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Supporting Information (SI):

# Tuning coupling interface of ultrathin $Ni_3S_2$@NiV-LDH heterogeneous nanosheet electrocatalysts for improved overall water splitting

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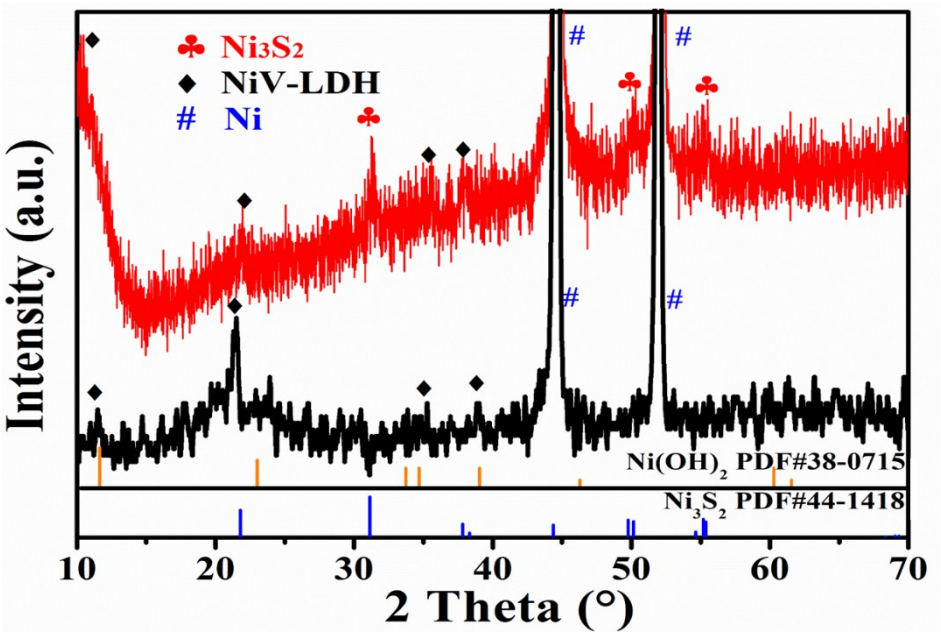


**Fig. S1** XRD patterns of NiV-LDH/NF and $Ni_3S_2$@NiV-LDH/NF.

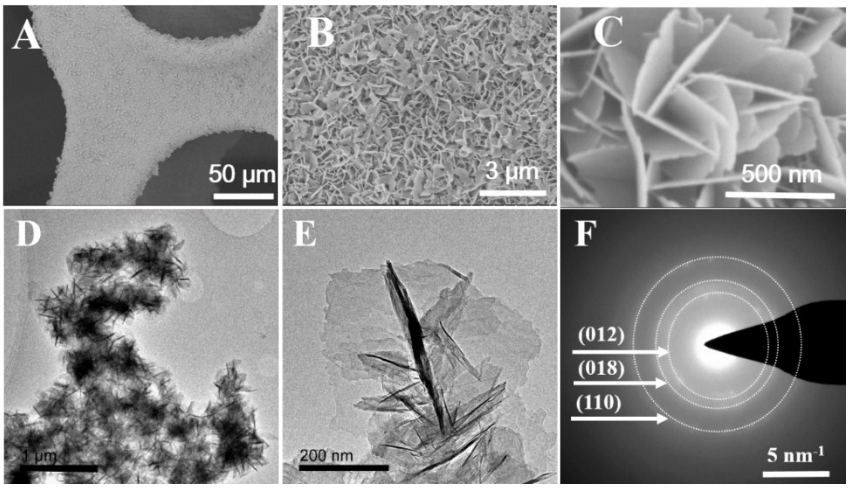


**Fig. S2** (A-C) FESEM images of the NiV-LDH/NF; (D)(E) TEM images of the NiV-LDH/NF architecture;(F)Selected area electron diffraction pattern.

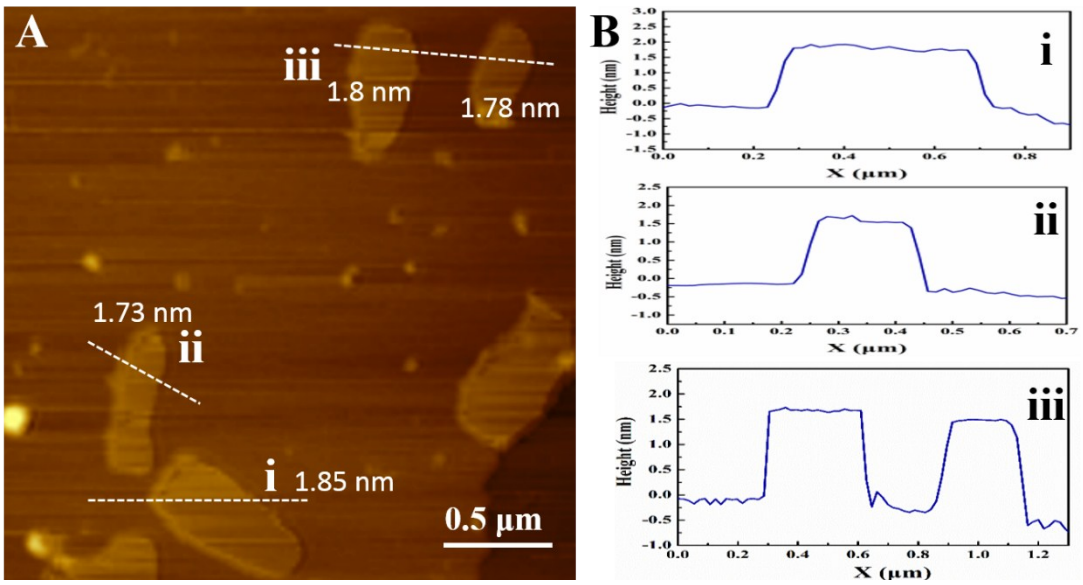


**Fig. S3** AFM image and the height profile of $Ni_3S_2$@NiV-LDH nanosheets.

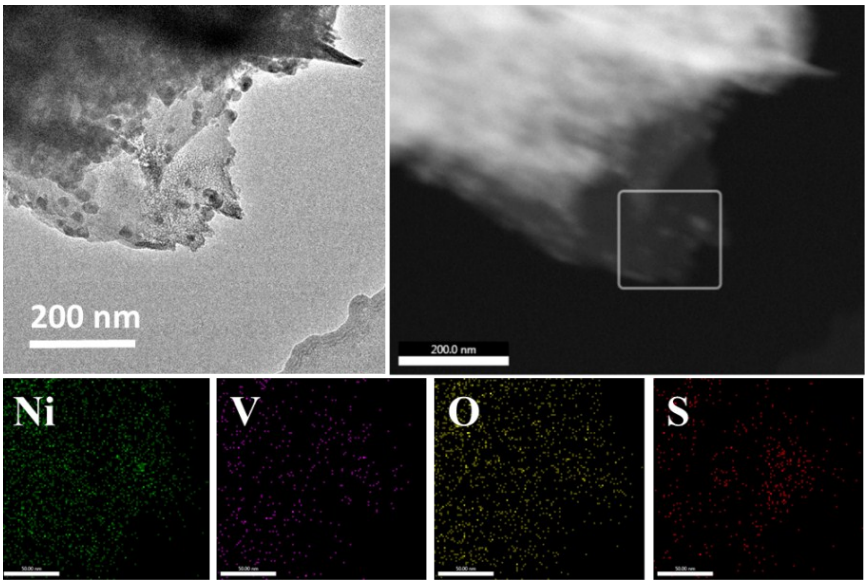


**Fig. S4** HAADF-STEM image and elemental mapping of Ni, V, O and S of $Ni_3S_2$@NiV-LDH nanosheet.

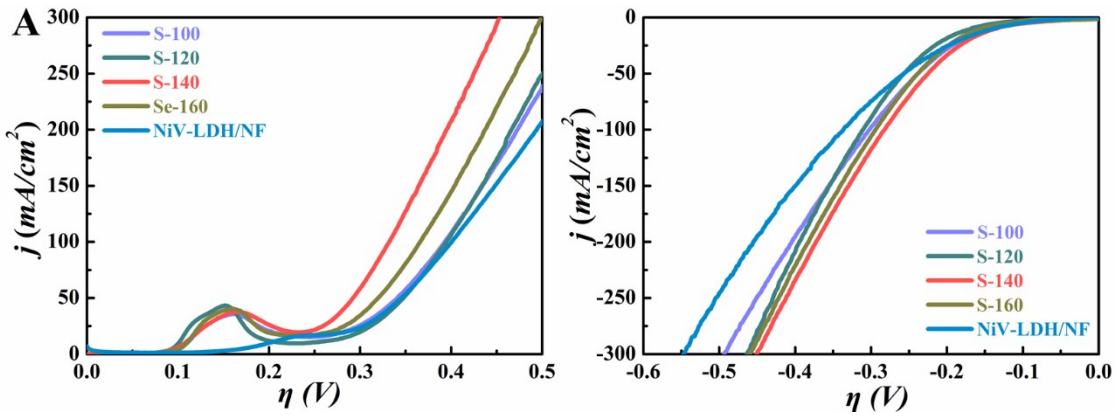


**Fig. S5**(A)OER and (B)HER polarization curves of NiV-LDH/NF and $Ni_3S_2$@NiV-LDH/NF at different reaction temperatures.

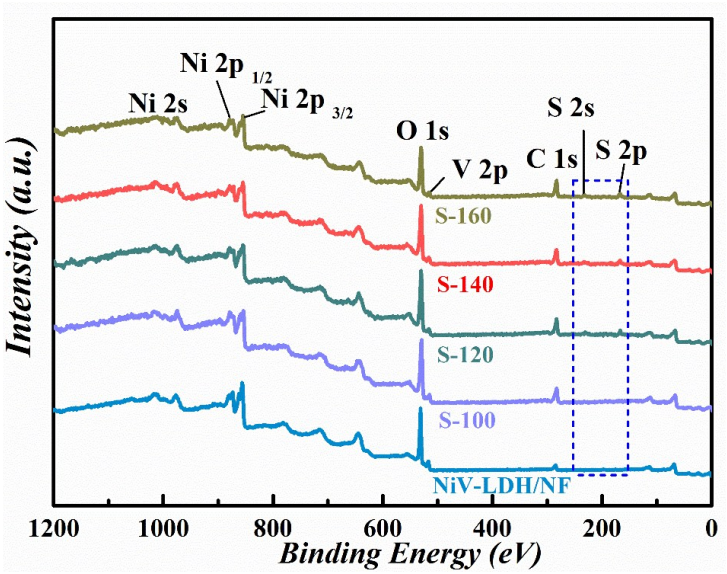


**Fig. S6** The survey spectra of the five samples (S-100, S-120, S-140, S-160 and NiV-LDH/NF).

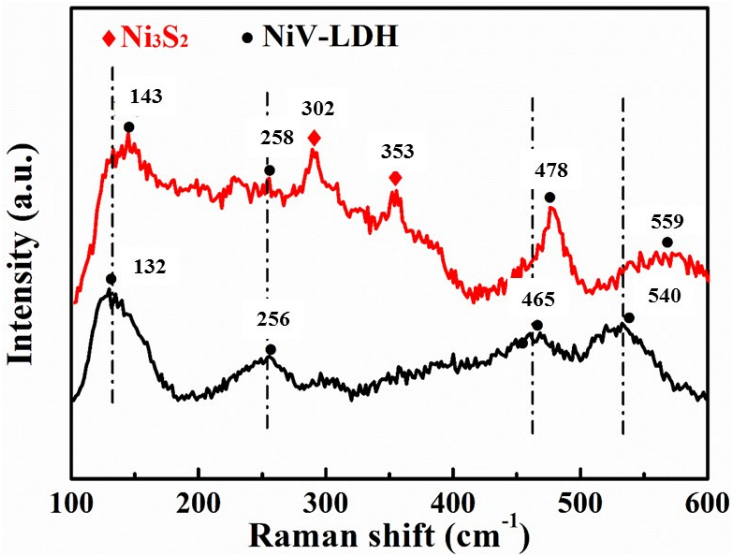


**Fig. S7.** Raman spectra of NiV-LDH/NF and $Ni_3S_2$@NiV-LDH/NF.

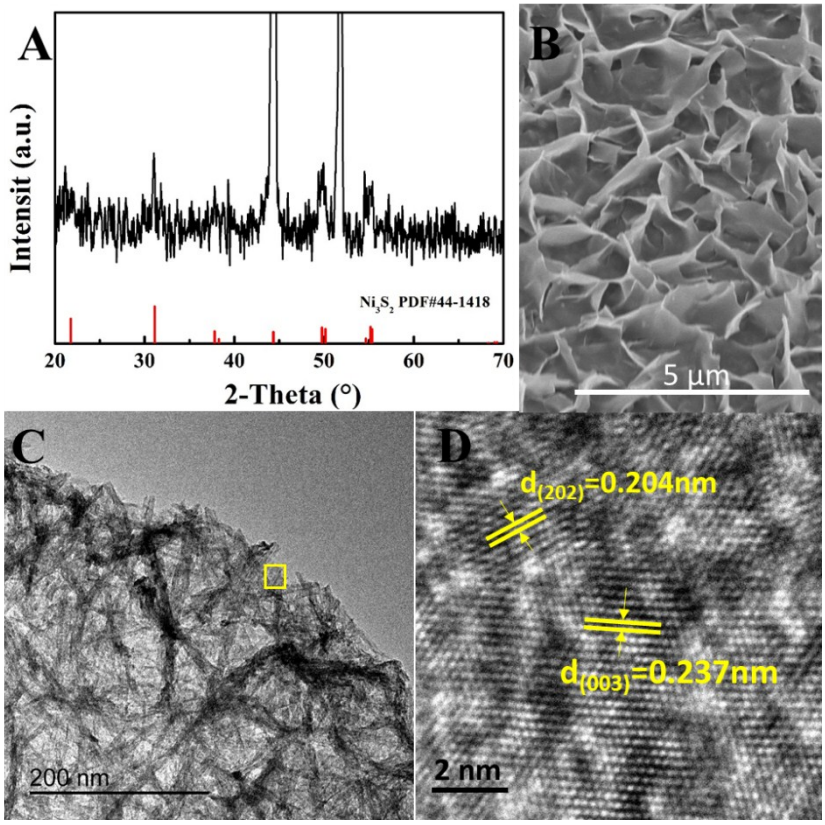


**Fig. S8** (A)XRD; (B) SEM; (C) TEM and (D) the high-resolution TEM images of $Ni_3S_2$/NF.

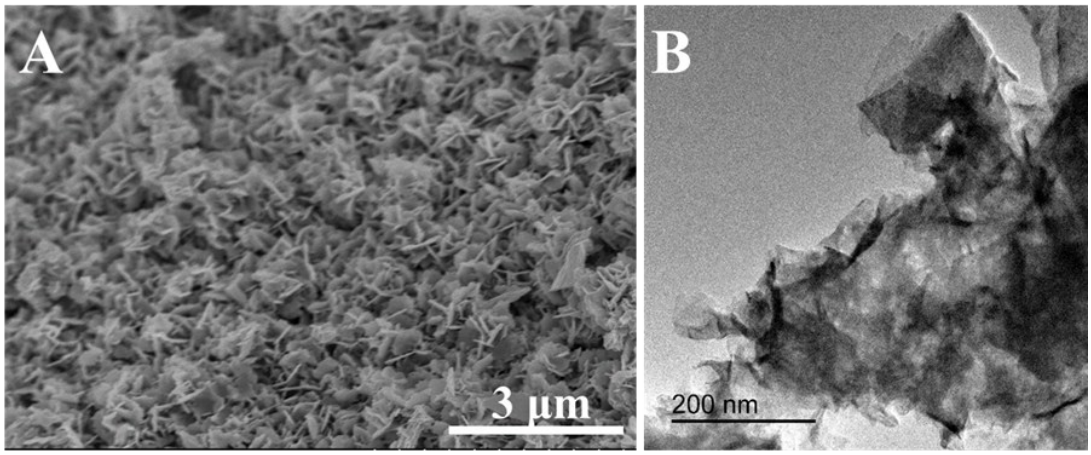


**Fig. S9** (A)SEM image and (B) TEM image of $Ni_3S_2$@NiV-LDH /NF after 100h OER electrocatalysis.

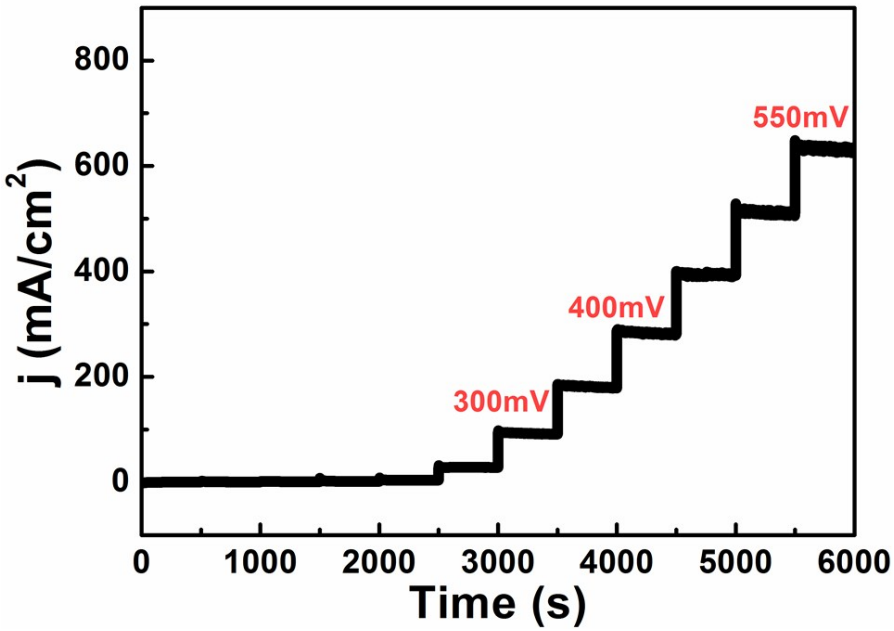


**Fig. S10** Multi-step chronoamperometric curve of OER over $Ni_3S_2$@NiV-LDH/NF in 1.0 M KOH.

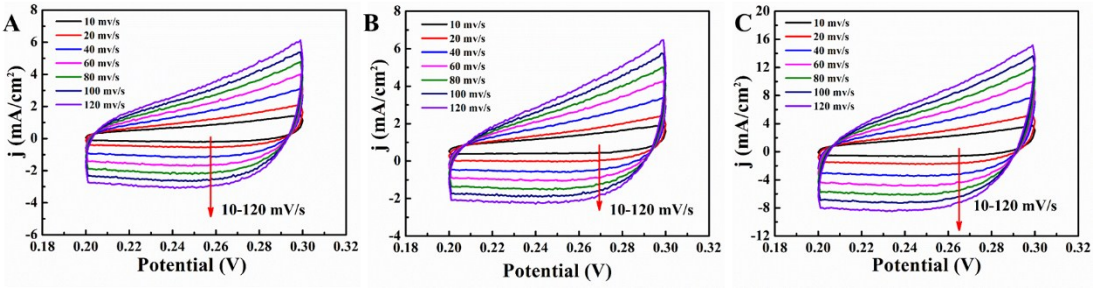


**Fig. S11** CV curves of (A)NiV-LDH/NF; (B)$Ni_3S_2$/NF and (C)$Ni_3S_2$@NiV-LDH/NF at different scan rates.

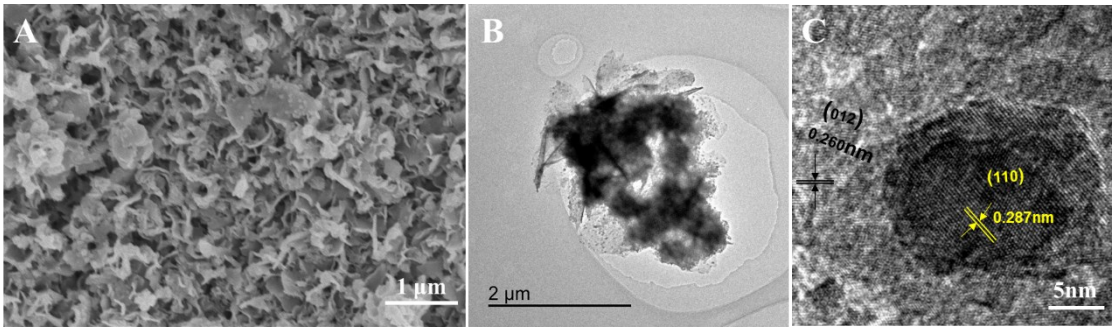


**Fig. S12** (A)SEM image; (B) TEM image and (C) the high-resolution TEM image of $Ni_3S_2$@NiV-LDH /NF after 100h HER electrocatalysis.

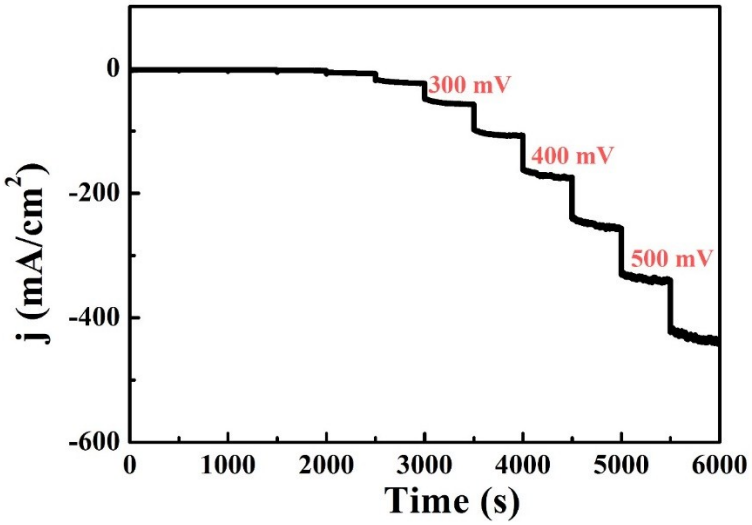


**Fig. S13** Multi-step chronoamperometric curve of HER over $Ni_3S_2$@NiV-LDH/NF in 1.0 M KOH.

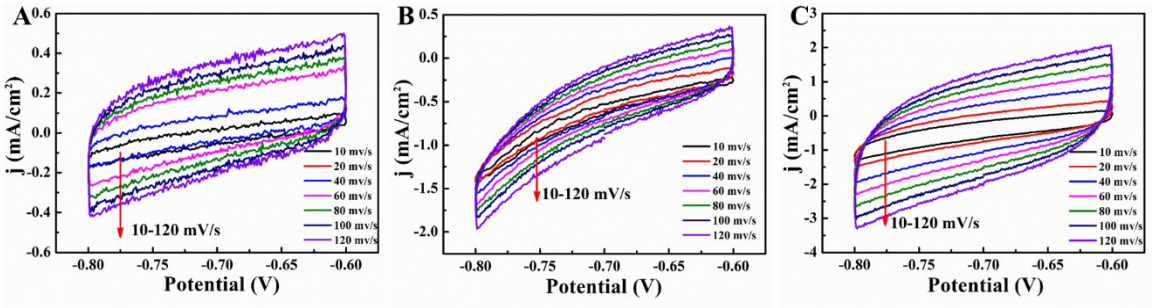


**Fig. S14** CV curves of (A)NiV-LDH/NF; (B)$Ni_3S_2$/NF and (V)$Ni_3S_2$@NiV-LDH/NF at different scan rates.

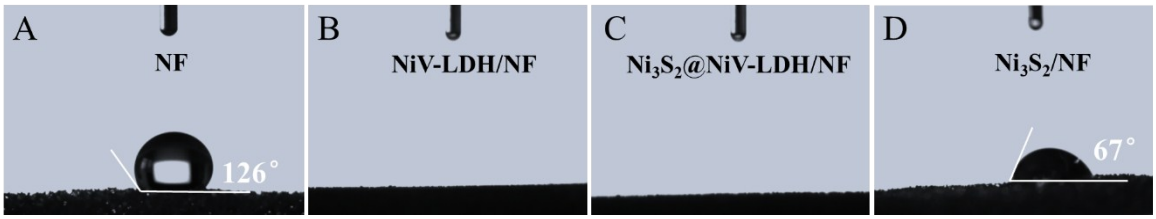


**Fig. S15** Contact angle measurements of different samples. (A) Ni foam; (B) NiV-LDH/NF; (C)$Ni_3S_2$@NiV-LDH/NF and (D)$Ni_3S_2$/NF.

**Table S1. Comparison of the electrocatalytic performance of $Ni_3S_2$@NiV-LDH/NF with other OER catalysts reported recently**

| Catalyst | Electrolyte solution | OER Overpotential for 100 mA/cm$^2$(mV) | Stability test | mass loading (mg cm$^{-2}$) | Reference |
|---|---|---|---|---|---|
| $Ni_3S_2$@NiV-LDH/NF | 1 M KOH | 320 | 100 | 0.71 | This work |
| NiFe LDH@ NiCoP/NF | 1 M KOH | 350 | 100 | 2 | Adv. Funct. Mater. 2018, 28, 1706847 |
| $Co(OH)_2$@NCNTs @NF | 1 M KOH | 400 | >200 | 0.72 | Nano Energy, 2018, 47, 96-104 |
| $NiCo_2S_4$@ NiFe LDH/NF | 1 M KOH | 230 | 10h | / | ACS Appl. Mater. Interfaces, 2017, 9 , 15364-15372 |
| $Co_1Mn_1$CH/NF | 1 M KOH | 340 | 18 | 5.6 | J. Am. Chem. Soc. 2017, 139, 8320−8328 |
| $Ni(OH)_2/Ni_3S_2$/NF | 1 M KOH | 490 | 10 | / | J. Mater. Chem. A, 2018, 6, 6938-6946 |
| $NiS/NiS_2$/CC | 1 M KOH | 416 | 24 | 2.4 | J. Mater. Chem. A, 2018, 6, 8233-8237 |
| $Ni_2P$@NiFe/NF | 1 M KOH | 230 | 25 | 1.0 | Chem. Sci., 2018,9, 1375-1384 |
| NiFe-LDH/ $NiCo_2O_4$/NF | 1 M KOH | 390 | 10 | 4.9 | Acs Appl. Mater. Interfaces, 2017, 9, 1488−1495 |
| CoNiP @ NiFe-LDH/NF | 1 M KOH | 230 | 500 | / | ACS Appl. Energy Mater., 2018, 1, 623–631 |
| $NiFe_2O_4$/NiFe LDH/NF | 1 M KOH | 213 | 20 | 2.8 | ACS Appl. Mater. Interfaces, 2018, 10, 26283–26292 |
| $Ni_xCo_{3-x}S_4$/ $Ni_3S_2$/NF | 1 M KOH | 330 | 30 | 0.56 | Nano Energy 2017, 35, 161-170 |
| $Ni_2P/Ni_3S_2$/NF | 1 M KOH | 330 | 24 | / | Nano Energy, 2018, 51, 26-36 |
| $CoSx/Ni_3S_2$@NF | 1 M KOH | 373 | 20 | 2.83 | ACS Appl. Mater. Interfaces, 2018, 10, 27712–27722 |
| $MoS_2$-$Ni_3S_2$ HNRs/NF | 1 M KOH | 340 | 48 | 13 | ACS Catal., 2017, 7, 2357–2366 |

| | | | | | |
|---|---|---|---|---|---|
| **Mo-W-S-2@$Ni_3S_2$/NF** | **1 M KOH** | **＞370** | **50** | **/** | **ACS Appl. Mater. Interfaces, 2017, 9, 26066–26076** |
| **NiS/$NiS_2$/CC** | **1 M KOH** | **416** | **24** | **2.4** | **J. Mater. Chem. A, 2018, 6, 8233-8237** |

**Table S2. Comparison of the electrocatalytic performance of $Ni_3S_2$/NiV-LDH/NF with other HER catalysts reported recently**

| Catalyst | HER Overpotential for 10 mA/cm$^2$(mV) | Electrolyte solution | Stability test (h) | mass loading (mg/cm$^2$) | Reference |
|---|---|---|---|---|---|
| $Ni_3S_2$@NiV-LDH/NF | 126 | 1 M KOH | 100 | 0.71 | This work |
| NiFe LDH@ NiCoP/NF | 120 | 1 M KOH | 100 | 2 | Adv. Funct. Mater. 2018, 28, 1706847 |
| $Co_5Mo_{1.0}P$ NSs@NF | 173 | 0.5 M $H_2SO_4$ | 20 | / | Nano Energy, 2018, 45, 448-455 |
| $NiS_2/MoS_2$HNW | 204 | 1 M KOH | 6 | / | ACS Catal. 2017, 7, 6179−6187 |
| $Co(OH)_2$@NCNTs @NF | 170 | 1 M KOH | 600 | 0.72 | Nano Energy, 2018, 47, 96-104 |
| Cu@CoFe-LDH/Cu | 171 | 1 M KOH | 48 | 1.8 | Nano Energy, 2017, 41, 327–336 |
| $Co_5Mo_{1.0}P$ NSs@NF | 173 | 0.5 M $H_2SO_4$ | 20 | / | Nano Energy, 2018, 45, 448-455 |
| $Ni_2P$@NiFe/NF | 75 | 1 M KOH | 25 | 1.0 | Chem. Sci., 2018,9, 1375-1384 |
| $NiCo_2S_4$@ NiFe LDH/NF | 200 | 1 M KOH | 10 | / | ACS Appl. Mater. Interfaces 2017, 9, 15364−15372 |
| $Ni(OH)_2/Ni_3S_2$/NF | 150 | 1 M KOH | 10 | / | J. Mater. Chem. A, 2018,6, 6938-6946 |
| NiFeLDH/ $NiCo_2O_4$/NF | 192 | 1 M KOH | 10 | 4.9 | ACS Appl. Mater. Interfaces, 2017, 9, 1488−1495 |
| $NiFe_2O_4$/NiFe LDH/NF | 101 | 1 M KOH | 20 | 2.8 | ACS Appl. Mater. Interfaces, 2018, 10, 26283–26292 |
| $Ni_2P/Ni_3S_2$/NF | 80 | 1 M KOH | 24 | / | Nano Energy, 2018, 51, 26-36 |
| CoSx/$Ni_3S_2$@NF | 204 | 1 M KOH | 20 | 2.83 | ACS Appl. Mater. Interfaces, 2018, 10, 27712–27722 |
| $MoS_2$-$Ni_3S_2$ HNRs/NF | 98 | 1 M KOH | 48 | 13 | ACS Catal., 2017, 7, 2357–2366 |
| Mo-W-S-2@$Ni_3S_2$/NF | 98 | 1 M KOH | 50 | / | ACS Appl. Mater. Interfaces, 2017, 9 ,26066–26076 |

| | | | | | |
|---|---|---|---|---|---|
| **$MoS_2/Ni_3S_2$/NF** | **110** | **1 M KOH** | **10** | **9.7** | **Angewandte Chemie, 2016, 55, 6702-6707.** |
| **$Ni_xCo_{3-x}S_4$/ $Ni_3S_2$/NF** | **136** | **1 M KOH** | **50** | **0.56** | **Nano Energy 2017, 35, 161-170** |

**Table S3. Comparison of the electrocatalytic water splitting performance of $Ni_3S_2$@NiV-LDH/NF *vis-à-vis* heterostructured catalysts reported in alkaline media.**

| Catalyst | Electrolyte | η @10 mA $cm^{-2}$ (V) | Stability Test(h) | Reference |
|---|---|---|---|---|
| $Ni_3S_2$@NiV-LDH/NF | 1 M KOH | 1.54 | 160 | This work |
| NiFe LDH@ NiCoP/NF | 1 M KOH | 1.57 | 100 | Adv. Funct. Mater. 2018, 28, 1706847 |
| Cu@CoFe-LDH/Cu | 1 M KOH | 1.68 | 48 | Nano Energy, 2017, 41, 327–336 |
| $Ni_2P$@NiFe LDH/NF | 1 M KOH | 1.51 | 100 | Chem. Sci., 2018, 9, 1375-1384 |
| $NiCo_2S_4$@ NiFe LDH/NF | 1 M KOH | 1.60 | 12 | Acs Appl. Mater. Interfaces, 2017, 9, 15364-15372 |
| NiFe LDH/ $NiCo_2O_4$/NF | 1 M KOH | 1.60 | 12 | ACS Appl. Mater. Interfaces 2017, 9, 1488−1495 |
| $NiFe_2O_4$/NiFe LDH/NF | 1 M KOH | ~1.54 | 20 | ACS Appl. Mater. Interfaces, 2018, 10, 26283–26292 |
| $MoS_2/Ni_3S_2$/NF | 1 M KOH | 1.56 | 10 | Angewandte Chemie, 2016, 55, 6702-6707. |
| Ni $(OH)_2/Ni_3S_2$/NF | 1 M KOH | 1.57 | / | J. Mater. Chem. A, 2018, 6, 6938-6946 |
| $Ni_xCo_{3-x}S_4$/ $Ni_3S_2$/NF | 1 M KOH | 1.53 | ＞200 | Nano Energy 2017, 35, 161-170 |
| CoSx/$Ni_3S_2$@NF | 1 M KOH | ~1.57 | 30 | ACS Appl. Mater. Interfaces, 2018, 10, 27712–27722 |
| $MoS_2$-$Ni_3S_2$ HNRs/NF | 1 M KOH | 1.5 | 50 | ACS Catal., 2017, 7, 2357–2366 |
| Mo-W-S-2@$Ni_3S_2$/NF | 1 M KOH | 1.62 | 50 | ACS Appl. Mater. Interfaces, 2017, 9, 26066–26076 |
| $MoS_2/Ni_3S_2$/NF | 1 M KOH | 1.56 | 10 | Angewandte Chemie, 2016, 55, 6702-6707. |