Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Accelerated electrocatalytic hydrogen evolution of non-noble metal containing trinickel nitride by introduction of vanadium nitride

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Turnover frequency calculations

The corresponding turnover frequency values (TOF) were calculated according to the following formula: [1-3]

$$TOF = \frac{*\ total\ hydrogen\ turn\ overs/cm^2 geometric\ area}{*\ surface\ active\ sites\ /cm^2\ geometric\ area}$$

The corresponding total hydrogen turnovers and surface active sites are calculated using following two equations:

$$*_{H_2} = \left(\frac{1C\ s^{-1}}{1000\ mA}\right)\left(j\frac{mA}{cm^2}\right)\left(\frac{1\ mol\ H_2}{2\ mol\ e^-}\right)\left(\frac{1\ mol\ e^-}{96485.3\ C}\right)\left(\frac{6.02\ \times 10^{23}\ H_2\ molecules}{1\ mol\ H_2}\right)$$

$$= 3.12\ \times 10^{15}\ \frac{H_2/s}{cm^2}\ per\ \frac{mA}{cm^2}$$

and $\frac{*\ surface\ sites}{cm^2\ geometric\ area} = Roughness\ factor \times \frac{*\ surface\ sites\ (flat\ standard)}{cm^2\ geometric\ area}$

The electrochemical double-layer capacitance (EDLC) is proportional to the ECSA. We can obtain the ECSA values from the corresponding EDLC values. The roughness factor can also obtain from corresponding ECSA values. According to previous reports, the C_{dl} of the flat standard is about 60 μF cm^{-2}, and the number of surface sites for the flat standard electrode is about 2×10^{15}.[1] Therefore, according to above values, we can calculate the number of the surface active sites of the Ni_3N@VN-NF-2 electrode: $2 \times 10^{15} \times \frac{148.3 \times 10^3}{60} = 4.94 \times 10^{18}$ surface sites cm^{-2}.

Therefore, the TOF values of the Ni_3N@VN-NF-2 electrode at different overpotentials are calculated as following:

$$\eta = \text{-X mV},\ \ TOF = \left(\frac{3.12 \times 10^{15}\ \frac{H_2/s}{cm^2} per \frac{mA}{cm^2} \times Y \frac{mA}{cm^2}}{4.94 \times 10^{18}\ surface\ sites\ per\ cm^2}\right) = Z\ s^{-1}$$

X, Y, Z refer to the corresponding overpotential, current density and the calculated TOF values.

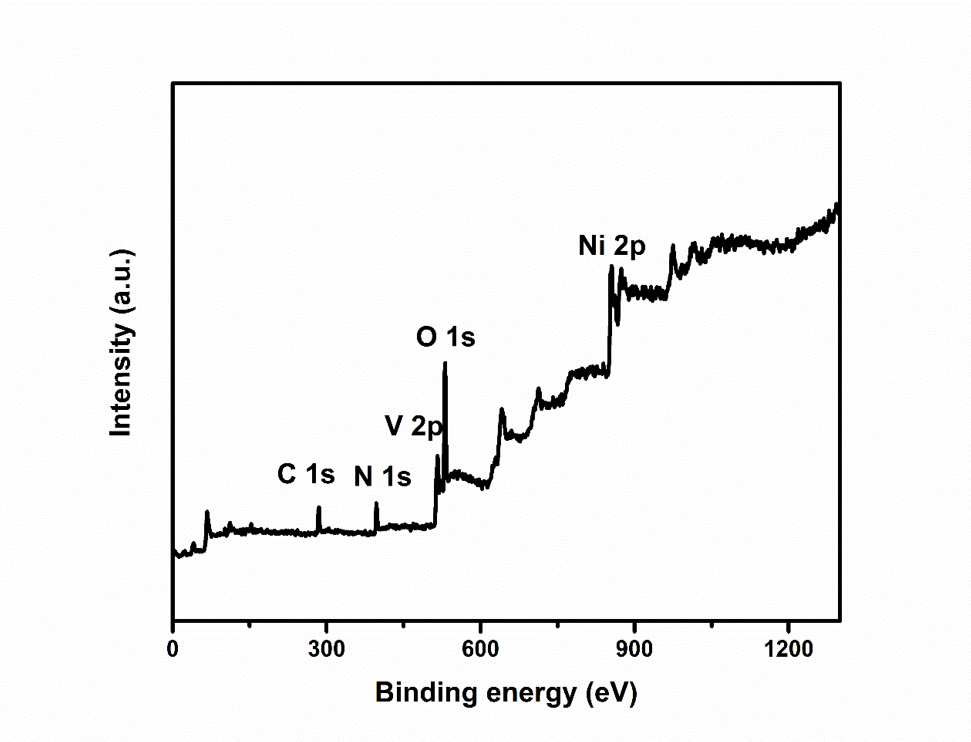

Fig. S1. The corresponding survey spectrum of Ni_3N@VN-NF-2 electrode.

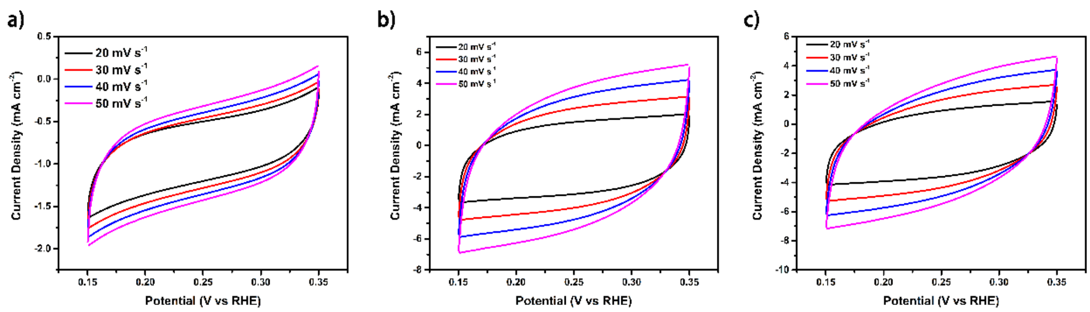

Fig. S2. The corresponding electrochemical double-layer capacitance (EDLC) measurements of Ni_3N-NF, Ni_3N@VN-NF-2 and VN-NF electrodes.

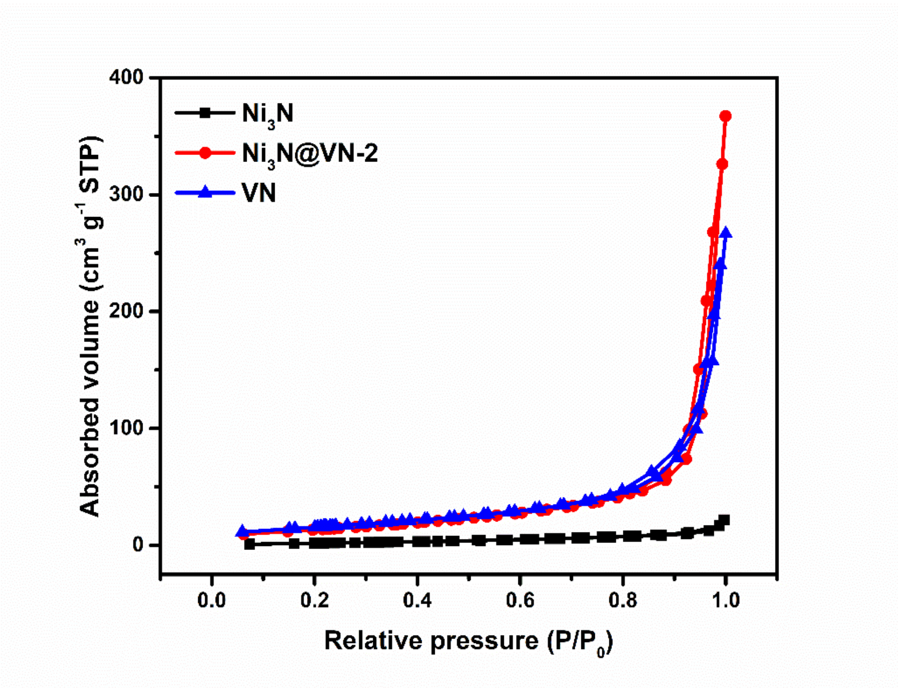

Fig. S3. N_2 adsorption–desorption isotherms of the powders Ni_3N, Ni_3N@VN-2 and VN samples.

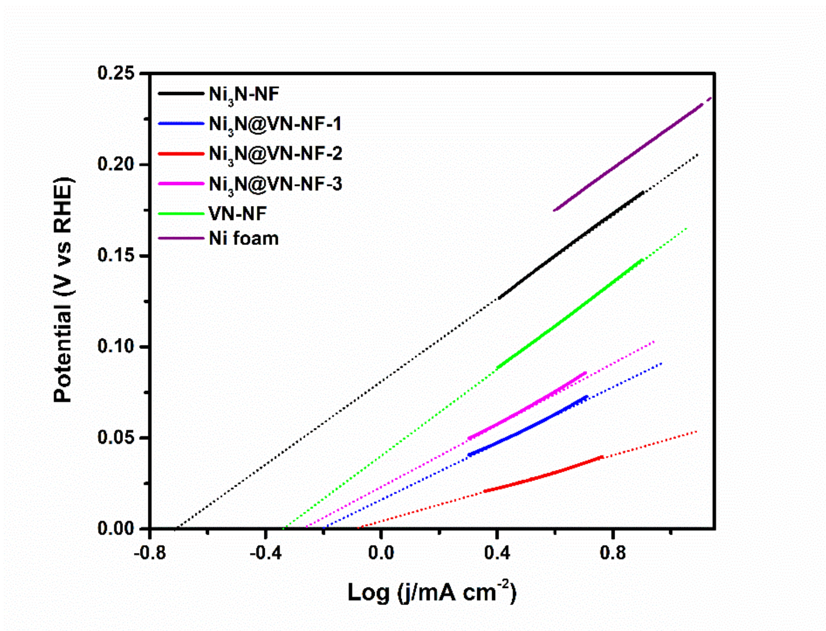

Fig. S4. The exchange current density plots of different electrodes derived from Tafel plots.

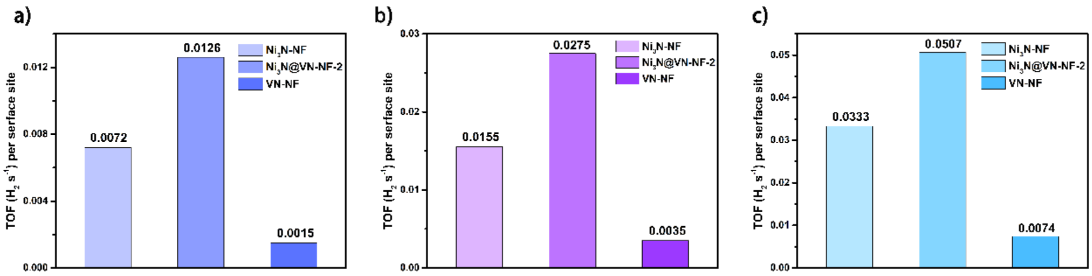

Fig. S5. The TOF values of different electrodes at -80, -120 and -160 mV (vs. RHE).

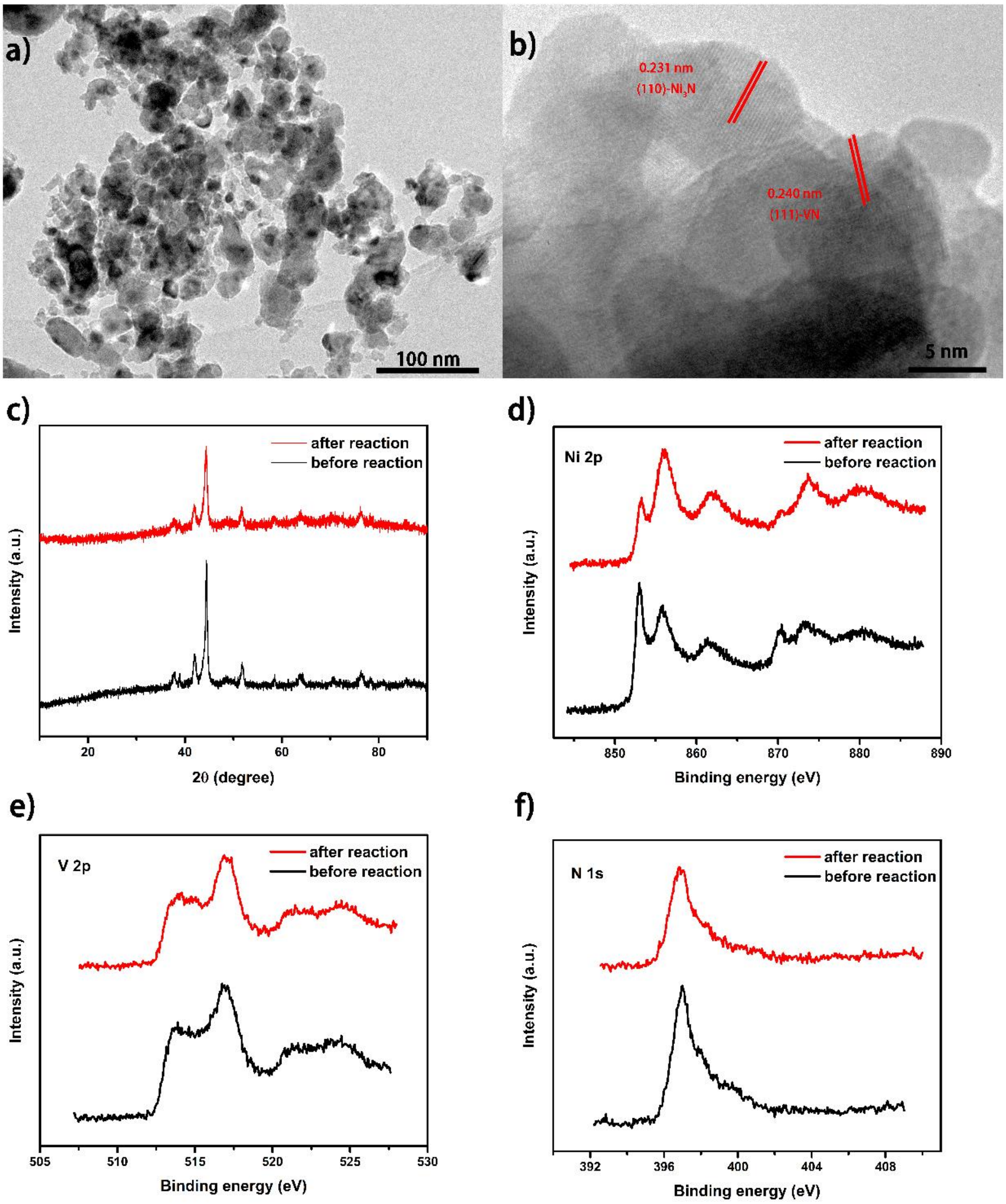

Fig. S6. (a-b) TEM and HRTEM images of Ni_3N@VN-NF-2 electrode after long time overall water splitting test; (c) XRD spectra of Ni_3N@VN-NF-2 electrode before and after long time overall water splitting test; (d-f) XPS spectra of Ni, V and N elements of Ni_3N@VN-NF-2 electrode before and after long time overall water splitting test.

Table S1. Comparison of HER performance of different electrodes

Catalyst	Overpotential at 10 mA cm^{-2} (mV)	Tafel slope (mV $decade^{-1}$)	Electrolyte	Source
Ni_3N@VN-NF-2	56	47	1 M KOH	This work
Ni_3N@CoN	68	69	1 M KOH	[4]
Metallic Ni_3N	59	59.8	1 M KOH	[5]
Ni_3N@C	115	52	1 M KOH	[6]
Ni_3N_{1-x}	55	54	1 M KOH	[7]
Ni_3N-Ni foam	100	120	1 M KOH	[8]
Ni_3N-NA	136	172	1 M KOH	[9]
Co- Ni_3N	194	156	1 M KOH	[10]
S-CoP	109	79	1 M KOH	[11]
Ni_2P-NiP_2	59.7	58.8	1 M KOH	[12]
NiMo	92	76	1 M KOH	[13]
CoP_3-Ni_2P	115	49	0.5 M H_2SO_4	[14]
Ni@MoS_2	98	75	1 M KOH	[15]
MoS_2@Ni_3S_2	110	83	1 M KOH	[16]
Ni_3S_2@Ni_2P	80	65	1 M KOH	[17]

Table S2. Comparison of the overall water splitting performance of different systems

Catalyst	Overpotential at 10 mA cm^{-2} (V)	Electrolyte	Source
Ni_3N@VN-NF-2//NiFe-LDH-NF	1.55	1 M KOH	This work
Ni_3N@CoN//Ni_3N@CoN	1.59	1 M KOH	[4]
Ni_3N-CMF//Ni_3N-CMF	1.59	1 M KOH	[6]
NiMo//NiMo	1.64	1 M KOH	[13]
MoS_2@Ni_3S_2//MoS_2@Ni_3S_2	1.56	1 M KOH	[16]
CVN//CVN	1.64	1 M KOH	[18]
O_3-V-Ni_2P//O_3-V-Ni_2P	1.56	1 M KOH	[19]
Ni@Mo_2C//Ni@Mo_2C	1.66	1 M KOH	[20]
$NiSe_2$//$NiCo_2S_4$	1.58	1 M KOH	[21]
$NiCo_2S_4$//$NiCo_2S_4$	1.63	1 M KOH	[22]
Ni_3FeN//Ni_3FeN	1.62	1 M KOH	[23]
NiCoP//NiCoP	1.58	1 M KOH	[24]
NiMo-PVP//NiMo-PVP	1.66	1 M KOH	[25]
NiMoP//NiMoP	1.6	1 M KOH	[26]
NiFe/$NiCo_2O_4$//NiFe/$NiCo_2O_4$	1.67	1 M KOH	[27]

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