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Supplementary Materials

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

Yajie Guo [1], Yongjie Liu [1], Yanrong Liu [2], Chunrui Zhang [1], Kelun Jia [1], Jibo Su [1] and Ke Wang [2,*]

[1] School of Materials Science and Engineering, Chang'an University, Xi'an 710064, China; yjguo@chd.edu.cn (Y.G.); 2021131039@chd.edu.cn (Y.J.L.); 2018131016@chd.edu.cn (C.Z.); 2020131033@chd.edu.cn (K.J.); 2019904173@chd.edu.cn (J.S.)

[2] Beijing Key Laboratory of Ionic Liquids Clean Process, CAS Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China; yrliu@ipe.ac.cn

* Correspondence: kewang@ipe.ac.cn

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^{-2} 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^{-1}, 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

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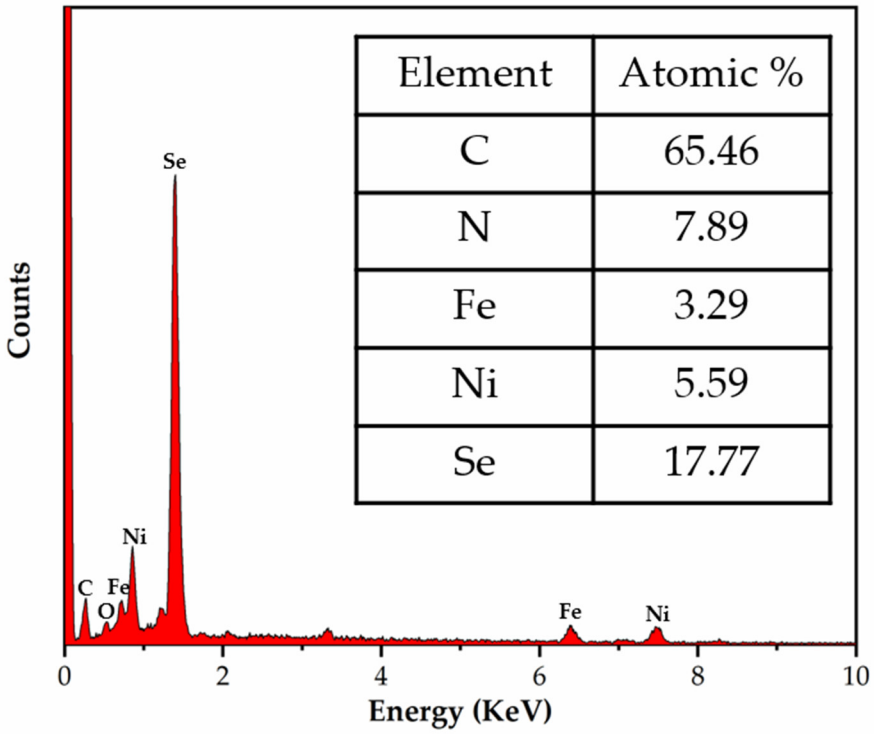

Figure S1. EDS spectrum of NiFeSe/CFP in FESEM.

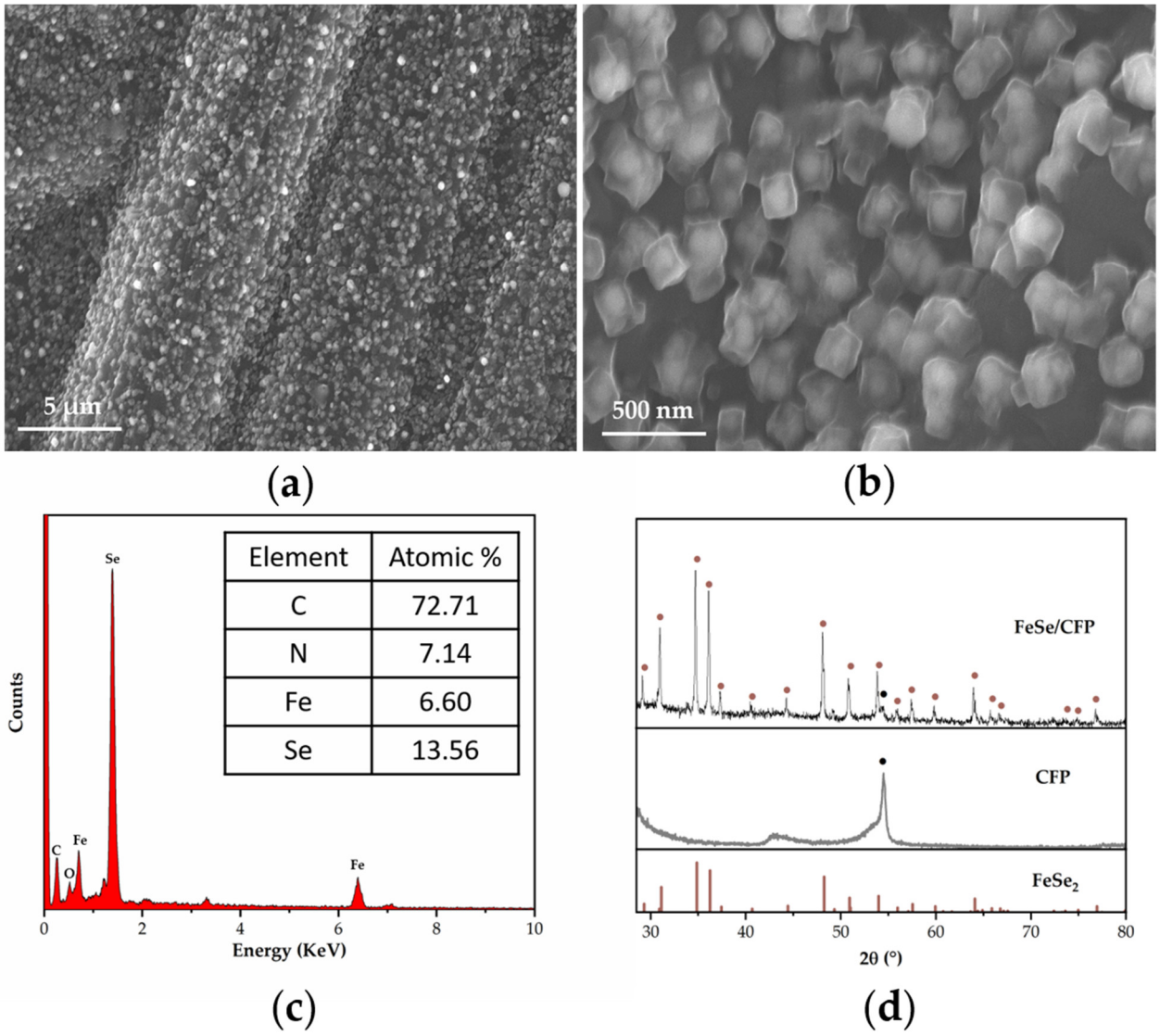

Figure S2. (**a**,**b**) FESEM images, (**c**) EDS spectrum, (**d**) XRD pattern of FeSe/CFP and the reference pattern of $FeSe_2$ (brown, ICDD: 97-004-2115). The peaks marked with black dots correspond to CFP substrate.

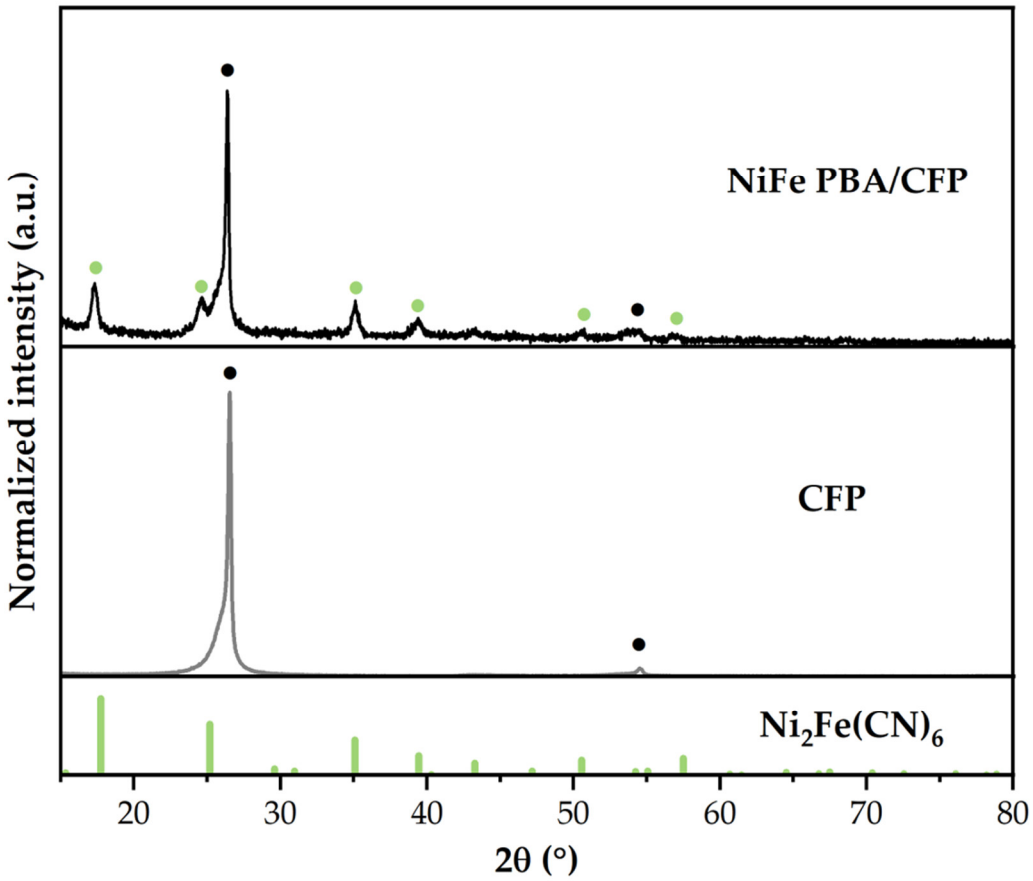

Figure S3. XRD spectra of NiFe PBA/CFP and the reference pattern of $Ni_2Fe(CN)_6$ (green, ICDD: 01-075-0037). The peaks marked with black dots corre-spond to CFP substrate.

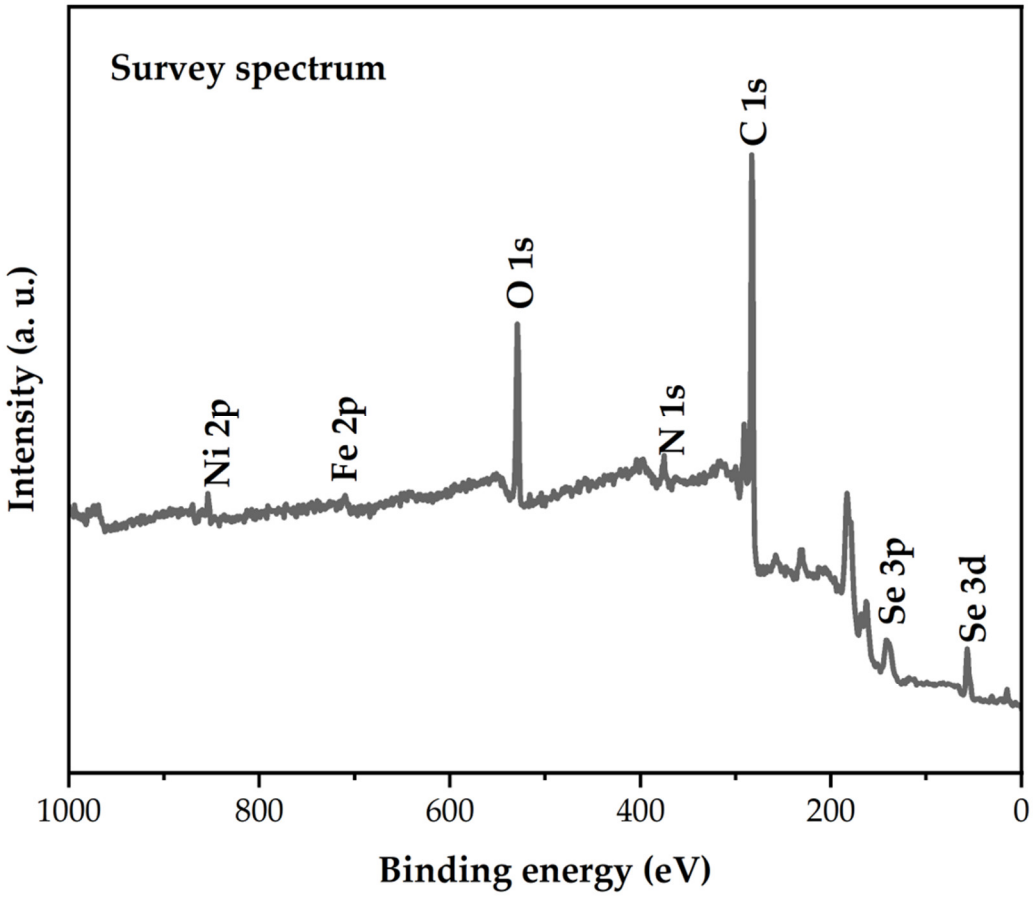

Figure S4. Survey XPS spectra of NiFeSe/CFP.

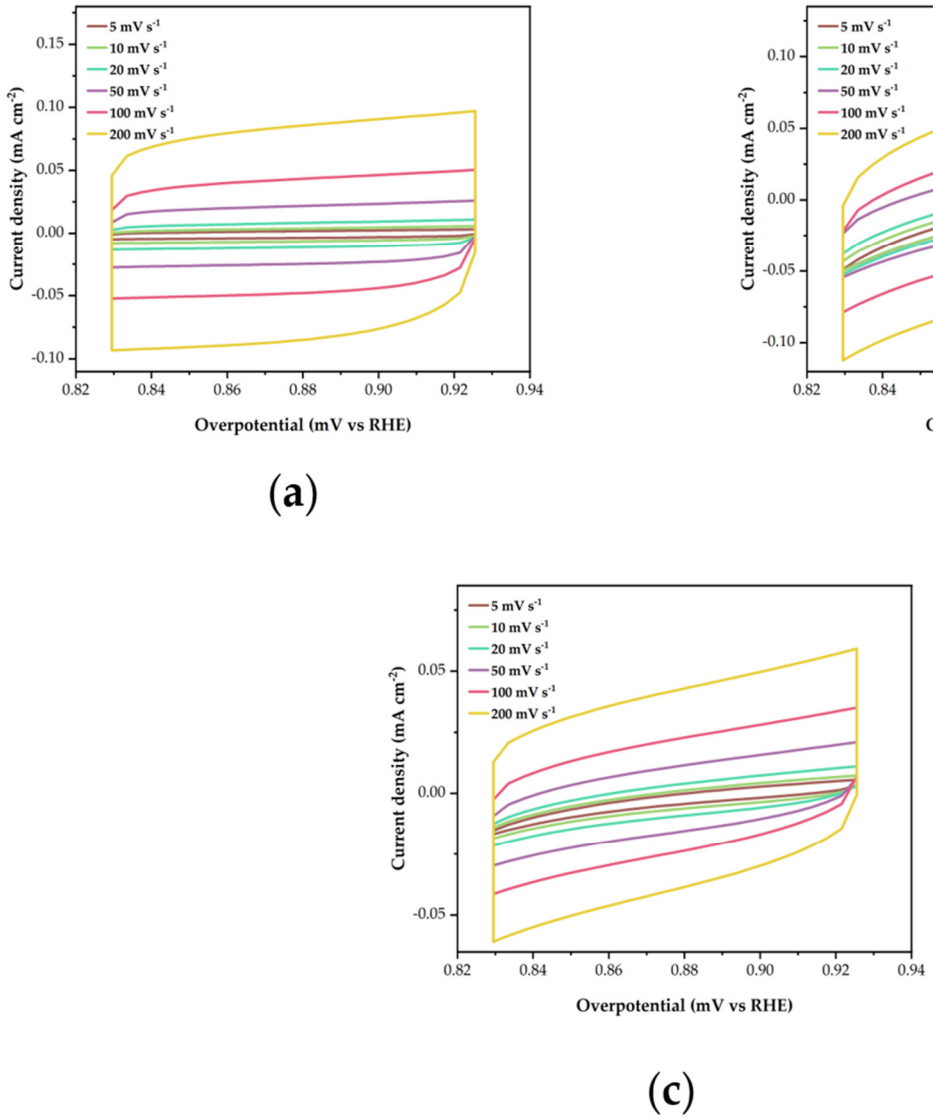

Figure S5. CV curves in the double layer region with various scan rates from 5 to 200 mV s^{-1} for (**a**) NiFeSe/CFP, (**b**) FeSe/CFP and (**c**)NiFe PBA/CFP.

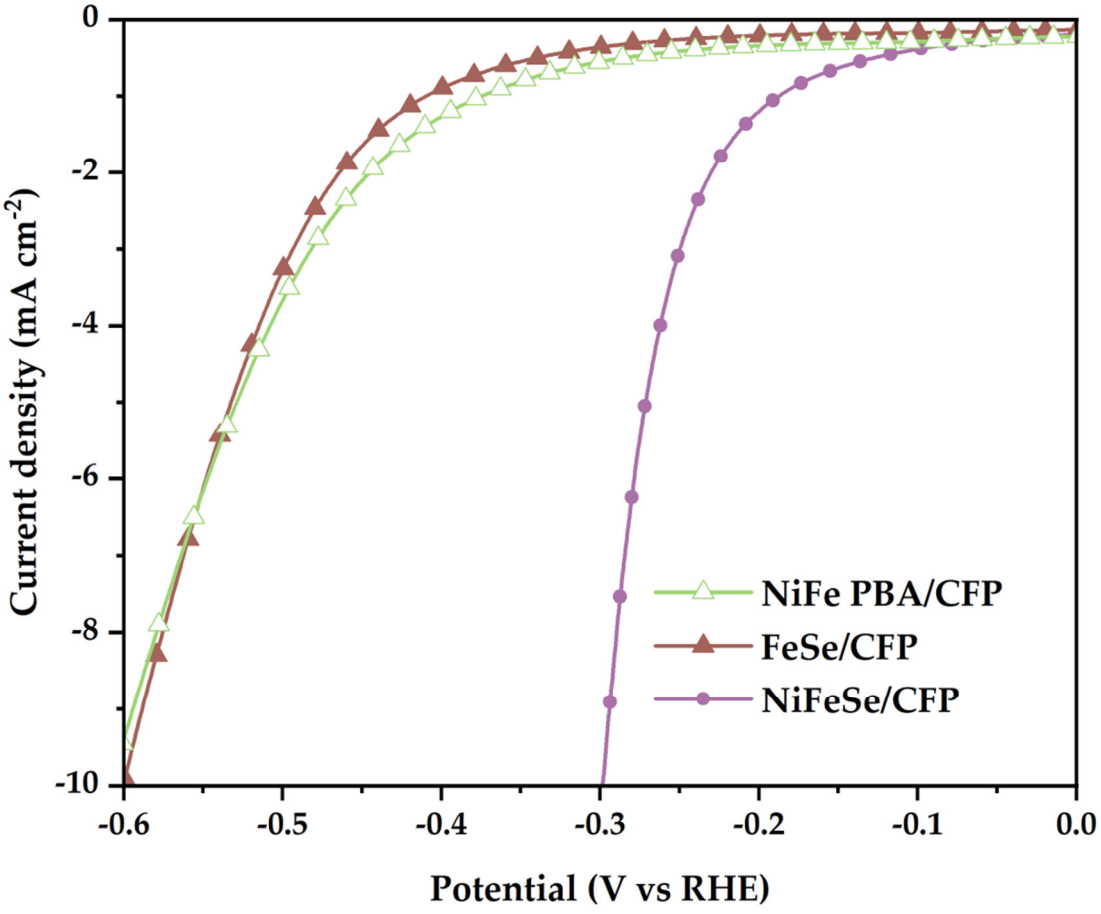

Figure S6. The ECSA normalized HER curves.

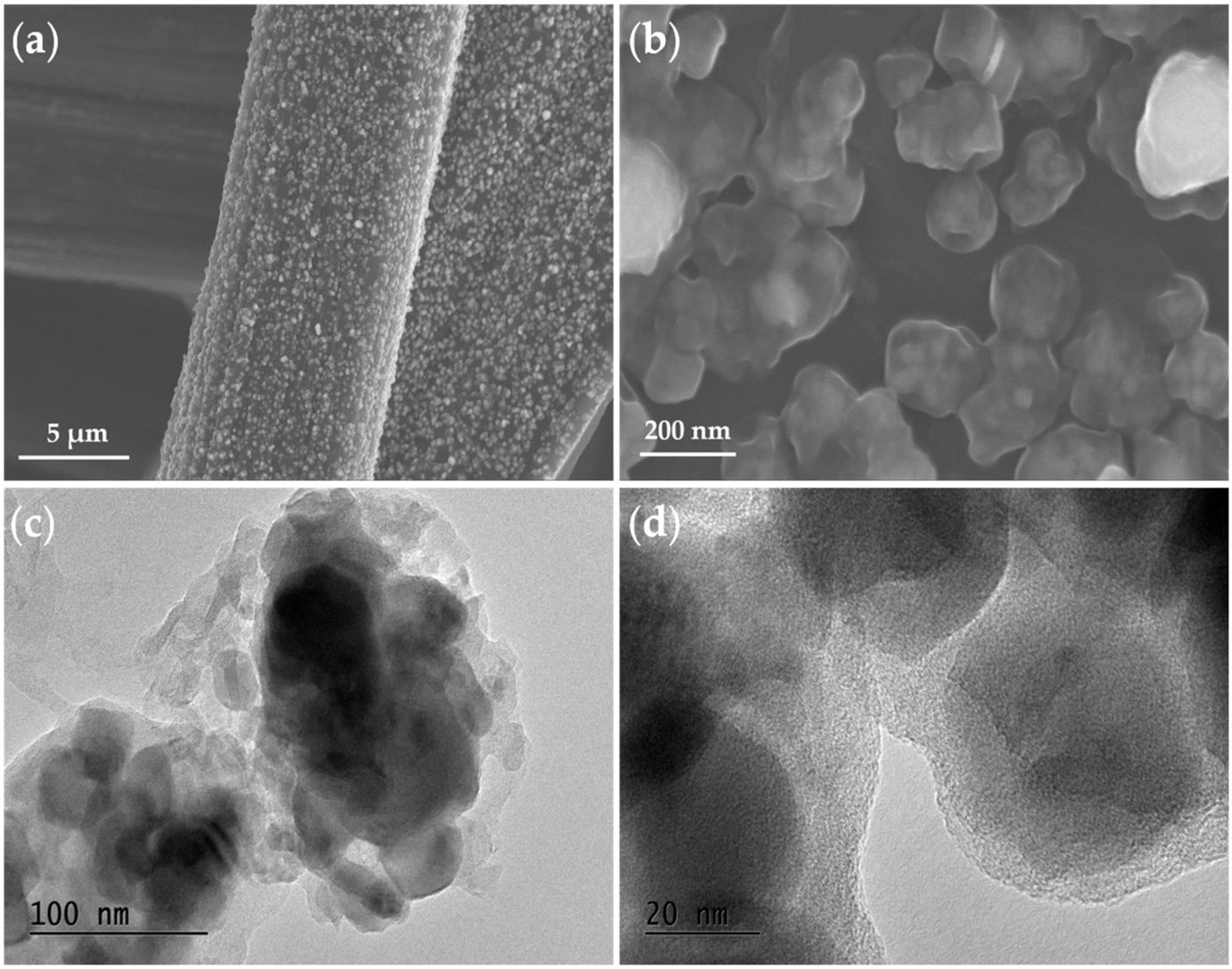

Figure S7. (**a**,**b**) FESEM and (**c**,**d**) TEM images of NiFeSe/CFP after HER stability test.

Table S1. ECSA determination of the CFP supported nanocubes.

Samples	C_{dl} [mF cm^{-2}]	ECSA [cm^2]
NiFeSe/CFP	0.41	10.25
FeSe/CFP	0.34	8.5
NiFe PBA/CFP	0.20	5

Table S2. Comparison of the HER electrochemical performance overpotentials (η_{10}) and Tafel slopes for similar composite materials reported in literature.

Catalysts	Electrolytes	η_{10} [mV]	Tafel slope [mV dec^{-1}]	Refs.
NiFeSe/CFP	1.0 KOH	186	52	This work
FeSe/CFP	1.0 KOH	423	81	This work
NiFe PBA/CFP	1.0 KOH	445	116	This work
NiFeSe/CFP	6.0 KOH	132	-	This work
FeCo-FeCoNi	1.0 KOH	211	77	1
$Ni_{90}Fe_{10}$/CP	1.0 KOH	246	95.4	2
$NiMoO_x$/NiMoS	1.0 KOH	236	96	3
Fe_3C-Co/NC	1.0 KOH	238	108.8	4
Mn-MoP	1.0 KOH	198	110.69	5
NiFeP@N-CS	1.0 KOH	186	112	6
CoSe/NiFe LDH	1.0 KOH	260	125	7
Ni_3S_2	1.0 KOH	240	113	8
$Ni_{0.85}Se$ flims/GS	1.0 NaOH	200	-	9
$Ni_{0.75}Se$ nanocrystal	1.0 KOH	233	86	10
Ra-Ni	6.0 KOH	22	-	11

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