Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

The controlled synthesis of V doped MoS_2-Ni_xS_y hollow nanosphere and its electrocatalytic performance for hydrogen evolution reaction

Wensi Wang[a], Huimin Zhao[a], Yunmei Du[a], Yu Yang*[a], Shaoxiang Li[b], Yanru Liu*[a] and Lei Wang[a,b]

a. Key Laboratory of Eco-chemical Engineering, Key Laboratory of Optic-electric Sensing and Analytical Chemistry of Life Science, Taishan Scholar Advantage and Characteristic Discipline Team of Eco Chemical Process and Technology, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China

b. Shandong Engineering Research Center for Marine Environment Corrosion and Safety Protection,College of Environment and Safety Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China

* Corresponding author. Email: liuyanru@qust.edu.cn (Y.R. Liu)
yangyu@qust.edu.cn (Y. Yang)

Experimental

1. The preparation of electrocatalysts

V doped MoS_2/Ni_xS_y/NF were prepared by a one-step hydrothermal method. VMNS/NF catalyst was prepared as follows: 60 mg sodium orthovanadate ($Na_3VO_4 \cdot 12H_2O$), 80 mg $Na_2MoO_4 \cdot 2H_2O$ and 110 mg TAA were put into 30 mL deionized water and then stirred for one hour to form a clean solution. Meanwhile, a piece of Nickel foam (1 cm*4 cm) was treated in acetone, 1 M HCl solution and ethanol, respectively, for 10 minutes to clear the oxide layer on the surface of the Ni foam. The as-prepared solution and Ni foam was transferred to a 50 mL Teflon-lined stainless autoclave. The sealed vessel was heated at 160 °C for 24 h. After cooling to room temperature, the as-synthesized VMNS/NF on Ni foam substrate was collected and subsequently rinsed with distilled water, ethanol for three times, and dried in vacuum oven at 60 °C for 12 h. For comparison, the VNS/NF (V doped Ni_3S_2), MNS/NF(MoS_2/Ni_3S_2), VMNS/NF-0.5(30 mg $Na_3VO_4 \cdot 12H_2O$), VMNS/NF-0.75(45 mg $Na_3VO_4 \cdot 12H_2O$), VMNS/NF-1.5(90 mg $Na_3VO_4 \cdot 12H_2O$) and VMNS/NF-2(120 mg $Na_3VO_4 \cdot 12H_2O$) are obtained in the same ways.

Firstly, 5 mg commercial Pt/C (20%) was poured into a sample tube containing 1 mL of the mixed solution of Nafion and ethanol, and then ultrasonicated for half an hour. At the same time, we used two different particle sizes of aluminum powder (50 nm, 1μm) to polish the glassy carbon electrode, and then ultrasoni-cally cleaned with deionized water and ethanol. Finally, 20 μL catalyst ink was dripped onto the surface of the clean glassy carbon electrode and electrochemical tests were performed after

drying half minute in oven.

2. Electrochemical measurements

Different ratio of crystal structure was presented by the powder X-ray diffraction D-MA 2500/PC). The morphology of different samples coated on Ni foam was characterized by SEM eiss sigma 500 in Germany. The elemental valence of the different sample surface is tested by Multifunctional imaging electron spectrometer Thermo ESCALAB 250Xi). The morphology of the nanoparticles of the sample is further analyzed by transmission electron microscope FEI Tecnai G2F20) and TEM mapping was recorded with Bruker QUANTAX.

3. Characterization

The hydrogen evolution reaction performance was tested by a gamry (reference 3000) workstation at a room temperature in a 1 M KOH solution through a three-electrode system with the sample supported on foamed nickel as the working electrode, the calomel electrode and the graphite rod as the reference and counter electrodes, respectively. Typically, the A linear sweep voltammetry (LSV) curve is performed at a scan rate of 1 mV s^{-1}. The Electrochemical impedance spectroscopy (EIS) test is tested at the frequency range from 100 KHz to 0.01 Hz with an overpotential of 150 mV. The time-dependent current density curve last 24 hours to prove its stability. The calculation of transfer electron number (n) and TOF is performed using CV at different sweep speeds in 1.0 M PBS (PH= 7) solution.

Fig. S1 XRD of the (a) NS/NF; (b) VNS/NF and (c) MNS/NF.

Fig. S2 XRD of the VMNS/NF-β (β=0.5, 0.75, 1, 1.5, 2).

Fig. S3 (a and b) SEM images of the NS/NF; (c and d) SEM images of the VNS/NF.

Fig. S4 (a and b) SEM images of the VMNS/NF-0.5; (c and d) SEM images of the VMNS/NF-0.75; (e and f) SEM images of the VMNS/NF-1.5; (g and h) SEM images of the VMNS/NF-2.

Fig. S5 XPS spectra of the VMNS/NF-β (β= 0.5, 1, 2): (a) Ni 2p, (b) Mo 3d, (c) V 2p, and (d) S 2p spectrum.

Fig. S6. HER polarization curves of VMNS/NF-β (β= 0.5, 0.75, 1, 1.5, 2).

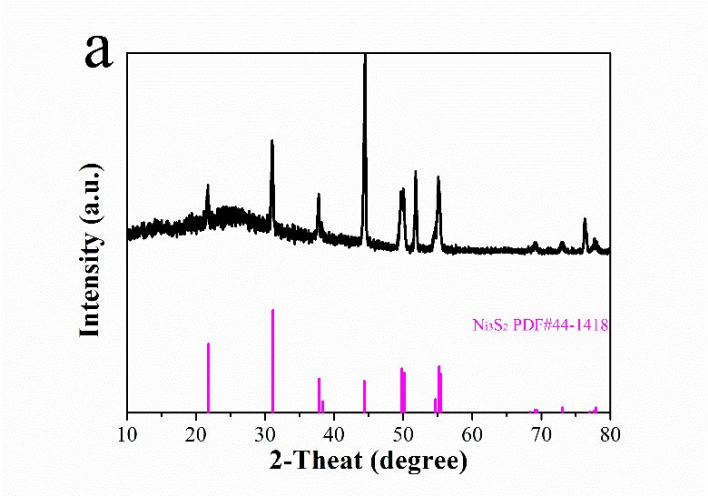
Fig. S7. The n value of NS/NF, VNS/NF, MNS/NF and VMNS/NF.

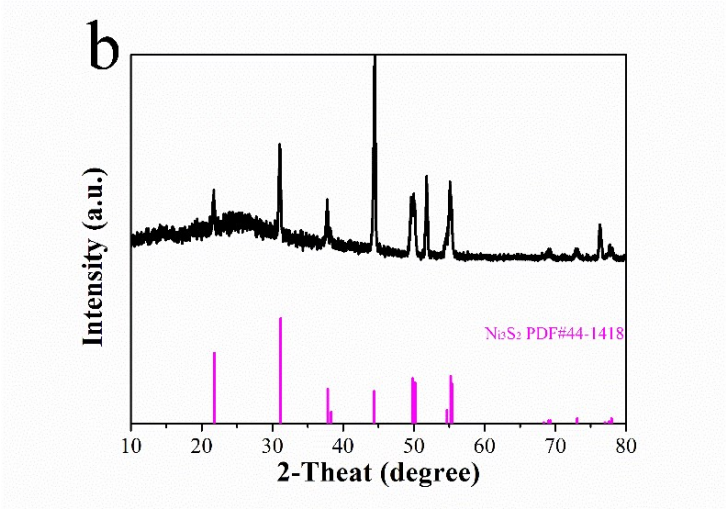
Fig. S8 (a) XRD (b) SEM images of the VMNS/NF after HER durability test.

Fig. S9 XPS spectra of the VMNS/NF after HER reaction: (a) Ni 2p, (b) Mo 3d, (c)V 2p, and (d) S 2p.

Table. S1 Comparison of HER activity in alkaline media for VMNS/NF with recently reported HER electrocatalysts.

Table. S2 EDS results of the as-prepared catalysts.





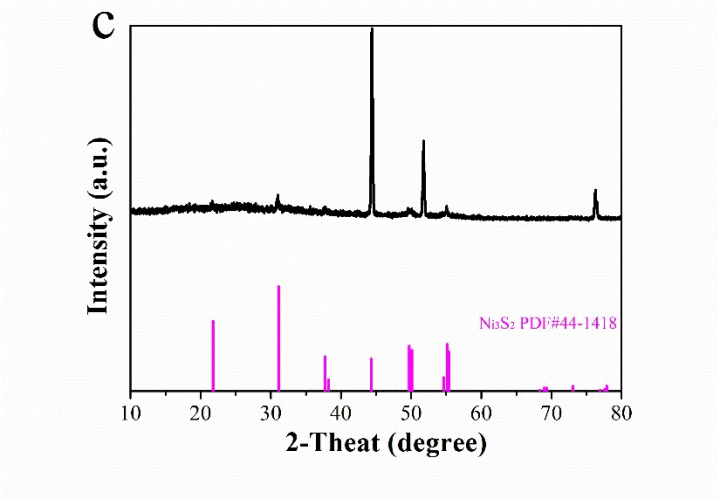


Fig. S1 XRD of the (a) NS/NF; (b) VNS/NF and (c) MNS/NF.

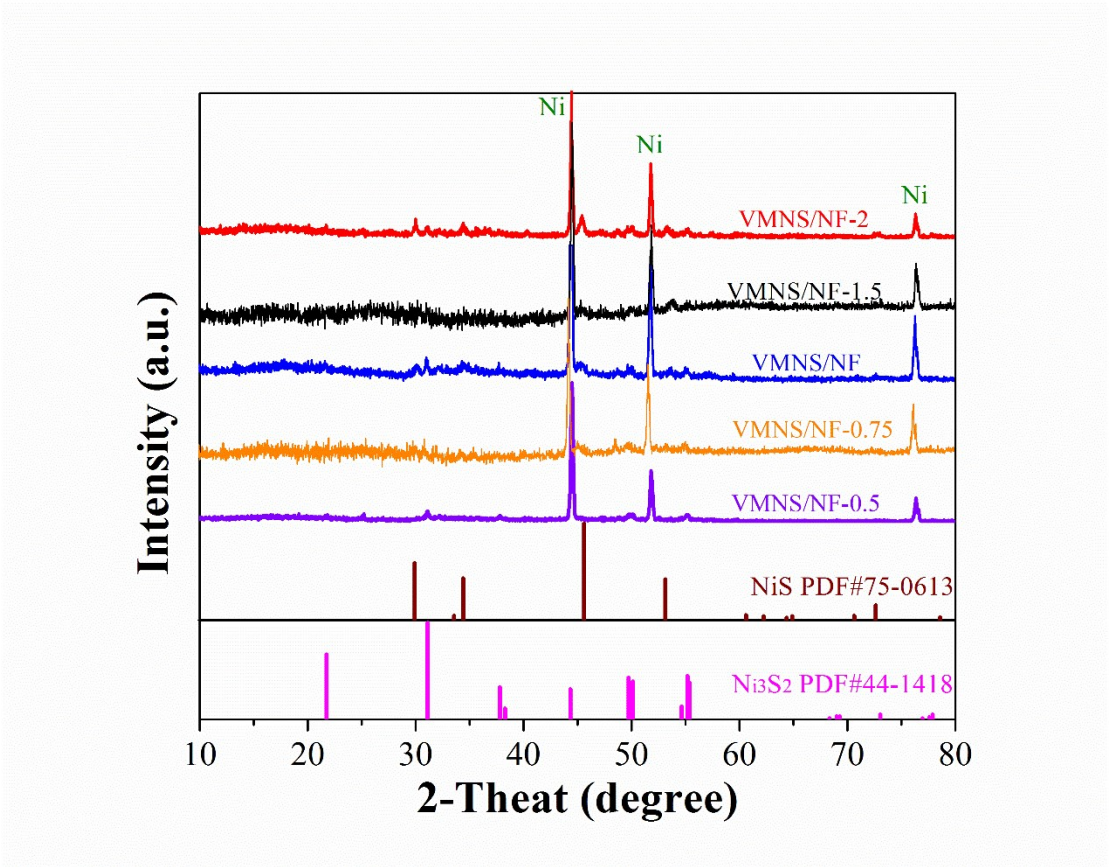


Fig. S2 XRD of the VMNS/NF-β (β=0.5, 0.75, 1, 1.5, 2).

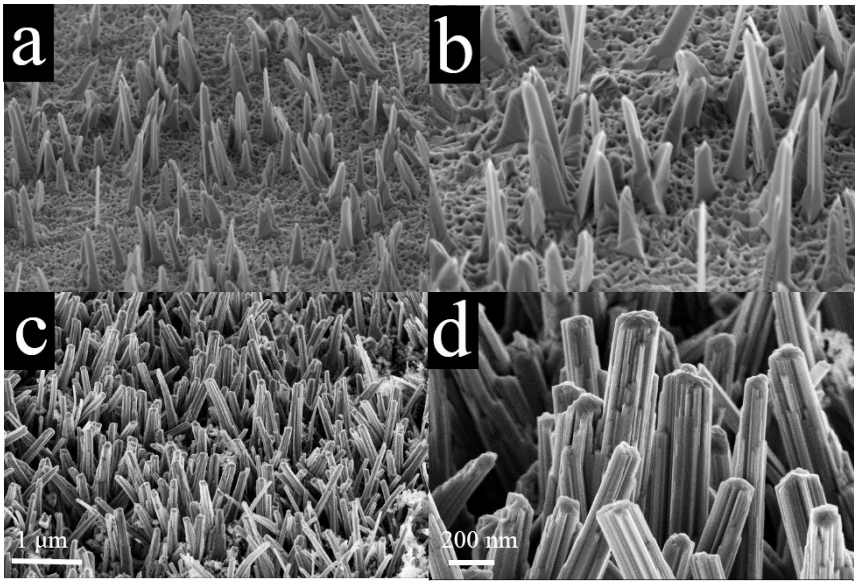


Fig. S3 (a and b) SEM images of the NS/NF; (c and d) SEM images of the VNS/NF.

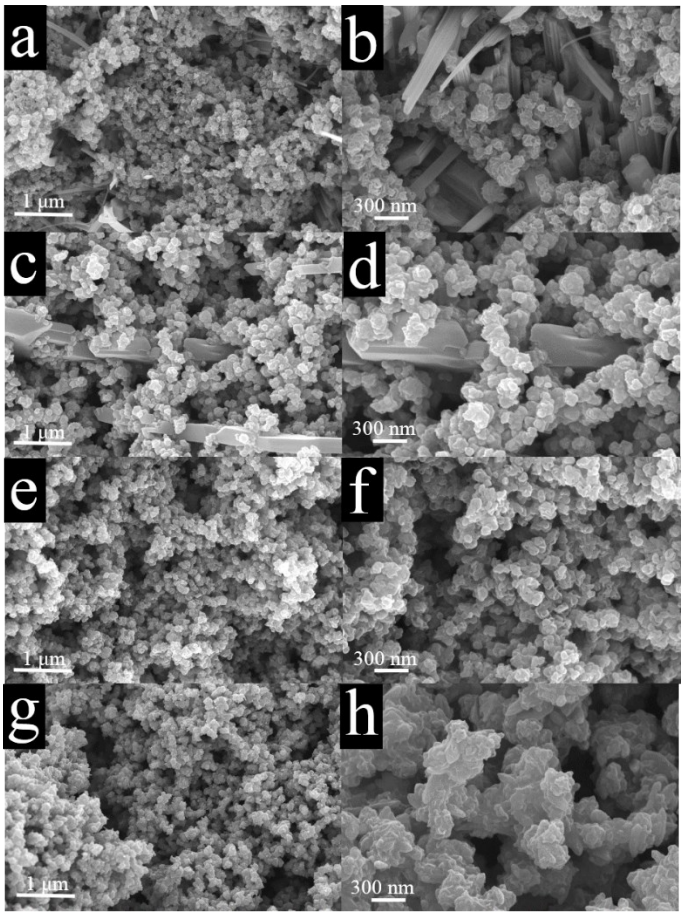


Fig. S4 (a and b) SEM images of the VMNS/NF-0.5; (c and d) SEM images of the VMNS/NF-0.75; (e and f) SEM images of the VMNS/NF-1.5; (g and h) SEM images of the VMNS/NF-2.

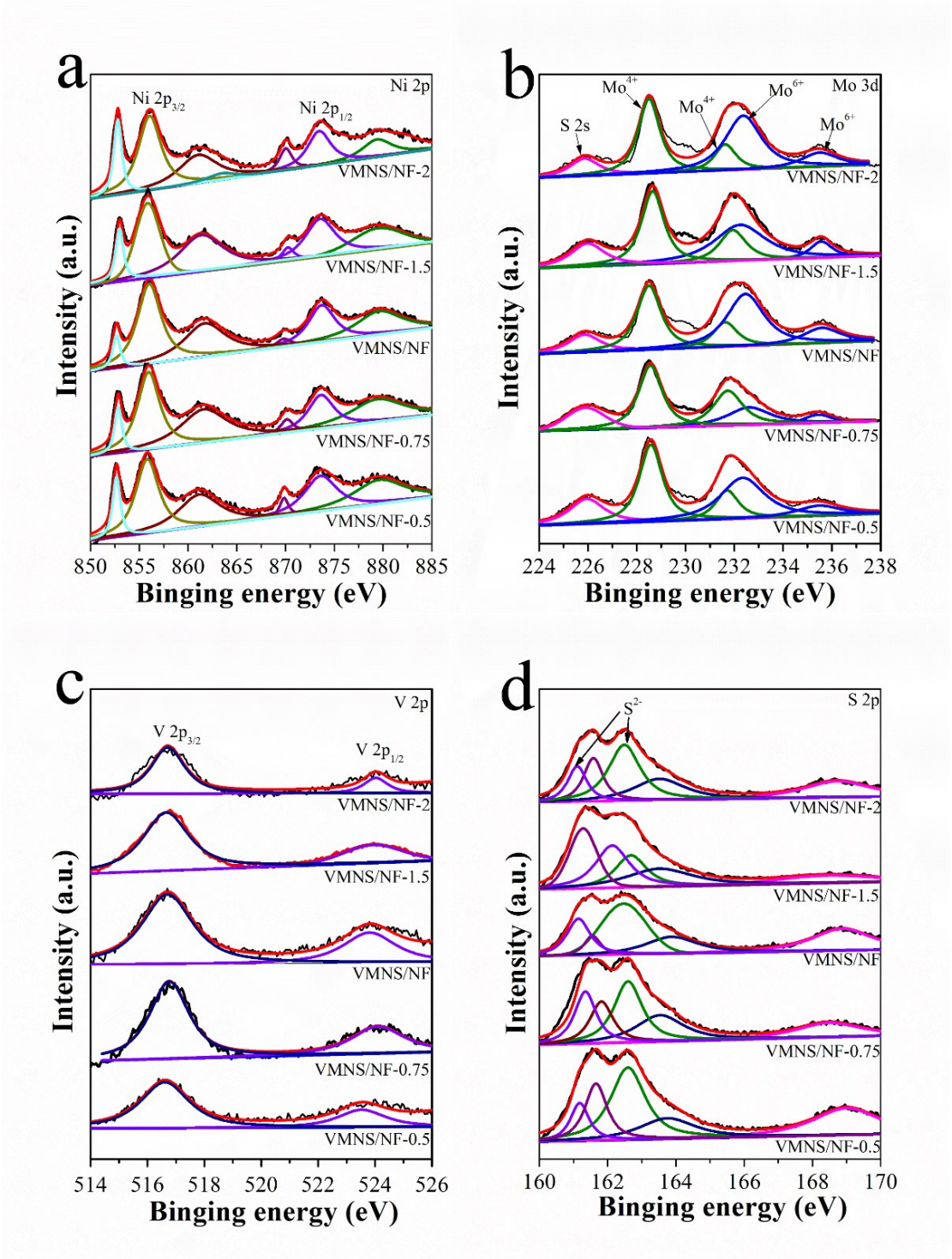


Fig. S5 XPS spectra of the VMNS/NF-β (β= 0.5, 0.75, 1, 1.5, 2): (a) Ni 2p, (b) Mo 3d, (c) V 2p, and (d) S 2p spectrum.

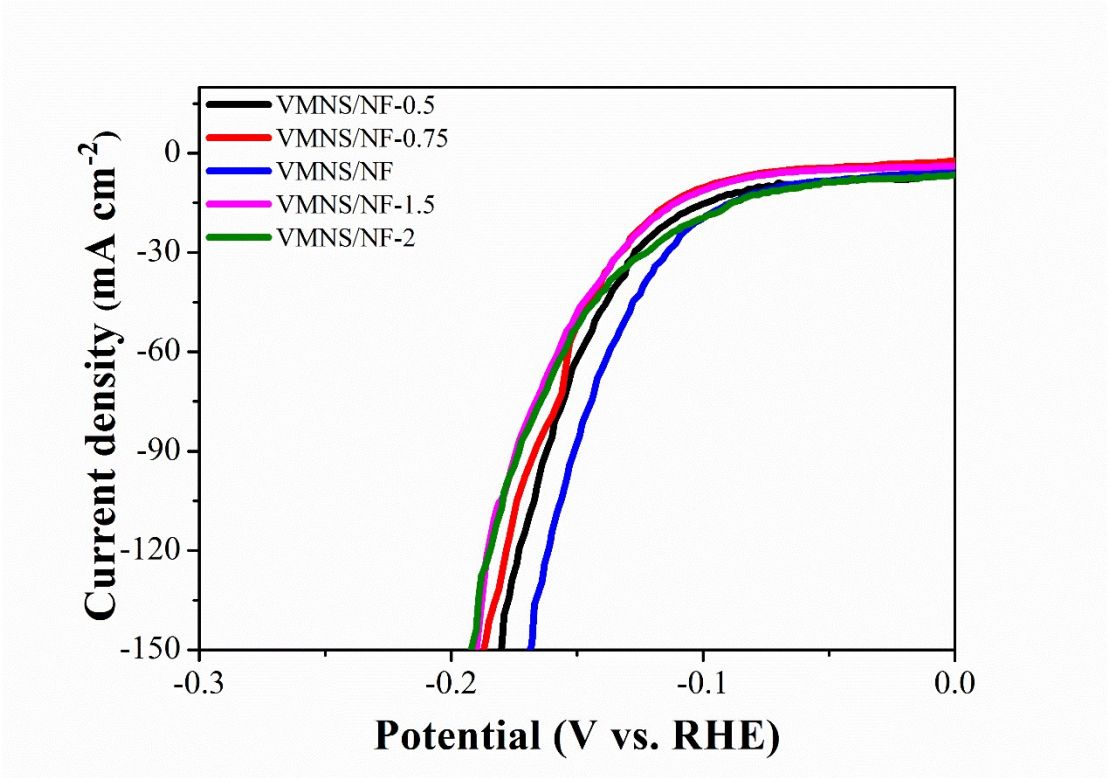


Fig. S6. HER polarization curves of VMNS/NF-β (β= 0.5, 0.75, 1, 1.5, 2).

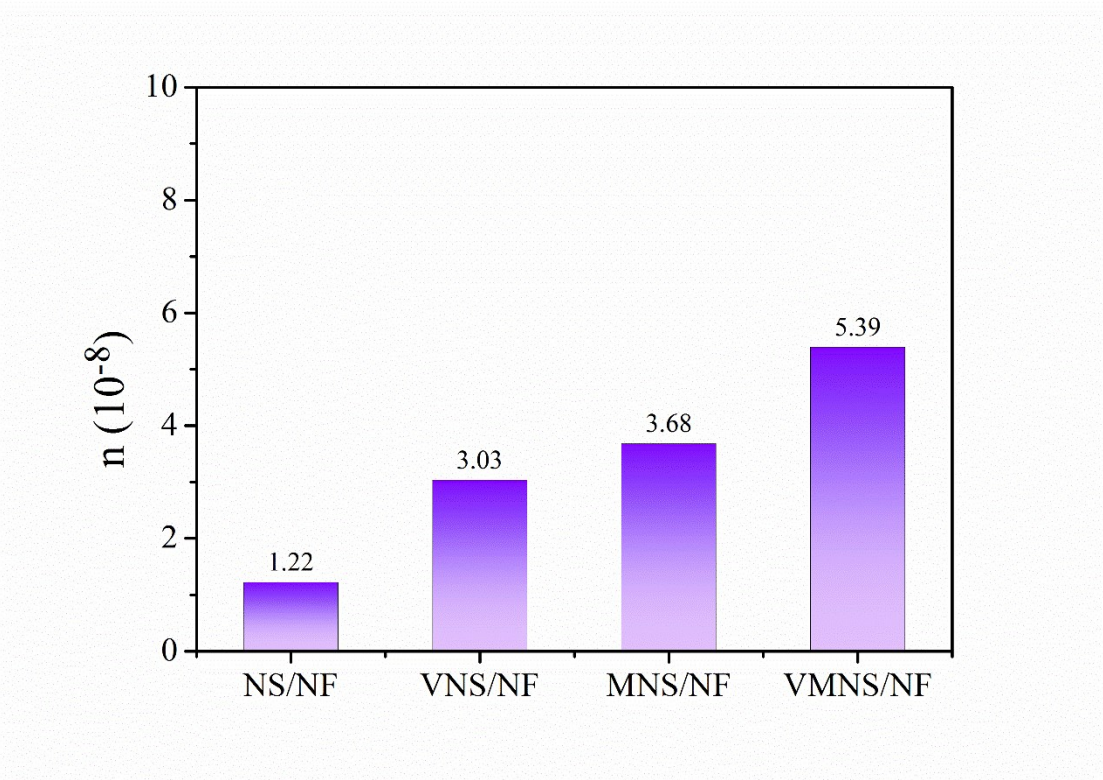


Fig. S7 The n value of NS/NF, VNS/NF, MNS/NF and VMNS/NF.

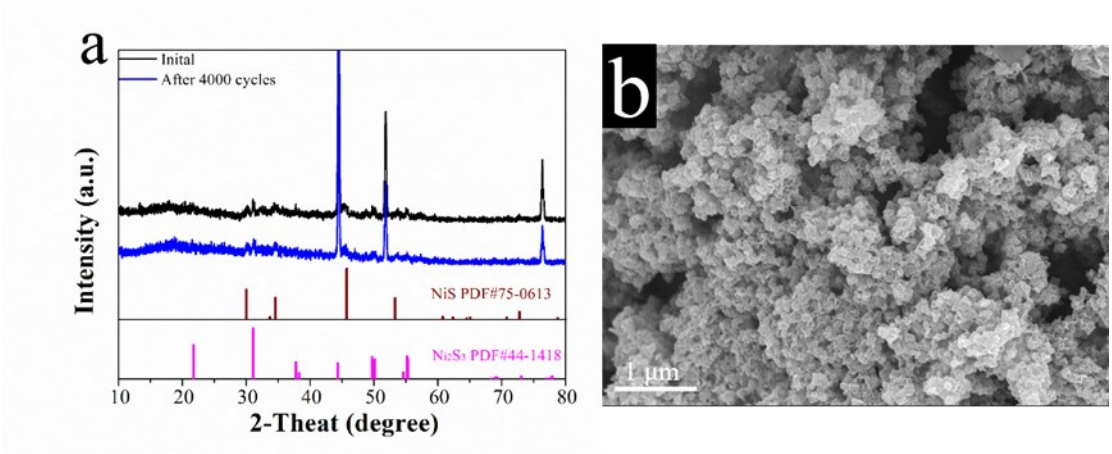


Fig. S8 (a) XRD (b) SEM images of the VMNS/NF after HER durability test.

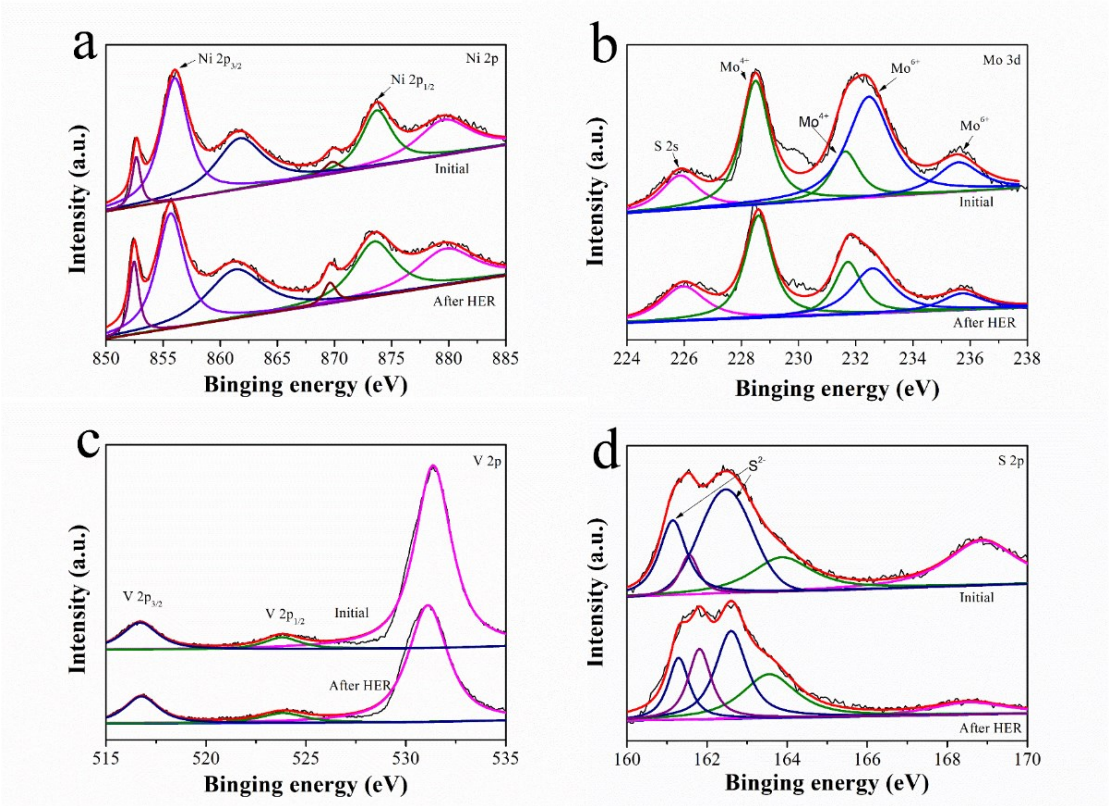


Fig. S9 XPS spectra of the VMNS/NF after HER reaction: (a) Ni 2p, (b) Mo 3d, (c) V 2p, and (d) S 2p.

Table. S1 Comparison of HER activity in alkaline media for VMNS/NF with recently reported HER electrocatalysts.

Catalysts	Electrolytes	Overpotential@j (mV@ mA cm^{-2})	Tafel slope (mV dec^{-1})	Ref.
VMNS/NF	1 M KOH	68@10	80.4	**This work**
Ni_3S_2@NGCLs/NF	1 M KOH	132@10	84	Chemical Engineering Journal, 2020, 401: 126045
a-MoS_2-Ni_3S_2/NF	1 M KOH	81@10	90.7	Electrochimica Acta, 2020, 332: 135454
NF@G-5@Ni_3S_2	1 M KOH	119@10	101.9	Journal of Energy Chemistry, 2020, 46: 178-186.
CoS_2/MoS_2	1 M KOH	75@10	86.2	J. Mater. Chem. A, 2020, 8, 11435-11441
3-Co-1T-MoS_2	1 M KOH	240@10	70	Materials Chemistry and Physics, 2020, 244: 122642
NiWO4/Ni_3S_2-16	1 M KOH	136@10	112	Applied Catalysis B: Environmental, 2020: 119120
H-MoS_2/MoP	1 M KOH	92@10	59.8	Small, 2020, 16(32): 2002482
V-Ni_3S_2@NiO/NF	1 M KOH	112@10	69	J. Am. Chem. Soc., 138 (2016) 16174-16181
Co_9S_8/Ni_3S_2	1 M KOH	128@10	97.6	Applied Catalysis B: Environmental, 2019, 253: 246-252

Table. S2 EDS results of the as-prepared catalysts.

Atomic % / **Sample**	V	Ni	Mo	S
VMNS/NF-0.5	4.04	16.69	10.02	28.56
VMNS/NF-0.75	4.16	18.24	11.96	29.71
VMNS/NF	5.06	16.9	10.51	25
VMNS/NF-1.5	3.85	19.03	9.28	26.43
VMNS/NF-2	3.31	13.11	11.75	25.31