Charge Transfer of Interfacial Catalysts for Hydrogen Energy

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Abstract

The development of multifunctional non-precious transition metal electrocatalysts is of technological significance in hydrogen and oxygen electrochemistry but challenging. Here we exploit interface engineering to construct a novel interface catalyst of Ni₃N and Co₂N, which exhibits multifunctional hydrogen and oxygen electrochemical activities in alkaline media. The interface catalysts of Ni₃N/Co₂N show superior bifunctional activity for hydrogen electrochemistry comparable to the state-of-the-art Pt, as well as high oxygen evolution reaction activity. Furthermore, the multifunctional Ni₃N/Co₂N interface electrocatalysts demonstrate the excellent applications in water splitting for H₂ generation and a highly stable Swagelok-type Ni-H battery for H₂ utilization. Density functional theory calculations further confirm that the interfacial charge transfer from Ni to Co and N in Ni₃N/Co₂N efficiently enhances the dissociative adsorption of H₂ and optimizes the adsorption configurations and binding energies of the intermediate hydrogen and hydroxide in the multifunctional reactions.

Introduction

The environmentally-benign water cycle is one of the key energy-environmental cycles for a clean energy option in renewable energy conversion and storage.¹⁻⁹ Both hydrogen and oxygen electrochemistry plays a pivotal role in the water cycle, including hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) for electrolyzers as well as HER and hydrogen oxidation reaction (HOR) for metal-H

batteries.¹⁰⁻¹⁸ To minimize energy penalties and increase energy conversion efficiencies, efficient electrocatalysts are required to speed up the kinetics of these reactions.¹⁹⁻²³ In particular, a multifunctional electrocatalyst could simplify the configuration of a working system and lower the cost of its preparations for commercial applications.²⁴⁻²⁸ At present, platinum-group metal (PGM) based materials are the most efficient electrocatalysts for the hydrogen and oxygen electrochemistry under acidic conditions, where few PGM-free electrocatalysts show comparable catalytic activity and stability.^{10, 29} Increasing research efforts have directed to the development of electrocatalysts in neutral or alkaline media,³⁰⁻³⁷ where earth-abundant electrocatalysts could compete with the PGM catalysts for the OER.^{38, 39} However, it still remains a great challenge to obtain highly efficient and cost-effective PGM-free electrocatalysts for the hydrogen electrochemistry.⁴⁰ Therefore, it is of both fundamental and technological significance to develop highly competent and earth-abundant PGM-free electrocatalysts for both hydrogen and oxygen electrochemistry.

Interface engineering is one of the promising strategies to develop efficient PGM-free electrocatalysts through modifying the catalytic activities and binding behaviors of reactants, intermediates, and products.^{41,42} Previous studies demonstrated that modifications of interfaces of PGM-based catalysts improved hydrogen and oxygen electrochemistry.^{19, 30, 43-45, 46-49} However, a majority of those focused on bifunctional HER/OER electrocatalysts and fewer works have been focused on multifunctional PGM-free electrocatalysts for HER/HOR/OER. Recently, earth-abundant metal nitrides were found to act as promising electrocatalysts due to its nearly metallic character with excellent electroconductivity and high corrosion resistance.⁵⁰⁻⁵³ Through interface engineering, the charge transfer between heterogeneous interface, resulting in optimized binding adsorption energies of versatile intermediated species for hydrogen and oxygen electrochemistry. Furthermore, the *d*-band of a parent metal can be efficiently re-modulated due to the inclusion of interstitial nitrogen atoms, leading to improvements in its catalytic properties.⁵⁴ Therefore, such an interface engineering represents a promising strategy for synthesis of multifunctional hydrogen and oxygen electrocatalysts for hydrogen-based device applications to meet future industrial applications.

In this work, we aim to develop interface electrocatalysts composed of first-row transition nitrides for hydrogen and oxygen electrochemistry in alkaline media for multifunctional HER/HOR/OER. We present a novel interface electrocatalyst of Ni₃N and Co₂N (Ni₃N/Co₂N) via a facile approach of cathodic electrodeposition and low-temperature nitridation. The low-cost multifunctional electrocatalysts efficiently facilitate the HER/HOR kinetics with extremely high activities in electrolyzer as well as highly stable Ni-H battery.

Experimental section

Syntheses of NiCo/carbon paper (NiCo/CP) and Ni₃N/Co₂N/carbon paper (Ni₃N/Co₂N/CP)

The Ni₃N/Co₂N/CP was synthesized by cathodic electrodeposition of NiCo particles on CP, followed by thermal nitridation. Typically, a piece of clean carbon paper (0.5 cm \times 0.5 cm) was put into 10 mL electrolyte consisting of 2.0 M NH₄Cl, 0.07 M NiCl₂, and 0.03 M CoCl₂. The electrodeposition was carried out in a two-electrode configuration, in which a carbon rod was used as a counter electrode. Porous NiCo microspheres were deposited in CP under a constant current of -0.25 A for 500 s. Subsequently, the resultant NiCo/CP was put in the center of a quartz tube and subjected to nitridation at desired temperatures under NH₃ flow, where NiCo was converted into Ni₃N/Co₂N/CP. The NH₃ flow of 20 sccm was kept throughout the whole process. As a comparison, electrodeposited NiCo/CP, Co₂N/CP, Ni₃N/CP, and commercial Pt/C catalysts loaded on CP with optimized loading were also used as working electrodes for electrocatalytic properties. The optimal loading of Pt/C on carbon paper (Pt/CP) was 1.0 mg cm⁻².

Results

Preparation and characterization of Ni₃N/Co₂N interface catalysts.

A detailed description of the preparation of Ni₃N/Co₂N is found in Method. Briefly, the preparation of Ni₃N/Co₂N catalysts started from the cathodic electrodeposition of porous NiCo nanoparticles (NPs) on commercial current collectors of carbon paper (CP). Subsequently, the NiCo/CP was nitridated by controllable thermal conditions in ammonia flow, resulting in desired Ni₃N/Co₂N supported on CP (Ni₃N/Co₂N/CP). Both hexagonal Ni₃N and orthorhombic Co₂N phases were formed as shown in the powder X-ray diffraction (XRD) pattern (Figure S1), upon nitridation at 350 °C for 3 h. X-ray photoelectron spectroscopy (XPS) was carried out to investigate chemical states and compositions of Ni₃N/Co₂N. For the core-level Co2p_{3/2} region in Figure 1a, the peaks at 780.8 and 785.7 eV were assigned to Co-N, in agreement with cobalt nitride reported in the literature.^{55, 56} The N1s peak at 397.6 eV was associated with the binding energy of metal-N (Figure 1c). Figure 1b shows XPS peak at 853.1 eV of Ni 2p_{3/2} spectrum, which was attributed to Ni⁺ in Ni₃N with its satellite peaks at 861.4 eV. The peak at 855.7 eV was attributed to oxidized nickel species adventitiously formed during the sample preparation for XPS measurement.^{45, 57, 58} A broad peak at 398.2 eV was due to the residual NH moieties from NH₃ incomplete reaction.⁴⁵ It was found that the binding energies of Ni2p for Ni-N were positively shifted with respect to those of pure Ni₃N, indicating charge transfer from Ni₃N to Co₂N.^{34, 58} This charge transfer is also verified by our Bader charge calculations described later. To further investigate fine structures of the Ni₃N/Co₂N interfaces. high-resolution transmission electron microscopy (HRTEM) was carried out. Figure 1d displays the HRTEM image of Ni₃N/Co₂N interfaces. Two well-resolved lattice fringes with inter-planar spacings of 0.133 and 0.217 nm were observed, corresponding to the (300) plane of hexagonal Ni₃N and (002) plane of cubic Co₂N, respectively. The line-scan elemental curves of Ni₃N/Co₂N interface have been supplied. As shown in

Figure S2, the EDS line scan curves suggest a distinct heterogeneous distribution between the Ni and Co elemental counts on cross-over interface, suggesting the formation of the Ni₃N/Co₂N heterojunction. The slightly increasing Co counts within the Ni rich area may be attributed to the presence of overlapping nanoparticle.

Morphologies and elemental distribution of Ni₃N/Co₂N/CP were characterized by scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX), respectively. The SEM images in Figure 1e display a macro-porous network structure in Ni₃N/Co₂N/CP, where numerous flower-like particles were stacked over the skeleton surface. Such a unique structure comes mainly from the pristine NiCo/CP (Figures S3-S4), suggesting that the nitridation reaction did not change the surface morphology of the catalysts. EDX was used to confirm the major composition of Ni, Co, and N in Ni₃N/Co₂N, and the molar ratio of Ni and Co was found to be close to 7:3 in Figure 1f, which is agreeing with ICP results. In addition, the corresponding elemental mappings demonstrate the homogeneous distribution of Ni, Co, and N elements over the entire sample surface in Figures 1g, S5 and S6d. These characterization results demonstrate the formation of the Ni₃N/Co₂N interfaces.



Figure 1. (a-c) XPS spectra of Ni2p_{3/2}, Co2p_{3/2},and N1s for Ni₃N/Co₂N/CP; (d) HRTEM image of Ni₃N/Co₂N; (e) SEM images of Ni₃N/Co₂N/CP under different magnifications; (f) EDX spectrum of Ni₃N/Co₂N/CP; (g) elemental mapping images of Ni₃N/Co₂N. Scale bars: 2 nm (d); 5 μ m (e); 500 nm inset of (e); 200 nm (g).

Electrocatalytic H₂ evolution. The Ni₃N/Co₂N catalysts under different preparation temperatures show distinct HER activities (Figure S7). We found that the Ni₃N/Co₂N catalysts nitridated at 350 °C exhibit the best HER catalytic activity. This is possibly due to more interfacial catalytic sites for the catalysts at 350 °C since Ni₃N starts to decompose above 400°C.⁵⁹ Here we employed the optimal Ni₃N/Co₂N for further electrochemical characterizations unless noted otherwise. Ni₃N/CP, Co₂N/CP, pristine NiCo/CP, and commercial Pt/C with an optimal loading of 1.0 mg cm⁻² supported on CP (Pt/CP) (Figure S8) were also prepared as a comparison. Figure 2a presents the iR-corrected linear sweep voltammetry curves (LSVs) of Ni₃N/Co₂N/CP, Ni₃N/CP, Co₂N/CP, NiCo/CP, and Pt/CP for HER in 1.0 M KOH at a scan rate of 5 mV s⁻¹. It is seen that an overpotential of only 10 mV was required to deliver a benchmark current density of -10 mA cm⁻² (η_{10}) for Ni₃N/Co₂N/CP. Such an overpotential is lower than those for Pt/CP (12 mV), Ni₃N/CP (19 mV), and Co₂N/CP (25 mV). Furthermore, the Ni₃N/Co₂N/CP catalysts show an overpotential as low as 70 mV to deliver an industrial-level HER current density of -100 mA cm⁻² (η_{100}) as compared to those for Pt/CP (85 mV), Ni₃N/CP (108 mV), and Co₂N/CP (128 mV) under the similar conditions. In contrast to Ni₃N/Co₂N/CP, the pristing NiCo/CP exhibits poor HER activity with a larger η_{10} of 159 mV and a larger η_{100} of 263 mV, suggesting that the nitridation plays a critical role in promoting the HER activity for Ni₃N/Co₂N.



Figure 2. LSV curves (a), Tafel plots (b), and (c) comparison of overpotentials at -10 mA cm⁻² and Tafel slopes of Ni₃N/Co₂N/CP, Ni₃N/CP, Co₂N/CP, NiCo/CP, and Pt/CP (1.0 mg cm⁻²) for HER in 1.0 M KOH at a scan rate of 5 mV s⁻¹; (d) Nyquist plots of Ni₃N/Co₂N/CP and NiCo/CP at -100 mV vs RHE; (e) Chronopotentiometry curves of Ni₃N/Co₂N/CP at -10 and -100 mA cm⁻² in 1.0 M KOH; (f) Comparison of overpotentials of selected HER electrocatalysts to deliver -10 mA cm⁻² for HER in 1.0 M KOH.

To reveal the kinetics mechanism for the HER of Ni₃N/Co₂N, Tafel plots of each electrocatalyst were depicted in Figure 2b and the corresponding Tafel slopes were summarized in Figure 2c. A linear fitting to

the Tafel plot for Ni₃N/Co₂N/CP gives a slope of 45.1 mV dec⁻¹, indicating that the Volmer-Heyrovsky reaction pathway dominates in the HER catalyzed by Ni₃N/Co₂N/CP.^{5, 60, 61} The fast HER kinetics for Ni₃N/Co₂N/CP was also verified by electrochemical impedance spectroscopy (EIS) analysis. Figure 2d exhibits the EIS plots for both Ni₃N/Co₂N/CP and NiCo/CP under the frequent region from 10⁶ Hz to 0.01 Hz. The obtained Nyquist plots were well fitted to a modified Randel model (Figure S9). The charge-transfer resistance (R_{ct}) was estimated to be 1.7 Ω and 265 Ω for Ni₃N/Co₂N/CP and NiCo/CP, respectively, suggesting that the Ni₃N/Co₂N catalysts exhibit a much faster electron transfer than the NiCo catalysts in the HER process.

Intrinsic specific activity is also an important criterion to assess an electrocatalyst. Although the aforementioned HER performance could be normalized by geometric areas, it possibly overestimates the HER activity of electrocatalyst due to its three-dimensional porous structure (Figures 1e and S6). To correctly assess the difference in HER between the interface catalyst Ni₃N/Co₂N and the state-of-the-art Pt, the electrocatalytic HER activities were normalized by their electrochemically active surface area (ECSA) (Figures S10-S11). It was found that the Ni₃N/Co₂N/CP presents better HER performance than Pt/CP in the whole applied potential window, indicating the superior intrinsic specific activity of Ni₃N/Co₂N/CP towards electrocatalytic H₂ evolution.

To further probe the stability of Ni₃N/Co₂N/CP electrocatalyst, chronopotentiometry experiments at -10 and -100 mA cm⁻² were carried out in 1.0 M KOH solution. The Ni₃N/Co₂N/CP electrocatalysts were found to retain a steady HER activity and had an increase of only 4 mV in an overpotential at -10 mA cm⁻² under alkaline condition after a period of 100 h for hydrogen production (Figure 2e). Similar stability was observed even at -100 mA cm⁻² for 100 h, further exhibiting its long-term robustness for electrocatalytic H₂ evolution. Post-electrolysis characterizations show no apparent change in the morphology and structure of Ni₃N/Co₂N/CP (Figure S12-S13), confirming its excellent structural robustness and mechanical stability. The generated H₂ amount well agreed with the theoretically calculated quantity (Figure S14) and all the passed charge was used for hydrogen evolution, suggesting a Faradaic efficiency close to 100% of Ni₃N/Co₂N/CP. These outstanding electrocatalytic performances make Ni₃N/Co₂N/CP a promising candidate for electrocatalytic H₂ evolution, ranking the top-tier noble-metal-free HER electrocatalysts reported to date (Figure 2f and Supplementary Table 1).^{5, 11, 57, 62-69}



Figure 3. Water splitting of the Ni_3N/Co_2N interface catalysts. (a) LSV of $Ni_3N/Co_2N/CP$ served as both cathode and anode electrocatalysts in a two-electrode configuration in 1.0 M KOH at a scan rate of 5 mV s⁻¹. (b) Chronopotentiometry curves of $Ni_3N/Co_2N/CP$ at 10 and 100 mA cm⁻² in 1.0 M KOH without iR correction.

Water splitting. The Ni₃N/Co₂N interface catalyst also acts as a bi-functional electrocatalyst with both excellent HER and OER for water splitting. We evaluated the OER activity of Ni₃N/Co₂N/CP in 1.0 M KOH solution via a three-electrode configuration (Figures S15-S16). The obtained Ni₃N/Co₂N/CP electrocatalysts exhibit a superior OER property than Ni₃N/CP, Co₂N/CP, and NiCo/CP, which is even comparable to many noble metal-free OER catalysts reported recently, as summarized in Table S2. Besides, the long-term stability test at current densities of 10 and 100 mA cm⁻² in Figure S17, strongly demonstrates the great robustness of $Ni_3N/Co_2N/CP$ for long-term O_2 evolution under alkaline condition. Given the excellent bifunctional HER/OER activities in 1.0 M KOH, a two-electrode cell configuration was further assembled for overall water splitting using two identical Ni₃N/Co₂N/CP electrodes as an anode and a cathode, respectively. Figure 3a shows that one of the assembled cells at current densities of 100, 300, and 500 mA cm⁻² provided voltages as low as 1.73, 1.96, and 2.15 V, respectively. Moreover, the Ni₃N/Co₂N/CP couple also maintained the robust stability, as manifested by the steady chronopotentiometric curves at 10 and 100 mA cm⁻² for 100 h in Figure 3b. Furthermore, the water-splitting cell operated at a current density as high as 500 mA cm⁻², and no apparent deterioration was observed for 70 h (Figure S18). Furthermore, the Ni₃N/Co₂N/CP exhibits a FE of closed 100%, with the ratio of generated hydrogen and oxygen amounts being closed to 2:1, as shown in Figure S19. These results demonstrate that the Ni₃N/Co₂N/CP electrodes possess extraordinary electrocatalytic efficiency and long-term electrocatalytic stability under alkaline conditions and are a promising candidate for practical water splitting applications (Table S3).



Figure 4. (a) Steady-state polarization curves of Ni₃N/Co₂N/CP, Ni₃N/CP, Co₂N/CP, NiCo/CP, Pt/CP, and Ni₃N/Co₂N/NF for HOR in H₂-saturated 0.1 M KOH; (b) Chronoamperometry curves of Ni₃N/Co₂N/CP in H₂- and Ar-saturated 0.1 M KOH at 100 mV vs. RHE.

Electrocatalytic H₂ oxidation. The electrocatalytic HOR property of Ni₃N/Co₂N/CP was examined in H₂and Ar-saturated 0.1 M KOH aqueous solution (Figure S20). An apparent anodic current was obtained in the presence of H₂. The optimized Ni₃N/Co₂N/CP catalysts exhibit excellent electrocatalytic HOR performance (normalized by the geometric areas and ECSA) comparable to that of Pt/C in the positive potential range applied (0 - 0.10 V vs RHE) (Figures 4a and S21-S23). The Ni₃N/Co₂N/CP catalysts produce a superior HOR current density of 2.12 mA cm⁻² (normalized by the geometric area) at 0.10 V vs RHE, which is higher than those of Ni₃N/CP (1.53 mA cm⁻²) and Co₂N/CP (1.17 mA cm⁻²). The exchange current density (j₀) was further evaluated for the HOR kinetics of Ni₃N/Co₂N/CP, Pt/CP, Ni₃N/CP, and Co₂N/CP in a micro-polarization region from -0.01 to 0.01 V vs RHE shown in Figure S24. The jo value of Ni₃N/Co₂N/CP was calculated to be 2.13 mA cm⁻², which is higher than those of Pt/CP (1.45 mA cm⁻²), Ni₃N/CP (1.82 mA cm⁻²), and Co₂N/CP (1.27 mA cm⁻²). Furthermore, the stability of Ni₃N/Co₂N/CP for H₂ oxidation was conducted at 0.10 V vs RHE in Figure 4b. The Ni₃N/Co₂N/CP electrode exhibits negligible HOR activity degradation over 100 h of continuous H₂ oxidation. Surprisingly, the Ni₃N/Co₂N catalysts demonstrate a champion HOR current density as high as 10.5 mA cm⁻² at 100 mV vs RHE when supported on commercial nickel foam (Ni₃N/Co₂N/NF) as shown in Figures 4a and S25. This was mainly attributed to that the nickel foam serves as a favorable H₂ gas diffusion layer in addition to its roles of current collector and catalyst support for the HOR. The robust nickel foam with a 3D macroporous network may facilitate H_2 diffusion, accounting for the higher HOR current density of Ni₃N/Co₂N/NF than those of Ni₃N/Co₂N/CP. Furthermore, we also compared the HOR properties of Ni₃N/Co₂N/NF, Pt/NF, Ni₃N/NF, Co₂N/NF and NiCo/NF under alkaline condition. As shown in Figure S26, the Ni₃N/Co₂N/NF exhibit the best HOR performance among the all samples, which suggest that the superior HOR activity of Ni₃N/Co₂N/NF arise from intrinsic activity of interfacial catalytic sites. Overall, such a HOR current is the best as compared to

the most active nonprecious HOR electrocatalyst (Table S3),^{10, 12-14, 23, 31-35} showing the potential applications of Ni_3N/Co_2N in Ni-H battery.

Swagelok-type Ni-H battery. The excellent HOR/HER properties make the Ni₃N/Co₂N interface electrocatalysts promising anodic materials in applications of Ni-H battery. We designed a novel Swageloktype Ni-H battery by using Ni₃N/Co₂N as an anode to catalyze hydrogen evolution in charging and hydrogen oxidation in discharging. The Swagelok-type Ni-H cell is composed of a cathode made of commercial Ni(OH)₂ on nickel foam, a glass fiber separator, an anode made of Ni₃N/Co₂N/NF, in a steel vessel filled with 30 wt% KOH electrolyte (Ni(OH)₂||Ni₃N/Co₂N). The reactions during charging and discharging are at the cathode: Ni(OH)₂ + OH⁻ \leftrightarrow NiOOH + H₂O + e⁻; and at the anode: H₂O + e⁻ \leftrightarrow 1/2 H₂ + OH⁻. Figure 5 presents the electrochemical performance of a Swagelok-type Ni-H battery of Ni₃N/Co₂N/NF. As shown in Figure 5a, the Ni-H cell exhibited a typical battery discharge behavior with a trajectory between 1.3 V and 1.0 V. When charging to a capacity of 1 mAh cm⁻², the Coulombic efficiency of the first cycle can achieve to \sim 85% and finally reach at \sim 91% at the fifth cycle. The rate capability as well as cycle stability is of importance for commercial applications of Ni-H battery. Figure 5b shows the performance of the Ni-H battery under different discharge current densities. When the discharge current density increases from 10 mA cm⁻² for 5.25 min to 100 mA cm⁻² for 0.53 min, the Ni-H battery maintained a stable capacity as high as 0.91 mAh cm⁻², and the corresponding Coulombic efficiency achieved at 91%. Such a high discharge rate is in agreement with the capacity retention at different discharge rates during cycling as shown in Figure 5c. Together, these results indicate a remarkably stable rate capability of the Ni-H battery made of Ni₃N/Co₂N/NF. Although its discharge plateau gradually decreases with increasing discharge current density, the capacity retained a stable value conducted at different current densities. More intriguingly, the Ni-H battery demonstrates outstanding long-term cycle stability with a negligible capacity decay over 5,000 cycles in Figure 5d. Such excellent electrochemical performance is comparable to those of the other metal-H batteries reported in the literature,^{70,71} leading to its potential for large-scale practical applications.



Figure 5. Swagelok-type Ni-H battery of Ni(OH)₂||Ni₃N/Co₂N. (a) Galvanostatic discharge curves of the Swagelok battery at a current density of 10 mA cm⁻²; (b) The discharge curves of the Swagelok battery at different current densities; Long-term cycle (c) and stability behaviors from 10 mA cm⁻² to 100 mA cm⁻², then back to 10 mA cm⁻²; (d) of the battery at a current density of 10 mA cm⁻². The Ni-H Swagelok batteries were fabricated using Ni(OH)₂ as a cathode and Ni₃N/Co₂N as an anode in 30% KOH electrolyte.

DFT Calculations. To reveal the mechanism of the multifunctional catalysis of Ni₃N/Co₂N, DFT calculations were carried out. Hydrogen adsorption free energy (ΔG_{H^*}) is considered as a key descriptor in evaluating the HER/HOR activity of an electrocatalyst.^{19, 72, 73} The optimal ΔG_{H^*} of an ideal catalyst is close to 0 eV.^{11, 14 74} We examined ΔG_{H^*} for various possible sites, including Ni, Co, and N sides near the interface of Ni₃N and Co₂N (Figures S27-S29 and Table S5). The optimal adsorption sites were found to be located in both the N and Co catalytic sites of Ni₃N/Co₂N as shown in Figure 6a. The energies for hydrogen adsorption (ΔG_{H^*}) onto the N and Co of Ni₃N/Co₂N interfaces were calculated to be 0.038 and 0.057 eV,

respectively. On the other hand, Co₂N and Ni₃N alone exhibit more negative hydrogen adsorption energies of -0.232 eV and -0.606 eV, respectively (Figures 6b and S30-S34). These results suggest a stronger hydrogen affinity for Co₂N and Ni₃N alone, which is not beneficial to efficient hydrogen electrochemistry. Furthermore, we evaluated the adsorption energies of H₂ onto Ni₃N/Co₂N, Ni₃N, and Co₂N (Figures S35-S38 and Table S6). The Ni₃N/Co₂N interfaces demonstrate the strongest H₂ adsorption with one of the two H atoms approaching the edge Co in Ni₃N/Co₂N (Figure S35). Such a configuration of H₂ adsorption on the Ni₃N/Co₂N is favorable to its subsequent hydrogen oxidation. Therefore, the dissociative adsorption of H₂ and weak binding of the intermediate H in Ni₃N/Co₂N contributes greatly to the excellent hydrogen electrochemistry.

In addition to the adsorptions of H₂ and the intermediate hydrogen, hydroxide species adsorbed onto catalyst surfaces could enhance the kinetics of the overall HOR process in alkaline media.⁴⁸ The adsorption free energies of hydroxide species onto Ni₃N/Co₂N, Ni₃N, and Co₂N were also calculated. As shown in Figures 6c, S39-S45 and Table S7, the Ni₃N/Co₂N interfaces exhibit a much stronger hydroxide adsorption energy (-1.27 eV) than those of Ni₃N alone (-0.41 eV) and Co₂N alone (0.35 eV). Interestingly, hydroxide species was found to preferentially adsorb onto the Co catalytic site of Ni₃N/Co₂N, near the optimal hydrogen adsorption site of N. Together, these binding configurations of the intermediate hydrogen and hydroxide facilitate the charge transfer between the interfacial sites of Ni₃N/Co₂N.



Figure 6. (a) Optimized interfacial structures of hydrogen (H) adsorbed on Ni_3N/Co_2N ; (b) Free energy changes (ΔG_{Had}) of the H adsorption onto different locations of Ni_3N/Co_2N ; (c) OH adsorption energies onto Ni_3N/Co_2N . As a comparison, the adsorption energies of the H and OH onto Ni_3N and Co_2N are shown. (d) Optimized structures of interfacial Ni_3N/Co_2N (left); Charge density at Ni_3N/Co_2N interface (right).

Yellow and cyan iso-surface represents electron accumulation ($\Delta \rho = +3 \times 10^{-3} \text{ e bohr}^{-3}$) and depletion ($\Delta \rho = -3 \times 10^{-3} \text{ e bohr}^{-3}$), respectively. Color code: Ni (grey), Co (green), N (blue), and H (white).

Discussion

As a multifunctional catalyst for HER/HOR/OER, constituted materials should possess lattice matching for heterojunctions. There are six possibilities for complexation, including nitridation, oxidation, sulfurization, phosphidation, hydrogenation, and halogenation. The hydrogenation and halogenation complexation could be excluded due to their experimental complications. Of the non-precious metals, Ni and Co are the best pair in terms of their abundance. Besides, charge redistribution is expected to occur in interface catalysts. In general, heterogeneous interfaces can introduce the charge transfer and modulate the orbitals of catalytic sites. The *d*-band center of one metal should act as a donor to transfer electrons to that of the other metal or their complexes. It turns out that we are limited to the nitridation of Ni and Co since the sulfurization, phosphidation, and oxidation could not provide satisfactory HOR or HER activities. Computationally, we constructed the Ni₃N(001)/Co₂N(111) interface. Figure 6d illustrates the charge density difference for the interface due to the formation of Ni-N-Co hybridizations. A quantitative analysis of the interfacial charge density difference shows electron accumulation ($\Delta \rho = +3 \times 10^{-3}$ e bohr⁻³) on the Co₂N side and electron depletion ($\Delta \rho = -7 \times 10^{-3}$ e bohr⁻³) on the Ni₃N side in Figure 6d. Such hybridizations are beneficial to the charge transfer from Ni to Co and both the N moieties in Ni₃N/Co₂N, leading to modulation of the orbitals of Co and N and the formation of the charge-rich catalytic sites.

The interface engineering strategy can efficiently improve the catalytic properties towards hydrogen/oxygen electrochemistry. As compared to the previous metal/metal nitride such as Ni₃N/Ni and Co₂N/Co,^{45,75} this novel heterojunction of two dissimilar metal nitrides (Ni₃N/Co₂N) demonstrate superior catalytic properties of HER/HOR in alkaline solution. Especially, for HOR, the interface catalysts Ni₃N/Co₂N produce a record-breaking HOR current density as high as 10.5 mA cm⁻² at 0.10 V vs RHE. These outstanding hydrogen/oxygen electrocatalytic properties of Ni₃N/Co₂N could be rationalized by the following aspects: 1) The Ni₃N/Co₂N interface efficiently lowered the $|\Delta G_{H^*}|$. The results show that N catalytic site at the interface unexpectedly reduced the $|\Delta G_{H^*}|$ to 0.038 eV, which can favor the formation of H* intermediate adsorbed on the catalyst surface to enhance the hydrogen electrochemistry, as revealed by the DFT calculations. In addition, the more negative H₂ binding energy of Ni₃N/Co₂N interface indicated that the H₂ dissociative adsorption is thermodynamically spontaneous on the interface and beneficial to the HOR; 2) The Ni₃N/Co₂N interface introduced charge redistribution and caused charge transfer from Ni to nearby Co and N, due to the interfacial hybridizations of the Ni3d-N2p-Co3d. Charge transfer near the interface modulated the *d*-orbital of Co and *p*-orbital of N. As a result, the electron-rich Co and N catalytic sites were formed, leading to the stabilization of the intermediates and thereby improvement of the HER/HOR kinetics; 3) The intimate contact between the Ni₃N/Co₂N microspheres ensured an effective 3D

conductive network and hence improved the current collection. The microspheres maintained strong mechanical adhesion and robustness even after the long-term durability tests. These features explained the remarkable catalytic stability for hydrogen electrochemistry and Ni-H battery.

In summary, we reported a facile strategy for the construction of the Ni₃N/Co₂N interface catalysts on commercial carbon paper and nickel foam for hydrogen and oxygen electrochemistry. The interface catalysts of Ni₃N/Co₂N exhibited excellent multifunctional catalytic properties of HER, HOR, and OER in alkaline solution. As HER/HOR electrocatalysts, the Ni₃N/Co₂N interfaces displayed superior hydrogen electrocatalytic performances comparable to the state-of-the-art Pt/C catalyst, with robust long-term stability. The Ni₃N/Co₂N electrocatalysts further acted as both an anode and cathode electrode in water electrolyzer. This electrolyzer split water with a current density of 10 and 100 mA cm⁻² for a long time of 100 h were as low as 1.55 and 1.73 V, respectively. In addition, the interface catalysts of Ni₃N/Co₂N acted as an anode material in a Swagelok-type Ni-H battery, which exhibited superior rechargeability over 5,000 cycles. DFT calculations further shed light on the charge transfer of the Ni₃N/Co₂N interfaces. The charge redistribution from Ni to Co and N at the Ni₃N/Co₂N interface efficiently enhanced the dissociative adsorption of H₂ and optimized the adsorption energies of the intermediate hydrogen and hydroxide. This work provides a new interface engineering strategy for low-cost and high-performance hydrogen and oxygen electrochemistry of earth-abundant electrocatalysts.

Supporting Information

Additional experimental details, including the following: chemicals used for synthesis; methods to prepare samples for characterization; instrumentation used to characterize samples; additional synthetic procedures to fabricate electrocatalysts; and a section on density functional theory calculations and methods. The following supporting figures are provided in the Supporting Information: XRD patterns of Ni₃N/Co₂N/CP, Ni₃N/CP and Co₂N/CP, Figure S1; STEM-HAADF image and corresponding EDS line-scan profile of Ni₃N/Co₂N interface, Figure S2; SEM images of pristine NiCo/CP, Figure S3; Elemental mapping and EDX result of NiCo/CP, Figure S4; SEM and elemental mapping images of Ni₃N/Co₂N/CP, Figures S5-S6; LSV curves of Ni₃N/Co₂N/CP synthesized at different nitridation temperatures, Figure S7; LSV curves of Pt/CP with varying mass loadings for HER in H₂-saturated 1.0 M KOH, Figure S10; The ECSA-normalized LSV curves of Pt/CP and Ni₃N/Co₂N/CP for HER in H₂-saturated 1.0 M KOH, Figure S11; SEM images of Ni₃N/Co₂N/CP after HER electrolysis, Figure S12; XPS spectra of Ni₃N/Co₂N/CP after HER/HOR electrolysis, Figure S13; Comparison of measured and theoretically calculated H₂ amounts during the electrolysis, Figure S14; LSV curves of Ni₃N/Co₂N/CP, and NiCo/CP for OER in 1.0 M KOH,

Figure S16; Chronopotentiometry curves of Ni₃N/Co₂N/CP collected at 10 and 100 mA cm⁻² in 1.0 M KOH, Figure S17; Chronopotentiometry curve of Ni₃N/Co₂N/CP served as both cathode and anode electrocatalysts in 1.0 M KOH, Figure S18; Gas yield of H₂ and O₂ evolved over the Ni₃N/Co₂N/CP electrodes, Figure S19; Steady-state polarization curves of Ni₃N/Co₂N/CP for HOR in Ar and H₂-saturated 0.1 M KOH, Figure S20; Steady-state polarization curves Ni₃N/Co₂N/CP synthesized at different nitridation temperatures, Figure S21; Steady-state polarization curves Pt/CF with different mass loadings of Pt/C for HOR in H₂-saturated 0.1 M KOH, Figure S22; The ECSA-normalized steady-state polarization curves of optimized Pt/CP and Ni₃N/Co₂N/CP for HOR in H₂-saturated 0.1 M KOH, Figure S23, The steady-state polarization curves of Ni₃N/Co₂N/CP, Pt/CP, Ni₃N/CP, and Co₂N/CP, in the micro-polarization region in H₂-saturated 0.1 M KOH, Figure S24; Steady-state polarization curves of Ni₃N/Co₂N/NF for HOR in Ar and H2-saturated 0.1 M KOH, Figure S25; Steady-state polarization curves of Ni₃N/Co₂N/NF, Pt/NF, Ni₃N/NF, Co₂N/NF and NiCo/NF for HOR in H₂-saturated 0.1 M KOH, Figure S26; Hydrogen adsorption structures of Ni₃N/Co₂N N, Figure S27; Hydrogen adsorption structures of Ni₃N/Co₂N Ni, Figure S28; Hydrogen adsorption structures of Ni₃N/Co₂N Co, Figure S29; Hydrogen adsorption structures of Ni₃N N, Figure S30; Hydrogen adsorption structures of Ni₃N Ni hollow, Figure S31; Hydrogen adsorption structures of Ni₃N Ni hollow 1, Figure S32; Hydrogen adsorption structures of Ni₃N Ni hollow 2, Figure S33; Hydrogen adsorption structures of Co₂N Co, Figure S34; H₂ adsorption structures of Ni₃N/Co₂N, Figure S35; H₂ adsorption structures of Co₂N, Figure S36; H₂ adsorption structures of Ni₃N, Figure S37; H₂ adsorption energies on of Ni₃N/Co₂N, Ni₃N and Co₂N, Figure S38; Hydroxide adsorption structures of Ni₃N/Co₂N Co, Figure S39; Hydroxide adsorption structures of Ni₃N/Co₂N Co 1, Figure S40; Hydroxide adsorption structures of Ni₃N/Co₂N Ni, Figure S41; Hydroxide adsorption structures of Ni₃N Ni, Figure S42; Hydroxide adsorption structures of Ni₃N N, Figure S43; Hydroxide adsorption structures of Co₂N Co, Figure S44; Hydroxide adsorption structures of Co₂N N, Figure S45; Swagelok-type Ni-H cell, Figure S46.

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