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Supporting Information

Hybrid Engineering of crystalline $NiSe_x$ nanorod arrays with amorphous Ni-P film towards promoted overall water electrocatalysis

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Materials

All chemicals were of analytical grade and used without further purification in the experiments. Hydrochloric acid (HCl), potassium hydroxide (KOH), anhydrous ethanol, acetone, Se powders, sodium borohydride ($NaBH_4$), sodium hypophosphite (NaH_2PO_2) and nickel nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Nickel foam (NF) was obtained from the KunShan Kunag Xun Electronics Co., Ltd. Pt/C (20 wt % Pt), ruthenium(IV) oxide (RuO_2) and Nafion (5 wt %) were purchased from Aladdin Ltd. The deionized (DI) water used in all experiments with a resistivity of 18.2 $MΩ·cm^{-1}$ was purified through a Millipore system.

Characterization

X-ray diffraction (XRD) patterns were obtained by X-ray diffractometer (Bruker D8-Advance) equipped with a Cu Kα radiation source (λ =1.5418 Å) to record the crystal diffraction patterns of samples. The morphology and structure of all samples were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi, SU-8010) and high-resolution transmission electron microscopy (HR-TEM, JEM-2100, 200 kV) with X-ray energy-dispersive spectroscopy. The surface composition and valence state of the samples were characterized by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD). Raman characterization was performed on a Renishaw-inVia Raman spectrometer with 532 nm laser excitation. The static contact angle is measured by JY-82B Kruss DSA system at room temperature.

Electrochemical measurements

All electrochemical data tests were achieved by CHI 760E electrochemical workstation (CH Instruments, China) with a three-electrode system in an O_2 saturated 1.0 M KOH. The as-prepared samples supported on Ni foam, a mercury oxide electrode (Hg/HgO) and a carbon rod (4 mm in diameter) were employed as the working, reference and counter electrode, respectively. Cyclic Voltammetry (CV) measurements for OER and HER were scanned in the potential range from 0 to 1 V (vs. Hg/HgO), -1.5 to -1 V (vs. Hg/HgO) at a scanning rate of 200 $mV\cdot s^{-1}$, respectively. And the corresponding polarization curves were obtained by using Linear Sweep Voltammetry (LSV) with a scan rate of 3 and 5 $mV\cdot s^{-1}$, respectively. The stability test was implemented using chronopotentiometric method at certain potentials. In addition, the polarization curve of the OWS was measured from 1.0 to 2.0 V at a sweep rate of 5 mV s^{-1} via a two-electrode configuration in 1 M KOH, and the chronopotentiometric curve was recorded at a constant potential of 1.52 V. The electrochemical data were not collected until the signals of working electrodes stabilized after scanning several times. Electrochemical impedance spectroscopy (EIS) experiments were conducted in the frequency range from 100 KHz to 1 Hz with an amplitude potential of 5 mV. All the potentials with regard to Hg/HgO were calibrated to the reversible hydrogen electrode (RHE) according to the following equation: $E\ (RHE) = E\ (vs.\ Hg/HgO) + 0.059 \times pH + 0.098$. All the measurements above were corrected by manual iR compensation using the current and the solution resistance. Furthermore, all experiments were repeated at least three times to ensure reliability and reproducibility.

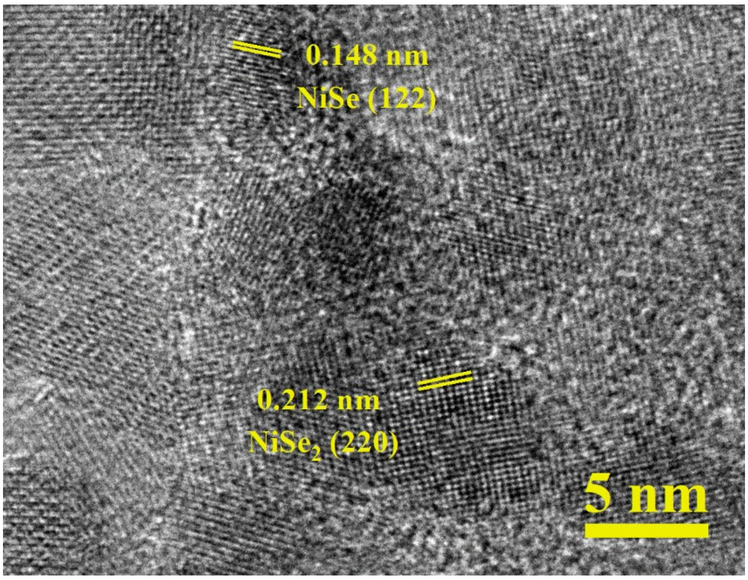
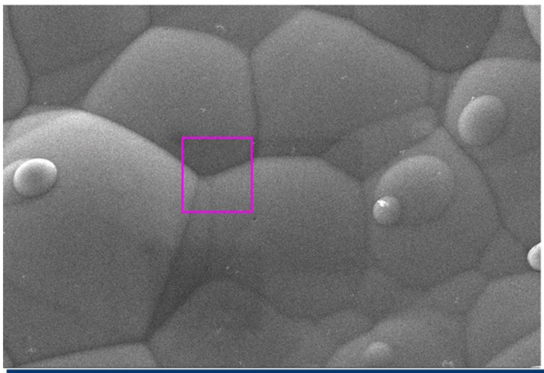


Fig. S1. HRTEM images of Ni-P/$NiSe_x$.



Element	Atomic %
Ni	80.90
P	17.88
Se	1.22
total	100

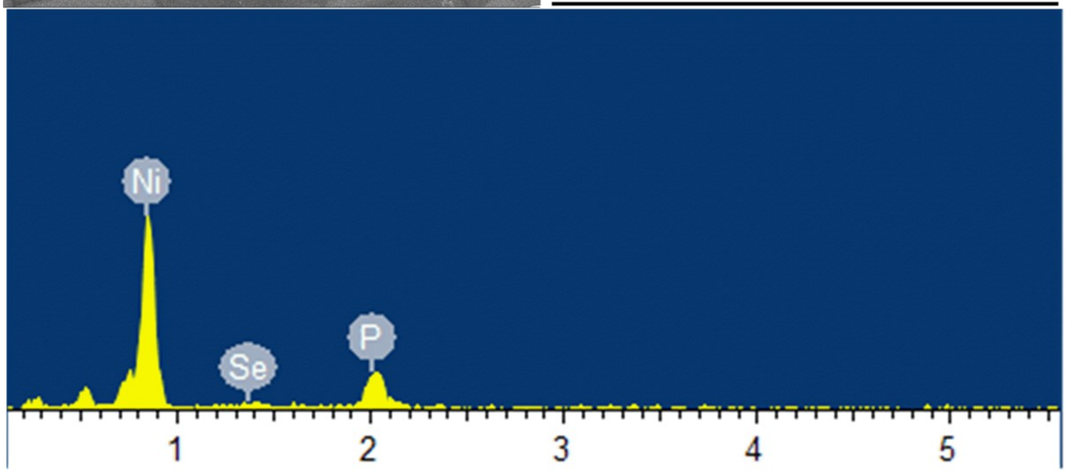


Fig. S2. Corresponding EDX plot of the Ni-P/$NiSe_x$/NF catalyst.

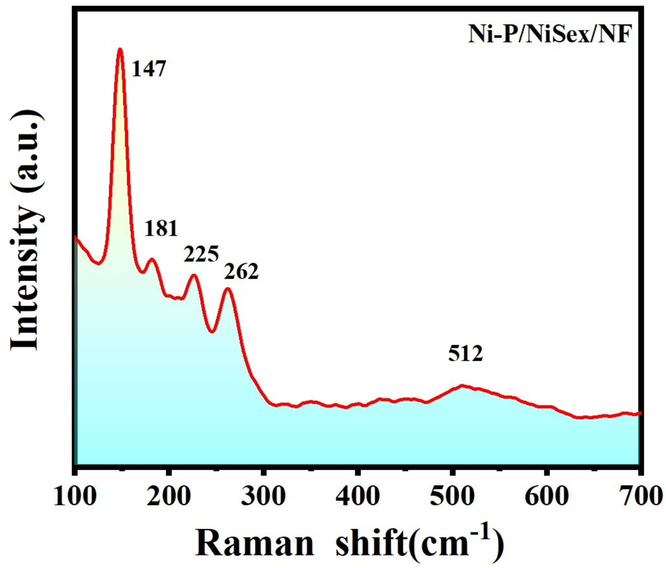


Fig. S3. Raman spectrum of as-prepared Ni-P/NiSe$_x$/NF.

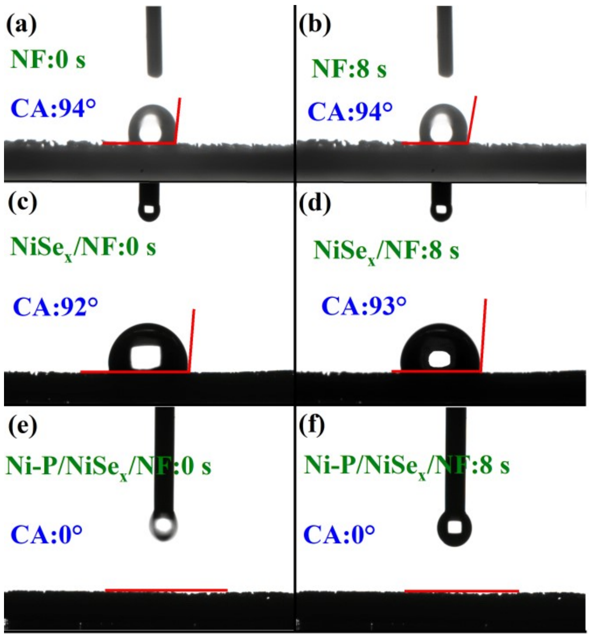


Fig. S4. Contact angle measurement of samples NF (a, b), NiSe$_x$/NF (c, d) and Ni-P/NiSe$_x$/NF (e, f) catalysts at 0 and 8 s standing time (using a drop of 1.0 M KOH solution).

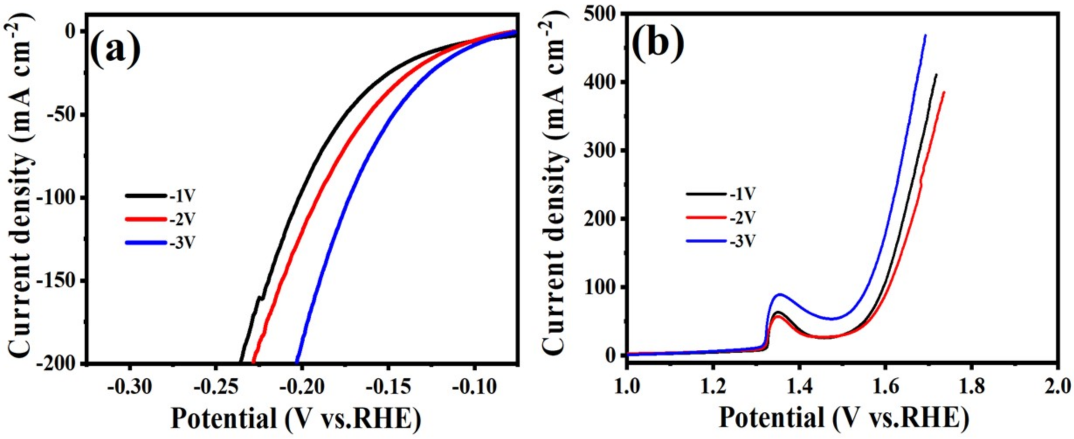


Fig. S5. (a) HER and (b) OER polarization curves of Ni-P/$NiSe_x$/NF synthesized with different deposition potential (-1, -2, -3 V).

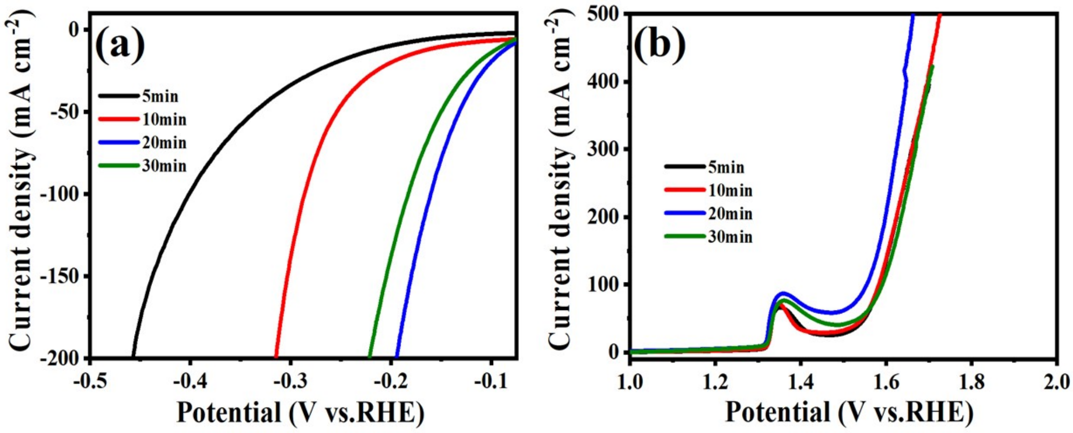


Fig. S6. (a) HER and (b) OER polarization curves of Ni-P/$NiSe_x$/NF synthesized with different deposition time (5, 10, 20, 30 min).

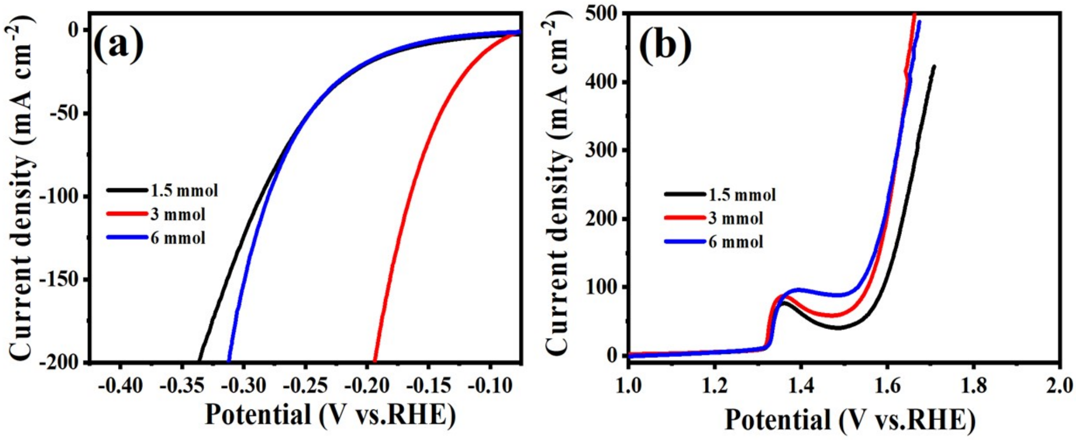


Fig. S7. (a) HER and (b) OER polarization curves of Ni-P/$NiSe_x$/NF samples synthesized with different amounts of NaH_2PO_2 (1.5, 3, 6 mmol).

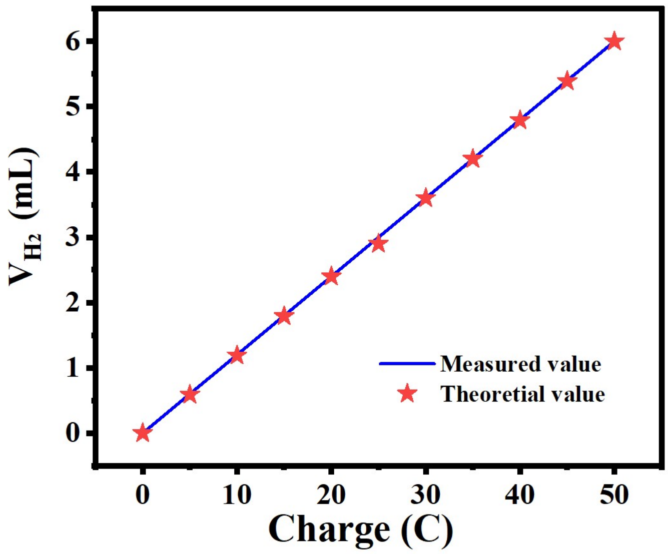


Fig. S8. Quantitative H_2 measurement via water displacement.

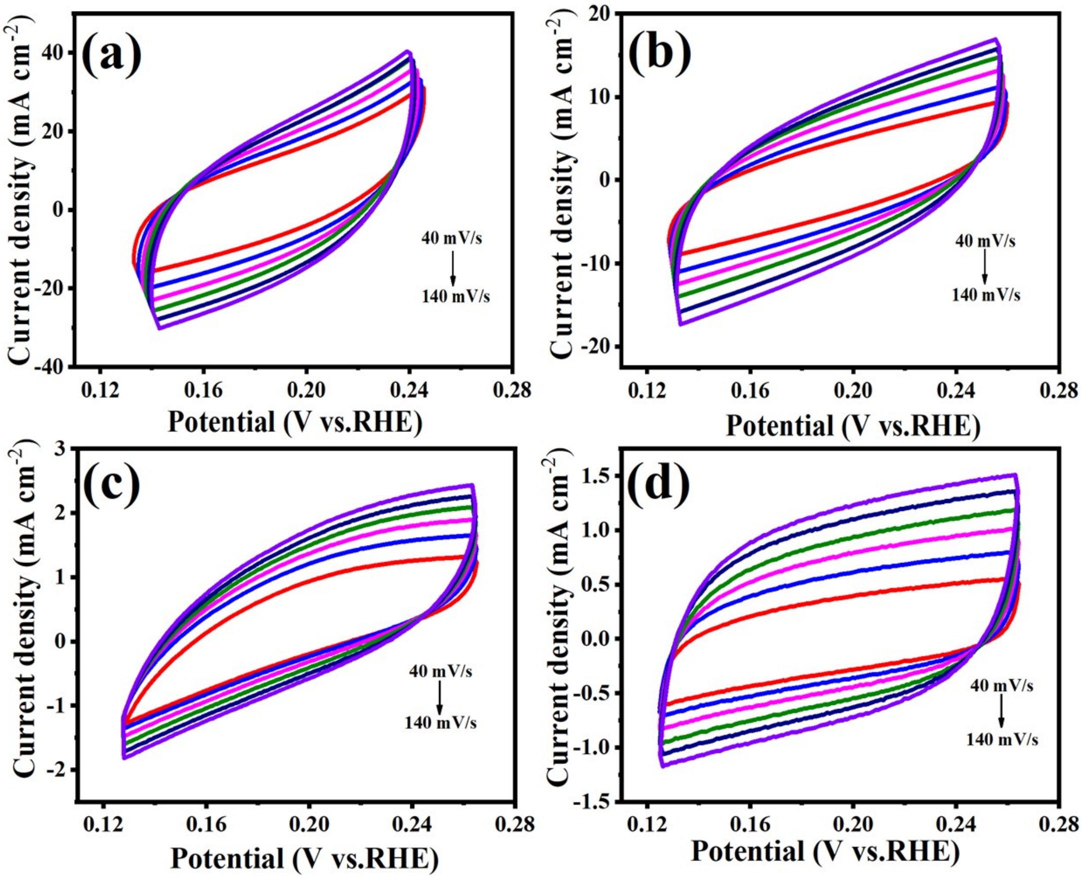


Fig. S9. CV curves of (a) Ni-P/NiSe$_x$/NF, (b) Ni-P/NF, (c) NiSe$_x$/NF, (d) NF in the non-faradaic region with different scanning rates from 40 to 140 mV·s^{-1}.

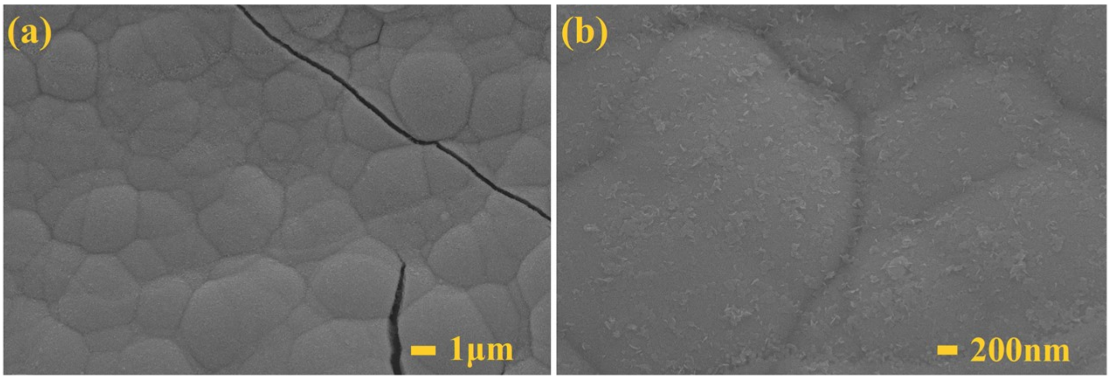
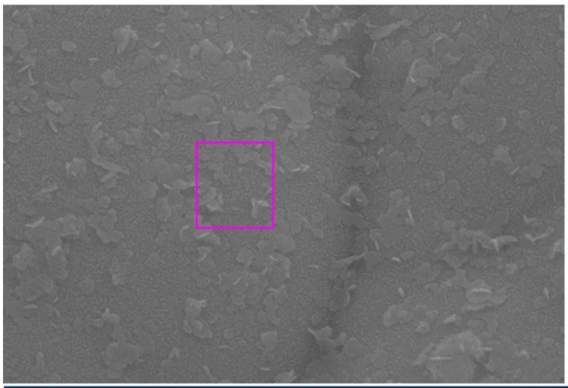


Fig. S10. Representative SEM images of the Ni-P/NiSe$_x$/NF catalyst after continuous 100 h for HER.



Element	Atomic %
Ni	56.07
P	1.02
Se	42.91
total	100

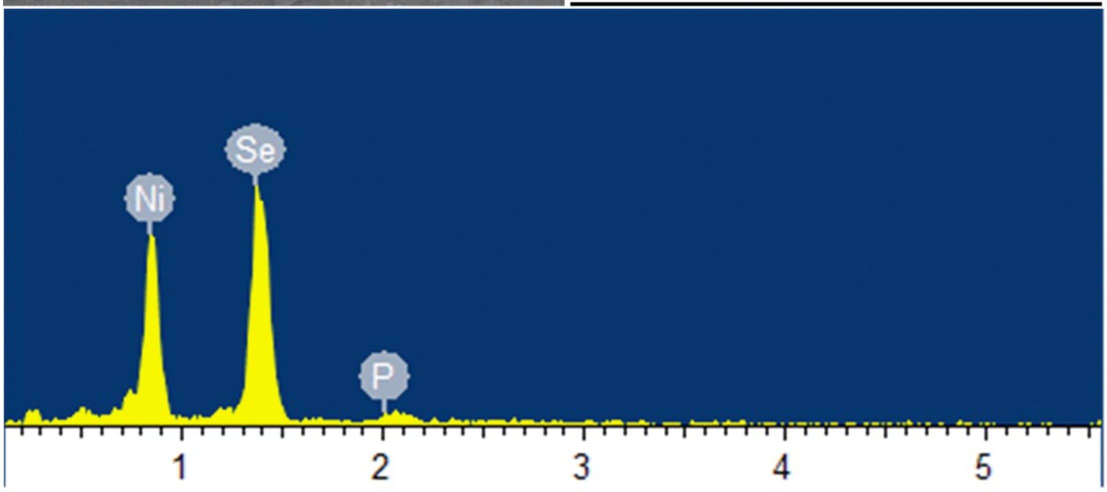


Fig. S11. Corresponding EDX plot of the Ni-P/NiSe$_x$/NF catalyst after continuous 100 h for HER.

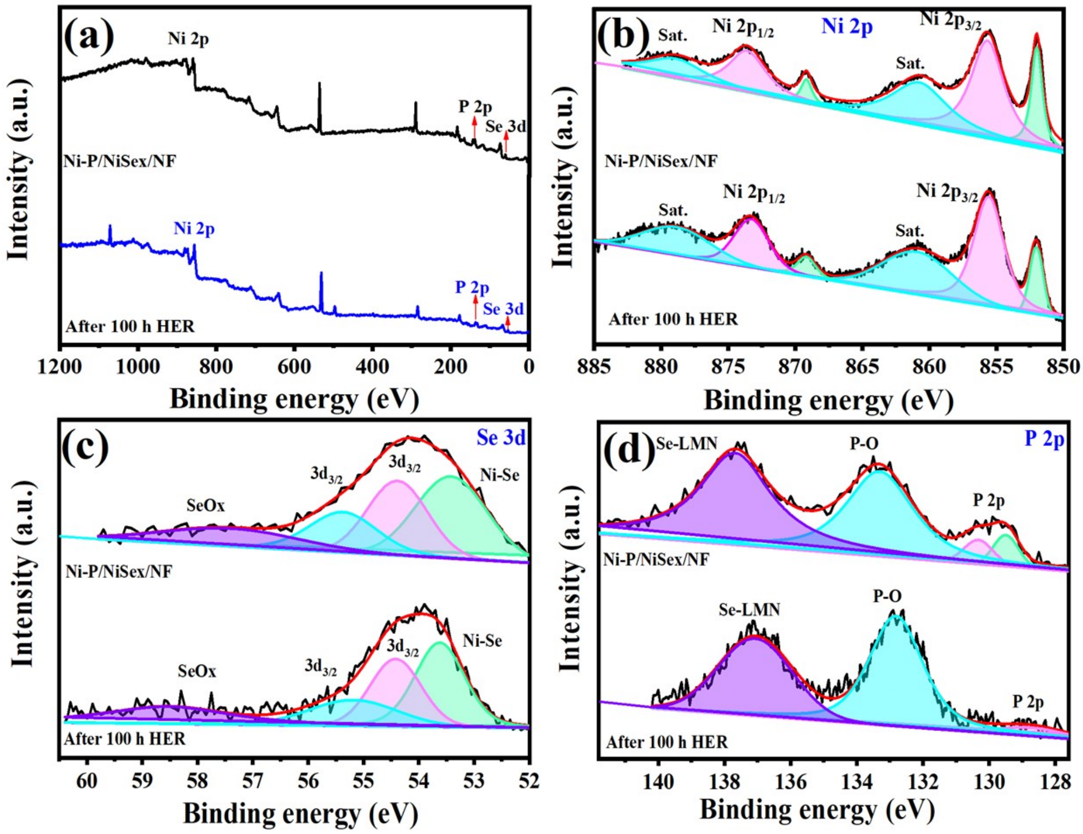


Fig. S12. (a) XPS full survey spectrum of Ni-P/$NiSe_x$/NF after HER electrolysis. High-resolution XPS spectrum: (b) Ni 2p, (c) Se 3d, and (d) P 2p.

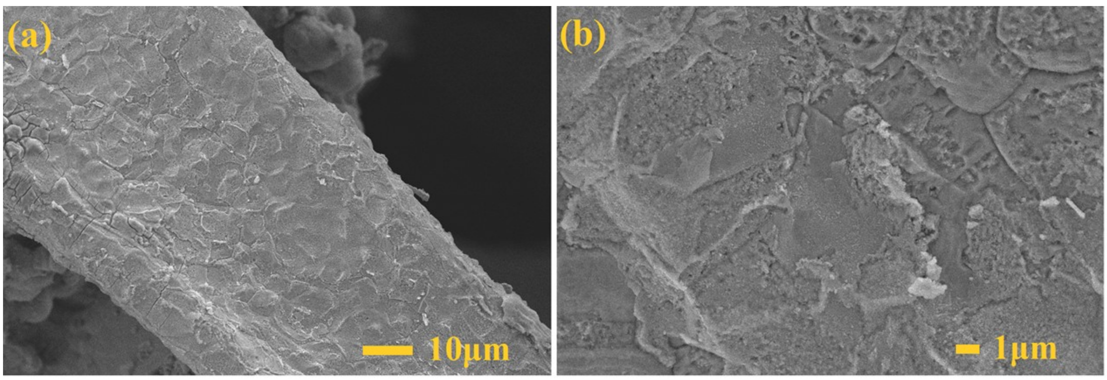
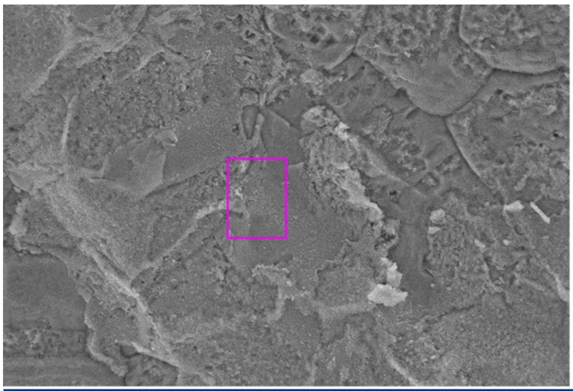


Fig. S13. Representative SEM images of the Ni-P/$NiSe_x$/NF catalyst after continuous 100 h for OER.



Element	Atomic %
Ni	71.50
P	0.95
Se	27.55
total	100

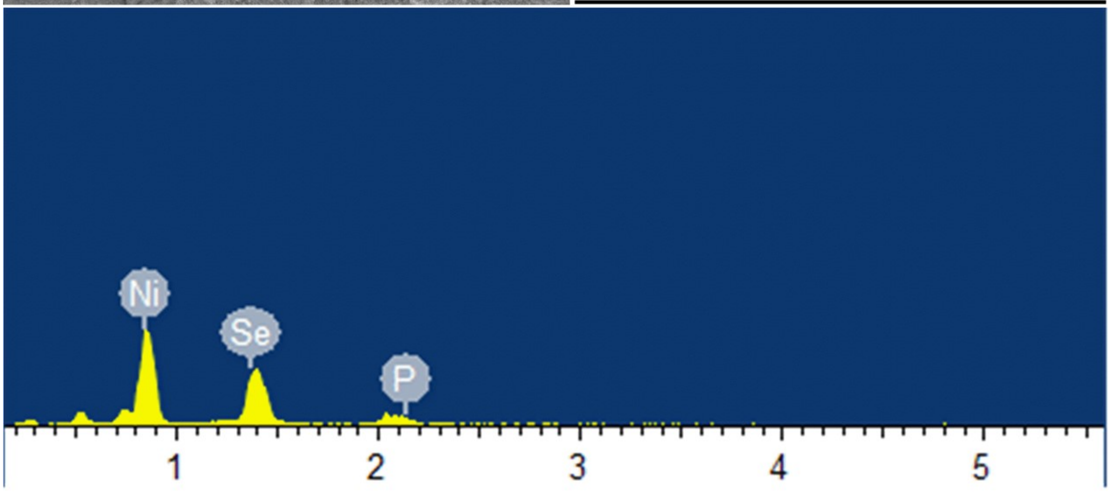


Fig. S14. Corresponding EDX plot of the Ni-P/$NiSe_x$/NF catalyst after continuous 100 h for OER.

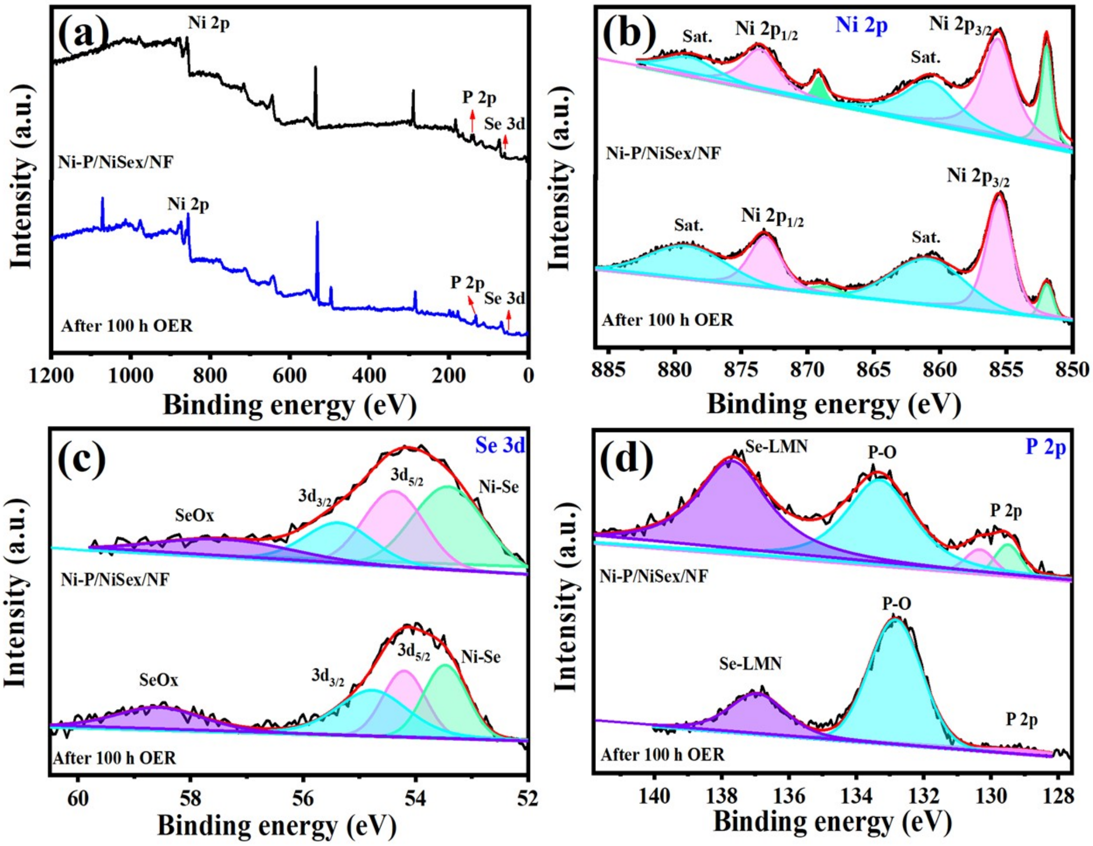


Fig. S15. (a) XPS full survey spectrum of Ni-P/$NiSe_x$/NF after OER test. High-resolution XPS spectrum: (b) Ni 2p, (c) Se 3d, and (d) P 2p.

Table. S1. Comparisons of HER catalytic activity of Ni-P/$NiSe_x$/NF with some previous reported catalysts in 1 mol/L KOH solution.

Material	Substrate	Overpotential HER@ $10mAcm^{-2}$	Overpotential HER@ $100mA\ cm^{-2}$	Reference
Ni-P/$NiSe_x$	Ni foam	98	165	This work
$Co_{0.85}Se$|P	Graphene	150	180 @$20mAcm^{-2}$	Adv. Mater 2017, 29,1701589[1]
Ni_3Se_2	Ni foam	203	279	Nano Energy 2016, 24,103[2]
$MoSe_2$@$Ni_{0.85}Se$	Ni foam	117	204	Electrochim. Acta 2017, 712[3]
$NiSe_2$@NiO_x	Glassy	132	-	

	carbon			Small 2017, 13, 1701487[4]
Fe,Co-$NiSe_2$	carbon fiber cloth	92	245 @200mAcm^{-2}	Adv. Mater. 2018, 30, 1802121[5]
NiSe	Ni foam	177	-	Adv. Energy Mater. 2018, 8, 1702704[6]
NiSe	Ni foam	96	270 @20mAcm^{-2}	Angew. Chem. Int. Edit. 2015,54, 9351[7]
Ni_2P	Glassy carbon	220	290	Energy Environ. Sci 2015,8, 2347[8]
Ni/Ni_8P_3	Ni foam	130	270 @30mAcm^{-2}	Adv. Funct. Mater. 2016, 26,3314[9]
NiSe-$Ni_{0.85}Se$	Carbon Paper	101	131	Small 2018, 14, 1800763[10]
CP@Ni-P	Carbon Fiber Paper	117	250	Adv. Funct. Mater. 2016, 26, 4067[11]
$Ni_{90}P_{10}$	Ti plate	234	-	Chem. Commun. 2018, 54, 12408[12]
O_3-V_{10}-Ni_2P	Glassy carbon	108	-	Nano Energy 2018,54,82[13]
EG/Ni_3Se_2 /Co_9S_8	graphene foil	170 @20mAcm^{-2}	230 @50mAcm^{-2}	Nano Lett. 2017, 17, 4202[14]
o-$CoSe_2$|P	Glassy carbon	104	-	Nat. Commun. 2018, 9, 2533[15]
$NixCo_3{-}xS_4$/ Ni_3S_2	Ni foam	136	258	Nano Energy 2017,35,161[16]
Mo_2C	Ni foam	130	215	Electrochim. Acta 2019,298, 305[17]

$Co_{0.9}Fe_{0.1}$-Se	Ni foam	125	229	J. Energy Chem. 2021,60,194 201[18]
NiSe/RGO	Ni mesh	102	-	J. Mater. Chem. A 2016,4,14789[19]
$NiSe_2$	Ti foam	100	-	Nanoscale 2016,8,3911-3915[20]
$NiSe_2$ nanoparticles	Glassy carbon	190	-	ACS Appl. Mater. Inter. 2016,8,5327-5334[21]
$Fe_{7.4\%}$-NiSe	Ni foam	163	265	J. Mater. Chem. A 2019,**7**,2233-2241[22]

Table. S2. Comparison of OER catalytic performance of Ni-P/$NiSe_x$/NF with other recently reported non-precious metal electrocatalysts in 1 mol/L KOH solution.

Catalyst	**Substrate**	**Overpotential (mV) @ 100 mA·cm^{-2}**	**Reference**
Ni-P/$NiSe_x$	Ni foam	320	This work
$Co_{0.9}Fe_{0.1}$-Se	Ni foam	287	J. Energy Chem. 2021,60,194-201
Co_2P/CoNPC	Glassy carbon	326@10	Adv. Mater. 2020,32,2003649.
O-CoP	Glassy carbon	310@10	Adv. Funct. Mater. 2020,30,1905252.
$NiSe_2$	Ti foam	295@20	ACS Appl. Mater. Inter. 2016,8,4718
Co-NiSe	Ni foam	330@50	ACS Sustainable Chem. Eng. 2019,7,19257-19267
Co_9S_8@NiCo-LDH	Ni foam	330	Sci. Bull. 2019,64 (3),158-165
$Co_{0.13}Ni_{0.87}Se_2$	Ti foam	320	Nanoscale 2016;8:3911-3915

P-NiS$_2$-500	Ni foam	350	Chem. Eng. J. 2021,420,127630
Ni$_3$Se$_2$ nanoforest	Ni foam	353	Nano Energy, 2016,24,103-110
NiSe nanowire film	Ni foam	270@20	Angew. Chem. Int. Ed. 2015,54,9351-9355
Ni$_x$P$_y$	Carbon fiber paper	320@10	ACS Appl. Mater. Inter. 2016,8,10826-10834
NiP	Ni foam	350@50	J. Energy Chem. 2017,26,1196-1202

Table S3. Comparison cell voltage of hierarchical Ni-P/NiSe$_x$/NF with other bifunctional electrocatalysts in 1 mol/L KOH solution.

Catalyst	**Substrate**	**cell voltage (V) @ j=10 mA·cm^{-2}**	**Reference**
Ni-P/NiSe$_x$	Ni foam	1.536	This work
NiSe-Ni0.85Se	Carbon fiber paper	1.62	Small 2018,14,1800763
Co$_{0.85}$Se/FeNi-LDH	Graphene foil	1.67	Energ. Environ. Sci., 2016,9(2),478-483
NiCo$_2$S$_4$/NiFe-LDH	Ni foam	1.60	ACS Appl. Mater. Inter. 2017,9(18),15364-15372
Co$_{0.9}$Fe$_{0.1}$-Se	Ni foam	1.55	J. Energy Chem. 2021,60,194-201
Co$_3$S$_4$@NiCo-LDH	Ni foam	1.59	New J. Chem. 2021,45,15429
Co$_{0.75}$Ni$_{0.25}$Se	Ni foam	1.60	Nanoscale 2019,11,7959-7966
NiCoSe$_2$	Carbon cloth	1.62	J. Mater. Chem. A 2018,6,17353-17360
Ni$_8$P$_3$	Ni foam	1.61	J. Am. Chem. Soc. 2016,26,3314-3323
Ni$_2$P	Glassy carbon	1.63	Energy Environ. Sci. 2015,8,2347-2351
NiP	Ni foam	1.63	J. Energy Chem. 2017,26,1196-1202
Porous Co$_{0.75}$Ni$_{0.25}$(OH)$_2$ nanosheets	Carbon fiber paper	1.56	Small 2019,15,1804832

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