Comprehensive Evaluation of Transition Metal Doped Ni_3N to Construct High-Efficiency Hydrogen Evolution Catalyst

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Abstract

Density functional theory (DFT) calculation indicators (ΔG , densities of state, D-band and bader charge) are commonly used to predict and analyze the hydrogen evolution reaction (HER) activity of catalysts, and most studies discuss only one or few of these indicators' impact on catalysis, but still no report has comprehensively evaluated the influence of all these indicators on catalytic performance. Herein, foreseen by comprehensive consideration first, we report transition metal doped Ni_3N nanosheets combined on Ni foam for ultra-efficient alkaline hydrogen evolution. For dual transition metals doped Ni_3N , Co,V- Ni_3N exhibits remarkable HER performance with a significantly low overpotential of only 10 mV in alkaline electrolyte and 41 mV in alkaline seawater electrolyte at 10 mA cm^{-2} ; while for single transition metal doped Ni_3N , V- Ni_3N exhibits the best performance with an overpotential of 15 mV and a Tafel slope of 37 mV dec^{-1} . Our work highlights the importance of comprehensive evaluation of DFT calculation indexes, and opens up a new method for the rational design of efficient and low-cost catalysts.

Introduction

The global energy pattern is undergoing a profound shift from relying on traditional fossil energy to pursuing clean and efficient energy. Countries are vigorously developing clean energy, reducing the use of traditional fossil energy, and actively looking for alternative energy sources.¹⁻⁴ As an ideal secondary energy carrier, hydrogen only emits water during its use and does not emit other harmful gases or solid particles.^{5,6} Hydrogen evolution reaction (HER) provides a promising path to generate high-purity hydrogen toward energy and environmental sustainability.⁷ Currently, one of the challenging issues in HER is to explore earth-abundant, long-term available, corrosion resistant, and efficient electrocatalysts for the practical application of hydrogen-energy technology.⁸ Commercial noble metals (such as Pt and Ru) are the most remarkable HER electrocatalysts due to their unique electronic properties, low Gibbs free energy for desorption and adsorption of hydrogen and low energy barrier for splitting water molecules.⁹⁻¹¹ However, their high cost, rarity and not-durability restrict the actual application in the water electrolysis industry. Another challenging issue is alkaline water splitting systems use pure water as the hydrogen source, which requires a lot of water resources. We know that freshwater resources on the earth are very rare, and large-scale freshwater electrolysis will exacerbate the problem of water scarcity. Seawater, which accounts for roughly 97% of the water volume on the earth, would be the most appropriate substitute for high purity freshwater in industrial production, and various anions and cations rich in seawater can also enhance the conductivity of the electrolyte.^{3,12} However, unlike freshwater, the composition of seawater is very complex, and the high concentration of chloride ions will not only compete with the oxygen evolution reaction (OER) of the electrolyzed water at the anode to release chlorine,⁷ but also severely corrode most of the catalysts containing metal elements. The highly corrosive hypochlorite by-products of chlorine evolution reaction (CER) will also block the active sites of the noble metal catalysts, and thus

the noble metal catalysts for HER can not be used.^{9,13} Therefore, the development of stable, high-activity and corrosion-resistant electrocatalysts is crucial to the hydrogen production industry.

Transition metal nitride (TMN) is one of the excellent electrocatalysts towards HER due to its outstanding conductivity and corrosion resistance.¹⁴ Nevertheless, most of the bulk TMNs reported have two existing drawbacks: the sluggish kinetics which needs extra energy to yield protons by the water dissociation, and destabilization in alkaline water. Therefore, many significant studies have been devoted to solving these problem. Apart from the usual modification strategy of vacancy engineering^{15,16}, heterojunction engineering¹⁷ and introducing metal-organic frameworks (MOFs)^{18,19}, transition metal doping (TMD) has been one of the most facile and effective methods to modulate physicochemical properties and lattice structures of each individual electrocatalyst to improve HER catalytic performance and stability.²⁰⁻²² It is worth noting that transition metal doping is directly related to local electron redistribution, valence states, free energy of adsorption (ΔG) and D-band center shift, and all of these indicators also deeply affect the performance of electrocatalysts.^{20,21} For example, RuIr bifunctional nanocrystals incorporated with transition metal (Co, Ni and Fe) exhibit a low overpotential for water splitting through modification of electronic structure, and this report highlights that the concentration of O-based species and valence states of catalysts are essential for catalytic performance.²³ Density functional theory (DFT) computations and physicochemical characterizations confirm that densities of states (DOS) of Co doped Ni_3N (Co- Ni_3N) are larger than those of pristine Ni_3N which boost electron and mass transfer to the surface during electrocatalytic process.²⁴ Zhang et al.²² proposed favorable hydroxyl adsorption free-energy could observably promote the kinetics of high-valence transition metal (Mo, W and V) doped Ni_3N , and found the downshift of the D-band center weakened the bond energy of the adsorbed species, resulting in remarkable electro-catalytic property. A novel Cr-doped Co_4N catalyst was prepared and the bader charge analysis indicated that Cr atom with much higher positive valence would be much easier to attract negatively charged oxygen atoms in the water molecules through strong electrostatic interaction, and thus to promote subsequent HER reaction steps.²⁰ Furthermore, Li et al.²⁵ verified that the incorporation of Mn into CoP nanowires noticeably made the catalyst expose more active site, facilitating adsorption behavior, and further manipulated the reaction activity for HER. In short, the existing literatures mostly start from one or a few of these recognized indicators to study the function of TMD. However, HER process is a comprehensive expression of the physical and chemical characteristics of the catalyst. It is one-sided and inaccurate to explore its impact on HER performance around a single index, thus leaving plenty of room for comprehensively considering all the calculation indicators to more scientifically and thoroughly evaluate their impact on HER. Furthermore, significant issues in TMD are all about single transition metal doping (STMD) and there are rare reports on dual transition metals doping (DTMD). Therefore, we ask whether the reasonable adjustment of DTMD will achieve a synergistic effect and further enhance HER performance?

Herein, a new method is provided to predict HER performance by comprehensively evaluating various DFT indicators, which points out a new way for the preparation of HER electrocatalysts guided by DFT

calculation. A series of STMD and DTMD Ni_3N were evaluated by the new method, and we found that V- Ni_3N and Co,V- Ni_3N possessed the optimizing comprehensive indicators (ΔG , DOS, D-band center and bader charge). All the evaluated STMD and DTMD Ni_3N were fabricated as well and the electrochemical test verified the rationality of the new evaluation method. DFT calculation reveals that the main function of V doping is to optimize the conductivity (DOS), charge distribution (bader charge) and ΔG_{H^*} of the catalyst. Physicochemical characterizations and electrochemical test confirm that Co doping increases the real active sites (Ni^{2+}) exposed on the catalyst surface. The Co,V- Ni_3N produced from the nitridation of the Co,V-Ni(OH)₂ precursor shows ultra-efficient alkaline HER activity ($\eta_{10}=10$ mV) with a small Tafel slope of 43 mV dec^{-1} , as well as ultra-long robust stability over 100 h, while V- Ni_3N exhibits the overpotential of 15 mV with a Tafel slope of 37 mV dec^{-1} . For practical application, we further examined the HER performance in alkaline seawater (pH = 13.1) and Co,V- Ni_3N exhibits an low overpotential of 41 mV at 10 mA cm^{-2} with a small Tafel slope of 46 mV dec^{-1} .

Results

Comprehensive analysis of DFT calculation indicators

To elucidate systematically the intrinsic effect of TMD on the HER performance, theoretical calculations of ΔG_{H^*} , $\Delta G_{\text{H}_2\text{O}^*}$, DOS, D-band and bader charge, several commonly accepted descriptors for HER performance, were carried out. Ni_3N models with various metals doping were established by replacing Ni with corresponding transition metals (Fe, Mo, W, V, Mn, Co and Cr) as shown in supplementary Fig. 1. HER is a combination of proton adsorption and desorption on the catalyst surface. According to Sabatier principle²⁶, the optimal value of H^* adsorption ($|\Delta G_{\text{H}^*}|$) is required to be much closer to the theoretical ideal value ($\Delta G_{\text{H}^*} = 0 \text{ eV}$) for easy H adsorption and release of H_2 . Foreseen by computational study, Cr- Ni_3N , V- Ni_3N and Co- Ni_3N possess superior ΔG_{H^*} on the above mentioned sites (Supplementary Fig. 2) of 0.098 eV, 0.102 eV and 0.117 eV (Fig. 1a), respectively. However, Ni_3N , W- Ni_3N , Mo- Ni_3N , Mn- Ni_3N and Fe- Ni_3N show too weak or too strong ΔG_{H^*} (Supplementary Table 1). Furthermore, we chose representative Co, V and Cr to construct a series of dual doping molecular models (Co,V- Ni_3N , Co,Cr- Ni_3N and Cr,V- Ni_3N). The ΔG_{H^*} of Co,V- Ni_3N , Co,Cr- Ni_3N and Cr,V- Ni_3N are -0.076 eV , 0.078 eV and -0.111 eV , respectively, which reveals that Co,V- Ni_3N exhibits the most optimal ΔG_{H^*} among all samples. (Fig. 1a, Supplementary Fig. 3 and Table 2). Alkaline HER consists of prior water adsorption ($^*\text{H}_2\text{O}$) and dissociation to form adsorbed hydrogen ($^*\text{H}$) followed by H_2 generation. Therefore, the adsorption of water is a significant step in alkaline HER that directly affects whether the catalyst can be put into industrial application. The most-energy negative of water absorption of Mn- Ni_3N demonstrates that Mn- Ni_3N is most conducive to water adsorption (Fig. 1b). As shown in Supplementary Figs. 4–5 and Tables 3–4, V- Ni_3N , Co,V- Ni_3N , Mo- Ni_3N , W- Ni_3N and Co,Cr- Ni_3N exhibit very high negative $\Delta G_{\text{H}_2\text{O}^*}$ (-0.265 , -0.197 , -0.176 , -0.139 and -0.068 eV , respectively), indicating strong attraction for water while Cr- Ni_3N , Co- Ni_3N , Fe- Ni_3N and Cr,V- Ni_3N show very weak interactions with water as their $\Delta G_{\text{H}_2\text{O}^*}$ are very high (0.138 , 0.195 , 0.202 and 0.299 eV ,

respectively) It is worth noting that Co,V-Ni₃N shows the largest density of state (DOS) near the Fermi level among all the STMD or DTMD Ni₃N. Notably, Co,V-Ni₃N has superior electroconductibility and faster interfacial electronic transfer kinetics (Fig. 1c).¹⁴ Meanwhile, STMD V-Ni₃N and Cr-Ni₃N show a relatively high DOS value, indicating that they also have better conductivity (Supplementary Fig. 6). The DOS near the Fermi level which is mainly derived from the D-band was investigated as well. Figure 1d displays the D-band center (E_d) of Ni atom for Co,V-Ni₃N, Co,Cr-Ni₃N and Cr,V-Ni₃N (-1.35, -1.32 and - 1.38 eV, respectively), which are lower than those of the STMD Ni₃N (Supplementary Fig. 7), clearly implying the DTMD is conducive to the deviation of the metal D-band from the Fermi level. According to the D-band theory, it suggests more electron filling (higher occupation) of anti-bonding states between adsorbate and catalyst's D-band, leading to a weakened interaction between adsorbate and surface. Besides, the charge density difference of the various doped Ni₃N was performed (Fig. 1e and Supplementary Figs. 8–16). In all models, the electron exchange between V atom and Ni₃N in V-Ni₃N reaches the maximum of 6.92 e⁻. A large number of electrons transfer will change the physicochemical properties of the catalyst surface and improve the catalytic performance, which is consistent with the mechanism of pumping effect.²⁷ The above results show that these optimized calculation indicators will more or less improve the HER performance of the electrocatalysts. However, the HER process is controlled by multiple factors. Analysis of a single indicator can't accurately and comprehensively predict the HER performance of the catalysts. Only by comprehensively considering all the calculation indexes, can DFT accurately and scientifically guide us to synthesize excellent catalysts. Therefore, the above calculation indicators were normalized and present in radar charts (Fig. 1f-g). It should be noted that STMD and DTMD were considered separately due to the different doping contents. The larger the area occupied in the radar chart, the higher the catalytic activity of HER. The specific area value is shown in Supplementary Table 5. We speculate that the catalytic performance is roughly following the trend of V-Ni₃N > Cr-Ni₃N > Mn-Ni₃N > Mo-Ni₃N > Co-Ni₃N > W-Ni₃N > Fe-Ni₃N in STMD Ni₃N, while the order of DTMD Ni₃N is Co,V-Ni₃N > Cr,V-Ni₃N > Co,Cr-Ni₃N. This means V-Ni₃N and Co,V-Ni₃N will exhibit the most remarkable HER catalytic performance (Fig. 1h) in STMD and DTMD Ni₃N, respectively.

Morphology and elemental characteristics

Guided by the theoretical calculations, Ni₃N nanosheets with TMD (Fe, Mo, W, V, Mn, Co and Cr) assembled on microporous nickel foam were fabricated via a novel straightforward two-step process (Fig. 2). We prepared the final catalysts by using nickel and transition metal salts as raw materials to synthesize nano-array precursors (Ni(OH)₂) through a simple hydrothermal method; and then following by annealing Ni(OH)₂ at 450°C for 2 h under an NH₃ atmosphere (See methods and Experimental Section for details). Figure 3a-b show the typical low-magnified scanning electron microscopy (SEM) images of DTMD Co,V-Ni₃N with a thin (typically around 20–30 nm) nanosheets morphology. The optimized STMD V-Ni₃N exhibits a sheet-like morphology with a thickness of 50–100 nm (Supplementary Fig. 17). For microstructure of Ni₃N, however, the nanosheets are made up of total nano-particles and collapse to varying degrees with the average thickness of 200–400 nm (Supplementary Figs. 18–19). According to

previous research, the thinner nanosheet structure possesses higher surface area with more active sites exposed.²⁸ Furthermore, by comparing the SEM images of different samples (Supplementary Fig. 19), it can be verified that the microscopic morphology of the catalysts has a lot to do with the doping element type. Figure 3d-e displays transmission electron microscopy (TEM) images which can provide sufficient evidence to prove the typical nanosheet structure of Co,V-Ni₃N. The high-resolution transmission electron microscopy (HR-TEM) images (Fig. 3f) of Co,V-Ni₃N indicate the (201) plane of Ni₃N (JCPDS No. 89-5144) with a lattice fringe of 0.18 nm, suggesting the incorporation of Co and V does not cause lattice distortion, in accordance with the later XRD results (Supplementary Figs. 20–22).

Furthermore, on the basis of selected area electron diffraction (SAED) and elemental mappings, we further identify that Ni, Co, V and N elements uniformly distribute in this region in Fig. 3g-l, providing more definitive evidence for the successful preparation of Co,V-Ni₃N. The TEM image of V-Ni₃N shows the sheet-like structure. The lattices of Ni₃N (002) can be distinctly observed, showing the formation of V doped Ni₃N. The STEM images and corresponding EDX mapping show homogeneous distributions of Ni, V and N in V-Ni₃N (Supplementary Fig. 17d).

Analysis of physical properties of samples.

To further study the chemical composition and unique information about the interaction of electrons for the prepared catalysts, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and electron paramagnetic resonance (EPR) analyses were conducted. As shown in Supplementary Figs. 20–22, the XRD patterns demonstrate the existence of Ni (JCPDS No. 04-0850) and Ni₃N (JCPDS No. 89-5144) in the catalyst, where Ni is from nickel foam (NF). After a fine comparison of the diffraction peaks of XRD patterns, it can be well indexed to (002) planes of hexagonal Ni₃N. Moreover, according to the latest research, when the nitriding temperature is higher than 350°C, part of the Ni₃N on the catalyst surface is decomposed, which also causes the disappearance of some peaks.^{29–31} Supplementary Table 6 exhibits the details of crystal structures of phases in samples. In Supplementary Fig. 23a, the XPS survey spectra exhibit the fundamental elements of Co,V-Ni₃N, further confirming its chemical composition. In the high-resolution Ni 2p spectra (Fig. 4a), the peak at 852.79 eV is ascribed to Ni^(δ+).³² The binding energies at 856.02, 873.76, 861.97 and 879.38 eV are corresponding to Ni 2p_{3/2}, Ni 2p_{1/2} of Ni²⁺ and the satellite peaks (defined as Sat.), respectively.^{22,33} The peak fitting analysis of N 1s displays in Fig. 4b, in which the binding energy at 397.04 eV shows existence of N-M (Ni, Co and V).^{17,14,34} The small peak at 399.72 eV is ascribed to residual NH, which originates from the incomplete reaction part of NH₃.³⁵ For the Co 2p spectra (Fig. 4c), the peaks at 781.26 and 787.39 eV are corresponding to Co 2p_{3/2} of Co-N bond (Co³⁺) and shakeup satellite, respectively. The fitting peak at 774.14 eV of Co-Co bond (Co⁰) suggests the formation of efficient active sites for water splitting.^{21,36} Meanwhile, the peaks with binding energies of 516.84 eV and 524.25 eV correspond to V 2p_{3/2} and V 2p_{1/2} of the V-N bond, and the peak located at 517.73 eV is attributed to V⁵⁺ (Fig. 4d).^{21,37,38} The appearance of Co-N and V-N species further manifests the successful doping of Co and V into Ni₃N. By

comparison with pristine Ni_3N , the Ni 2p peaks of Co,V- Ni_3N are apparently upshifted by 0.6 eV, while N 1s peaks show a positive shift of 0.1 eV. The various peak binding energies imply significant electron transfer and strong electronic interaction after Co, V dual doping. The both increased binding energies of Ni 2p and N 1s indicate the electrons transfer from Ni to N, which leads to the conversion of Ni^+ to Ni^{2+} on Co,V- Ni_3N surface.³⁹ The XPS survey spectra of V- Ni_3N exhibit the fundamental elements of V- Ni_3N (Supplementary Fig. 24). High-resolution Ni 2p spectra reveal the existence of Ni^{2+} (856.36 and 874.03 eV), Ni^{3+} (857.93 eV), and a satellite peak (862.34 and 880.1 eV). Supplementary Fig. 24c shows the presence of N-M (Ni,V). The peaks at 516.6 and 525.2 eV correspond to the V $2p_{3/2}$ of the V-N bond, and the peak located at 517.9 is corresponding to V^{5+} . Meanwhile, the various peak binding energies of Ni $2p_{3/2}$ for V- Ni_3N (856.36 eV) and fresh Ni_3N (856.16 eV) suggest Ni in V- Ni_3N was oxidized, while the binding energies of N-M (Ni,V) for V- Ni_3N (396.93 eV) and fresh Ni_3N (397.02 eV) show that N in V- Ni_3N has lost electrons. Compared with Co,V- Ni_3N , the bonding energy of V has shifted negatively by 0.2 eV, indicating that V atom in V- Ni_3N has acquired electrons. Generally, the XPS analysis accurately verifies the result of the charge distribution in DFT. The XPS spectra and bonding energies of Co,Cr- Ni_3N , Cr,V- Ni_3N , Cr- Ni_3N , Co- Ni_3N , Mn- Ni_3N , Mo- Ni_3N , W- Ni_3N and Fe- Ni_3N are shown in Supplementary Figs. 26–33, confirming the chemical composition of these catalysts. In addition, the semi-quantitative analysis on XPS of Ni^{2+} concentration further confirms the valence conversion ($\text{Ni}^+ \rightarrow \text{Ni}^{2+}$) after TMD.^{33,40} As shown in Table 1, Co- Ni_3N , Co,V- Ni_3N and Co,Cr- Ni_3N show more higher concentration of Ni^{2+} . It has been reported that the active HER site in Ni_3N was on Ni cations, and Ni^{2+} could help to accelerate the kinetic rate of the HER.^{17,41,42} Thus, we propose that the main function of Co doping is to promote the exposure of active sites on the catalyst surface which contributes to excellent catalytic performance. Raman spectra (Fig. 4e and Supplementary Fig. 25a) reveal that the vibrational bands below 1000 cm^{-1} can be attributed to the Ni_3N nanosheets, further confirming the fabrication of the Ni_3N . The characteristic peak of the Ni vacancy can be clearly detected at 3510 Guss from EPR spectra, where the introduction of transition metal increases the concentration of nickel vacancies (Fig. 4f and Supplementary Fig. 25b).² According to previous reports, vacancies and defects are also the real active sites of catalysts.^{15,43} Next, the band structure of Ni_3N catalysts was collected by UPS (Fig. 4g-h). The cutoff energies (E_{cutoff}) of Ni_3N , Co,V- Ni_3N , Co,Cr- Ni_3N and Cr,V- Ni_3N are 16.91, 17.93, 17.06 and 16.99 eV, respectively. Accordingly, the work functions (e_ϕ) can be calculated to be 4.31, 3.29, 4.19 and 4.23 eV by the equation ($e_\phi = h\nu - |E_{\text{cutoff}} - E_F|$), while all the E_F are 0 eV (Fig. 2e). The e_ϕ of V- Ni_3N is 3.54 eV, as shown in Supplementary Fig. 25c. The reduction of e_ϕ facilitates the electron exchange and mass transfer on the surface of the electrocatalyst, therefore, accelerating the HER catalytic process, which agrees well with the DOS of DFT calculation. The valence band maximum values (E_V) are determined to be 2.90, 3.34, 3.19 and 2.95 eV of Ni_3N , Co,V- Ni_3N , Co,Cr- Ni_3N and Cr,V- Ni_3N , respectively, while E_V of V- Ni_3N is 2.93 eV (Supplementary Fig. 25c). According to the D-band theory, shifting away from the Fermi level (down-shifting of the D-band center) mainly contributes to higher occupation of the anti-bonding states of catalysts, hence a weaker adsorption.⁷ As shown in Fig. 4h, the increased valence band maximum indicates that ΔG of

electrocatalysts after transition metal doping becomes smaller, thus benefiting for the desorption of intermediate and hydrogen.³⁰ Similarly, the experimental results perfectly confirms our DFT calculation.

Table 1
XPS semi-quantitative analysis for the content of divalent Ni.

sample	Co,V-Ni ₃ N	Co,Cr-Ni ₃ N	Cr,V-Ni ₃ N	V-Ni ₃ N	Cr-Ni ₃ N
content of Ni ²⁺ (%)	65.16	65.16	59.03	64.92	57.98
sample	Co -Ni ₃ N	Mn-Ni ₃ N	Mo-Ni ₃ N	W-Ni ₃ N	Fe-Ni ₃ N
content of Ni ²⁺ (%)	68.18	61.97	64.22	53.97	59.14

Electrochemical properties and catalytic activity

To further confirm the superior electrochemical catalytic performance of TMD Ni₃N toward the HER, electrochemical test was carried out in 1.0 M KOH using a standard three-electrode setup and the commercial Pt/C was also tested for comparison. To verify the DFT predicted results and more comprehensively analyze the effect of transition metals on the catalytic performance of Ni₃N, we also evaluated STMD Ni₃N for comparison (Supplementary Fig. 34).

As shown in Fig. 5a and e, the linear sweep voltammetry (LSV) curves display the overpotentials of Co,V-Ni₃N (10 mV), Co,Cr-Ni₃N (70 mV), Cr,V-Ni₃N (82 mV), Ni₃N (141 mV) and commercial Pt/C (38 mV) at 10 mA cm⁻² in 1M KOH solution. The overpotentials of V-Ni₃N, Cr-Ni₃N, Co-Ni₃N, Mn-Ni₃N, Mo-Ni₃N, W-Ni₃N and Fe-Ni₃N are 15, 22, 30, 80, 97, 100 and 142 mV, respectively, at 10 mA cm⁻² in 1M KOH solution. As our comprehensive forecast, the as-synthesized Co,V-Ni₃N has the most remarkable alkaline-electrochemical hydrogen evolution performance in DTMD Ni₃N, while V-Ni₃N shows the best performance in STMD Ni₃N, and their activity even surpasses the commercial Pt/C significantly. Here, the smaller Tafel slope (43 mV dec⁻¹) compared with counterparts of Co,Cr-Ni₃N (75 mV dec⁻¹), Cr,V-Ni₃N (94 mV dec⁻¹) and Ni₃N (123 mV dec⁻¹), directly, demonstrates more favorable HER kinetics on Co,V-Ni₃N (Fig. 5b). The Tafel slope of V-Ni₃N, Cr-Ni₃N, Co-Ni₃N, Mn-Ni₃N, Mo-Ni₃N, W-Ni₃N and Fe-Ni₃N are 37, 46, 47, 62, 70, 64 and 96 mV dec⁻¹, respectively (Supplementary Fig. 34b). Apparently, among all the catalysts, V-Ni₃N shows the smallest Tafel slope, which may be related to the large amount of electron transfer in V-Ni₃N. As observed in Fig. 5c, the charge-transfer resistance (R_{ct}) was investigated by electrochemical impedance spectroscopy (EIS). Co,V-Ni₃N possesses a small R_{ct} value of approximately 0.98 Ω , which is considerably lower than those of counterparts (Co,Cr-Ni₃N: 2.4 Ω , Cr,V-Ni₃N: 4.3 Ω , and Ni₃N: 7.0 Ω). Furthermore, the EIS of single-doped Ni₃N was collected in Fig. 34b and it confirms type of

doping element is crucial for yielding a distinguished electrocatalyst for HER again. The fast electron transport of V-Ni₃N and Co,V-Ni₃N with a favorable charge-transfer resistance and the better reaction kinetics would contribute to their enhanced catalytic activity toward HER. Next, typical cyclic voltammetry (CV) in the non-Faradaic region under with various scan rates (10–60 mV s⁻¹) was recorded to further study the innate activities of Ni₃N (Supplementary Fig. 35). Electrochemically active surface area (ECSA) is determined by the C_{dl} curve, which was acquired via CV. As shown in Fig. 5d, the C_{dl} value of Co,V-Ni₃N (11.8 mF cm⁻²) is higher than those of Co,Cr-Ni₃N (10.1 mF cm⁻²), Cr,V-Ni₃N (5.5 mF cm⁻²), and Ni₃N (2.6 mF cm⁻²). Throughout all the samples, Co-Ni₃N (15.6 mF cm⁻²) possesses largest C_{dl} and samples containing Co also show a larger C_{dl}, which once again confirms that the main impact of Co is to increase the ECSA of the catalyst and expose more active sites (Supplementary Fig. 34d). Corroborating the operation durability of the electrocatalys is another indispensable indicator. The overpotential after 3000 CV cycles was negligible higher than pre-test overpotential at 100 mA cm⁻² and the result of chronopotentiometry demonstrates its preeminent stability as well (Fig. 5h). As shown the inset in Fig. 5h and Supplementary Fig. 36, neither the macroscopic morphologies nor the main XPS peaks of the elements have changed, which also proves that the catalyst has excellent catalytic corrosion resistance after even 100 h of continuous operation at -10 mA cm⁻² (Fig. 5g). The stability test of V-Ni₃N is shown in Supplementary Fig. 37. In addition, the turnover frequency (TOF) of Co,V-Ni₃N and V-Ni₃N with the best catalytic performance at 100 mV, calculated based on the previously reported method, is 8.78 s⁻¹ and 3.64 s⁻¹ in alkaline solutions (Supplementary Fig. 38), indicating its high intrinsic catalytic activity towards the HER.^{44,45} The volcano map drawn based on the exchange current density (*j*₀) and Δ*G*_{H*} is shown in Fig. 5f and the trend basically in line with DFT prediction (Fig. 5f). The loading is shown in the Supplementary Table 7. To our knowledge, the performance of V-Ni₃N and Co,V-Ni₃N is superior to all the present state-of-the-art transition metals HER electrocatalysts reported so far (Supplementary Tables 8–9).

All in all, the trend of HER performance of these catalysts is basically consistent with our DTF prediction results, which shows that comprehensive consideration of the DFT calculation indicators proposed by us can accurately forecast the activity of catalysts. However, we need to point out that the normalization of this comprehensive consideration does not involve the weight of the impact of each indicator on the catalyst performance, which may cause a certain error but the comprehensive evaluation is still better than the single indicator evaluation, and we will follow up the discussion on weights in future research.

For practical application, we explored the catalytic performance of the catalysts in seawater electrolysis. As shown in Supplementary Fig. 39, the pure seawater was collected from the local coast in Qingdao (pH ≈ 8.1). The natural seawater is not suitable for electrolyte.⁹ Firstly, chlorine evolution reaction (CER) occurs at the anode of seawater electrolysis, competing with OER. The generated chlorine and the hypochlorite dissolved in the electrolyte will corrode cathode material.

Secondly, the high concentration of toxic cations (Ca^{2+} and Mg^{2+}) in natural seawater will be electrodeposited on the surface of the cathode, which block the active sites. Thirdly, CER is more competitive than OER in natural seawater, and there will be more chlorine and hypochlorite produced and corrode the electrode. Hence, we further examined the HER performance of Ni_3N catalysts in alkaline seawater (pH = 13.1). Co,V- Ni_3N achieves an overpotential of only 41 mV at 10 mA cm^{-2} and a small Tafel slope of 46 mV dec^{-1} (Fig. 6a-c), which are superior than those of Ni_3N and other previously reported catalysts (Supplementary Table 10). Other than activity, the most critical catalytic performance index is the stability. In contrast, Co,V- Ni_3N and Ni_3N were conducted a continuous chronoamperometry for 6 h (Fig. 6d). ICP results showed that after 6 hours of chronoamperometry, the concentration of Ca and Mg in the electrolyte became smaller due to the formation of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$. The dissolved Ni concentration of Co,V- Ni_3N is much less than that of Ni_3N , confirming excellent corrosion resistance of Co,V- Ni_3N (Table 2). The overpotential after 3000 CV cycles was negligible higher than pre-test overpotential at 100 mA cm^{-2} (Fig. 6e). The above analysis demonstrates preeminent activity, corrosion resistance and stability of Co,V- Ni_3N in the chloride environment. After the HER test in 1M KOH/seawater, XRD, XPS, SEM, HR-TEM and EDS mapping were employed to probe stable chemical components and micro morphology of the samples. The XRD is shown in Supplementary Fig. 40, and there is no change compared to the original sample. Furthermore, XPS shows except for the disappearance of the $\text{Ni}^{(6+)}$ and the exposure of Ni^{3+} caused by surface dissolution, there is no shift in the Ni 2p spectra (Fig. 6f).^{46,47} HR-TEM images (Fig. 6g-i) of the post-HER demonstrate a nanosheet morphology very similar to the original morphology. EDS mapping images (Supplementary Fig. 41) show that its chemical element composition is still Ni, Co, V and N. These results indicate that the continuous long-term HER process hardly corrodes the surface structure of Co,V- Ni_3N .

Table 2
Concentration of elements obtained from alkaline seawater, Co,V- Ni_3N and Ni_3N in alkaline seawater after chronoamperometry test at a current density of 10 mA cm^{-2} for 6 h.

	Concentration of elements (mg/L)			pH
	Ca	Mg	Ni	
Alkaline seawater	28.105	16.783	-	8.1
Co,V- Ni_3N in alkaline seawater	0.190	8.073	0.018	13.1
Ni_3N in alkaline seawater	0.321	8.091	0.031	13.1

Discussion

In summary, a new method for comprehensive consideration of DFT calculation indicators is proposed, which can comprehensively and accurately predict the catalytic performance of the catalysts. Guided by the theoretical calculations, the as-prepared Co,V-Ni₃N and V-Ni₃N exhibit remarkable performance as well as distinguished durability (up to 100 h) in alkaline media. Co,V-Ni₃N delivers 10 mA cm⁻² at a low overpotential of only 10 mV in alkaline electrolyte and 41 mV in alkaline seawater at a current density of 10 mA cm⁻², while V-Ni₃N exhibits the overpotential of 15 mV with a Tafel slope of 37 mV dec⁻¹ in alkaline medium. Such alkaline HER performances are compared with commercial Pt/C and superior to most reported noble metals and non-noble metals catalysts. Our work provides a new scientific method for DFT prediction of catalyst performance and opens up opportunities for exploring high-efficiency and lost-cost electrocatalysts for HER.

Methods

Synthesis of Co,V-Ni(OH)₂ / V-Ni(OH)₂

Typically, 0.05 mmol NH₄VO₃, 0.05 mmol Co(NO₃)₂·6H₂O, 0.90 mmol Ni(NO₃)₂·6H₂O, 5 mmol of CO(NH₂)₂ and 2 mmol NH₄F were dissolved in 20 mL deionized water under stirring to form a homogeneous solution. The solution and a piece of nickel foam (NF, 2cm*3cm) were transferred into a 50 mL Teflon-lined autoclave, sealed and kept at 120 °C for 8h, to obtain dual doped nickel hydroxide (Co,V-Ni(OH)₂) nanosheets array, which was further cleaned with water and ethanol, respectively. The V-Ni(OH)₂ was also synthesized with similar procedure without adding Co(NO₃)₂·6H₂O.

Synthesis of catalysts

The nanosheets was fabricated by nitridation of the prepared nickel hydroxide nanosheets in a tube furnace system at 450 °C for 2h under the high purity NH₃ atmosphere which was named as Co,V-Ni₃N and V-Ni₃N.

Materials characterization

X-ray diffraction was conducted on a PANalytical X'Pert Powder. Field-emission scanning electron microscopy (FESEM) analysis was performed on the JEOL JSM-7800F. High-resolution transmission electron microscopy, and energy-dispersive spectroscopy mapping were performed on the Talos F200S. X-ray photoelectron spectroscopy experiments were performed on the ESCALAB250Xi. Ultraviolet Photoemission Spectroscopy experiments were collected at ThermoFisher ESCALAB 250Xi. Electron paramagnetic resonance (EPR) spectra were measured by Bruker A300 spectrometer at 20°C. ICP- OES analysis was conducted using an Optima 8000 instrument.

Electrochemical measurement

All electrochemical measurements were performed on CHI660E electrochemical work station (Shanghai Chenhua Instrument Co., Ltd., China) by using the typical three-electrode set-up at 25°C. Transition metal doped Ni₃N was used directly as the work electrode (1 cm⁻² electrode area), and a Hg/HgO electrode and a graphite rod served as the reference electrode and the counter electrode, respectively.

DFT calculations

In the calculations, work functions were calculated use clean and M (M = Fe, Mo, W, V, Mn, Co and Cr) doped Ni₃N (002) surfaces. Plane-wave density functional theory (DFT) calculations were performed on CASTEP code of the Materials Studio package of Accelrys Inc. Generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE) functional was employed for the DFT exchange correlation energy and ultrasoft pseudo-potentials are used for the core electrons. A plane-wave basis set with an energy cutoff energy of 500 eV was assigned. The force atomic relaxation was 0.01 eV Å⁻¹. The Ni₃N (001) surface was modeled by a periodic five-layer slab repeated in 2×2 surface unit cell with a vacuum width of 15 Å between the slabs along the Z axis, where all atoms were fully relaxed. The water adsorption energy E_{H2O} is calculated by $E_{\text{H2O}} = E_{(\text{surf}+\text{H2O})} - E_{(\text{surf})} - E_{\text{H2O}}$, where $E_{(\text{surf}+\text{H2O})}$ and $E_{(\text{surf})}$ are the total energies of the surface with and without the H₂O adsorbate, and $E_{(\text{H2O})}$ is the energy of a free water molecule. Additionally, the hydrogen adsorption free energy ΔG_{H^*} is calculated by $\Delta G_{\text{H}^*} = E_{(\text{surf}+\text{H})} - E_{(\text{surf})} - 1/2E_{(\text{H}_2)} + \Delta E_{\text{ZPE}} - T\Delta S$, where ΔE_{ZPE} and ΔS are the difference in the zero-point energy and entropy between the adsorbed H atom and the gaseous phase H₂. At T = 289.15 K, ΔG_{H^*} can be calculated by $\Delta G_{\text{H}^*} = E_{(\text{surf}+\text{H})} - E_{(\text{surf})} - 1/2E_{(\text{H}_2)} + 0.24 \text{ eV}$.

Data Availability

The authors declare that the data supporting the findings of this study are available within the article and its Supplementary Information files. Additional data are available from the corresponding authors upon reasonable request.

Declarations

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Meng Wang and Prof. Jie Dang conceived the idea and co-wrote the paper. Dr. Zepeng Lv helped with the material characterization. Prof. Xuwei Lv guided all aspects of the work. Prof. Qian Li contributed to theoretical calculations.

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Ethics declarations

Competing interests

The authors declare no competing interests.

Supplementary information

Supplementary information

Supplementary Figs. 1–41 and Tables 1–10.

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Figures

Figure 1

DFT prediction. (a) H and (b) H₂O adsorption free-energy for different catalysts. (c) Density of states (DOS) of different systems. (d) Projected density of states (PDOS) of Ni atom. (e) Charge density distributions of Co,V-Ni₃N. Blue and yellow contours represent electron depletion and accumulation, respectively. Radar chart after normalization for (f) STMD Ni₃N and (g) DTMD Ni₃N. (h) Schematic diagram of electrolyzed water.

Figure 2

Schematic illustration of the fabrication process

Figure 3

Characterizations of Co,V-Ni₃N. (a-c) SEM; (d-e) TEM, and (f) HRTEM images of the prepared Co,V-Ni₃N nanosheets. (g) SAED. (h-l) HAADF-STEM image and the elemental mapping images of Ni, Co, V and N.

Figure 4

Surface electronic structure of samples. High-resolution Ni 2p (a), N 1s (b) Co 2p (c) and V 2p (d) XPS spectra; Raman spectra (e), EPR spectra (f) and UPS spectra (g, h).

Figure 5

HER performance of $\text{Co,V-Ni}_3\text{N}$. (a) LSV curves in 1 M KOH, (b) Tafel plots derived from the polarization curves, and (c) the Nyquist plots (inset: magnified image). (d) The Cdl values of different samples. (e) Comparison of overpotential at 10 and 100 mA cm^{-2} of the catalysts in this study. (f) Volcano map of TMD catalysts. (g) I-t curves for $\text{Co,V-Ni}_3\text{N}$ at different current densities for 100 h. (h) Durability test before and after 3000 CV cycles (inset: SEM of $\text{Co,V-Ni}_3\text{N}$ after durability test).

Figure 6

HER performance in alkaline seawater. (a) LSV curves; (b) Tafel plots derived from the polarization curves; (c) Comparison of overpotential at 10 and 100 mA cm^{-2} of the catalysts in this study; (d) L-t curves for $\text{Co,V-Ni}_3\text{N}$ and Ni_3N at 10 mA cm^{-2} for 6 h; (e) Durability test before and after 3000 CV cycles; (f) XPS, (g-i) TEM of $\text{Co,V-Ni}_3\text{N}$ after HER.

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