Supporting Information

Bi-Cation Incorporated Ni₃N Nanosheets Boosts Water Dissociation

Kinetics for Enhanced Alkaline Hydrogen Evolution Activity

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Experimental section Contd.

Electrocatalytic Measurements

The electrochemical measurements were studied in a three-electrode test system and employing the CHI760E electrochemical workstation purchased from (Shanghai Chenhua Instrument Co., Ltd., China) as the testing apparatus. To maintain the contact area of the catalysts with the 1.0 M KOH electrolyte solution to be uniform, the catalyst was sealed with an epoxy resin leaving only a 1.0 cm² area for contact with the solution and also another small area at the other end for ohmic contact. The active material loadings on the CC are 1.82, 1.79, 1.71, 1.69, and 1.75 mg cm⁻² for Ni₃N, V-Ni₃N, Fe-Ni₃N, and V-Fe-Ni₃N, respectively. Both carbon rod and Hg/HgO in the saturated solution were employed as the counter and reference electrodes respectively. The polarization curves of the samples were measured at a scanning speed of 5.0 mV s⁻¹. The exact overpotential values (mV) were calculated based on the equation:

HER Overpotential (mV) = [E (Hg/HgO) +
$$0.099 + 0.059 \times pH$$
] × $1000 - 0 mV$ (1)

OER Overpotential (mV) =
$$[E (Hg/HgO) + 0.099 + 0.059 \times pH] \times 1000 - 1230 mV$$
 (2)

The Tafel slope is calculated from $\eta = b \log j + a$, where η is the overpotential, b is the Tafel slope, and j is the current density. Electrochemical impedance spectroscopy (EIS) was performed using an AC amplitude of 5 mV and frequency range of 1000000 Hz to 0.01 Hz. During the stability test, the electrolyte was vigorously stirred. The polarization curves are not iR-corrected and all electrochemical performance experimental were carried out under Ar atmosphere.

Turnover Frequency (TOF)

TOF is the number of times of reaction per unit time and unit active site. TOF values were calculated from the following equations:

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Where J is the current density [mA cm⁻²] at specified overpotentials, S is the geometric surface area [cm²] of the catalyst, n is the stoichiometric number of electrons consumed in the electrode reaction (n = 2 for the HER and n = 4 for the OER), F is the Faraday constant (96 485.3 C mol⁻¹), and N is the loading of active material per unit area. The active material loadings are 1.82, 1.79, 1.71, 1.69 and 1.75 mg cm⁻² for Ni₃N, V-Ni₃N, Fe5%-Ni₃N, Fe10%-Ni₃N and V-Fe-Ni₃N, respectively. Here we assumed all the metal sites were actively involved in the electrochemical reaction ¹.

Conversion of C_{dl} to ECSA

The specific capacitance for a flat surface is generally found to be in the range of 20 - 60 μ F cm⁻². In the following calculations of ECSA, we assume specific capacitance as 40 μ F cm⁻².

$$ECSA = \frac{Cdl}{40\,\mu F\,cm-2} \tag{4}$$

DFT Calculations

All the calculations were performed with the ABINIT software package. Total energy calculations were performed to study the properties of Ni₃N structure using the periodic density functional theory (DFT) and density functional perturbation theory (DFPT) which were implemented in ABINIT code. ABINIT stands for "Open-Source Package for Research in Electronic Structure, Simulation, and Optimization" ². *Exchange-correlation energy* was treated with the generalized gradient approximation (GGA) using the Perdew, Burke, and Enzerholf (PBE) parameterization ³. A 20 Å vacuum space between sheets was set to prevent the interaction between two membrane layers. The Brillouin zone of the fibre was sampled by $1 \times 3 \times 1$ k-points. The electronic structure of the system was treated using the generalized gradient approximation with the PBE functional

⁴. The van der Waals interactions were added to the standard DFT description by Grimme's D2 scheme ⁵. All calculations include spin polarization. In all calculations the convergence parameters were 10^{-6} eV for the energy, 0.01 eV Å⁻¹ for the forces and an energy cut-off of 500 eV. A Gaussian smearing of 0.05 eV was applied. The electron-ion interaction was modeled using the pseudo-potential generated by Van Setten et al., which gives very transferable norm conservation pseudo-potentials ⁶. Integrations in the reciprocal lattice were made using the kpoints generation method of Monkhorst and Pack⁷. Population analysis has been performed on the optimized structures in the ground state. Charge transfer analysis and electron density differences were performed with Multiwfn 3.2.1⁸. Models of Ni₃N were used to simulate the V-Ni₃N, Fe-Ni₃N, and V-Fe-Ni₃N samples. In the Supporting Information, we have outlined the models and how they have been built. We use the bridge site between the dopant element (V or Fe) and Ni element as the active site to simulate the catalytic reaction of the as-prepared catalyst. The two cations with a relatively short distance were chosen in the DFT calculations and the distance between two cations using DFT calculations to obtain the lowest energy and best catalytic activity for the co-doped structure were optimized. A similar small calculation model has been used in the calculations of many works of electrocatalytic water splitting ^{9, 10}. Based on the ICP results in Table S1, the content of V is about 2-3% and the content of Fe is about 3-9%, which is close to the atomic content we used in the DFT calculation (V-Ni₃N, V 3%; Fe-Ni₃N, Fe 5%; Fe-V-Ni₃N, Fe 3%, and V 2%).



Figure S1. The controlled experiment of the electrocatalysts. HER polarization curves of (a) V- Ni_3N with different V compositions and (b) Fe- Ni_3N with different Fe compositions compared with pristine Ni_3N . (c) LSV curves of Ni_3N and V-Fe- Ni_3N with different V and Fe compositions.

Three different concentrations of V and Fe with respect to Ni (2%, 5%, and 10%) were separately selected (details can be found in the experimental section). The 5%-V-Ni₃N achieved the best HER and selected for further discussion (Supporting Information, Figure S1a). For the Fe-doped catalysts, 5%-Fe-Ni₃N showed the best HER (Supporting Information, Figure S1b) and also selected for further discussion. Different doping concentrations of both V and Fe (2.5%-V-2.5%-Fe-Ni₃N and 5%-V-5%-Fe-Ni₃N) were also studied and the 5%-V-5%-Fe-Ni₃N (denoted V-Fe-Ni₃N, optimized catalyst in this work) exhibited the best catalytic performance (Supporting Information, Figure S1c). The Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) analysis was performed on V-Ni₃N, Fe-Ni₃N, Fe-Ni₃N, and V-Fe-Ni₃N) and the results are shown in Supporting Information, Table S1.

Sample	Elements	Atomic Percentage (At%)
Ni ₃ N	Ni	100%
V-Ni ₃ N	Ni	93.04%
	V	2.66%
5%Fe-Ni₃N	Fe	4.83%
	Ni	91.45%
5%V-Fe10%-Ni ₃ N	Fe	2.50%
	Ni	91.32%
	V	2.10%
10%Fe-Ni₃N	Fe	9.49%
	Ni	85.04%

Table S1. ICP data of Ni₃N, V-Ni₃N, Fe5%-Ni₃N, Fe10%-Ni₃N and V5%-Fe10%-Ni₃N

Based on the ICP results, the samples chemical formulas include: Ni₃N, V-Ni₃N, Fe-Ni₃N, Fe-Ni₃N and V-Fe-

Ni₃N



Figure S2. Low magnification SEM images of (a) Ni_3N , (b) V- Ni_3N , (c) Fe- Ni_3N , and (d) V-Fe- Ni_3N samples.



Figure S3. XRD spectra of the Ni₃N, V-Ni₃N, Fe-Ni₃N, and V-Fe-Ni₃N samples.



Figure S4. Polarization curve of the pristine CC.

	η@	Tafel slope	Loading	
Catalysts	10 mA cm ⁻²	(mV dec ⁻¹)	(mg cm ⁻²)	Reference
V-Fe-Ni ₃ N	70	65	1.75	This work
Co-Ni ₃ N	194	156	2.91	11
Ni₃FeN/r-GO	94	90	0.5 (GCE)	12
PO-Ni/Ni-N-CNFs	262	97.42	2.0	13
Co-Ni/Ni ₃ N	60	76	0.7(GCE)	14
FeNi ₃ N/NF	75	98	0.8 (GCE)	15
Cu ₁ Ni ₂ -N	71.4	106.5	1.70	16
NC–NiCu–NiCuN	93	55	1.50	17
Ni₃N@C	284		0.2 (GCE)	18
NiCo ₂ N-NF	290	79	-	19

Table S2. HER Performance of the recently reported Nickel nitride-based electrocatalysts.

 η represents overpotential (mV); OWS represents overall water splitting; GCE represents glassy

carbon electrode

	HER	Tafel slope	HER	Tafel slope
Catalyst	η @10 mA cm ⁻²	(mV dec ⁻¹)	η @ 100 mA cm ⁻²	(mV dec ⁻¹)
Ni ₃ N	185	103	407	388
V-Ni ₃ N	85	77	301	345
Fe-Ni₃N	182	120	394	394
V-Fe-Ni₃N	70	65	261	375

Table S3. HER performance comparison of the compared electrocatalysts

 η represents overpotential (mV).



Figure S5. CV curves of the (a) Ni_3N , (b) V- Ni_3N , (c) Fe- Ni_3N , and (d) V-Fe- Ni_3N at different current

scan rates to determine the ECSA at the HER region.

C_{dl} conversion to ECSA for HER

$$ECSA = \frac{9.15 \ mF \ cm - 2}{40 \ \mu F \ cm - 2} = 228.75 \ cm^2_{ECSA} \ for \ Ni_3N$$

$$ECSA = \frac{53.30 \text{ } mF \text{ } cm - 2}{40 \text{ } \mu F \text{ } cm - 2} = 1332.50 \text{ } cm^2_{ECSA} \text{ for V-Ni}_{3}\text{N}$$

$$ECSA = \frac{20.66 \ mF \ cm - 2}{40 \ \mu F \ cm - 2} = 516.50 \ cm^2_{ECSA} \ for \ Fe-Ni_3N$$







Figure S6. (a-b) SEM of V-Fe-Ni₃N after HER stability test. (c-d) TEM and HRTEM images of V-Fe-Ni₃N after HER stability test. (e) XRD spectra of the V-Fe-Ni₃N before and after HER stability test. (f) Ni 2pXPS spectra of V-Fe-Ni₃N before and after HER stability test.



Figure S7. (a) XRD spectra of the V-Fe-Ni₃N before and after stability test. (b) Raman spectrum of V-Fe-Ni₃N after stability test. (c) Ni 2pXPS spectra of V-Fe-Ni₃N before and after stability test.

Sample	Elements	Original Sample Solution Element Concentration (mg/L)	Test Solution Element concentration (mg/L)
After HER	Ni	<0.20	<0.02
LSV	V	<0.20	<0.02
	Fe	<0.20	<0.02
After HER	Ni	<0.20	<0.02
stability	V	<0.20	<0.02
	Fe	<0.20	<0.02

Table S4. ICP data of the KOH solution used in testing V-Fe-Ni₃N before and after electrolysis



Figure S8. Optimized structural models of (a) Ni₃N, (b) V-Ni₃N, (c) Fe-Ni₃N, and (d) V-Fe-Ni₃N.



Figure S9. (a) Optimized structural model and (b) models of the adsorbed species on V-Fe- $Ni_3N/NiOOH$ electrocatalyst for the HER steps.

Models	d-band
Ni ₃ N	-0.1636
V-Ni ₃ N	-0.2468
Fe-Ni ₃ N	-0.9612
Fe-V-Ni ₃ N	-1.0484

Table S5. The d-band center of the proposed models

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