelerate HER. These results suggest that a combination of rational chemical and structural design is a potential way to further improve the performances of TMC catalysts. Despite widely used MOFs such as ZIF [22,24,25] and MIL [26,27] as precursors, Prussian blue analogues (PBAs) are a kind of MOF with a relatively low price. It has been demonstrated that the construction of three-dimensional (3D) architectures from TMC nanomaterials prepared with PBAs as a template also effectively boosted the HER activity due to their relative abundance of highly active sites brought about by high porosity [28–30].

Enlightened by the literature mentioned above, in the present work, we synthesized nickel–iron diselenide (NiFeSe) nanocubes (NCs), which were converted from PBA precursors deposited on carbon fiber paper (CFP). For HER in 1.0 M KOH at ambient temperature, the NiFeSe/CFP catalyst requires an overpotential of only 186 mV to sustain a current density of 10 mA cm<sup>-2</sup>. The remarkable activity of the synthesized NiFeSe/CFP can be assigned to its appropriate electronic structure and desired nanostructure inherited from the PBA precursor. Moreover, the NiFeSe/CFP displayed high stability during 20 h in alkaline HER conditions. Its good stability is believed to benefit from the residual carbon shell that serves as a protection layer to prevent structural change during electrocatalysis.

## 2. Results and Discussion

## 2.1. Microstructure and Phase Identification

As demonstrated here, the NiFe selenides based on PBA CNs were facilely synthesized by selenizing pre-deposited PBA NiFe NCs (Figure 1). First, the typical FESEM images displayed successful synthesis of NiFe PBA NCs with a uniform size distribution, welldefined cubic morphology and smooth surface through the CV electrochemical deposition method (Figure 2a,b). After selenization treatment, the NiFe PBA NCs were converted to NiFeSe NCs, which inherited the uniform cubic morphology with a rough surface (Figure 2c). A single cube consisted of multiple particles with an average size of ~25 nm and visible hollow voids, as can be seen in the TEM images (Figure 2d,e). The transformations from PBA precursors to porous nanostructures are commonly observed during pyrolysis processes due to the nonequilibrium interdiffusion process [31]. On the other hand, the pyrolysis gas (NH<sub>3</sub>, H<sub>2</sub>O) gradually released in the selenization promotes the formation of a hierarchical porous structure, which facilitates the efficient diffusion of electrolytes and benefits the exposure of more active sites [24]. Notably, the TEM images also revealed the existence of an amorphous carbon shell about 5 nm outside the cube. The residual carbon was also reported in previous works based on PBA precursors [32]. The HRTEM image revealed distinct lattice fringes with interplanar spacings of 0.268 nm and 0.181 nm, respectively, which corresponded to the (210) and (311) planes of the NiSe<sub>2</sub>. Furthermore, the interplanar distances of 0.270 nm and 0.265 nm were attributed to the  $(\overline{1}12)$  and (112)planes of the Fe<sub>2</sub>NiSe<sub>4</sub>, respectively (Figure 2f). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and associated elemental mapping images confirmed that the Se, Ni, Fe, O and C elements were distributed evenly in NiFeSe NCs (Figure 2g). The corresponding EDS spectrum is presented in Figure S1. The atomic ratio of Ni, Fe and Se was 3.29:5.59:17.77. Additionally, FeSe NCs as control-group samples

were also synthesized by similarly altering the precursor (Figure S2a,b). The magnified SEM images demonstrated that the FeSe NCs were uniformly deposited on the CFP. The samples kept a Fe/Se ratio of ~2:1 according to the EDS characterization (Figure S2c), suggesting that FeSe<sub>2</sub> NCs were successfully prepared.



Figure 1. Schematic illustration of the formation process of NiFeSe/CFP.



**Figure 2.** Morphology and structure characterizations. (**a**,**b**) FESEM images of PBA/CFP: (**c**) FESEM, (**d**,**e**) TEM, and (**f**) HRTEM images of NiFeSe/CFP. (**g**) HAADF-STEM and elemental mapping images of selected NiFeSe NCs.

The phase composition of the selenides for NCs was further investigated. In the XRD pattern of the NiFe-based precursor, the distinctive peaks at 17.7°, 25.2° and 35.9°, respectively, correspond to the (200), (220) and (400) planes of  $Ni_2Fe(CN)_6$ , as shown in Figure S3 (ICDD: 01-075-0037), which is in accordance with a previous report [33]. The NiFebased precursor completely changed into bimetallic selenides after selenization, which was verified via the XRD pattern of NiFeSe/CFP (Figure 3a). The NiFeSe/CFP catalyst was well indexed to a mixture of the cubic-pyrite NiSe<sub>2</sub> (ICDD: 04-003-1991) and Fe<sub>2</sub>NiSe<sub>4</sub> (ICDD: 01-089-1968) crystal phases. The peaks at 20 values of  $33.6^\circ$ ,  $36.9^\circ$  and  $50.7^\circ$  were attributed to the (210), (211) and (311) planes of NiSe<sub>2</sub>. The peaks at  $2\theta$  values of  $33.2^{\circ}$ ,  $33.9^{\circ}$  and  $44.0^{\circ}$  were attributed to the (202), (114) and (114) planes of Fe<sub>2</sub>NiSe<sub>4</sub>. This result further confirmed the formation of NiSe<sub>2</sub>/Fe<sub>2</sub>NiSe<sub>4</sub> on CFP, as revealed by the HRTEM image. For comparison, the crystal structure of the FeSe/CFP was also characterized. The peaks at  $2\theta$  values of  $34.9^\circ$ ,  $36.2^\circ$  and  $48.2^\circ$  were assigned to the (111), (120) and (211) planes FeSe<sub>2</sub> (Figure S2d). Generally, during the selenization process, the cyanide tends to decompose at ~300 °C. The metal ions are reduced by the liberation of CN groups to the metallic state and then react with Se to form heterometallic selenides [34].

The chemical composition and valence states of the as-prepared NiFeSe/CFP were further examined via XPS. The survey spectrum in Figure S4 confirmed the existence of Ni, Fe, Se and O elements in the NiFeSe NCs, which coincided with the result of EDS results. In addition, the C and N elements were also detected, which came from the decomposition of the CN group in the PBA precursors. Although the appearance of C peaks in the survey spectra may also be related to the CFP substrates, the existence of N species commonly indicates the formation of residual carbon, according to the results provided by Varnell et al. [35]. For the Ni 2p<sub>3/2</sub> region (Figure 3b), the peaks at ~853.5 eV corresponded to the Ni<sup>2+</sup> species, which further verified the formation of NiSe<sub>2</sub>. The binding energies of Ni 2p<sub>3/2</sub> located at 853.9 and 855.7 eV, respectively, are the characteristics of nickel oxides [36,37]. For the Fe  $2p_{3/2}$  region (Figure 3c), the deconvoluted peak centered at 707.0 eV was assigned to the Fe-Se bonds; the peaks at 708.5 eV and 710.6 eV were deemed as the Fe-O bonds [38]. In the Se 3d high-resolution spectrum (Figure 3d), the peak at 58.4 eV was ascribed to the oxidation state of the Se species caused by surface oxidation in ambient air, while the major peak at 55.4 eV (Se  $3d_{5/2}$ ) was attributed to the Se bonded to Ni or Fe in the form of metallic selenide. The O 1s high-resolution spectrum (Figure 3e) was deconvoluted into three peaks, which could be explained by the coexistence of Se-O, M-O (M=Ni and Fe) and hydroxyl (-OH) groups. The formation mechanism of -OH groups is not clear and deserves to be investigated in future work, but it is considered to promote the absorption of  $H_2O$  in alkaline solutions due to hydrogen bonding effects [39].



**Figure 3.** X-ray characterizations: (**a**) XRD spectra of NiFeSe/CFP and the reference patterns of NiSe<sub>2</sub> (yellow, ICDD: 04-003-1991), Fe<sub>2</sub>NiSe<sub>4</sub> (cyan, ICDD: 01-089-1968). The peaks marked with black dots correspond to CFP substrate. XPS spectra of (**b**) Ni 2p, (**c**) Fe 2p, (**d**) Se 3d and (**e**) O 1s in NiFeSe/CFP.

## 2.2. HER Performance Testing

We investigated the HER activities of NiFeSe/CFP in 1.0 M KOH at room temperature. Figure 4a shows the LSV polarization curves of catalyzed HER at a scan rate of 5 mV s<sup>-1</sup>. It can be easily observed that the bare CFP (black curves) showed a very small capacitive and no significant faradic current at 500 mV applied potential. Relatively, the NiFe PBA/CFP (green curves) and FeSe/CFP (red curves) required the overpotential of 445 mV and 423 mV, respectively, to drive the current density of 10 mA cm<sup>-2</sup>. The NiFeSe/CFP displayed a substantially smaller overpotential of 186 mV at 10 mA  $cm^{-2}$ , as predicted (purple curves). This value is comparable to most of the state-of-the-art TMCs catalysts (Table S2). Notably, there is still a gap between the NiFeSe/CFP and industrial Ra-Ni [40]; thus, further enhancement of the performance of TMCs is urgently needed. Compared with FeSe/CFP, NiFeSe/CFP exhibited remarkably enhanced activity, indicating that the synergetic electronic interactions between the different components formed a better electronic structure and reduced HER energy barriers [41]. To assess HER kinetics, the Tafel slope was calculated. The observed Tafel slope for NiFe PBA/CFP was around 116 mV  $dec^{-1}$ , as shown in Figure 4b. FeSe/CFP had a Tafel slope of roughly 81 mV dec<sup>-1</sup>, whereas NiFeSe/CFP had a Tafel slope of 52 mV dec $^{-1}$ . The Volmer–Heyrovsky mechanism [42], which consists of a quick discharge of a proton and a slow coupling of the discharged proton with an extra proton  $[H_{ad} + H_3O^+ + e^- \rightarrow H_2 + H_2O]$ , had a minimal Tafel slope of 51.63 mV dec $^{-1}$ . As per the EIS, the faster electrode reaction kinetics of NiFeSe/CFP was more apparent. At an overpotential of 532 mV, the Nyquist plots of NiFeSe/CFP (purple curves), FeSe/CFP (red curves) and NiFe PBA/CFP (green curve) are shown in Figure 4c. The EIS analysis suggested that the NiFeSe/CFP electrode had a lower charge transfer resistance ( $R_{ct}$  4.6  $\Omega$ ) than FeSe/CFP (6.9  $\Omega$ ) and NiFe PBA/CFP (12.5  $\Omega$ ), implying that the electron transfer and catalytic kinetics during HER are favorable. This is due to the distinctive electronic structure and the ohmic contact of the NiFeSe/CFP [43]. For an advanced electrocatalyst, a large surface area is required. We tested the electrochemical  $C_{dl}$  of the catalysts using the CV method (Figure S5) to evaluate the ECSA. As shown in Figure 4d, the  $C_{dl}$  of NiFeSe/CFP was 0.41 mF cm<sup>-2</sup>, which was larger than FeSe/CFP and NiFe PBA/CFP. The same sequence is also observed in Figure S6, in which LSV curves are normalized against the ECSA. The mass activity for HER at selected potentials for NiFeSe/CFP possessed the highest value of 24.5 A  $g^{-1}$ , which significantly outperforms NiSe<sub>2</sub>/CFP and NiS<sub>2</sub>/CFP, as reported in our previous works [19,20].

Robust operational stability is another crucial prerequisite for an HER catalyst. We used CV and constant current measurements to evaluate the NiFeSe/CFP electrode for this purpose. After 1000 CV cycles, the polarization curve was almost identical to that of the initial one (Figure 4e, solid lines), showing a very small negative shift (Figure 4e, dotted lines). Moreover, the potential in 1.0 M KOH needed to achieve 10 mA cm<sup>-2</sup> increased slightly at first 1 h but stayed stable within 20 h (Figure 4f). The remaining amorphous carbon may enhance durability [44,45]. The morphology, composition and structure of the NiFeSe/CFP after the long-time HER operations for 20 h were systematically investigated. It can be seen that NiFeSe NCs preserved their initial morphology after the stability test (Figure S7), regardless of the rougher surface. The elemental mapping images (Figure 5a) demonstrated an even distribution of the Ni, Fe, Se and O elements in NCs, implying no aggregation of particles during the reaction. The corresponding EDS spectrum in FESEM (Figure 5b) displayed an acceptable proportional change in atomic composition compared with the selenides before HER. Additionally, the phase structure remained virtually unaltered, as confirmed by XRD (Figure 5c). These facts clearly pointed to the high HER stability of the NiFeSe/CFP. Similarly, the comparison between the XPS fine spectra before and after testing showed no significant change with respect to Ni 2p, Fe 2p and Se 3d of NiFeSe/CFP (Figure 5d–f), apart from the increase in Se-O peaks due to the surface oxidation of Se in strongly alkaline solutions [46].



**Figure 4.** HER performance of the as-prepared catalysts in 1.0 M KOH at room temperature. (a) LSV polarization curves (b) Tafel plots, (c) EIS Nyquist plots and (d)  $C_{dl}$  for the HER of NiFe PBA/CFP, FeSe/CFP and NiFeSe/CFP. (e) HER polarization curves of NiFeSe/CFP before and after 1000 CV tests. (f) The plot of the extracted corresponding overpotential at a current density of 10 mA cm<sup>-2</sup>.

The outstanding HER performance of the NiFeSe/CFP can be mainly attributed to the following factors: (i) the porous architecture of NiFeSe/CFP inherited from the PBA precursors enable the larger number of exposed active sites; (ii) the synergistic effects in the bimetallic phase enhance charge transfer occurring at the heterogeneous interface; (iii) the existence of amorphous carbon layer improves the conductivity and reaction kinetics; (iv) the surface -OH groups promote the adsorption of initial H<sub>2</sub>O, accelerating the HER catalytic activity [47–49].



**Figure 5.** Composition and structure characterizations. (**a**) Elemental mapping images and (**b**) EDS spectrum in FESEM of selected NiFeSe/CFP after HER stability test. (**c**) XRD spectra of NiFeSe/CFP and the reference patterns of NiSe<sub>2</sub> (yellow, ICDD: 04-003-1991), Fe<sub>2</sub>NiSe<sub>4</sub> (cyan, ICDD: 01-089-1968). The peaks marked with black dots correspond to CFP substrate. XPS spectra of (**d**) Ni 2p, (**e**) Fe 2p and (**f**) Se 3d in NiFeSe/CFP.

## 3. Materials and Methods

# 3.1. Preparation of Electrodes

The CFP substrates were cleaned via ultrasonication with Milli-Q water for 15 min. CFP pretreatment and subsequent electrodeposition were performed with an electrochemical workstation (Shanghai Chenhua, CHI 760E) in a classical three-electrode configuration using a platinum wire and Ag/AgCl electrode (saturated with KCl) as counter electrode and reference electrode, respectively. To enhance hydrophilicity, the CFP electrodes were activated by conducting cyclic voltammetry (CV) treatments in 2.0 M H<sub>2</sub>SO<sub>4</sub> aqueous solution with a scan range from 0.2 to 1.2 V (vs. Ag/AgCl) at a rate of 50 mV s<sup>-1</sup> until a

stable CV profile was reached. The samples were further rinsed thoroughly with Milli-Q water before electrodeposition of the PBA precursor. The exposed geometric area of the CFP electrodes was 1.0 cm<sup>2</sup>.

## 3.2. Electrodeposition of NiFe PBA/CFP and Fe PBA/CFP Precursors

NiFe PBA catalyst was electrodeposited onto CFP substrates in a potassium nitrate buffer containing Ni(II) and Fe(III) ions. The 0.6 mM nickel(II) nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99.5%, Aladdin, Shanghai, China) and 0.6 mM iron(III) cyanide (K<sub>3</sub>Fe(CN)<sub>6</sub>, 99.5%, Aladdin, Shanghai, China) were sequentially added into the potassium nitrate buffer solution (KNO<sub>3</sub>, 99.5%, Aladdin, Shanghai, China). The NiFe PBA precursors were deposited on a CFP substrate for 200 consecutive cycles at 50 mV s<sup>-1</sup> under CV between 0.4 and 1.2 V (vs. Ag/AgCl). The electrode was cleaned thoroughly using Milli-Q water and then conditioned in saturated KNO<sub>3</sub> solution for 24 h. After deposition, the product was washed with Milli-Q water and ethanol, successively, for a few cycles and dried at 60 °C for 8 h before selenization. Fe PBA/CFP precursors were electrodeposited onto CFP substrates in a similar way to prepare FeSe/CFP, except for replacing nickel(II) nitrate with iron(III) chloride (FeCl<sub>3</sub>·3H<sub>2</sub>O, 99.5%, Aladdin, Shanghai, China).

## 3.3. Fabrication of NiFeSe/CFP and FeSe/CFP Electrocatalysts

The as-deposited NiFe PBA/CFP (downstream side) and 80 mg of Se (99.9%, Aladdin, Shanghai, China) powder (upstream side) were placed in a porcelain boat in a tube furnace. The samples were calcinated at 450 °C for 30 min with a heating ramp of 5 °C min<sup>-1</sup> under an Ar atmosphere. The fabrication of the FeSe/CFP catalyst was similar to that of the NiFeSe/CFP catalyst.

## 3.4. Material Characterizations

The morphologies and crystal structures of NiFeSe/CFP were investigated using field-emission scanning electron microscopy (FESEM, S4800, Hitachi, Tokyo, Japan) and transmission of electron microscopy (TEM, FEI Talos F200, Tokyo, Japan). The high-resolution TEM (HRTEM) analysis and elemental mapping were conducted with the FEI Talos F200. The compositions of the productions were determined by energy-dispersive spectroscopy (EDS). A D8 Advance, Bruker Phaser X-ray diffractometer was used to characterize the X-ray diffraction (XRD) patterns using Cu K $\alpha$  radiation in the region of 15°~80°. X-ray photoelectron spectroscopy (XPS, PHI-5400, Physical Electronics, Inc., Chanhassen, MN, USA) was used to reveal the chemical and elemental information.

### 3.5. Electrochemical Measurements

To evaluate the electrocatalytic performance of the as-prepared samples for HER, a standard three-electrode system was used, and the tests were conducted with an electrochemical workstation (Shanghai Chenhua, CHI 760E). The CFP substrates loaded with NiFeSe NCs  $(0.5 \text{ mg cm}^{-2})$  were adopted as the working electrodes. A platinum mesh and saturated calomel electrode (SCE) were serving as the counter and reference electrodes, respectively. All electrochemical tests were performed in 1.0 M KOH electrolyte at room temperature. All potentials shown in this work were calculated with respect to the reversible hydrogen electrode (RHE) using the equation of  $E_{vs RHE} = E_{vs SCE} + E_{SCE} + 0.059 \text{ pH}$ . At a scan rate of 5 mV s<sup>-1</sup>, the activity of catalysts towards HER was evaluated using linear sweep voltammetry (LSV) from 0.8 V to 0 V vs. RHE. Tafel plots were determined to assess the reaction kinetics by plotting  $\eta$  vs. the logarithm to base 10 of current density. The Tafel slope was extracted from the Tafel equation,  $\eta = b \log j + a$ , where b is the Tafel slope and j denotes the current density. Electrochemical impedance spectroscopy (ElS) was carried out by applying a 532 mV overpotential with an amplitude of 5 mV across a frequency window of 100 kHz to 0.1 Hz. The double-layer capacitance ( $C_{dl}$ ) obtained utilizing CV scans between 0.85 and 0.91 V vs. RHE at varied scan speeds ranging from 5 to 200 mV s<sup>-1</sup>,

$$ECSA = C_{dl}/C_s,$$
 (1)

The specific capacitance ( $C_s$ ) of TMCs catalysts is typically at 0.04 mF cm<sup>-2</sup>. These measured values are summarized in Table S1. The mass activity of each sample was calculated with the following formula:

mass activity = 
$$j/m$$
, (2)

where m is the mass loading. The mass activity calculated in this study was obtained at the current density with 200 mV HER overpotentials. In addition, 1000 CV cycles and constant current measurements were conducted for long-term stability.

# 4. Conclusions

In summary, we synthesized a hierarchical nanostructure of a NiFeSe/CFP catalyst where the porous NC films converted from the PBAs precursors were uniformly grown on CFP. Benefiting from the highly porous configuration stemming from the PBA and the manipulating of hybridization of multi-component metallic selenides, the as-prepared NiFeSe/CFP displayed outstanding catalytic activity for HER in 1.0 M KOH. A current density of 10 mA cm<sup>-2</sup> was derived by a small overpotential of 186 mV, making it one of the most promising transition metal chalcogenides HER catalysts. The Tafel slope was only 52 mV dec<sup>-1</sup>, revealing the reaction process followed the Volmer–Heyrovsky mechanism. The formation of a residual carbon layer could effectively promote the electron transfer ability of the NiFeSe/CFP for which the R<sub>ct</sub> was 4.6  $\Omega$ . It provides a promising approach to fabricating a high-performance and durable catalyst for HER by using nonnoble bimetallic chalcogenides.

**Supplementary Materials:** The following supporting information can be downloaded at https: //www.mdpi.com/article/10.3390/catal12070739/s1, Figure S1: EDS spectrum of NiFeSe/CFP in FESEM; Figure S2: (a,b) FESEM images, (c) EDS spectrum, (d) XRD pattern of FeSe/CFP and the reference pattern of FeSe<sub>2</sub> (brown, ICDD: 97-004-2115). The peaks marked with black dots correspond to CFP substrate; Figure S3: XRD spectra of NiFe PBA/CFP and the reference pattern of Ni<sub>2</sub>Fe(CN)<sub>6</sub> (green, ICDD: 01-075-0037). The peaks marked with black dots correspond to CFP substrate; Figure S4: survey XPS spectra of NiFeSe/CFP; Figure S5: CV curves in the double layer region with various scan rates from 5 to 200 mV s<sup>-1</sup> for (a) NiFeSe/CFP, (b) FeSe/CFP and (c)NiFe PBA/CFP; Figure S6: the ECSA normalized HER curves; Figure S7: (a,b) FESEM and (c,d) TEM images of NiFeSe/CFP after HER stability test; Table S1: ECSA determination of the CFP supported nanocubes; Table S2: comparison of the HER electrochemical performance overpotentials ( $\eta_{10}$ ) and Tafel slopes for similar composite materials reported in the literature [40,52–61].

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