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Cobalt nickel phosphide nanoparticles decorated carbon nanotubes as advanced hybrid catalyst for hydrogen evolution

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Abstract

Exploring new hybrid catalyst to replace Pt-based catalysts for the hydrogen evolution reaction (HER) is important to various renewable energy applications. However, the design and synthesis of such catalysts are still challenging. Herein, we focus on the development of a series of hybrid materials consisting of cobalt nickel phosphide nanoparticles (NPs) decorated carbon nanotubes $(Co_{2,x}Ni_xP/CNTs)$ as efficient catalysts for enhanced HER catalytic activity. All the X-ray spectra including X-ray diffraction, X-ray photoelectron spectroscopy and X-ray adsorption spectroscopy demonstrate that the crystalline phase structure, valence and coordination environment of hexagonal Ni₂P are changed with increasing Co atoms. Electrochemical measurements show that the Co_{2-x}Ni_xP/CNTs hybrids exhibit high activity and stability for HER in acidic solution. The as-synthesized $Co_1 e^{Ni_0 P/CNTs}$ hybrid exhibits the highest electrocatalytic activity with low onset overpotential (36.1 mV), a small Tafel slope (46.7 mV·dec⁻¹), a much larger exchange current density (1.86×10⁻⁵ A·cm⁻²), lower HER activation energy (57.3 kJ·mol⁻¹), and good stability. Such enhanced catalytic activity originates from the introduction of Co and strong synergistic effects between CNTs and $Co_{2,x}Ni_xP$. Meanwhile, density functional theory calculations also confirm that the higher HER catalytic activity of the $Co_{2,x}Ni_xP/CNTs$ can be attributed to the splendid migratory aptitude of adsorbed single H atom and the lower energy barrier for H₂ formation after the introduction of Co atoms. The as-synthesized Co_{2-x}Ni_xP/CNTs hybrid catalysts have great potential practical application in water splitting.

Keywords: Cobalt nickel phosphide, X-ray adsorption spectroscopy, hydrogen evolution reaction, density functional theory.

1. Introduction

Electrocatalytic water splitting into hydrogen and oxygen using an effective electrocatalyst has been regarded as an attractive way to solve global energy demand and environmental problems. The hydrogen evolution reaction (HER, $2H^+ + 2e \rightarrow H_2$), which is the main reaction of water electrolysis, needs an effective catalyst to improve the hydrogen production efficiency¹. Pt-based noble metal catalysts exhibit the highest catalytic activity, but their applications are limited due to the high cost and scarcity². Therefore, it is necessary to rationally design low-cost bulk quantities of non-noble metal HER catalysts for practical application.

The first generation non-noble metal HER electrocatalyst is molybdenum sulfide³, which date back to the 1970s. After that, many Mo-based non-noble metal catalysts and alloy compounds emerged as the times require, such as MoB⁴, Mo₂C⁵, MoSe₂⁶, Ni-Mo⁷, Ni-Mo-Zn⁸, and Ni-Fe⁹. Since the first transition-metal phosphide (TMPs), nanostructured Ni₂P, has been reported as attractive HER electrocatalysts by the Schaak group¹⁰, many other TMPs, such as CoP¹¹, MoP¹², FeP¹³, Cu₃P¹⁴, and InP¹⁵ also have been developed as new types of HER catalysts.

Recent efforts involving TMPs have primarily focused on enhanced HER activity and durability, and all kinds of strategies have been developed to further enhance the catalytic activity. The first strategy is that the hybridization of various TMPs nanoparticles (NPs) and carbon materials may improve the catalytic performance due to the high electrical conductivity and huge surface area of carbon materials¹⁶. The high electrical conductivity can promote the electron transfer, while the huge surface of carbon materials can increase the dispersity of the active components. For example, Zhang et al.¹⁷ reported that FeP NPs grown on graphene sheets can significantly improve the HER activity compared to pure FeP NPs. Liu et al.¹⁸ synthesized a nanohybrid consisting of

carbon nanotubes (CNTs) decorated with CoP nanocrystals by a low-temperature phosphidation method. This hybrid catalyst also exhibited high catalytic activity. Our group mainly focused on the development of Ni₂P-based catalysts for improving the HER activity. For example, we developed a thermal decomposition synthesis of Ni₂P NPs on CNTs¹⁹, carbon nanospheres²⁰ and nitrogen-doped reduced graphene oxide²¹, which exhibited superior electrocatalytic activity in HER relative to our previously reported pure Ni₂P NPs²².

Recently, many literatures²³ reported that the catalytic performance can be further enhanced by doping heteroatoms such as nitrogen (N) and boron (B) into above mentioned carbon materials. and this method can be regarded as another strategy to improve the catalytic activity of HER. For example. Huang et al.²⁴ reported that a hybrid catalyst comprising Fe₂P NPs and N-doped graphene showed excellent electrocatalytic activity for HER in both acidic and basic solutions. The third strategy, namely metal-doped metal phosphides and carbon materials, is a novel method to enhance the HER activity, because the hydrogen adsorption energy and kinetic energy barrier of the hydrogen evolution pathway could be decreased by varying the type of atom or crystal phase structure²⁵. Some literatures have reported that the HER activity of metal sulfide catalysts can be improved by doping other metal atoms²⁶. For example, Wang et al. demonstrated that the HER activity of FeS₂ nanosheets can be improved by introducing Co atoms²⁷. Long et al. designed a highly active catalyst composed of Fe-doped nickel sulfide ultrathin nanosheets²⁸. Therefore, in our studies, we think that the electrocatalysis activity may also be enhanced by introducing another metal atoms into Ni₂P. However, the effect of metal introduction for the HER by nickel phosphide-based hybrid catalysts is not well established yet.

On the basis of our previous work, we designed and synthesized a series of highly active and

stable cobalt nickel phosphide NPs on carbon nanotubes (Co2-xNixP/CNTs) hybrid catalysts for the

HER. All the X-ray spectra including X-ray diffraction, X-ray photoelectron spectroscopy and

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X-ray adsorption spectroscopy demonstrate that the crystalline phase structure, valence and coordination environment of hexagonal Ni₂P was changed with increasing Co atoms. In addition, electrochemical measurements showed that the catalytic activity of the $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts is strongly related to the introduction of Co atoms. The as-synthesized $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid exhibits the highest electrocatalytic activity with low onset overpotential (36.1 mV), a small Tafel slope (46.7 mV·dec⁻¹), a much larger exchange current density (1.86×10⁻⁵ A·cm⁻²), lower HER activation energy (57.3 kJ·mol⁻¹), and good stability. The superior catalytic activity is attributed to the introduction of cobalt and strong synergistic effects between CNTs and $Co_{2-x}Ni_xP$. Furthermore, density functional theory (DFT) calculations also revealed that Co atoms in $Co_{2-x}Ni_xP$ structure were appropriate for proton adsorption and reduction. The detailed reaction kinetic pathway and the energy barrier of hydrogen atom adsorption for HER were also investigated. To the best of our knowledge, this is the first systematic study to reveal the relative activity of $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts for HER. We believe that the present work could be a guideline in designing and synthesizing effective non-noble metal HER catalyst.

2. Results and discussion

2.1 Characterization of the as-synthesized Co_{2-x}Ni_xP/CNTs hybrid catalysts

X-ray diffraction (XRD) was used to analyze the crystalline phase structure after the introduction of Co atoms. Fig. 1 shows the XRD patterns of the as-synthesized $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts. It can be seen that a phase transformation process occurred with increasing Co

ratio. When the Co: Ni precursor ratio was 0.33, the crystalline phase was hexagonal Ni₂P (PDF # 03-065-3544), and no crystalline impurities were detected. The diffraction peaks at 41° , 44.9° , 47.5°, 54.4°, 66.4°, 72.6°, 75.6°, 80.8°, and 88.9° are attributed to the (111), (201), (210), (300), (310), (311), (400), (401), and (321) crystal planes, respectively, which indicates that the crystalline phase structure of Ni₂P was not changed at low Co ratio. However, when the Co: Ni precursor ratio was increased to 1.22, the crystalline phase was a mixture of Ni₂P (major phase) and CoP (minor phase). The diffraction peaks at 31.7°, 35.3°, 36.5°, and 52.2° can be attributed to the (011), (200), (102) and (103) crystal planes of CoP. Upon further increasing the Co: Ni precursor ratio to 3, the major crystalline phase was CoP (PDF # 03-065-2593). The diffraction peaks at 31.7°, 35.3°, 36.5°, 46.2°, 48.3°, 52.2° and 56.4° can be attributed to the (011), (200), (102), (112), (202), (103) and (212) crystal planes of CoP. Thus, it can be concluded that the structure of the crystalline phase was changed with increasing Co ratio. This is due to the limitation of the doping amount in the Ni₂P lattice. In addition, all the Co_{2-x}Ni_xP/CNTs hybrid catalysts showed a diffraction peaks at 26.1° , which can be attributed to the (002) planes of hexagonal graphite²⁹. These results indicate that the CNTs were decorated with Co_{2-x}Ni_xP NPs successfully.

The morphologies and elemental compositions of the as-synthesized Co_{2-x}Ni_xP/CNTs hybrid catalysts were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution TEM (HRTEM), selected area electron diffraction (SAED), energy dispersive X-ray (EDX) and STEM EDX elemental mapping. The SEM images (Fig. S1) demonstrated that the Co_{2-x}Ni_xP NPs were grown on CNTs with high density and well homogeneous distribution. The TEM images (Fig. 2a-c) showed that monodispersed Co_{2-x}Ni_xP

NPs exhibit typically solid spherical shape structure with an average particle size of 3.65 ± 0.68 , 4.52 ± 0.98 , and 5.35 ± 1.48 nm (inserted in Fig. 2). They are exclusively dispersed on the CNTs and no any free NPs can be observed, indicating the existence of strong interaction between $Co_{2-x}Ni_xP$ and CNTs. The HRTEM image of $Co_{0.5}Ni_{1.5}P/CNTs$ hybrid catalyst (Fig. 2d) reveals two clear lattice fringe with the spacing of 1.68 Å and 2.11 Å, corresponding to the (002) and (111) crystalline plane of Ni₂P, which further indicates that the crystalline phase structure of Ni₂P was not changed after the introduction of Co atoms at low ratio. However, the HRTEM image of $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst (Fig. 2e) reveals two clear lattice fringe with the spacing of 2.11 Å and 2.83 Å, corresponding to the (111) crystalline plane of Ni_2P and (011) crystalline plane of CoP, which further indicates that the coexistence of Ni₂P and CoP. Additionally, several bright diffraction rings can be observed from the SAED image of $Co_0 5Ni_1 5P/CNTs$ hybrid catalyst (Fig. 2f), however, for the $Co_{11}Ni_{0.9}P/CNTs$ hybrid catalyst (Fig. 2g), besides bright diffraction rings, a lot of discrete spots also can be observed, and more discrete spots can be observed in $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst (Fig. 2h), further indicating the crystalline phase structure was changed. The corresponding EDX spectra (Fig. S2) confirmed the existence of C, Co, Ni and P elements in the as-synthesized $Co_{2,x}Ni_xP/CNTs$ hybrid catalysts. The STEM and the elemental mapping images of $Co_0 SNi_1 SP/CNTs$ (Fig. 2i) and $Co_1 SNi_0 P/CNTs$ hybrid catalysts (Fig. 2j) also reveal a homogeneous distribution of Co, Ni, P, and C elements over the $Co_{2,x}Ni_xP/CNTs$ hybrid catalysts.

X-ray photoelectron spectroscopy (XPS) spectra were recorded to investigate the elemental composition and chemical state of the as-synthesized $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts. The XPS survey spectra (Fig. 3a) of all the hybrid catalysts indicate the presence of the elements C, O, Co,

Ni, and P. Three peaks can be observed in the C 1s spectra (Fig. 3b) at about 284.5, 285.7, and 289.1 eV. They can be assigned to sp² hybridized graphite-like carbon atoms, carbon atoms bound to one oxygen atom by a single bond and a double bond, respectively³⁰. Two characteristic Ni₂P peaks at about 853 and 870.5 eV were observed of each hybrid (Fig. 3c), which can be attributed to Ni $2p_{3/2}$ and Ni $2p_{1/2}$ energy levels, respectively. These values are very close to those reported for Ni₃P³¹. Two other peaks at about 856.4 and 874.3 eV as well as two satellites at about 861 and 878.6 eV correspond to oxidized Ni species³². Similarly, for the Co 2p spectra (Fig. 3d), two peaks at about 778.5 and 793.5 eV of each hybrid are attributed to Co $2p_{3/2}$ and Co $2p_{1/2}$ energy levels of CoP, respectively³³. The peaks at about 781.7 and 798 eV as well as two satellites at 786 and 803.5 eV correspond to oxidized Co species. The intensity of the Ni $2p_{3/2}$ peak decreased gradually, but the intensity of the Co $2p_{3/2}$ peak increased gradually with increasing Co atoms ratio. For the P 2p spectra (Fig. 3e), two peaks were observed at 129.1 and 130 eV, which can be attributed to P $2p_{3/2}$ and P $2p_{1/2}$ energy levels of three hybrids, respectively, while the peak at about 133.5 eV is due to oxidized P species formed on the surface of $Co_{2x}Ni_xP/CNTs$ hybrid catalysts³⁴. Note: The atomic molar ratio of Co: Ni: P of the as-synthesized $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts in this paper were confirmed from the XPS fitting results.

The contents of Co, Ni and P in the $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts were estimated by inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis (Table S1). The Ni content decreased gradually while the Co content increased with increasing of Co atoms. In addition, we estimated the Co: Ni: P molar ratio to be about 0.44:1.58:1, 1.02:0.91:1, and 1.4:0.44:1, respectively, which is consistent with the XPS results.

X-ray adsorption spectroscopy (XAS) was performed to further study the Co and Ni bonding

environment of the as-synthesized Co2-xNixP/CNTs hybrid catalysts. The Ni K-edge (Fig. 4a) and Co K-edge (Fig. 4b) X-ray adsorption near-edge spectra (XANES) were measured and the absorption edge positions are shown in Table S2. Both Ni K-edge and Co K-edge XANES spectra show two regions with a pre-edge peak and a main edge peak. The pre-edge peak represents the electronic transitions from the 1s orbital to an unoccupied 3d orbital, while the main edge peak corresponds to the electronic transitions from the 1s to the 4p orbital³⁵. In addition, the valence state of both Co and Ni species in $Co_{2x}Ni_xP$ have a small positive charge by comparing with Ni-foil (Ni⁰), NiO (Ni²⁺), Co-foil (Co⁰), CoO (Co²⁺) and Co₃O₄ (Co²⁺, Co³⁺). We also found that the absorption edge position of Co and Ni in $Co_{1.6}Ni_{0.4}P/CNTs$ catalyst are located at 7716.7 eV and 8338.5 eV, respectively, these values are higher than that of the $Co_0 {}_5Ni_1 {}_5P/CNTs$ catalyst, which indicate that the charge of the Co and Ni species in the Co_{1.6}Ni_{0.4}P/CNTs catalyst is higher than that of the $C_{0,5}Ni_{1,5}P/CNTs$ catalyst. Because a higher positive charge on a metal is about favors the production of hydrogen in HER^{11, 39}, the Co_{1.6}Ni_{0.4}P/CNTs catalyst exhibits the highest HER catalytic activity. This can be attributed to the change of crystalline phase structure due to the increase of Co ratio (as proved by XRD results). In the $Co_0 \,_5Ni_1 \,_5P/CNTs$ catalyst, some Co atoms replace Ni atoms in Ni₂P, but the crystalline phase did not change. However, in the $Co_{1.6}Ni_{0.4}P/CNTs$ catalyst, the crystalline phase structure of Ni₂P was changed, accompanied the formation of CoP and a change in the charge of the Co and Ni species. To support our opinion, the bonding environment of the Ni and Co atoms was investigated by Fourier transform k³-weighted extended X-ray absorption fine structure spectra (EXAFS) at the Ni and Co edges for the $Co_{16}Ni_{04}P/CNTs$ and $Co_{05}Ni_{15}P/CNTs$ catalysts (Fig. S3) with their fitting parameters summarized in Table S3. The results indicate that, in the Co_{0.5}Ni_{1.5}P/CNTs catalyst, the Co-Ni, Co-P and Ni-P bonding were observed but no Co-Co distance was found. The Co-Ni distance is 2.66 Å, and is coincides with the Ni-Ni distance (2.67 Å) in the Ni₂P/CNTs reference, suggesting that the Co atoms were successfully introduced into the crystalline phase structure of Ni₂P without phase separation. However, in the Co_{1.6}Ni_{0.4}P/CNTs catalyst, the Co-Co bond has coordination number and bond distance that are very close to those of the CoP reference. This indicates the formation of CoP. The strong interaction between Co_{1.6}Ni_{0.4}P and CNTs can enhance the HER catalytic activity.

Because the hydrogen binding energy can reflect the HER activity, we carried out hydrogen temperature-programmed desorption (H₂-TPD) measurements (Fig. S4) of the as-synthesized $Co_{2,x}Ni_xP/CNTs$ hybrid catalysts. All H₂-TPD profiles showed two hydrogen desorption peaks at different temperature. Generally, the hydrogen species desorbed at lower temperature can be assigned to hydrogen species adsorbed on the metal surface, whereas those desorbed at higher temperature can be attributed to spillover hydrogen species³⁶. The H₂ desorption temperature of $Co_{1.6}Ni_{0.4}P/CNTs$ was in the range of 500-750 °C with a peak at 598 °C. The $Co_{1.1}Ni_{0.9}P/CNTs$ catalyst showed a broader desorption temperature of 500-780 °C and higher peak temperature of 632 °C. The $Co_{0.5}Ni_{1.5}P/CNTs$ catalyst exhibited the highest peak temperature of 665 °C. It can be concluded that the hydrogen binding energy is weakened with the increase of Co atoms, revealing the highest HER catalytic activity for the $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst. In addition, the appearance of another peak at higher temperature in each catalyst further suggests the existence of spillover hydrogen species, which can promote the diffusion of adsorbed hydrogen from $Co_{2-x}Ni_xP$

N₂ adsorption-desorption was used to analyze the textural properties (BET surface area, pore

volume, and pore size) of the as-synthesized $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts (Table S4). The BET surface area and pore volume increased gradually with increasing Co atoms. The $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid exhibited the highest surface area of 68.8 m²·g⁻¹ and the largest pore volume of 0.31 cm³·g⁻¹, which indicates that it exposed more active sites than the $Co_{1.1}Ni_{0.9}P/CNTs$ and $Co_{0.5}Ni_{1.5}P/CNTs$ hybrid catalysts, as confirmed by electrochemical activity measurements, which revealed that the $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid had the highest catalytic activity for the HER. Moreover, N₂ sorption (Fig. S5a) of the $Co_{2-x}Ni_xP/CNTs$ hybrids revealed type IV isotherms with a distinct hysteresis loop, which is characteristic of mesoporous materials. The Barrett-Joyner-Halenda (BJH) pore-size distribution (Fig. S5b) confirmed the nanoporous nature of the as-synthesized $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts.

2.2 Electrocatalytic properties of Co_{2-x}Ni_xP/CNTs hybrid catalysts for HER

The HER activities of the $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts were evaluated under acidic conditions (0.5 M H₂SO₄) in a typical three-electrode system. For comparison, we also synthesized and characterized Ni₂P, CoP and Co_{2-x}Ni_xP NPs without CNTs in order to demonstrate the merits of mixed phosphides and the synergistic effect between Co_{2-x}Ni_xP and CNTs. The XRD patterns confirm the crystalline phase of the as-synthesized pure Ni₂P and CoP catalysts (Fig. S6a). All the diffraction peaks matched well with the hexagonal structure of Ni₂P (PDF # 03-065-3544) and the orthorhombic structure of CoP (PDF# 03-065-2593). The XRD patterns of the Co_{2-x}Ni_xP NPs (Fig. S6b) also show the similar diffraction peaks with Co_{2-x}Ni_xP/CNTs hybrids except for without the peak of CNTs. TEM images indicate that Ni₂P exhibits a nanosphere structure with a size of about 8 nm (Fig. S7a) and CoP shows a nanorod structure with a size of about 18 nm (Fig. S7b). The as-synthesized Co_{0.5}Ni_{1.5}P also shows nanosphere-like structure with an average size of

about 9 nm (Fig. S7c). However, with the increase of Co atoms in Co_{2-x}Ni_xP, the morphology becomes irregular (Fig. S7d-e). This is difference with the $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts, suggesting the existence of the strong interaction between $Co_{2-x}Ni_xP$ and CNTs. Fig. 5a shows the linear sweep voltammetry (LSV) polarization curves of the Co_{2-x}Ni_xP/CNTs hybrids, Co_{2-x}Ni_xP NPs. Ni₂P. CoP. bare GCE, and Pt/C catalyst with a scan rate of 5 mV s⁻¹ at 298 K. The Pt/C catalyst showed the lowest overpotential, indicating the highest catalytic activity, while the bare GCE showed very poor catalytic activity. Pure Ni₂P exhibits higher catalytic activity with an onset overpotential of 110 mV than CoP with an onset overpotential of 187 mV. For driving the current density of 10 and 20 mA·cm⁻², Ni₂P need overpotentials of about 213 and 250 mV, CoP need overpotentials of about 352 and 410 mV, respectively (Fig. 5b). To our surprise, we found that the catalytic activity of bimetallic phosphides is higher than monometallic phosphides. The onset potentials for the $Co_0 {}_5Ni_1 {}_5P$, $Co_1 {}_1Ni_0 {}_9P$ and $Co_1 {}_6Ni_0 {}_4P$ catalysts were 124, 108 and 91 mV, respectively. Overpotentials of 199, 176 and 165 mV are needed to achieve current densities of 10 mA·cm⁻². The needed overpotentials of 225, 201 and 195 mV to achieve current densities of 20 $mA \cdot cm^{-2}$, respectively (Fig. 5b), indicating positive role of the mixed phosphides. However, the catalytic performance can be further increased after the decoration of CNTs. The onset potentials for the $Co_0 SNi_1 SP/CNTS$, $Co_1 Ni_0 P/CNTS$, and $Co_1 SNi_0 P/CNTS$ hybrid catalysts were 76.4, 57.6 and 36.1 mV, respectively. Overpotentials of 169.8, 135.4, and 118.8 mV are needed to achieve current densities of 20 mA·cm⁻², respectively (Fig. 5b). All these values are smaller than that of the compared catalysts, suggesting the existence of strong the synergistic effect between $Co_{2-x}Ni_xP$ and CNTs. Furthermore, the electrocatalytic performance of the $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst is superior to some reported HER catalysts, as shown in Table S5. The above comparison strongly

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suggests that the presence of Co is very beneficial for decreasing the overpotential and onset

potential values, both of which improve the HER. The excellent catalytic activity can be attributed

to the strongly synergistic effects between $Co_1 e^{Ni_0 A}P$ NPs and CNTs. Due to the introduction of

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Co atoms, the valence and coordination environment were changed. XPS and XANES analyses demonstrated that both Co and Ni species in $Co_{1.6}Ni_{0.4}P$ have more positive charge, indicating that excess electrons are located near the P atoms, which can promote proton discharge and enhance the HER catalytic activity.³⁸ Previous studies indicated covalency for Ni-P or Co-P bonds in pure

Ni₂P or CoP with charge separation because of charge transfer from metal to P^{39} . In our case, due to the excess Co atoms, the crystalline phase was changed, the synergistic effects between Ni_2P and CoP in the same system further accelerated the electron transfer and improved the catalytic activity. These catalytic mechanisms are similar to those previously reported for metal complex HER catalysts, which incorporate proton transfers from pendant acid-base groups positioned near the metal center accompanied by the occurrence of hydrogen production⁴⁰. In addition, the catalytic sites for hydrogenase also feature pendant base proximate to metal centers⁴¹. Therefore, for the $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst, with the pendant base P close to the metal center of Co and Ni, the metal centers (Co and Ni) and basic P function act as the hydride-acceptor and proton-acceptor centers, respectively, both of which facilitate the HER⁴². Furthermore, due to the $Co_{1.6}Ni_{0.4}P$ NPs in-situ grown in the CNTs, the electrons can be easily transferred from CNTs to Co_{1.6}Ni_{0.4}P NPs because of their strong contact during cathodic polarization, these results lead to the formation of the hydride at the metal center. Meanwhile, by the electrochemical desorption process, P atoms also facilitate the formation of a metal-hydride for subsequent hydrogen evolution43.

The Tafel plots of the pure Ni₂P, CoP, Co_{2-x}Ni_xP NPs, Co_{2-x}Ni_xP/CNTs hybrids and Pt/C catalyst

are shown in Fig. 5c. The linear portions of the Tafel plots were fitted by the Tafel equation ($\eta = a$ + blog j, where j is the current density and b is the Tafel slope), yielding Tafel slopes of 30, 46.7, 53.1, 60.9, 68.2, 68.1, 72.3, 78.9, 92.8 mV·dec⁻¹ for Pt/C, Co_{1.6}Ni_{0.4}P/CNTs, Co_{1.1}Ni_{0.9}P/CNTs, $Co_0 SNi_1 SP/CNTS$, $Co_1 SNi_0 P$, $Co_1 Ni_0 P$, $Co_0 SNi_1 SP$, Ni_2P and CoP catalysts, respectively, which indicates that the HER rate of these catalysts follows the order of $Pt/C > Co_{1.6}Ni_{0.4}P/CNTs >$ $Co_{1.1}Ni_{0.9}P/CNTs > Co_{0.5}Ni_{1.5}P/CNTs > Co_{1.6}Ni_{0.4}P > Co_{1.1}Ni_{0.9}P > Co_{0.5}Ni_{1.5}P > Ni_2P > CoP.$ For the $Co_{2,x}Ni_xP/CNTs$ hybrid catalysts, the smaller Tafel slope of the $Co_{1,6}Ni_{0,4}P/CNTs$ hybrid demonstrates that the catalytic performance is better than that of the $Co_{1,1}Ni_{0,0}P/CNTs$ and $Co_0 SN_{15}P/CNTs$ hybrid catalysts. It is well known that the HER reaction mechanism can be explained by Tafel analysis. There are three reaction steps including Volmer, Heyrovsky, and Tafel reactions in acidic medium⁴⁴. The first step is a Volmer reaction that occurs for the discharge of H⁺ and adsorption of hydrogen, as shown in Equation (1). The second step is a Heyrovsky reaction that follows the Volmer reaction concludes with the electrochemical desorption of free H^+ and the adsorbed hydrogen (Equation (2)). The third step is a Tafel reaction in which two adsorbed hydrogen atoms form hydrogen by chemical desorption (Equation (3)). The reported Tafel slopes of the above three reactions are about 120, 40, and 30 mV dec⁻¹. Therefore, from the Tafel slope values of the as-synthesized Co_{2-x}Ni_xP/CNTs hybrid catalysts, it can be concluded that the HER reaction took place via a fast Volmer step followed by a rate-determining Heyrovsky step⁴⁵.

 $H_{3}O^{+} + e^{-} \rightarrow H_{ads} + H_{2}O \qquad (1)$ $H_{3}O^{+} + e^{-} + H_{ads} \rightarrow H_{2} + H_{2}O \qquad (2)$ $H_{ads} + H_{ads} \rightarrow H_{2} \qquad (3)$

Additionally, the exchange current densities (j₀) for the $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts were calculated by applying the extrapolation method to the Tafel plots (Fig. S12, 298 K). The $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid displayed the largest exchange current density of 1.86×10^{-5} A·cm⁻² (Table S7, 298 K), which indicates that it has the best catalytic activity of the $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts.

The electrochemically-active surface area (ECSA), which is also an important factor to reflect the catalytic activity of the catalysts¹⁴. Figure 5d shows the ECSA of $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts in 0.5 M H₂SO₄ measured from the electrochemical double-layer capacitance (C_{dl}) by testing cyclic voltammograms (CVs) from 40 to 300 mV·s⁻¹ in a non-Faradaic region (Fig. S8). It can be seen that $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst exhibits the highest C_{dl} value of 6.79 mF·cm⁻², which is 1.18 and 1.23 times that of the $Co_{1.1}Ni_{0.9}P/CNTs$ (5.77 mF·cm⁻²) and $Co_{0.5}Ni_{1.5}P/CNTs$ (5.5 mF·cm⁻²) catalysts, respectively. The much larger ECSA for $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst indicates the existence of much more catalytic active sites, which is beneficial for the HER.

For a good HER electrocatalyst, the long-term stability is another important criterion. The stability of the as-synthesized $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid was investigated by continuous CVs in 0.5 M H₂SO₄ with a scan rate of 100 mV·s⁻¹. As shown in Fig. 5e, hardly any change in the polarization curve was observed after 500 cycles, indicating the excellent stability of the $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst in acid solution. In addition, the time-dependent current density curve under static overpotential of 120 mV shows that the $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst maintained its high catalytic activity for at least 40 000 s (inserted in Fig. 5e).

To obtain the TOF of the $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts, we first calculated the number of active sites by CV sweeps (Fig. S9a) with a scan rate of 20 mV·s⁻¹ over a range of -0.2 to 0.6 V vs.

RHE in a 1.0 M phosphate buffer solution (PBS, pH = 7). The calculated number of active sites of the $Co_{0.5}Ni_{1.5}P/CNTs$, $Co_{1.1}Ni_{0.9}P/CNTs$ and $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalysts were 3.3×10^{-8} , 3.64×10^{-8} , and 7.55×10^{-8} mol, respectively. The $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid has the highest numbers of active site, suggesting the highest catalytic activity among all the $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts. Fig. S9b shows the LSV polarization curves normalized by the number of active sites and expressed in terms of TOF. The obtained TOF values were 0.06, 0.22, and 0.21 s⁻¹ at an overpotential of 125 mV, further indicating the excellent catalytic activity of the $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst.

The electrical conductivity of the as-synthesized $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts were confirmed by electrochemical impedance spectroscopy (EIS) experiments at the same potential of 150 mV (Fig. 5f). The $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst exhibits the smallest semicircle, indicating the best electron-transfer ability and the highest HER catalytic activity among the $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts.

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The electrode kinetics of the $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst for HER were further studied by EIS. Fig. 6a shows the Nyquist plot of the EIS response of the $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid at various overpotentials in 0.5 M H₂SO₄. The Nyquist plot showed only one semicircle, which indicates that the model equivalent circuit can be characterized by one time constant for the electrocatalysis, the equivalent circuit including one unit of resistor and capacitor in parallel. Fig. 6b shows the Bode plot of the $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid. The phase angle is frequency dependent, which indicates that there is another resistor element in series. Thus, a model equivalent circuit (inserted in Fig. 6a) was obtained. Table S6 shows the electrode kinetic parameters obtained from fitting the experimental data to the model equivalent circuit. It has been reported that the Tafel slope can also

be obtained from the charge transfer resistance $(R_{ct})^{46}$. The Tafel slope of the Co_{1.6}Ni_{0.4}P/CNTs hybrid was obtained by fitting the log $(1/R_{ct})$ - η plot from 60 to 140 mV, as shown in Fig. 6c, yielding a Tafel slope of 59 mV·dec⁻¹, further revealing the Volmer-Heyrovsky mechanism for the HER.

2.3 Effect of temperature on catalytic activity of the as-synthesized $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts for HER

We further studied the influence of electrolytic temperature on the electrocatalytic performances of the as-synthesized Co_{2-x}Ni_xP/CNTs hybrid catalysts for HER. Fig. S10 shows the LSV polarization curves of the Co1.6Ni0.4P/CNTs, Co1.1Ni0.9P/CNTs and Co0.5Ni1.5P/CNTs hybrid catalysts from 298 to 328 K. The catalytic activity of three hybrid catalysts could be enhanced by increasing the electrolytic temperature. Besides, the $Co_1 e^{1/6}Ni_0 e^{1/6}P$ which exhibited a higher catalytic activity as the other hybrid catalysts at the same temperature. Fig. S11 and Fig. S12 show the Tafel plots and the corresponding exchange current densities of the Co_{2-x}Ni_xP/CNTs hybrids. The Tafel slopes and exchange current densities are listed in Table S7. These values also confirm the above experimental results. In addition, for the HER catalyst, it is well known that a high catalytic activity of a catalyst also reflects its low action energy (E_a). Therefore, the value of E_a often used to evaluate the catalytic activity of a catalyst⁴⁷. Here, the E_a values of the as-synthesized $Co_{2,x}Ni_xP/CNTs$ hybrid catalysts were calculated from the Arrhenius curves. Fig. 6d shows three linear Arrhenius curves of log j_0 on T^{-1} for the Co_{2-x}Ni_xP/CNTs hybrid catalysts. The calculated E_a values are shown in Table S7. The Co_{1.6}Ni_{0.4}P/CNTs showed the lowest E_a (57.3 kJ·mol⁻¹), indicating the highest HER activity among all the Co_{2-x}Ni_xP/CNTs hybrid catalysts.

2.4 Effect of CNTs content on catalytic activity of hybrid catalysts for HER

To study about the catalytic activity of the $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst is affected by the CNTs content, a series of $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalysts with different CNTs content were synthesized and characterized (see Supporting Information for details, Fig. S13, Table S4). Fig. S14 shows that the $Co_{1.6}Ni_{0.4}P$ NPs with no CNTs exhibited the lowest HER catalytic activity. The catalytic activity can be enhanced by increasing the CNTs content. However, an increase in the catalytic activity of the $Co_{1.6}Ni_{0.4}P/CNTs$ -50 hybrid catalyst compared with that of the $Co_{1.6}Ni_{0.4}P/CNTs$ -20 hybrid catalyst was not obvious. Actually, CNTs as a support can provide larger surface area and electrical conductivity, both of which can enhance the HER catalytic activity. However, the higher carbon content, which decreased the total available sites because of the fraction of $Co_{1.6}Ni_{0.4}P$ is decreasing. Therefore, the HER catalytic activity could not be further increased.

2.5 DFT calculations

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We further investigated the detailed HER pathways on both the Ni₂P/CNTs and Co_{2-x}Ni_xP/CNTs hybrid catalyst by DFT calculations (see details in Supporting Information) to understand the Co effect on catalytic HER activity. Our Tafel analysis proved that the HER process of the $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts according to a Volmer-Heyrovsky mechanism. Therefore, the HER pathway of the DFT calculation in acid solution can be described as follows: (i) a proton is adsorbed on the catalyst surface, (ii) another proton close to the above adsorbed proton (H_{ads}) forms adsorbed H₂ molecule, (iii) the adsorbed H₂ molecule desorbs from the catalyst surface and forms free H₂. Previously it was reported that the HER catalytic activity of a catalyst is related to the kinetic energy barrier of the pathway of hydrogen evolution⁴⁸. Therefore, we studied the kinetic energy barrier profiles of the Co_{2-x}Ni_xP/CNTs hybrid catalyst along the HER pathway by

DFT calculations to obtain the mechanism of enhanced catalytic activity by Co incorporation. Two H atoms were initially placed on the center hollow site of three Ni or Co atoms and on top of a P atom (Fig. S15a) of a Ni₂P and Co_{1.5}Ni_{0.5}P hybrid slab. In addition, the primarily center hollow site of three metal atoms assembled with the center hollow site of three metal atoms and two P atoms were taken into consideration for comparison (Fig. S15b). The energy barrier for transition state a and transition state b on the Co_{1.5}Ni_{0.5}P slab were calculated to be 1.451 and 0.203 eV (Fig. 8a and b), respectively. Moreover, the corresponding released energy between transition state and the product energy for the formation of H₂ on Co_{1.5}Ni_{0.5}P slab is 0.630 eV and 0.002 eV separately, while the results are stated that it is difficult to produce a H₂ molecule on Ni₂P/CNTs under the same initially set condition.

Some other H atomic adsorption sites on the Ni₂P slab (Fig. S15c and d) were inspected according to the geometry optimized H adsorption structure of the $Co_{1.5}Ni_{0.5}P$ slab (Fig. 7 IS1 configuration of a and b). The transition state geometries showed a relatively higher energy barrier on both bridge sites and one hollow site combined with one bridge site, with energy barriers of 0.505 and 0.255 eV (Fig. 8c and d), respectively. Furthermore, the processes from the initial two bridge sites adsorbed structure to the corresponding transition state as well as the relevant final state showed to be endothermic. All these results confirm the higher catalytic activity of $Co_{2-x}Ni_xP/CNTs$ than that of the corresponding hybrid catalyst without Co introducing. In conclusion, our calculation results are in accord with the experimental results. The higher HER catalytic activity of the $Co_{2-x}Ni_xP/CNTs$ can be attributed to the splendid migratory aptitude of adsorbed single H atom and the lower energy barrier for H₂ formation after Co introduce into Ni₂P/CNTs system.

3. Conclusions

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A series of cobalt nickel phosphide nanoparticles and carbon nanotubes ($Co_{2-x}Ni_xP/CNTs$) hybrid catalysts were synthesized by an *in situ* thermal decomposition method. The crystalline phase structure, valence and coordination environment of Ni₂P changed with the increase of Co atoms. As a novel hybrid catalysts, the $Co_{2-x}Ni_xP/CNTs$ hybrids exhibited high activity and stability for HER in acidic solution. Besides, the catalytic activity could be enhanced by increasing the Co atoms. The strong synergistic effects between CNTs and $Co_{2-x}Ni_xP$ contributed to the superior HER catalytic activity. DFT calculation results also demonstrated that the higher HER catalytic activity of the $Co_{2-x}Ni_xP/CNTs$ can be attributed to the splendid migratory aptitude of adsorbed single H atoms and the lower energy barrier for H₂ formation after Co into the Ni₂P/CNTs system. This work provides a general strategy for the synthesis of metal-doped non-noble metal phosphide/carbon nanotubes hybrid catalysts, and the excellent catalytic activity toward HER makes $Co_{2-x}Ni_xP/CNTs$ hybrids promising catalysts for hydrogen production in practical applications. Additionally, our strategy may also be applied to other metal phosphide-catalyzed reactions such as hydrodesulfurization and hydrodenitrogenation.

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Fig. 1 XRD patterns of the as-synthesized Co_{2-x}Ni_xP/CNTs hybrid catalysts.





Fig. 2 TEM and SAED images of the (a, f) $Co_{0.5}Ni_{1.5}P/CNTs$, (b, g) $Co_{1.1}Ni_{0.9}P/CNTs$ and (c, h) $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalysts. Inserts show the corresponding size distribution. HRTEM and STEM elemental mapping images of the (d, i) $Co_{0.5}Ni_{1.5}P/CNTs$, (e, j) $Co_{1.6}Ni_{0.4}P/CNTs$.



Fig. 3 XPS spectra of (a) survey, (b) C 1s, (c) Ni 2p, (d) Co 2p and (e) P 2p regions of the $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts.



Fig. 4 Normalized XANES spectra of the (a) Ni K-edge and (b) Co K-edge of the $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts. Inserted are the corresponding Ni and Co K-pre-edges of the $Co_{2-x}Ni_xP/CNTs$

hybrid catalysts.







Fig. 5 (a) LSV curves (iR corrected), (b) the histogram of η at j = 10 mA·cm⁻² and j = 20 mA·cm⁻² and (c) the corresponding Tafel plots of the Co_{2-x}Ni_xP/CNTs hybrid catalysts, Co_{2-x}Ni_xP NPs, Ni₂P, CoP and Pt/C catalyst in 0.5 M H₂SO₄. (d) The C_{dl} at 0.15 V as a function of scan rate for

 $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts. (e) LSV curves of the $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst in 0.5 M H_2SO_4 before and after long-term 500 cycles. Inserted is the corresponding time-dependent current density curve under a static overpotential of 120 mV. (f) Nyquist plots of the $Co_{2-x}Ni_xP/CNTs$ hybrid catalysts in 0.5 M H_2SO_4 with an overpotential of 150 mV.





Fig. 6 (a) Nyquist plots and (b) Bode plots of the $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst in 0.5 M H_2SO_4 . Inserted in (a) is the equivalent electrical circuit used to model the HER kinetics process. R_s , Q and R_{ct} are the solution resistance, element and charge transfer resistance, respectively. (c) Tafel slope of the $Co_{1.6}Ni_{0.4}P/CNTs$ hybrid catalyst fitted from EIS data from 60 to 140 mV. (d)



Linear Arrhenius curves of log j_0 on T⁻¹ for the Co_{2-x}Ni_xP/CNTs hybrid catalysts.

Fig. 7 Top views and side views of configurations for the two H atoms adsorbed on the $Co_{1.5}Ni_{0.5}P$ slab and Ni_2P slab along the minimum energy path via the HER mechanism, including the primary

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configurations (IS0), the initial states (IS1), the transition state (TS) and the final state. (a), (b), (c) and (d) corresponding to the primary configurations (a), (b), (c) and (d) in Fig. S12. (a) and (b) belong to structures of H atom adsorbed $Co_{1.5}Ni_{0.5}P$ slab, the transition state configuration and the final H₂ adsorbed slabs, correspondingly, (c) and (d) belong to structures of H atom adsorbed Ni₂P slab , the transition state configuration and the final H₂ adsorbed slabs.



Fig. 8 Schematic energy profile corresponding to configurations shown in Fig. 10 along the HER pathway. (a) The kinetic energy barrier profiles of HER on $Co_{1.5}Ni_{0.5}P$ slab with the primary H atoms on the H_P and T_P sites. (b) The kinetic energy barrier profiles of HER on a $Co_{1.5}Ni_{0.5}P$ slab with the primary H atoms on the H_P and H_M sites. Scheme (c) and (d) assign to the kinetic energy profiles of HER on Ni_2P with the primary two H atoms on both B_M-M sites and H-P site combined with B M-P sites.

Graphic Abstract



Cobalt nickel phosphide nanoparticles decorated carbon nanotubes $(Co_{2-x}Ni_xP/CNTs)$ as efficient hybrid catalysts for enhanced hydrogen evolution reaction catalytic activity.