Supporting Information (SI) *for*:

Generation of Ni_3S_2 nanorod arrays with high-density bridging S_2^{2-} by introducing a small amount of $Na_3VO_4 \cdot 12H_2O$ for superior hydrogen evolution reaction

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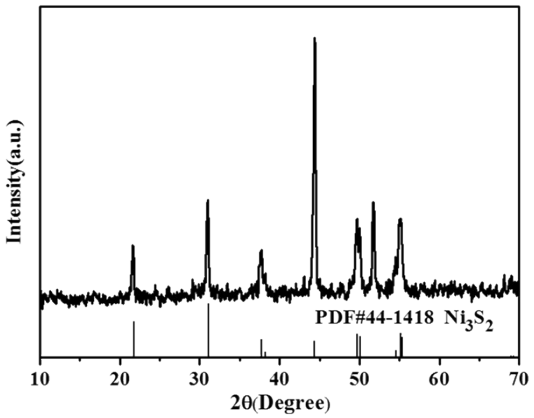


Fig. S1 XRD pattern of NS-film/NF.

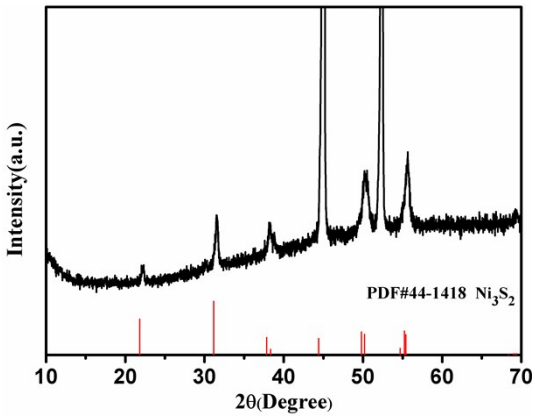


Fig. S2 XRD pattern of the control sample was prepared where the addition of $Na_3VO_4 \cdot 12H_2O$ was increased to 200 mg with keeping other experimental conditions unchanged.

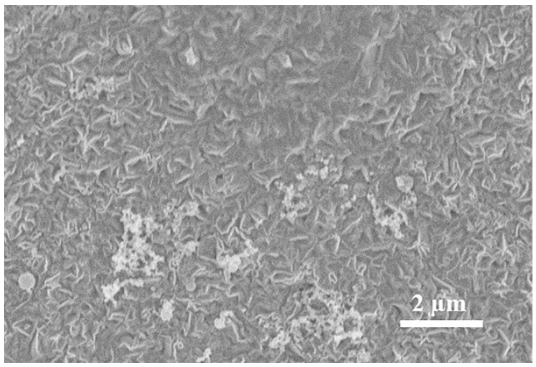


Fig. S3 SEM image of NS-film/NF.

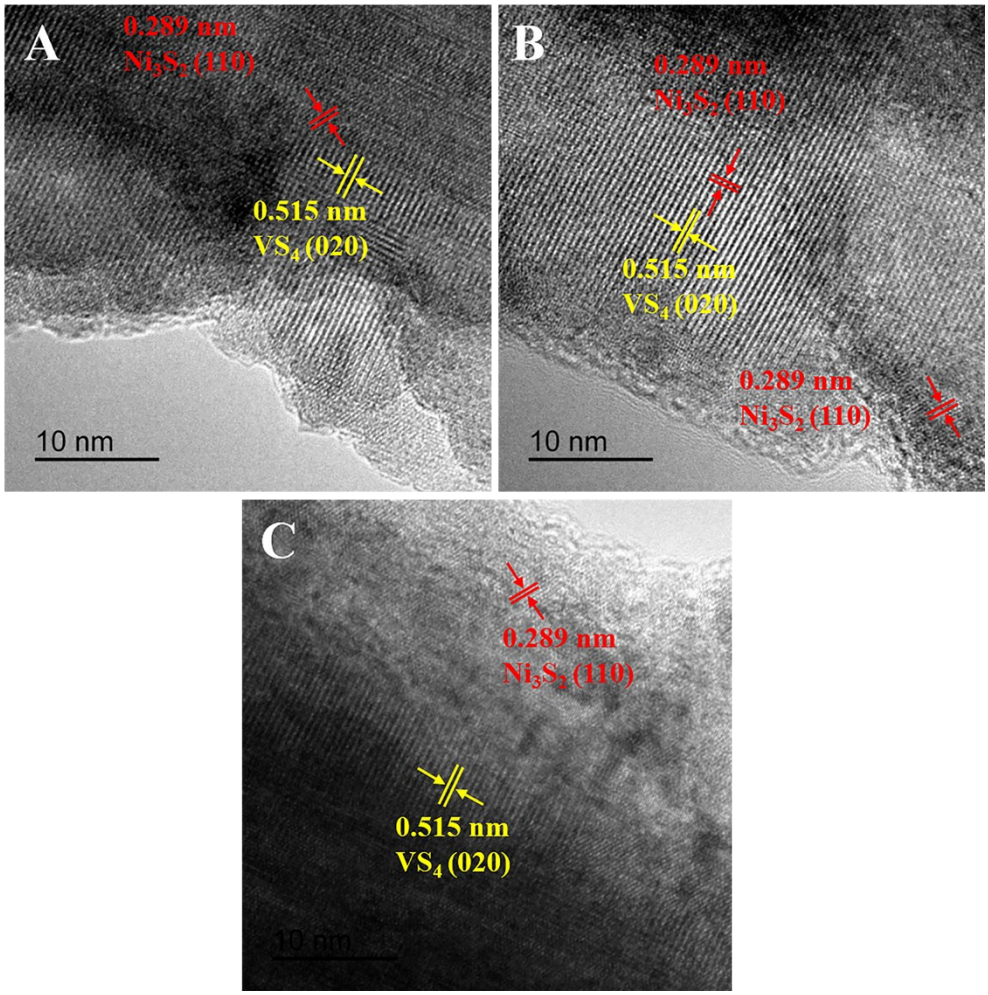


Fig. S4 HRTEM images of S_{hig}-NS-rod/NF.

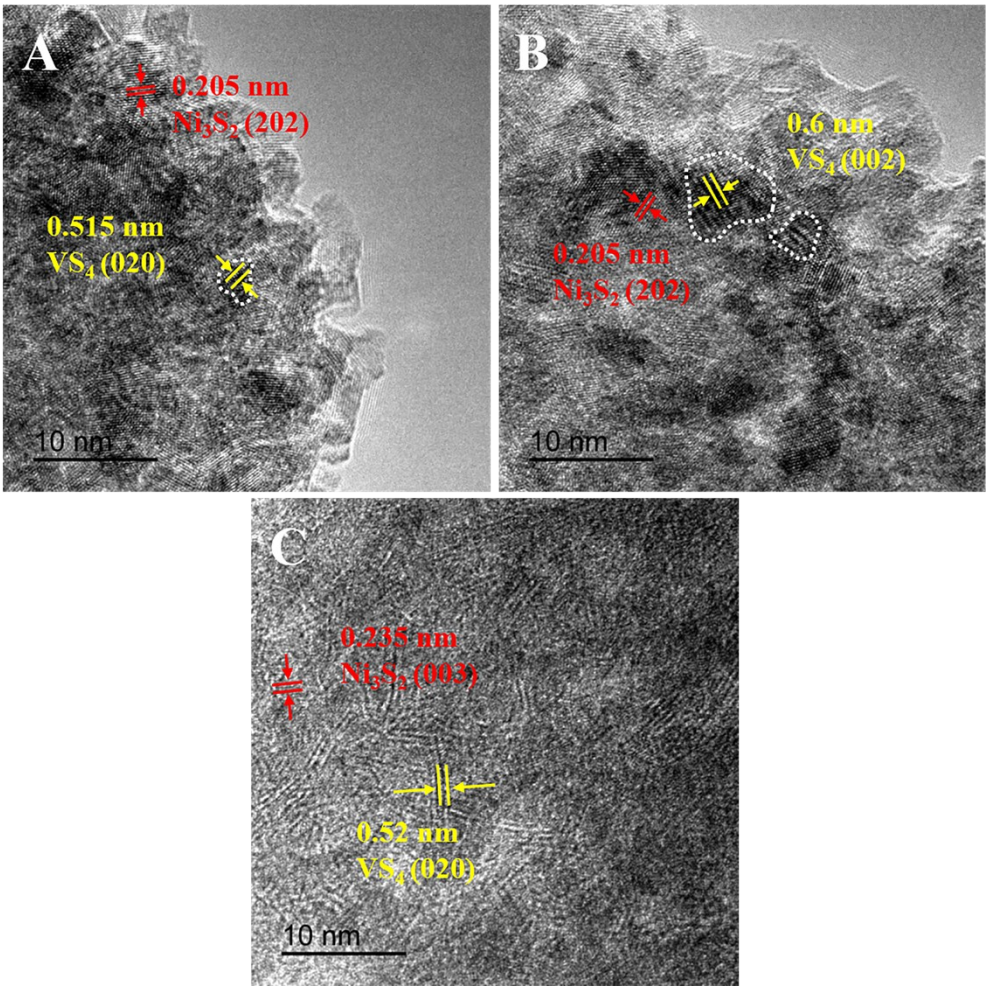


Fig. S5 HRTEM images of S_{low}-NS-rod/NF.

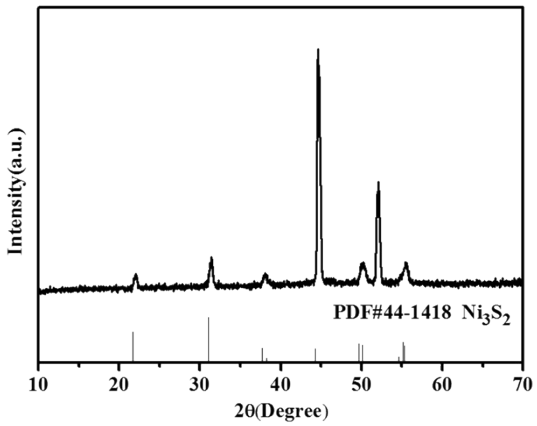
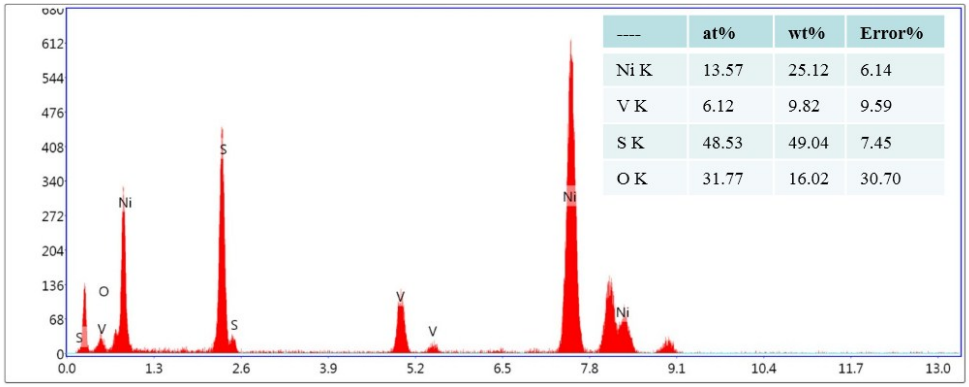


Fig. S6 XRD pattern of S_{low}-NS-rod/NF.



----	at%	wt%	Error%
Ni K	13.57	25.12	6.14
V K	6.12	9.82	9.59
S K	48.53	49.04	7.45
O K	31.77	16.02	30.70

Fig. S7 EDX spectrum of S_{hig}-NS-rod/NF.

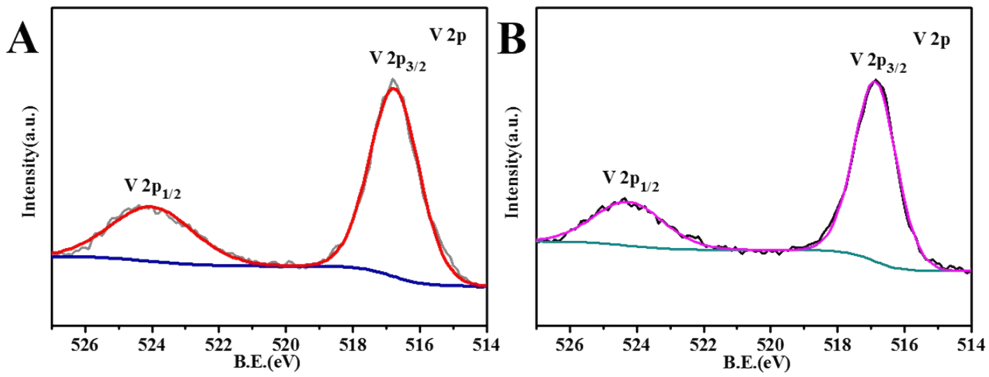


Fig. S8 High-resolution XPS spectra: V 2p of S_{hig}-NS-rod/NF (A) and S_{low}-NS-rod/NF (B).

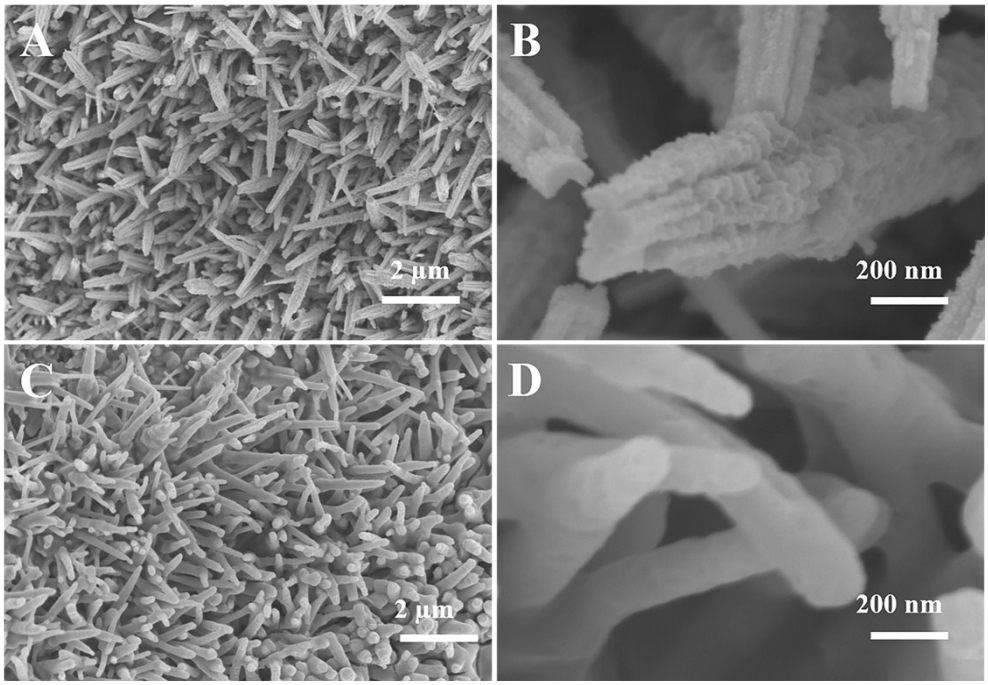


Fig. S9 SEM image of NS-rod/NF-100 (A, B) and NS-rod/NF-200 (C, D).

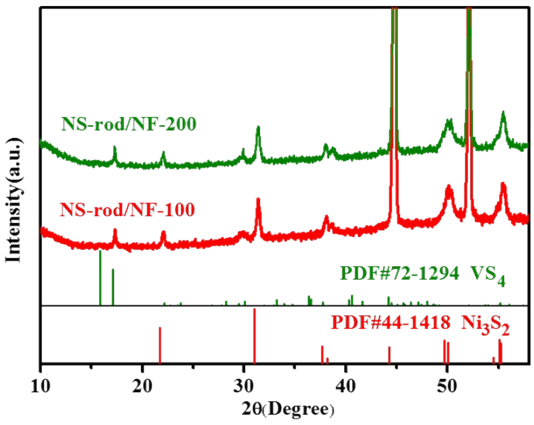


Fig. S10 XRD patterns of NS-rod/NF-100 and NS-rod/NF-200.

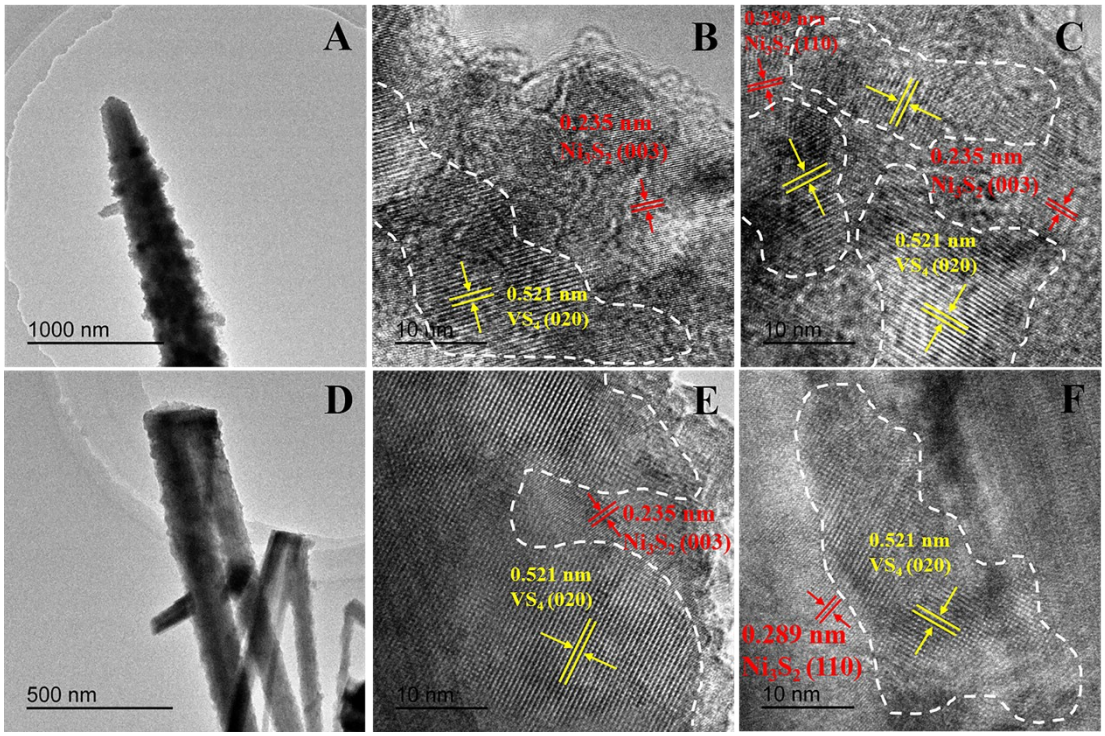


Fig. S11 TEM image and HRTEM patterns of NS-rod/NF-100 (A, B, C) and NS-rod/NF-200 (D, E, F).

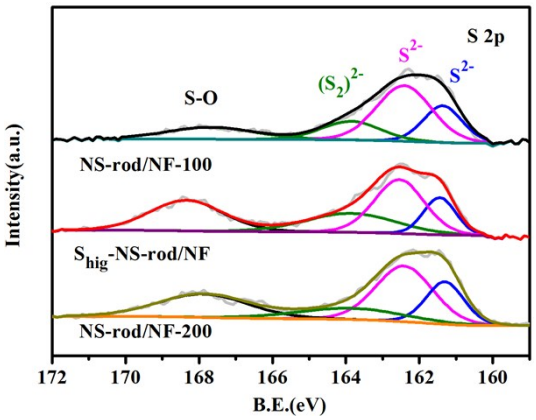


Fig. S12 High-resolution XPS spectra: S 2p of NS-rod/NF-100, S_{hig}-NS-rod/NF and NS-rod/NF-200.

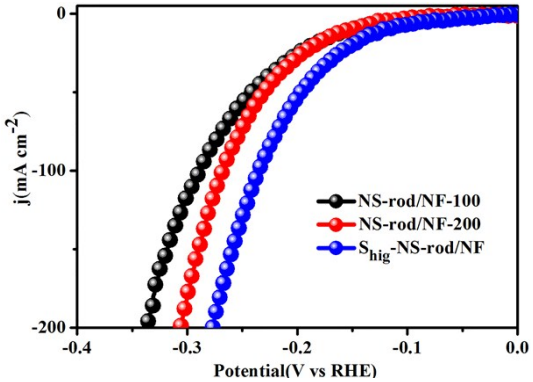


Fig. S13 LSV curves of NS-rod/NF-100, S_{hig}-NS-rod/NF and NS-rod/NF-200.

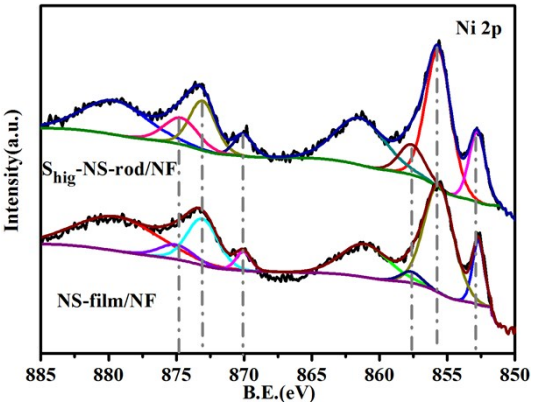


Fig. S14 High-resolution XPS spectra: Ni 2p of S_{hig}-NS-rod/NF and NS-film/NF.

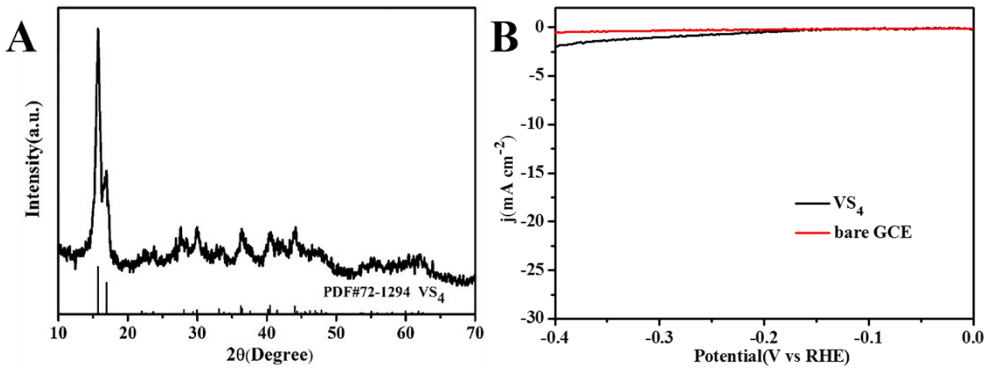


Fig. S15 (A) XRD pattern of pure VS_4, (B) The LSV curves for HER of pure VS_4 on GCE.

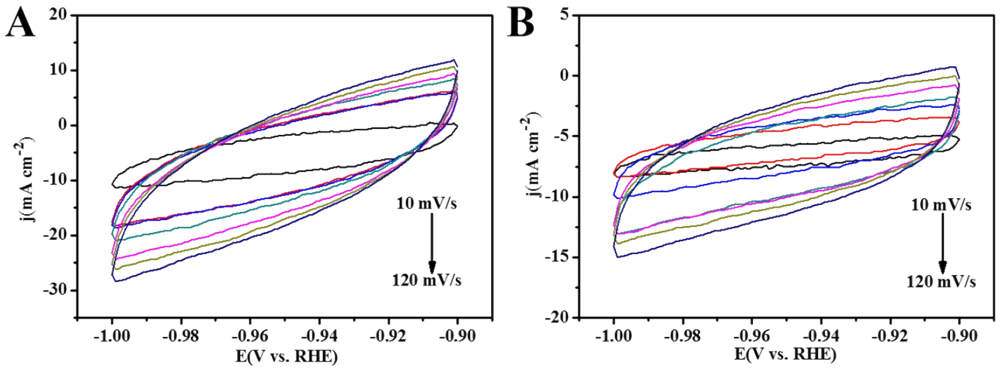


Fig. S16 CV curves of S_{hig}-NS-rod/NF (A) and S_{low}-NS-rod/NF (B).

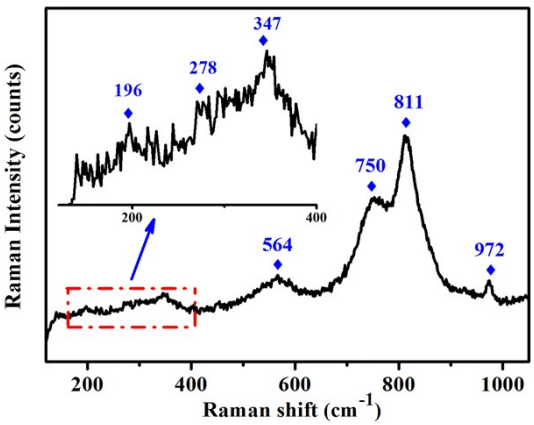


Fig. S17 Raman spectra of S_{hig}-NS-rod/NF after HER chronoamperometry test.

We very appreciate your valuable comments. We have carried out the Raman characterization of S_{hig}-NS-rod/NF after potentiostatic test. As shown in Fig. S17, one peak observed at 347 cm^{-1} can be assigned to Ni-S bond of Ni_3S_2[1], and the four weak peaks around 196 cm^{-1}, 278 cm^{-1}, 564 cm^{-1} and 972 cm^{-1} belong to the V-S bonds of VS_4[2,3]. Besides, the obvious peak located at 750 cm-1 can be attributable to the Ni-O bond of NiO [1,4], resulting from the oxidation of nickel sulfide during the HER test. Previous reports show that NiO is also a catalytically active material for the HER, so the electrocatalytic active sites are in the Ni_3S_2/NiO hybrid catalyst. Also, the peak at ~811 cm^{-1} corresponds to the asymmetric stretching υ_{as} (VO_4) vibration modes of the VO_4 groups [5], which could be originated from the unreacted sodium orthovanadate.

References:

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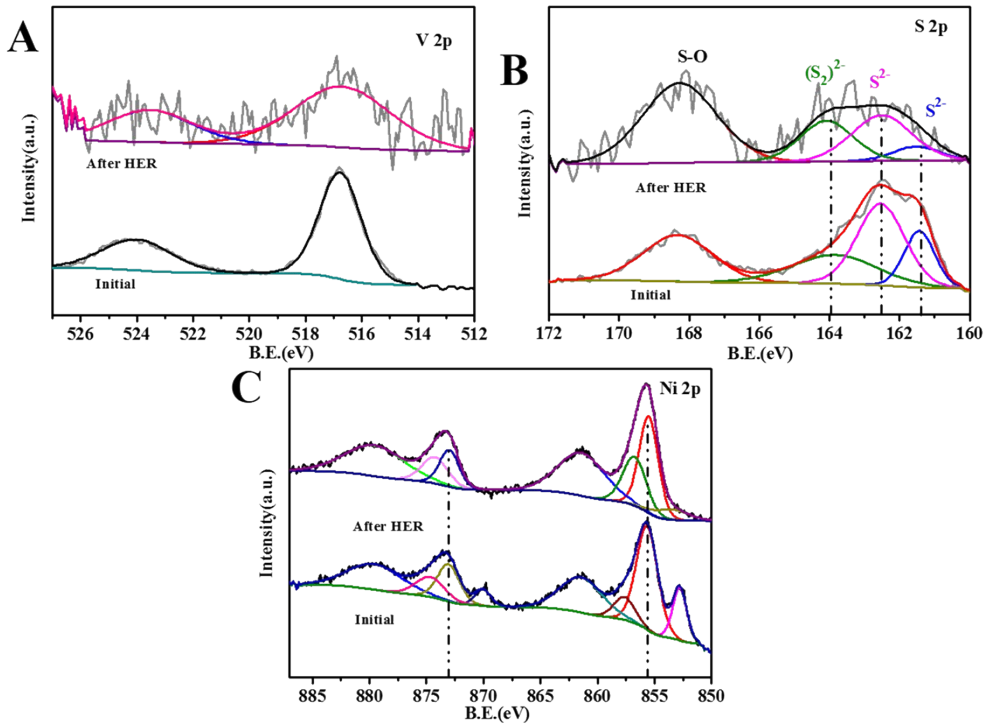

Fig. S18 XPS characterization of S_{hig}-NS-rod/NF before and after HER chronoamperometry test: (A) V 2p, (B) S 2p, (C) Ni 2p.

Table S1 The atomic percent contents of different S species investigated from X-ray photoelectron spectroscopy (XPS).

Products	S-O	$(S_2)^{2-}$	S^{2-}
S_{low}-NS-rod/NF	22.11%	16.45%	61.44%
NS-rod/NF-100	25.99 %	14.68%	59.33%
S_{hig}-NS-rod/NF	28.54%	21.66%	49.8%
NS-rod/NF-200	15.74%	16.48%	67.78%
$S_{hig,\ after\ HER}$-NS-rod/NF	51.55%	18.91%	29.54%

Table S2 Geometric values of electronic components extracted from the electrical equivalent circuit model.

Products	R_s (Ω)	Q_1 (Ss^{-n})	n	R_1(Ω)	Q_2(Ss^{-n})	n	R_2(Ω)
S_{hig}-NS-rod/NF	2.26	0.0077	0.7582	0.47	0.0045	0.9258	7.18
S_{low}-NS-rod/NF	3.89	0.0017	0.9732	0.32	0.0024	0.9248	10.38

Table S3 Comparison of the HER performance of S_{hig}-NS-rod/NF with some representative HER electrocatalysts reported recently.

Catalyst	Electrolyte	Overpotential(mV) @10 mA cm^{-2}	Stability test (h)	Reference
S_{hig}-NS-rod/NF	1 M KOH	137	20	This work
NS-horn/NF	1 M KOH	177	20	Appl. Catal. B: Environ. 2019, 257, 117911
Ni_3S_2 NTFs	1 M NaOH	177	30	Appl. Catal. B: Environ. 2019, 243, 693-702
Ni_3S_2/VO_2	1 M KOH	100	15	J. Mater. Chem. A, 2019, 7, 1196-1205
Cu NDs/Ni_3S_2 NTs-CFs	1 M KOH	128	30	J. Am. Chem. Soc. 2018, 140, 610-617
N-doped Ni_3S_2	1 M KOH	155	40	Adv. Energy Mater. 2018,8,1703538.
$NiCo_2S_4/Ni_3S_2$/NF	1 M KOH	119	24	ACS Appl. Mater. Interfaces, 2018, 10, 10890-10897
Ni_3S_2	1 M KOH	300	24	ACS Appl. Mater. Interfaces. 2018, 10, 12807-12815
$Ni(OH)_2/Ni_3S_2$	1 M KOH	165	10	J. Mater. Chem. A 2018, 6, 6938-6946
CoS_x/Ni_3S_2@NF	1 M KOH	204	20	ACS Appl. Mater. Interfaces, 2018, 10, 27712-27722
Co-Ni_3S_2@CNTs/GNF	1 M KOH	155	20	J. Mater. Chem. A, 2018, 6, 10490-10496
Ni_3S_2|P	1 M KOH	173	10	ACS Appl. Energy Mater. 2018, 1, 3488-3496
NF-Ni_3S_2/NF	1 M KOH	135	50	J. Mater. Chem. A, 2018, 6, 4485-4493
N-Ni_3S_2/NF	1 M KOH	110	10	Adv. Mater. 2017, 29, 1701584
$Ni_xCo_{3-x}S_4/Ni_3S_2$/NF	1 M KOH	136	50	Nano Energy, 2017, 35, 161-170
Ni_3S_2-GQDs/NF	1 M KOH	218	16.7	small 2017, 13, 1700264
MoS_2-Ni_3S_2 HNRs/NF	1 M KOH	98	48	ACS Catal. 2017, 7, 2357-2366
Ni_3S_2@NF	1 M KOH	182	12	J. Mater. Chem. A 2016, 4, 13916-13922