Supplemental Note

Materials and Methods

Chemicals. All chemicals are used as received without further purification. Vanadium chloride (VCl₃), nickel chloride (NiCl₂· $6H_2O$) and urea are supplied by Aladdin (Shanghai, China). A commercial sample of Pt on XC-72 carbon support (20 wt% Pt, HiSPEC 3000, Johnson Matthey) is used throughout.

Catalyst Preparation. In a typical preparation of Ni/VN catalyst, nickel chloride (NiCl₂·6H₂O, x g), vanadium chloride (VCl₃, 0.15 g) and urea (0.18 g) are dispersed in 30 mL water. The mixture is ultrasonicated for about 5 minutes to form a clear solution. The resulting homogeneous mixture is then placed in a hydrothermal reactor and heated to 120 °C, and kept at this temperature for 12 h. There after it is cooled to room temperature, the resulting solid product is collected using filtration, and subsequently washed three times with a water/ethanol mixture and dried at 60 °C. The grey powder obtained is finally pyrolysed in a tube furnace under flowing ammonia (99.999%, 30 mL min⁻¹), the temperature is kept at 350 °C for 2 hours and 500 °C for 2 hours in succession at a heating rate of 5 °C min⁻¹. After the heat treatment is completed, it is cooled to room temperature under the flow of ammonia gas. and argon gas (99.999%, 30 mL min⁻¹) is introduced for 2 h to remove the ammonia gas remaining in the furnace tube. A series samples with different mass ratio of NiCl₂· $6H_2O$:VCl₃ (x:0.15=1:1, 2:1, 3:1, 4:1) are prepared. Among them, the sample obtained by mass ratio of NiCl₂·6H₂O:VCl₃=3:1 presents the best HER performance and is labelled as Ni/VN in this work.

For comparison, the sample VN is synthesized via the same as the above procedures without nickel chloride. Notably, Ni₃N (PDF No. 89-5144) is obtained using the same procedures without VCl₃, suggesting the existence of valence changed vanadium

contributes to the generation of metal Ni during the preparation. To prepared the sample NiPs, the hydrothermally treated product without VCl₃ is reduced under flowing H_2/Ar (H_2 5%) at a heating rate of 5 °C min⁻¹, and then cooled to room temperature and passivated by maintaining it for 2 h under the flowing argon (30 mL min⁻¹).

Characterization. X-ray diffraction (XRD) is conducted using a powder X-ray diffractometer (Rigaku Miniflex 600) with Cu-K_a radiation ($\lambda = 1.54178$ Å) in a 2 θ range from 20° to 80° scanning at 1° min⁻¹. Transmission electron microscopy (TEM) and scanning TEM (STEM) are performed using JEOL JEM-2100F TEM/STEM (Tokyo, Japan) which are operated at 200 kV. Nitrogen sorption measurement is determined at -196 °C using an Autosrob-1(Quantachrome INSTRUMENTS). X-ray photoelectron spectroscopy (XPS, VG ESCALAB MKII) with Mg K_a as the excitation source is used to analyze surface valence of the materials with carbon as an internal standard (C 1s=284.8 eV). The nickel content in Ni/VN is tested using the inductively coupled plasma optical emission spectrometry (ICP-OES) on SPECTRO ARCOS^{II}. Before the test, the prepared Ni/VN is resolved by chloroazotic acid and diluted using deionized water.

Electrochemical tests. The counter and reference electrodes are a graphite rod and Ag/AgCl (saturated KCl aqueous solution), respectively. To fabricate the working electrode, the catalyst inks (10 mg mL⁻¹ for Ni/VN, VN or NiPs, and 4 mg mL⁻¹ for Pt/C) are prepared by dispersing the catalyst in a mixture of water and isopropyl alcohol at a volume ratio of 1 : 1 with 0.1 wt% Nafion as a binder. After sonicating for 30 min, 10.0 μ L of the uniform ink is deposited on the polished glassy carbon electrode (Φ =5.0 mm). There after post-drying at 35 °C, a mass loading of 0.5 mg cm⁻² for sample Ni/VN, VN or NiPs, and 0.2 mg cm⁻² for Pt/C (20 wt%) is found to have been achieved.

Cyclic voltammetry (CV) experiments are employed to activate the materials between -0.8 to -1.2 V vs Ag/AgCl. The polarization curves of modified disk electrode are recorded using linear sweep voltammetry (LSV) scanned positively at a rotation rate of 1600 rpm at 10 mV s⁻¹. Prior to CV and LSV tests, the electrolyte solution is bubbled with hydrogen for more than 20 min with a flowing rate of 100 mLmin⁻¹.

The double-layer capacitance (C_{dl}) is determined by measuring cyclic voltammetric stripping at scan rates of 5 mV s⁻¹, 10 mV s⁻¹, 20 mV s⁻¹, 50 mV s⁻¹ and 100 mV s⁻¹. The Cdl is estimated by plotting the $\Delta J = (J_a - J_c)$ at 0.87 V (where J_c and J_a are the cathodic and anodic current densities, respectively) versus RHE against the scan rate, in which the slope was twice that of C_{dl}.

Accurately, the accessible nickel (n_{Ni}) available as active sites for HER is quantified based on the reduction peak of Ni³⁺/Ni²⁺. To monitor the reduction peak of Ni³⁺/Ni²⁺, Cyclic voltammetry (CV) experiment is carried out between 0.8 to 0.1 V vs Ag/AgCl at a scan rate of 10 mV s⁻¹. And the TOF value is calculated using the following equation:

$$TOF = \frac{Iv}{2S}$$

I is the measured current density for HER, *v* is the scan rate of the CV curve (V s⁻¹), S is the integral area of Ni^{3+}/Ni^{2+} reduction peak (W).

The durability and Faraday efficiency (FE) are tested using nickel foam (NF, thickness: 1.6 mm) modified with Ni/NV as working electrode. Ni foam with a fixed area of 1 x 1 cm² is ultrasonically cleaned in deionized water and drop-

casted with 200µL of the catalyst ink (mass loading for Ni/VN and Pt/C is 2.0 and 0.8 mg cm⁻², respectively). Chronopotentiometry is used to record the electron consumption at specified current density. The hydrogen that is experimentally generated from the water splitting is collected using water–gas displacing method. The Faraday efficiency is calculated based on the following equation:

 $FE(\%) = \frac{2FV_{H2}}{\operatorname{It} V_{m}} \times 100$, where F is the Faraday constant (96485 C mol⁻¹), V_{H2} is the

volume of the produced H_2 (L), V_m is the molar volume of gas (24.1 L mol⁻¹ at 20 °C), I is the current (A), t is the time (s).

RHE calibration in 1.0 M KOH is performed in the high purity hydrogen saturated electrolyte with a Pt foil as the working electrode and a Pt wire as the counter electrode. Cyclic voltammometry (CVs) is run at a scan rate of 1.0 mV s⁻¹, and the average of two potentials at which the currents cross zero is taken as thermodynamic potential for the hydrogen electrode reactions. Thus, as shown in Figure S17, the potential measured against a Ag/AgCl electrode is converted to the potential versus the reversible hydrogen electrode (RHE) according to E(RHE) = E(Ag/AgCl) + 1.006 V.

Computational methodology. Density functional theory (DFT) calculations are useful for investigating surface properties related to HER performance. All the DFT calculations were performed using the Quantum Espresso Package, with generalized gradient approximation projector augmented wave (GGA-PAW) pseudopotentials.

Norskov computational hydrogen electrode method¹ is used to simulate the hydrogen evolution reaction (HER) using the Gibbs free energy change of each electrochemical

elementary step. In this method the overall HER mechanism is estimated with the aid of three state diagrams containing an initial H⁺ state, an intermediate H* state, (the asterisk represents one H atom adsorbed on the catalyst surface), and 1/2 H₂ as the final product. The Gibbs free energy change of H* (Δ GH*) is a simple but main indicator to characterize the HER catalytic activity of the catalyst^{1, 2}.

The Volmer-Tafel mechanism can be presented into two steps.

$$\mathrm{H}^{+} + \mathrm{e}^{-} + * \leftrightarrow \mathrm{H}^{*} \tag{S1}$$

 $H^* + H^* \leftrightarrow H_2 \tag{S2}$

The first one is related to the adsorption of hydrogen on the catalyst surface, known as Volmer mechanism. This will by continued by the Tafel mechanism in an acidic solution or the Heyrovsky mechanism in neutral solution, respectively.

The free energy change of each step is calculated as $\Delta G = \Delta E - T\Delta S + \Delta ZPE$. In this formula, ΔE is the total energy change for H adsorption, i.e. difference between the DFT calculated total energies of a surface with and without adsorbed hydrogen atom. ΔZPE is the zero-point energy changes and ΔS is entropy difference between the adsorbed H and H in the gas phase.

For an active HER catalyst, the optimum value for ΔG is around 0 eV and -0.2 eV $\Delta G < 0.2$ eV; this is the normal case for an active catalyst. Largely positive or negative ΔG means it would be harder for hydrogen to be attached on or be released from the surface of the catalyst.

Supplemental Figures



Figure S1. Comparison of Ni/VN with currently reported HER catalysts. η_{10} is the overpotential at current density of 10 mA cm⁻².



Figure S2. The XRD patterns of (a) Ni-V hydroxide and (b) Ni₃N. Without VCl₃, the thermal ammonolysis of Ni hydroxide give rise to the formation of pure Ni₃N with a crystal size of 36 nm, suggesting the crucial role played by vanadium in the formation of metal Ni.



Figure S3. The XRD of Ni/VN prepared with different mass ratio of $NiCl_2 \cdot 6H_2O:VCl_3$. Determined by ICP-OES, the content of Ni in Ni/VN (1:1), Ni/VN (3:1), Ni/VN (5:1) is 52.2, 64.6, 77.7 wt.%.



Figure S4. High-angle annular dark-field scanning TEM of Ni/VN. The inset is the grain size distribution.



Figure S5. Structure analysis of VN.(a) TEM image. Inset corresponds to selected area electron diffraction pattern. (b) HR-TEM image. Lattice fringes of VN with d-spacings of 2.0 and 2.4 Å are clearly seen. (c-f) High-angle annular dark-field scanning TEM and EELS mapping images of N, V and integrated mapping.



Figure S6. Structure analysis of NiPs.(a) TEM image. Inset is corresponding selected area electron diffraction pattern. (b) TEM image of single Ni cube. Inset is the corresponding SAED. (c) HR-TEM image. Lattice fringes of Ni with d-spacing of 1.8 and 2.0 Å, and NiO with d-spacings of 2.1 Å are clearly seen. (d-g) High-angle annular dark-field scanning TEM and EELS mapping images of Ni, O and integrated mapping. An oxide layer of NiO with 2.0 nm thickness is formed due to exposure of NiPs to air.



Figure S7. The linear sweep voltammetry (LSV) curves of Ni/VN prepared with different mass ratio of NiCl₂· $6H_2O$:VCl₃ in 1.0 M KOH. Among them, the sample obtained by mass ratio of NiCl₂· $6H_2O$:VCl₃=3:1 presents the best HER performance and is labelled as Ni/VN in this work.



Figure S8. HER performance. (a) Mass activity of Ni/VN and Pt/C (20 wt.%). (b) The cost of metal in electrode-modified catalysts normalized by specific current density at different potential.



Figure S9. EIS spectra. EIS comparison for VN, NiPs, Ni/VN and Pt/C in terms of Nyquist plots. The scatters are experimental results, and the solid lines are best-fit curves.



Figure S10. CVs at different scan rate for (a) NiPs, (b) VN and (c) Ni/VN.



Figure S11. ECSA-normalized LSVs based on the double-layer capacitance.



Figure S12. Cyclic voltammetry (CV) curves show the $Ni^{3+}/Ni^{/2+}$ reduction peak used for accessible Ni site quantification for Ni/VN and NiPs. Scan rate is 10 mV s⁻¹.



Figure S13. The CV and CO-stripping curve of the commercial Pt/C (20%) recorded at room temperature in CO-saturated 1.0 M KOH solution at scan rate of 50 mVs⁻¹. The current densities are normalized to the geometric area of the RDE (0.196 cm²).



Figure S14. Faraday efficiency determination. Time dependence of the potential at a current density of 10 and 20 mA cm^{-2} for three hours.



Figure S15. XPS analysis of Ni/VN after stability test. (a) Ni $2p_{3/2}$ and (b) V $2p_{3/2}$ region spectra.



Figure S16. Top (upper) and side (lower) views of the most stable configurations of (a) pure, (b) Ni-doped (c) O-doped (d) Ni-O co-doped VN-(200) surfaces in the presence of H atom.



Figure S17. CV curves for RHE calibration in H_2 -saturated 1.0 M KOH at 1.0 mV s⁻¹. A Pt foil and Pt wire are used as the working and counter electrode, respectively.

Supplemental Tables

Table S1. Comparison of HER performance in 1.0 M KOH for some noble metal free catalyst.

Sample	mass	load	$\eta_{10} (mV)^{ \mathfrak{b}}$	Tatel slop	HER pathway	$I_0 (mA cm^{-2})^{c}$	TOF of metal (s^{-1})	Ref.
	(mg cn	n ⁻²)		$(mV dec^{-1})$				
Cu-Ni nanocages	0.283		140	79	Volmer-Heyrovsky	N/A	N/A	3
Co@N-			108	55	Volmer-Heyrovsky	N/A	N/A	4
CNTs@rGO ^a								
WC-W ₂ C/PNCDs ^a	0.4		101	90	Volmer-Heyrovsky	0.74	0.11(100mV)	5
MoC-Mo ₂ C/PNCDs ^a	0.4		121	60	Volmer-Heyrovsky	0.15	0.06(100mV)	
NiCu@C ^a	0.38		94	74	Volmer-Heyrovsky	N/A	N/A	6
np-Ni ₃ N ^a	0.32		50	N/A	N/A	N/A	N/A	7
NC/NiCu/NiCuN ^a	1.50		93	55	Volmer-Heyrovsky	N/A	N/A	8
Ni ₂ P/MoS ₂	0.51		159	69	Volmer-Heyrovsky	0.1	N/A	9
Co-NiS ₂ NSs	0.26		80	43	Volmer-Heyrovsky	N/A	0.14	10
B,N:Mo ₂ C@BCN ^a	0.5		94	62	Volmer-Heyrovsky	N/A	N/A	11
MoSx@NiO	0.7		406	43	Volmer-Heyrovsky	N/A	N/A	12
$Meso-CoS_2$	0.2		358	116	Volmer-Heyrovsky	0.008	0.104	13
Meso-CoSSe-12h	0.2		56	52	Volmer-Heyrovsky	0.07	0.047	
B-CoP/CNT	0.51		56	69	Volmer-Heyrovsky	N/A	N/A	14
NiPs	0.5		238	123		0.12	0.028	This
Pt/C (20 wt%)	0.2		57	30	Volmer-Tafel	0.3	0.16	work
Ni/VN	0.5		43	33	Volmer-Tafel	0.53	0.15	

^a Carbon coated/supported material.

^b The overpotential at current density of 10 mA cm⁻².

^c Exchange current density.

Samples	Potential (V, vs. RHE)	$R_s(\Omega)$	$R_1(\Omega)$	$R_2(\Omega)$
NiPs	-0.2	6.8	197	>20000
VN	-0.2	7.0	5.1	233.5
Ni/VN	-0.05	6.9	3.1	11.3
	-0.1	6.9	3.1	7.6
	-0.2	6.9	3.1	3.5
Pt/C	-0.05	6.8	0.2	15.6
	-0.1	6.9	0.2	10.2
	-0.2	6.9	0.2	6.2

 Table S2. EIS analysis results of different catalysts.

 R_s is the electrolyte resistance, R_1 is related to the interface resistance, R_2 denotes the charge-transfer resistance.

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