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1 Introduction

The growing concerns regarding energy depletion and environmental issues have led to extensive investigation into renewable and clean energy. Currently, H₂, due to its environmental efficiency and high energy density, is considered an ideal alternative energy carrier for traditional fossil fuels.¹ Compared to traditional H₂ production with severe environmental pollution, water electrolysis powered by renewable energy sources (*e.g.* wind and solar) has attracted increasing attention and is a promising approach for high purity H₂ generation.^{2,3} Generally, water electrolysis includes the cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER), both of which, especially the OER process,

3D self-supported porous vanadium-doped nickel nitride nanosheet arrays as efficient bifunctional electrocatalysts for urea electrolysis[†]

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Electrocatalytic water splitting is an up-and-coming method to produce H₂, but it is mostly limited by the sluggish anodic oxygen evolution reaction (OER). Replacing the OER with the urea oxidation reaction (UOR) process with a low thermodynamic potential would significantly reduce energy consumption. Here we developed porous V-doped Ni₃N nanosheets arrays grown on nickel foam (labeled V–Ni₃N/NF) by a hydrothermal and subsequent nitridation process. As a bifunctional electrocatalyst, the V–Ni₃N/NF shows striking catalytic performances for the hydrogen evolution reaction (HER) and UOR, which require low potentials of -83 mV and 1.361 V to drive a current density of 10 mA cm⁻², respectively. Furthermore, when applying V–Ni₃N/NF as both the cathode and anode for the HER and UOR, the assembled electrolyzer needs small cell voltages of 1.416 and 1.543 V to achieve 10 and 100 mA cm⁻², which are 180 and 243 mV lower than that in traditional water electrolysis, as well as displaying remarkable stability over 200 h. The excellent catalytic performances can be attributed to the self-supported porous nanosheet arrays on 3D NF, the intrinsic conductivity of V–Ni₃N, and the optimized Gibbs free energy of hydrogen adsorption after V doping. Our result suggests that this attractive material has promising applications in energy-saving H₂ production and urea-related waste water treatment.

require additional energy to overcome the reaction barrier.^{4,5} Highly active electrocatalysts are therefore essential to improve the reaction rate and reduce the over-potentials of the HER and OER processes. Currently, noble metals and their oxides, such as Pt-based materials and RuO₂ and IrO₂, remain the state-ofthe-art electrode materials to catalyze the HER and OER, respectively.^{6,7} However, the exorbitant price and scarcity mainly restrict their widespread applications.

As we know, compared to the HER, the OER process involves multiple and complex proton-coupled electron-transfer steps, which leads to sluggish kinetics and significantly reduces the energy conversion efficiency of water electrolysis.8,9 To avoid its large anodic overpotential, replacing the OER with more readily oxidizable species e.g. hydrazine, urea, and glycerol is an effective and energy-saving method to generate H₂. Among them, urea, as one of the easily electro-oxidizable species, is mainly generated from fertilizers and animal waste, and its oxidation reaction (UOR, $CO(NH_2)_2 + 6OH^- \rightarrow N_2 + CO_2 + 5H_2O + 6e^-)$ with lower thermodynamic potential (0.37 V) than that of the OER (1.23 V) is a good process to replace the OER.10 Thus, urea electrolysis $(CO(NH_2)_2 + H_2O \rightarrow 3H_2 + N_2 + CO_2)$ by integrating the UOR and HER not only produces H2 more effectively, but treats urea-rich water contamination.11,12 However, the UOR process shows sluggish kinetics because of its six-electron transfer process, which certainly requires highly efficient catalysts to promote this reaction. Moreover, the HER's kinetics under alkaline conditions is

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also more sluggish than that in acidic electrolytes due to additional adsorption and dissociation of water molecules.¹³ Therefore, it is urgent to explore earth-abundant and high-performance bifunctional UOR and HER catalysts to realize urea electrolysis in the same electrolyte, which can avoid incompatibility and deterioration and reduce the cost of synthesis.

Recently, transition metal- and carbon-based materials including oxides, hydroxides, phosphides, nitrides, and sulfides have been developed as advanced catalysts.14-16 Nitrides have attracted great attention and are highly catalytic due to their unique electronic structure, intrinsic metallicity, and high corrosion resistance.17,18 For instance, Ni₃N catalysts have been applied in water electrolysis. Incorporating foreign metals, e.g. Co, Fe into Ni₃N to form bimetallic nitrides catalysts is an effective way to enhance the catalytic activity, which optimizes the electronic structure and reduces the reaction energy barriers.¹⁹⁻²¹ As one of the earth-abundant elements, vanadium shows more valencestate diversity and it has been applied in electrochemical fields.^{22,23} The vanadium-doped catalytic materials including NiV LDH, NiFeV LDH, and V-Co₄N exhibited improved catalytic activities for the OER and HER, which stems from the promoted catalytic dynamics by electron interactions.²⁴⁻²⁶ Nevertheless, as far as we know, the electronic structure and catalytic performances of Ni₃N with V modification are still rarely explored. On the other hand, the catalytic activities of materials also depend on the morphology and dimensionality.27,28 The uniform nanosheet structure can expose more catalytically active sites, promote fast diffusion of electrolyte ions, and generate gas bubbling.^{29,30} Furthermore, in situ growth of catalysts on a substrate can increase the dispersion of catalytically active sites and avoid possible mechanical shedding and catalyst degradation.^{31,32} Because of the above points, it is worthwhile to develop selfsupported Ni-V-based nitride nanosheet array electrodes as promising water and urea electrolysis catalysts.

Herein we developed 3D self-supported porous V-doped Ni_3N nanosheet arrays on nickel foam (denoted as V– Ni_3N/NF) *via* hydrothermal and subsequent nitridation methods. Benefiting from high conductivity, self-supported porous nanosheets on NF, and the modified electronic structure, the V– Ni_3N/NF electrode displays remarkable bifunctional catalytic activities for the HER and UOR. Notably, with the V– Ni_3N/NF electrode as both the anode and cathode, the assembled electrolyzer exhibits excellent catalytic performance and great stability for urea electrolysis.

2 Experimental

2.1 Chemicals and materials

 $Ni(NO_3)_2 \cdot 6H_2O$, VCl₃, and NH₄F were purchased from Sinopharm Chemical Reagent Co. Ltd. KOH, and urea was provided by Adamas-beta®. Pt/C (20 wt% Pt on Vulcan XC-72R) and RuO₂ were provided by Sigma-Aldrich. All reagents were utilized as received without further treatment.

2.2 Sample synthesis of V-Ni₃N/NF

V-Ni₃N/NF was synthesized through the following process. Typically, 1.9 mmol Ni $(NO_3)_2$, 0.1 mmol VCl₃, 10 mmol urea and

5 mmol NH₄F were dissolved in 40 mL water with magnetic stirring to form a homogeneous solution. Then, the solution and a piece of NF were transferred into a 50 mL Teflon-lined stainless-steel autoclave. After a hydrothermal reaction at 120 °C for 6 h, V-doped Ni(OH)₂ was uniformly grown on the surface of NF (V-Ni(OH)₂/NF). Then, the V-Ni(OH)₂/NF precursor was placed in the center of a quartz tube and calcined at 400 °C for 2 h to synthesize V-NiO/NF under an N₂ flow. Finally, the V-Ni₃N/NF product was fabricated after annealing the V-NiO/NF in an NH₃ atmosphere at 400 °C for 2 h. For comparison, the V-doped Ni₃N/NF samples with different ratios of Ni and V were prepared by a similar process except for adding different initial ratios (14 : 1 and 9 : 1) of Ni(NO₃)₂ and VCl₃ and named V-Ni₃N/NF-1 and V-Ni₃N/NF-2. The Ni₃N/NF was obtained using the same method without adding VCl₃.

2.3 Materials characterization

The morphological structure and composition were characterized using a scanning electron microscope (SEM, FIB Helios G4) operated at 10 kV and a transmission electron microscope (TEM, FEI Tecnai-F20) equipped with an energy dispersive X-ray (EDX) spectrometer at an acceleration voltage of 200 kV. The Xray diffraction (XRD) patterns were recorded using an X-ray diffractometer using Cu Ka radiation (Bruker D8AXS). The chemical states of samples were characterized using an X-ray photoelectron spectrometer (XPS, ESCALAB 250) with Al Kα radiation.

2.4 Electrochemical measurements

All electrochemical measurements were carried out in a threeelectrode electrochemical cell using an electrochemical workstation (CHI 760E) with a 1 M KOH electrolyte. The assynthesized electrode, Ag/AgCl, and a graphite rod were used as the working, reference, and counter electrodes, respectively. Polarization curves were obtained using linear sweep voltammetry (LSV) with a scan rate of 2 mV s^{-1} and were corrected for iR compensation. The electrochemical impedance spectra (EIS) were obtained by applying an AC voltage of 10 mV amplitude with frequency from 100 kHz to 0.1 Hz. Measurements of electrochemical double-layer capacitances were performed using cyclic voltammetry between 0.20 and 0.30 V. All potentials obtained were converted to the corresponding values based on the reversible hydrogen electrode (RHE) using the following equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + 0.21 \text{ V}$. For the water and urea electrolysis tests, the V-Ni3N/NF was used as both the cathode and anode in a two-electrode electrolyzer.

2.5 DFT calculations

All the DFT calculations were carried out using the projector augmented wave (PAW) approach to represent ion–electron interaction, as implemented in the Vienna *ab initio* Simulation Package (VASP).^{33–35} The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional was used to describe the electronic exchange and correlation effects.^{36,37} The kinetic energy termination was set to 500 eV. The convergence criteria for force and energy were set to 10^{-5} eV and

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 10^{-2} eV Å⁻¹, respectively. The Brillouin zones were sampled at 5 × 5 × 1 using Monkhorst–Pack mesh.³⁸ A vacuum region of 15 Å was set to avoid interactions between adjacent images. To describe the van der Waals interaction, the semi-empirical dispersion-corrected DFT-D3 scheme proposed by Grimme was used.³⁹ To understand the HER mechanism well, the Gibbs free energy of hydrogen adsorption (ΔG_{H^*}) was calculated using the following equation: $\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} - T \times \Delta S_{H^*}$, where ΔE_{H^*} , ΔE_{ZPE} , and ΔS_{H^*} are the hydrogen adsorption energy, the difference in zero point energy between the adsorbed hydrogen and hydrogen in the gas phase, and the entropy difference between the adsorbed state and the gas phase, respectively.

3 Results and discussion

The preparation process of 3D self-supported porous V-Ni₃N nanosheet arrays on NF is illustrated in Scheme 1. First, the NiV hydroxide precursor (denoted as V-Ni(OH)₂) with a uniform nanosheet-like structure was directly grown on NF via a facile hydrothermal reaction. The SEM images (Fig. 1a and b) show that the V-Ni(OH)₂ with uniform interconnected nanosheet arrays and a smooth surface directly grows on the surface of the NF skeleton, and the corresponding crystalline structure is obtained by XRD (Fig. 1d), in which the main characteristic diffraction peaks can be indexed to Ni(OH)₂ (JCPDS no. 73-1520) and Ni(OH)₂ · 0.75H₂O (JCPDS no. 38-0715). Then, after calcination in a N2 atmosphere, the precursor was successfully converted to V-NiO (JCPDS no. 71-1179). Moreover, it still retains the uniform nanosheets arrays with smooth surfaces, as presented in Fig. 1c and S1.† After thermal ammonolysis, the prominent characteristic diffraction peaks of the product correspond to Ni₃N (JCPDS no. 89-5144). The morphology of V-Ni₃N/NF was characterized using a SEM and TEM. In Fig. 1e, the V-Ni₃N nanosheet arrays are well preserved. Notably, close observation reveals that V-Ni₃N nanosheets display porous features, which may be caused by the corrosion of NH₃ and is consistent with previous reports.⁴⁰ The porous nanosheet-like structure was further confirmed using a TEM, as shown in Fig. 1f. The high-resolution TEM (HRTEM) image of V-Ni₃N shows well lattice fringes with an interplanar distance of 0.214 nm, which is corresponds well to the (002) plane of Ni₃N (Fig. 1g). In Fig. 1h, the selected area electron diffraction (SAED)



 $\label{eq:scheme1} \begin{array}{l} \mbox{Scheme1} & \mbox{Scheme1}$

pattern of V–Ni₃N displays ordered discrete spots and these diffraction rings are assigned to the (110), (111) and (202) planes, further indicating the successful formation of nitride. The EDX spectrum confirms the presence of Ni, V, and N elements in nitride (Fig. S2†). Furthermore, the high angle annular dark-field scanning TEM (HAADF-STEM) and EDX elemental mapping images (Fig. 1i) exhibit a uniform distribution of Ni, V, and N elements in the product, signifying the uniform doping of the V element.

To further analyze the surface composition and element states of the obtained V-Ni₃N/NF, XPS measurements were performed (Fig. 2). The survey spectrum (Fig. 2a) shows the presence of Ni, V, and N elements. The atomic ratio of Ni : V : N elements is calculated to be 19.4: 1.0: 6.1 in V-Ni₃N, which matches the feed ratio of Ni and V, indicating the highly controlled incorporation of V. In the high-resolution spectrum of Ni 2p (Fig. 2b), the peaks located at 853.3 and 854.5 eV are ascribed to Ni 2p_{3/2}, whereas the peaks at 871.2 and 872.4 eV are assigned to Ni 2p_{1/2}.⁴¹ Meanwhile, two satellite peaks at 860.0 and 877.9 eV can be observed. The V 2p spectrum shown in Fig. 2c displays two peaks at 513.6 and 514.4 eV assigned to the V-N and V-O bonds, respectively. The generation of V-O bonds may stem from surface oxidation.⁴² The N 1s spectrum shows the formation of Ni-N and V-N bonds (Fig. 2d). Also, the peak located at 401.3 eV can be attributed to the N-H group, suggesting the presence of abundant H species on the surface of the catalyst, which is beneficial for improving catalytic performance.43

The electrocatalytic performances of the obtained electrodes were analyzed in an alkaline electrolyte. Fig. 3a depicts the linear sweep voltammetry (LSV) curves for the HER. It is found that the commercial Pt/C has excellent catalytic HER performance, while the Ni₃N/NF displays moderate catalytic HER activity with an overpotential of 111 mV at 10 mA cm $^{-2}$. It is of importance to point out that the V-Ni₃N/NF electrode (Fig. 3a and c) shows the best catalytic HER activity with a low overpotential of 83 mV to achieve 10 mA cm^{-2} , which surpasses that of all other synthesized V-doped Ni₃N electrodes, indicating that the suitable introduction of V is of great importance to enhancing the catalytic performance. Remarkably, the V-Ni₃N/ NF electrode can afford large current densities of 100 and 300 mA cm⁻² at low overpotentials of 172 and 260 mV, respectively. Moreover, the V-Ni₃N/NF shows outstanding catalytic activity for the HER with a low overpotential of 90 mV to reach 10 mA cm^{-2} in a neutral electrolyte (1 M PBS). To reveal the catalytic mechanism for the HER, the Tafel slope obtained by the linear fitting of Tafel plots was analyzed.44,45 In Fig. 3b and c, the Tafel slope of V–Ni₃N/NF is 45 mV dec $^{-1}$, which is smaller than that of Ni_3N/NF (67 mV dec⁻¹), V- Ni_3N/NF -1 (52 mV dec⁻¹), and V- $Ni_3N/NF-2$ (76 mV dec⁻¹), revealing that the V- Ni_3N/NF is more favorable for facilitating HER reaction kinetics and undergoes the Volmer-Heyrovsky mechanism. The catalytic performances are superior to those of most of the recently reported state-ofthe-art HER catalysts (Table S1[†]). To better understand the origin of catalytic activity, the electrochemically active surface area (ECSA) was investigated according to the electrical doublelayer capacitance tests using cyclic voltammetry (CV) methods



Fig. 1 SEM images of (a and b) $V-Ni(OH)_2/NF$ and (c) V-NiO/NF. (d) XRD patterns of $V-Ni(OH)_2/NF$, V-NiO/NF and $V-Ni_3N/NF$. (e) SEM, (f) TEM, and (g) HRTEM images and (h) SAED pattern of $V-Ni_3N/NF$. (i) HAADF-STEM image and the corresponding elemental mapping images of Ni, V, and N elements for $V-Ni_3N$.



Fig. 2 (a) XPS survey and high-resolution spectra of the (b) Ni 2p, (c) V 2p, and (d) N 1s of the V–Ni $_3$ N/NF electrode.

at various scan rates (Fig. S3[†]). In Fig. 3d, the double-layer capacitance value of the V–Ni₃N/NF electrode is 8.0 mF cm⁻², which is larger than that of the Ni₃N/NF (5.0 mF cm⁻²), V–Ni₃N/NF-1 (6.5 mF cm⁻²), and V–Ni₃N/NF-2 (2.7 mF cm⁻²), indicating the highest exposure of the electrochemically active surface area and accessible active sites.⁴⁶ To further explore the reactive kinetics, electrochemical impedance spectroscopy tests were conducted, and the Nyquist plots are shown in Fig. 3e. The V–

Ni₃N/NF with the highest catalytic activity exhibits the smallest charge transfer resistance (R_{CT}) in these electrodes, suggesting its rapid electron transfer for V-doped Ni₃N to accelerate the turnover of protons and adsorbed water molecules.47 Additionally, the intrinsic ohmic resistance (the first intercept along the real axis) of V-Ni₃N/NF is smaller than that of other electrodes (Fig. 3e), indicating that the electrical conductivity of the Ni₃N is improved after V doping. The catalytic durability is another key parameter to evaluate the catalyst. In Fig. 3f, the chronoamperometry tests of V-Ni3N/NF with continuous electrolysis at 10 mA cm⁻² for over 25 h exhibit excellent long-term durability in both alkaline and neutral media. The SEM images (Fig. S4a and b[†]) show that the porous nanosheet-like structures of V-Ni₃N/NF are well maintained after the stability tests demonstrating the magnificent robustness of the porous nanosheet array electrode in alkaline and neutral electrolytes. Moreover, the XRD phase matches well with the initial one (Fig. S5[†]), indicating the great stability of the crystallographic structure after the HER stability test.

To further understand the high HER activity of V–Ni₃N/NF, DFT calculations were performed. The optimized structural representations of Ni₃N (111), V–Ni₃N (111), Ni₃N (002) and V–Ni₃N (002) are presented in Fig. S6a–d.† As is well known, ΔG_{H^*} is a key indicator of the HER activity for a given catalytic site.⁴⁸ A smaller absolute value indicates a greater catalytic activity, and the value of ΔG_{H^*} of a good HER catalyst should be close to 0 to benefit the subsequent H₂ generation. We calculated ΔG_{H^*} values based on the (111) and (002) surfaces of Ni₃N and V–



Fig. 3 (a) HER polarization curves and (b) Tafel slopes of Ni₃N/NF, V–Ni₃N/NF, V–Ni₃N/NF-1, V–Ni₃N/NF-2, and Pt/C catalysts. (c) Comparison of the overpotentials at 10 mA cm⁻² and Tafel plots of these catalysts. (d) The double-layer capacitance and (e) EIS of Ni₃N/NF, V–Ni₃N/NF, V–Ni₃N/NF-1, and V–Ni₃N/NF-2. (f) Chronoamperometric curves of V–Ni₃N/NF at 10 mA cm⁻² in 1 M KOH and 1 M PBS electrolytes.

Ni₃N, respectively. As illustrated in the calculated free energy diagram (Fig. 4a), the ΔG_{H^*} values of clean Ni₃N (111) and Ni₃N (002) surfaces are -0.48 and -0.64 eV, respectively, suggesting its relatively high energy and that it is adverse to hydrogen desorption from the surfaces of the Ni₃N during the HER process. With the introduction of V, the ΔG_{H^*} values of V–Ni₃N (111) and V–Ni₃N (002) are reduced and shifted to -0.12 and -0.18 eV, respectively, indicating that the introduction of V is beneficial for optimizing the free energy of hydrogen adsorption and it can regulate the hydrogen adsorption that is neither too strong nor too weak on the surface, thereby enhancing the subsequent H₂ generation.

Furthermore, the d-band center as a descriptor for the HER activity was also investigated. We calculated the density of states (DOS) of the (111) and (002) surfaces of Ni₃N and V–Ni₃N, respectively. In Fig. 4b, the d-band center values (ε_d) of pure Ni₃N (111) and Ni₃N (002) are -1.81 and -1.78 eV, respectively. After V doping, the ε_d of V–Ni₃N (111) and V–Ni₃N (002) shift to more negative values (-1.93 and -2.02 eV), meaning that the antibonding states shift to lower energy levels and become more occupied, which leads to a decrease in the binding energy for hydrogen atoms. Thus, the interaction between hydrogen and



Fig. 4 (a) Calculated HER free–energy diagram on the surface of Ni₃N and V–Ni₃N. (b) Total electronic DOS calculated for Ni₃N (111), V–Ni₃N (111), Ni₃N (002), and V–Ni₃N (002). The Fermi level is set at zero.

the catalyst decreases with the ϵ_d downshifting, which is consistent with recent reported results. 49,50

We further evaluated the catalytic OER performances of the V-Ni₃N/NF electrode in alkaline media. As shown in Fig. 5a, the V-Ni₃N/NF exhibits high catalytic OER activity, achieving a current density of 10 mA cm⁻² at a low potential of 1.519 V, which is smaller than the values for Ni₃N/NF (1.547 V), V-Ni₃N/ NF-1 (1.526 V), V-Ni₃N/NF-2 (1.522 V), and RuO₂ (1.504 V). The catalytic performance of V-Ni3N/NF exceeds that of RuO2 when the current density is beyond 74 mA cm⁻², and it delivers high current densities of 200 and 400 mA cm⁻² at low potentials of 1.634 and 1.677 V, respectively. Generally, the anodic OER process is environment friendly. However, the high overpotential increases the energy consumption. Substituting the OER with other smart anodic reactions to perform hybrid water electrolysis can reduce the overall energy cost. As one of the common molecules, the urea molecule has a satisfying thermodynamic oxidation potential (0.37 V) and is an ideal candidate to energy-efficiently generate H2.51 Accordingly, the UOR activity of V-Ni₃N/NF was evaluated in a 1 M KOH electrolyte with 0.5 M urea. As depicted in Fig. 5a, the V-Ni₃N/NF exhibits a greatly improved anodic catalytic activity, and it only requires a low potential of 1.361 V to achieve 10 mA cm^{-2} , which is lower than the values for Ni₃N/NF (1.371 V), V-Ni₃N/NF-1 (1.365 V), V-Ni₃N/NF-2 (1.382 V), and RuO₂ (1.356 V). Moreover, the required potentials decrease to 1.437 and 1.510 V at large current densities of 200 and 400 mA cm⁻², respectively. In addition, the Tafel slope of V-Ni₃N/NF is lower than that of Ni₃N/NF, V-Ni₃N/ NF-1, and V-Ni₃N/NF-2, implying its enhanced UOR reaction kinetics (Fig. S7[†]). Such catalytic activities surpass those of most recently reported non-precious metal based UOR catalysts (Table S2[†]), suggesting that the V-Ni₃N/NF is a promising UOR catalyst. Then, the long-term UOR stability of V-Ni₃N/NF was evaluated by a chronoamperometry test. In Fig. 5b, the chronoamperometry test maintains the excellent durability at a fixed

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Fig. 5 (a) Polarization curves of the OER and UOR for different catalysts. (b) Chronoamperometric curve of V–Ni₃N/NF at 10 mA cm⁻² in 1 M KOH with a 0.5 M urea electrolyte.

current density of 10 mA cm⁻². We further analyzed the change of morphology and chemical composition of V-Ni₃N/NF after the stability measurement. In Fig. S8,† the SEM image of V-Ni₃N/NF shows that the morphology of porous nanosheet arrays is almost retained after the long-term UOR test. The XRD pattern of V-Ni₃N/NF (Fig. S9[†]) shows two new crystalline phases of NiOOH and VO(OH)₂ due to the partial surface oxidation during the UOR test. Additionally, the composition on the surface was observed by XPS. The content of high-valent Ni (854.5 and 872.4 eV) in the Ni 2p spectra (Fig. S10a⁺) increases compared with that before the stability test, indicating the partial oxidation to form NiOOH at high oxidation potential, which is consistent with the XRD results and considered to be the real surface active sites.^{52,53} In the V 2p spectra (Fig. S10b⁺), the ratio of the V-O bond to V-N bond increases, indicating that the vanadium ion in V-Ni₃N is oxidized to the high-valence hydroxide species during the UOR process, which is favorable for improving the catalytic activity.⁵⁴ In Fig. S10c and d,† the peak intensity of N 1s declines further demonstrating the surface oxidation of metal nitrides.

Based on the excellent HER and UOR performance of V–Ni₃N/NF, a two-electrode urea electrolyzer was constructed using V–Ni₃N/NF as both the anode and cathode electrodes in



Fig. 6 (a) Schematic illustration of the urea electrolyzer using V–Ni₃N/NF as the bifunctional electrocatalyst for both the HER and UOR. (b) Polarization curves of V–Ni₃N/NF for urea electrolysis and water electrolysis. (c) Long-term stability test performed at a constant current density of 10 mA cm⁻².

1 M KOH with a 0.5 M urea electrolyte (Fig. 6a). In Fig. 6b, the urea electrolyser needs low cell voltages of 1.416 and 1.543 to achieve 10 and 100 mA cm⁻², respectively, whereas traditional water electrolysis requires higher values of 1.596 and 1.786 V at identical current densities, suggesting the significant advantages of thermodynamics for urea electrolysis. The high catalytic activity is superior to that of recently reported catalysts (Table S3†). Furthermore, the urea electrolyzer shows excellent long-term stability upon 200 h of continuous electrolysis at 10 mA cm⁻² (Fig. 6c). All the above results demonstrate that the V–Ni₃N/NF electrode is promising for large-scale urea electrolysis for energy-efficient H₂ production.

Based on the above results, the marvelous catalytic activities of V-Ni₃N/NF can be ascribed to the following factors. First, the porous sheet arrays grown on NF not only provide a large electrochemically active surface area and abundant catalytically active sites, but also facilitate the diffusion of electrolyte ions and the release of generated gas from the surface of the catalyst during the reaction process. Second, the V ion doping improves the intrinsic electrical conductivity of Ni₃N, which is beneficial for facilitating electron transport during the catalytic process. As we know, cation doping is an effective strategy to regulate the electronic structure of materials, which is beneficial for optimizing the ΔG_{H^*} . Accordingly, the incorporation of V modifies the electronic structure of Ni₃N, bringing the ΔG_{H^*} of V–Ni₃N closer to the thermal neutral than that of Ni₃N, and provides more catalytically active sites.55 In addition, the formed hydroxides during the UOR process are considered to be the real catalytically active species and are favorable for water molecule adsorption for the UOR, and the V-doped Ni₃N has lower water dissociation energy than Ni₃N, similar to previous reports.⁵⁶ Finally, the self-supported electrode, due to directly integrating the V-Ni₃N on NF, avoids the use of a binder, which can block the active sites and decrease the catalytic activity. All the above merits contribute to enhancing the catalytic performance of V– $\rm Ni_3N/\rm NF.$

4 Conclusions

In summary, porous V doped Ni₃N nanosheet arrays on NF were synthesized by a hydrothermal and subsequent nitridation process. Benefiting from the abundant catalytically active sites, high electrical conductivity, and optimized ΔG_{H^*} , the V–Ni₃N/ NF electrode exhibits outstanding catalytic activity for the HER with low overpotentials of 83 and 90 mV at 10 mA cm⁻² in an alkaline and neutral electrolyte, respectively, and it also displays striking catalytic activity for the UOR. Based on the prominent bifunctional performance of the V–Ni₃N/NF electrode, a two-electrode urea electrolyzer was constructed which needs a low cell voltage of 1.416 V to afford 10 mA cm⁻², which is 0.180 V smaller than that required in water electrolysis. This work creates an avenue to rationally design and fabricate the promising 3D self-supported transition-metal nitride electrode for urea-assisted energy-efficient H₂ production.

Conflicts of interest

There are no conflicts to declare.

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