Rugae-like Ni$_2$P-CoP nanoarrays as a bi-functional catalyst for hydrogen generation: NaBH$_4$ hydrolysis and water reduction

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A B S T R A C T

Designing a bifunctional catalyst that performs hydrolysis of metal hydrides and water reduction spontaneously is an essential step towards developing an integrated H$_2$ storage system. Herein, a series of rugae-like CoP-Ni$_2$P arrays decorated Ni foam (Ni-Co$_{20}$-P@NF) are fabricated by two-step electrodeposition followed by phosphating treatment. The optimized Ni-Co$_{20}$-P@NF catalyst shows a superior catalytic H$_2$ generation by NaBH$_4$ hydrolysis, giving a specific H$_2$ generation rate of 4323.0 mL min$^{-1}$ g$^{-1}$ catalyst and good reusability, far better than most previously reported catalysts. Besides, the catalyst also exhibits an excellent electrocatalytic hydrogen evolution reaction with a low overpotential of 67.0 mV to reach ~10 mA cm$^{-2}$, small Tafel slope and long-term stability in 1.0 M KOH. The outstanding catalytic H$_2$ generation capacity is attributed to the synergistically catalytic effect between the Ni$_2$P and CoP species, as well as the unique composite structure with the benefit of solute transport and gas emission.

1. Introduction

Hydrogen (H$_2$) is clean energy sources that regarded as a future replacement of fossil fuel due to the highest energy per mass 142 MJ kg$^{-1}$ [1]. As an alternative of methane reforming, the electrochemical water splitting attracts a lot of attention due to the zero carbon emission and high purity H$_2$. Most importantly, H$_2$ can be generated using renewable energy such as solar and wind. However, the electrochemical water splitting requires a much higher voltage (1.8 ~ 2.0 V) than the theoretical limit of 1.23 V owing to the strong uphill reaction that requires high overpotentials [2]. As a result, it is critical to developing the efficient electrocatalysts that improve the sluggish kinetics thereof decrease the overpotential. The state-of-the-art hydrogen evolution reaction (HER) catalysts are based on the expensive noble metal Pt [3,4]. Hence, extensive efforts have been devoted to developing robust and cheap noble-metal-free transition metal catalyst including sulfides, selenides, phosphides, carbides, and nitrides, etc. [5]. Among them, the increasing attention has been paid to metal phosphides (Ni$_2$P, CoP, MoP, and FeP) as HER catalyst because of the thermostability, high conductivity, and low cost [6]. Besides, the metal phosphides show bulk activity as compare to the metal sulfides of which the electrocatalytic activity is limited to the edges [7]. Thus the metal phosphides often show better HER performance compare to those of others. Therefore, self-supported metal phosphide nanostructures in situ grown on 3D substrates have been widely exploited because the self-supported HER catalyst has several advantages as compared to a powder-based catalyst such as no binder, more active sites, better charge transfer and easy to be prepared [8-10]. However, the long term stability of the metal phosphides based HER catalyst is the primary concern.

Apart from the H$_2$ production, the H$_2$ storage is also a critical process for a sustainable “hydrogen economy”. H$_2$ storage is particularly challenging because of its low volumetric energy density. In general, there are two categories for storage H$_2$ including physical and chemical methods [11]. The physical storage based on forming either the high pressure (350 ~ 700 bar) compressed gas or low-temperature liquid. The hydrogen can also be stored on the surface of porous scaffold through physical absorption, for example, organic frameworks and polymers with intrinsic porosity [12,13]. On the other hand, the chemical storage is realized by a reversible chemical bonding between hydrogen and absorbents including liquid organic (HCOOH) [14-16], interstitial metal hydride (LaNiH$_6$) [17], complex hydride (NaAlH$_4$) [18-20], and chemical hydride (NaBH$_4$) [21,22].
However, developing high-density hydrogen storage for stationary and portable applications remains a significant challenge. Among all the chemical storage materials, chemical hydrides (NaBH₄, NH₃BH₃, and LiBH₄) are the best candidate in this regard because of the high hydrogen gravimetric storage capacity, stable chemical properties, and non-toxicity [23–25]. Nevertheless, boron hydride hydride synthesis generally suffers from sluggish reaction kinetics. At present, platinum-based materials are the best performing catalysts for hydrosynthesis of sodium borohydride [26,27] and a lot of efforts have been made to develop the earth’s abundant non-noble metal catalysts to replace the expensive platinum-based catalysts [28,29]. Among them, transition metal phosphides such as CoP/C nanoboxes [30], CoP nanowire [31], Ni₃P/Ni/FeAlO₄ [32], Ni – Cu – P nanotube [33], CoP/NiCoP [34], etc. become the hotspot. Wang et al. [35] and Zhang et al. [36] found that the bimetallic phosphides can significantly improve the catalytic performance as compared to single metal phosphides due to the synergistic effect. The maximum solubility of NaBH₄ in water is around 25% therefore only a quarter of the NaBH₄ solution is consumed after NaBH₄ electrodeposited on the surface of NF (Co@NF and Ni@NF). All of the Ni/Co for 1/20 [(Co₂Ni)P@NF]. Third, only Co or Ni species was reversed, while the ratio of Ni/Co was kept at 1/20 (Co₂₀Ni-P@NF). Second, a mixture of Ni-Co solution was prepared with the molar ratio of 15:1 and the mixture was pipetted onto the surface of NF (1 cm × 1 cm) and dried naturally in air.

2. Experimental section

2.1. Synthesis of Ni-Coₓ-species@NF

All chemicals are analytical grade and do not require further purification in experiments. Firstly, pretreatment of the nickel foam (1 cm × 1 cm × 1.6 mm) with 1.0 M HCl deionized water and ethanol for 5 min respectively, and then repeated 3 times to make sure the surface of the NF was well cleaned. To prepare the Ni-Co-species@NF, 1.5 mmol of Co(NO₃)₂·6H₂O and 1.0 mmol of Ni(NO₃)₂·6H₂O was ultrasonically dissolved into 40 mL deionized water to form uniform solutions, respectively. The electrodeposition experiments were carried out at room temperature in a standard three-electrode system to electrodeposits Co-species and Ni-species in sequence. The NF skeleton was used as the working electrode, a Pt sheet and a saturated calomel electrode SCE electrode used as the counter electrode and the reference electrode respectively. A series of composites with different Co/Ni molar ratios were synthesized by changing the deposition times at a constant current density of −10 mA cm⁻², in which the total electrodeposition time is kept at 1.0 h. After being thoroughly washed and dried at room temperature, the resulted products were labeled as Ni-Coₓ@NF (x = 5, 10, 15, 20 and 25).

We prepared a series of control materials by changing one parameter at a time. First, the order of electrodeposition of Co/Ni was reversed, while the ratio of Ni/Co was kept at 1/20 (Co₂₀Ni@NF). Second, a mixture of Ni-Co solution was prepared with the molar ratio of Ni/Co for 1/20 [(Co₂₀Ni)@NF]. Third, only Co or Ni species was electrodeposited on the surface of NF (Co@NF and Ni@NF). All of the above experiments were performed at −10 mA cm⁻² for a total deposition time of 1.0 h.

2.2. Synthesis of Ni-Coₓ-P@NF by vapor phase phosphidation

The phosphidation process was performed in a tube furnace, where a ceramic boat containing NaBH₄ as a phosphorus source was placed upstream, and all electrodeposited products were placed in another ceramic boat placed downstream. The furnace was heated to 350 °C with 2 °C min⁻¹ in Ar atmosphere (20 sccm), and kept at 350 °C for 2 h. After the phosphidation, the samples were cooled down to ambient temperature in flowing Ar gas. Thereafter, a series of samples were prepared and named as Ni-Coₓ-P@NF (x = 5, 10, 15, 20 and 20), Co₂₀Ni-P@NF, (Co₂₀Ni)P@NF, CoP@NF and Ni₃P@NF, etc., as the following studies.

As a control, commercial Pt/C modified NF was also prepared, where 10.0 mg of commercial 20 wt% Pt/C powder was ultrasonically dispersed in 0.5 mL of 0.2 wt% Nafion solution. After 30 min, the resulted mixture was pipetted onto the surface of NF (1 cm × 1 cm) and dried naturally in air.

2.3. Characterizations

The crystal structures of catalysts were analyzed by X-ray powder diffraction (XRD, Rigaku D/Max 2500 V/PC) with a sweep speed for 2.0 ° min⁻¹. The morphologies and microstructures of the catalysts were characterized by scanning electron microscope (SEM, FEI Quanta 200 FEG) and transmission electron microscope (TEM, JEM-2100 F). The X-ray photoelectron spectrometer (XPS, JPS-9010 Mg Kα) was used to analyze the chemical states of different elements. The actual loadings of different metals in the catalyst were checked by inductive coupled plasma atomic emission spectroscopy (ICP-AES, IRIS Intrepid II XP). The specific BET surface area of the as-prepared materials were measured on Quantachrome instrument. The conductivity of various materials were tested by four-point probe meter (RTS-9).

2.4. Catalytic hydrolysis of sodium borohydride studies

The catalytic activity, cycle stability and activation energy of the catalytic material were obtained by the following methods. Typically, 50 mL mixture solution (contained 150 mM NaBH₄ + 0.4 wt% NaOH) was kept in a three-necked round-bottom flask (100 mL), which was placed in a water bath at 25 °C. The volume of H₂ was monitored by a drainage which was connected to a computer to record the instantly changed water quantity. The catalytic reaction was started when the catalyst was added into the flask under constant magnetic stirring conditions. In order to test the recyclability of the catalyst, we continued to use the fresh NaBH₄ solution instead of the fully decomposed NaBH₄ solution for five consecutive cycles at 25 °C. After each stability test, we centrifuged the catalytic material, dried it under vacuum condition at room temperature, and weighed the catalytic material. All experiments were repeated three times to ensure the reliable results. The activation energy of the designed catalyst was evaluated in the same device in the temperature range of 25–45 °C.

2.5. Electrochemical hydrogen evolution studies

The electrocatalytic performance of different catalysts were performed in a standard three-electrode system with a Multi-channel electrochemical workstation (Bio-logic VMP3, France) at room temperature. The graphite plate and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Cyclic voltammetry (CV) tests were firstly carried out for about 3–5 cycles to stabilize the electrocatalytic performance of the catalyst at a scan rate of 20 mV s⁻¹. Then, linear sweep voltammetry (LSV) curves were performed at a scan rate of 5 mV s⁻¹, and electrochemical impedance spectroscopy (EIS) was evaluated near the onset potential in the frequency range from 200 kHz to 10 mHz. Cyclic voltammetry (CV) method was used to derive the electrochemical double-layer
of Ni-Co$_2$O$_3$-P@NF is dominated by the CoP peaks indicating the low-
rent crossed zero ($1.044$ V) was taken to be the thermodynamic po-
RHE by the average CV curves of the two potentials at which the cur-
0443) and Ni(OH)$_2$ (JCPDS: 38-0715), respectively. The Co and Ni were
stored energy can be calculated using the conventional capacitor
chemically double-layer is similar to the regular capacitors where the
energy stored in the $C_d$ by simply charge separation. Therefore, the
stored energy can be calculated using the conventional capacitor
equation [39]: $Q_a = C_d V = \varepsilon \varepsilon_0 \frac{d}{d}$, where $V$ is voltage, $A$ is electro-
chemically active surface area, $d$ distance between two layers, and $\varepsilon$
is the permittivity of the dielectric. Therefore, the $C_d$ is directly propor-
tional to the electrochemically active surface area (EASA) of the elec-
trocatalysts. All potentials (vs. SCE) in this work were calibrated to the
HRE by the average CV curves of the two potentials at which the cur-
rent crossed zero ($1.044$ V) was taken to be the thermodynamic po-

tential in $H_2$-saturated $1.0$ M KOH. Two clean Pt sheets are used as the
working and counter electrodes in the calibration system, respectively.
All reported curves had been corrected by iR compensation and all the
electrochemical tests were performed at room temperature ($25 \pm 1$ °C).

3. Results and discussion

The Ni-Co$_2$O$_3$-P@NF materials were fabricated by consecutive three
steps, in which Co-species were first electrodeposited onto the surface
of NF to form Co-species nanosheet arrays. Thereafter, the Ni species
were subsequently electrodeposited onto the surface of the Co-species
nanosheet arrays. Finally, after the gas phase phosphating treatment, a
series of the target Ni-Co$_2$O$_3$-P@NF composites with different Co/Ni ratios
were prepared (Fig. 1a). The XRD patterns were adopted to explore the
changes in crystal structure of the catalytic materials. Fig. S1a–b shows that
the prepared Co-species and Ni-species on the NF surface are consistent
with the standard XRD patterns of Co(OH)$_2$ (JCPDS: 30-0443) and Ni(OH)$_2$
(JCPDS: 38-0715), respectively. The Co and Ni were electrochemically deposited on the NF where they are in the metallic state initially, but they are subsequently oxidized in the air to Co(OH)$_2$
and Ni(OH)$_2$. After phosphating, the pure Ni-species on NF surface is
subsequently converted to Ni$_2$P (JCPDS: 03-0953), while the Co-species
are transformed to CoP (JCPDS: 65–2593) (Fig. 1b). The XRD patterns of
Ni-Co$_2$O$_3$-P@NF is dominated by the CoP peaks indicating the low-
content of Ni$_2$P in the hybrid composite. This phenomenon was si-
multaneously observed in the series of Ni-Co$_2$O$_3$-P@NF and Co$_2$O$_3$-Ni$_2$P@NF
materials (Fig. S1c). However, the XRD pattern of (Co$_2$Ni)$_2$P@NF
obtained by electroplating at the same time shows strong Ni$_2$P dif-
fraction peaks because more Ni species are electrodeposited on NF
surface due to the higher standard reduction potentials of Ni$^{2+}$ ($-0.23$
V) than Co$^{2+}$ ($-0.28$ V) under the same conditions (Fig. S1d).

SEM and TEM are used to investigate the morphologies and na-
nostructure of the catalysts. Fig. 2a shows that the fresh NF has a three-
dimensional structure and the surface is very smooth. After electro-
deposition of Co-species and phosphatization, the resulted rugue-like
CoP nanosheet arrays are vertically distributed on the surface of the NF
(Fig. S2a). It is worth noting that when the Co/Ni ratio is less than 10/
1, a large amount of Ni$_2$P clusters appear on the surface of CoP na-
sheet arrays (Fig. S2b–c), and as the Co/Ni ratio increases, the observed
Ni$_2$P clusters gradually decrease (Fig. 2b and Fig. S2d–e). Interestingly, the
Co/Ni ratios have little effect on the overall morphologies of Ni-Co$_{x}$
P@NF composites, except for the partial agglomeration of pure Ni$_2$P on
NF (Fig. S2f). As a control, the Co$_{20}$Ni$_{30}$P material presented irregular
morphology on the surface of NF at a high magnification SEM images
and was mainly composed by a large number of particulate materials
(Fig. S2g). Notably, the large spacings between these nano-sheets fa-
cilitate the mass transfer, thereby increasing in catalytic activity. The
TEM image of the ultrasonically exfoliated Ni-Co$_{20}$-P@NF nanosheets re-
veals that the Ni$_2$P clusters are uniformly distributed on the surface of
CoP with an average diameter of 6.0 nm (Fig. 2c). The high-resolution TEM image shows a set of lattice spacings of 0.25 and 0.19 nm, cor-
responding to the (111) and (211) crystal planes of CoP, respectively.
The other set of lattice spacings is 0.20 and 0.19 nm, which correspond
to the (201) and (210) crystal planes of Ni$_2$P, respectively (Fig. 2d).
Furthermore, the HAADF-STEM and corresponding element mappings
demonstrate that the elements of Co, Ni and P are uniformly dispersed
the entire architectures of Ni-Co$_{20}$P@NF (Fig. S2e).

Moreover, the specific surface areas of Ni-Co$_{20}$P@NF, Co$_{20}$Ni$_{30}$P@NF
and CoP@NF were investigated by Brunauer–Emmett–Teller (BET)
gas-sorption measurements (Fig. S3). The results reveal that the BET
surface area of Ni-Co$_{20}$P@NF is 18.2 m$^2$ g$^{-1}$, which is ca. 1.57- and
2.60-fold higher than that of Co$_{20}$-Ni$_{30}$P@NF and CoP@NF, respectively.
Interestingly, the Ni-Co$_{20}$P@NF also shows a high conductivity (2703 S
$^{-1}$), which is ca. 2.92-, 1.46- and 2.76-times larger than that of Co$_{20}$
Ni$_{30}$P@NF, CoP@NF and Ni$_2$P@NF, respectively (Table S1). It is known
that the high BET surface area helps to expose more active sites and
large conductivity enhances electron transport, an improved catalytic
performance is expected.

X-ray photoelectron spectroscopy (XPS) was used to further study the
changes in the surface chemical states of the composites and asso-
ciated electron transfer properties. As shown in Fig. S4a–b, the Ni-
Co$_{20}$P@NF material is composed of C, O, Co, Ni and P elements, in
which the high-resolution C1s region is deconvoluted into C–C (284.8
eV), CO (286.0 eV) and CO== (288.7 eV) as standard corrections for
other elements [40]. The Co 2p region of Ni-Co$_{20}$P@NF contains a pair of
Co 2p$_{3/2}$ and Co 2p$_{1/2}$, where the Co 2p$_{3/2}$ is fitted into three peaks of
Co–P (779.2 eV), CoO– (782.4 eV) and a satellite (786.4 eV), respecti-
vely (Fig. 3a). Compared to CoP@NF, the binding energy of Co–P of
Ni-Co$_{20}$P@NF is positively shifted by 0.82 eV. Besides, the Ni 2p$_{3/2}$
region of Ni-Co$_{20}$P@NF is also fitted with three peaks of Ni–P (854.7
eV), Ni–O (857.8 eV) and one satellite peak (862.8 eV). Contrary to Co
2p, the binding energy of the Ni–P of Ni-Co$_{20}$P@NF is negatively
shifted by 0.47 eV as compared to that of Ni$_2$P@NF (Fig. 3b). It is worth
noting that we have also studied the high-resolution Co 2p and Ni 2p of
Ni-Co$_{20}$P@NF and Ni-Co$_{30}$P@NF, and observed that they have a sim-
ilar chemical states distribution with Ni-Co$_{20}$P@NF (Fig. S4c–d).
Besides, the P 2p of Ni-Co$_{20}$P@NF is fitted in Fig. 3c, where the high-
resolution P 2p mainly includes P 2p$_{3/2}$ (130.6 eV) and P 2p$_{1/2}$ (131.7
eV) of Co–P or NiP, and additional PO– bonds (134.7 eV). One should
note that the positive shift on the Co–P and the negative shift on the
Ni–P binding energies in the Ni-Co$_{20}$P@NF indicates the charge
transfer from the CoP species to the Ni$_2$P species [41], implying the
synergy between CoP and Ni$_2$P species.
The catalytic hydrolysis of NaBH₄ for H₂ generation is carried out in an alkaline environment at 25 °C, wherein the generated H₂ gas is calculated by weighing the water mass produced by the drainage method (Fig. S5). Firstly, we explored the effect of Ni-Co₂₀-P@NF catalysts prepared by different ratios of Co/Ni on H₂ production by catalytic hydrolysis. It can find that the catalytic hydrolysis performance begins to increase gradually until the ratio for 20/1 and then decreases slightly with the increase of Co contents (Fig. 4a). When the ratio of Co/Ni is 20/1, the maximum catalytic hydrolysis H₂ generation rate is 4323.0 mL min⁻¹ g⁻¹ (Fig. 4b), wherein the calculated mass (g) is the total mass of Co and Ni, which is obtained by ICP test. To eliminate the influence of nickel form on the actual Co/Ni molar ratio, the carbon cloth (CC) was used as the support and prepared a series of Ni-Co₂₀-P modified CC composites. To monitor the Ni loading effect, the Ni loading was started from very low to high. The ICP-AES results were consistent with the original design, as shown in Tables S2 and S3. The Ni-Co₂₀-P@NF showed better catalytic performance than that of Co₂₀-Ni-P@NF on NaBH₄ hydrolysis due to the following reasons. Firstly, the catalyst of CoP is a much better catalyst than Ni₂P in terms of NaBH₄ hydrolysis [42,43]. Moreover, CoP@NF shows well-orientated nanosheet array structure as compare to that of the disorientated Ni₂P@NF where CoP@NF not only has better coverage but also offers higher surface area for Ni to attach (Fig. S3). The SEM images of both Ni-Co₂₀-P@NF and Co₂₀-Ni-P@NF reveal the same fact as a Ni₂P clusters decorated CoP@NF vs an irregular Co₂₀-Ni-P@NF morphology (Fig. S2). More surface area means more active sites as shown in Fig. 6c where the electrochemical capacitance (Cdl) of Ni-Co₂₀-P@NF is almost 1.82-fold higher than that of Co₂₀-Ni-P@NF which is directly proportional to the number of active sites [44,45]. Secondly, we explored the effects of different types of catalysts on the catalytic H₂ generation, in which the

![Fig. 2. Scanning electron microscopy (SEM) images of (a) NF, (b) Ni-Co₂₀-P@NF. The insets are the magnified SEM images. (c) Transmission electron microscopy (TEM) and (d) high-resolution TEM images of Ni-Co₂₀-P@NF.](image)

![Fig. 3. High-resolution XPS spectra of (a) Co 2p, (b) Ni 2p and (c) P 2p regions of Ni-Co₂₀-P@NF, CoP@NF and Ni₂P@NF, respectively.](image)
Ni-Co$_{20}$P@NF catalyst still showed the best catalytic performance compared with the control catalysts prepared by different methods (Fig. 4c). We can see that the H$_2$ generation rate of Ni-Co$_{20}$P@NF catalyst is approximate 1.71-, 1.20-, 2.02- and 55.42-fold higher than those of Co$_{20}$Ni-P@NF, (Co$_{20}$Ni)P@NF, CoP@NF and Ni$_2$P@NF, respectively (Fig. 4d). Meanwhile, the high catalytic H$_2$ generation rate is also superior to most of the previously reported catalysts (Table S4). Such excellent catalytic activity is mainly caused by the synergistic effect between CoP and Ni$_2$P species combined with more catalytically active sites.

The temperature effect to the catalytic performance of Ni-Co$_{20}$P@NF and CoP@NF in the alkalized NaBH$_4$ solution are further investigated (Fig. 5a and Fig. S6). The results revealed that the catalytic performance increases with the increasing reaction temperatures. Moreover, the activation energies of Ni-Co$_{20}$P@NF and CoP@NF are estimated to be 30.1 kJ mol$^{-1}$ and 56.1 kJ mol$^{-1}$ [40] respectively, and the activation energy of Ni-Co$_{20}$P@NF is almost half of the that of CoP@NF (Fig. 5b) once again implies the strong positive synergy between Co and Ni species in the Ni-Co$_{20}$P@NF. The reusability of Ni-Co$_{20}$P@NF catalyst was evaluated by the continuous recycling experiments in alkalized NaBH$_4$ solution. The results show that it takes 5 – 8 min to collect 200 mL of H$_2$ from the 1st to the 5th use (Fig. 5c) as
shown in Fig. 5d, the Ni-Co20-P@NF catalyst showed a good recyclability and retained 92% of initial catalytic activity after 5th cycle. The slight decay of catalytic activity could be attributed to the exfoliation of the catalytic materials and catalyst poisoning by BO2 species [23, 46].

In addition to the catalytic hydrolysis of NaBH4, the HER performance of the Ni-Co20-P@NF is also measured in 1.0 M KOH solution. All the HER results are corrected to the RHE potential, and the calibration parameter is obtained in an H2 saturated electrolyte (Fig. S7). We first studied the Ni-Co20-P@NF catalyst with different Co/Ni ratios and found that the HER catalytic activity increased with the increasing Co contents to reach the maximum at 20/1, and then decreased gradually (Fig. S8a). Similar to the NaBH4 hydrolysis results, the Co/Ni ratio of 20/1 shows the best HER performance meaning it has the lowest overpotential, the smallest Tafel slope (42.7 mV dec−1), and high double-layer capacitance (476.9 mF cm−2), which is the smallest among all other catalysts indicating the fastest electrocatalytic performance. We also compared the LSV polarization curves before and after the long-term stability, where the overpotential of the Ni-Co20-P@NF catalyst decayed by ca. 5 mV after the stability test at the current density of −10 mA cm−2 (Inset of Fig. 6d). This superior electrocatalytic stability is believed to be associated with a unique preparation process that effectively reduces the voids between the catalyst and the support, thereby avoiding catalyst exfoliation and increasing electron conductivity.

4. Conclusion

In summary, a high-performance bifunctional catalyst of the rugae-like Ni3P-CoP arrays decorated NF is fabricated by a two-step electrodeposition plus a vapor phase phosphatization treatment. The XRD patterns and SEM images have characterized the crystal structures and morphologies, and the TEM image shows that the Ni3P nanoclusters are distributed on the surface of the CoP nanosheet arrays with an average size of ≈6 nm. The XPS spectra indicate that there is a substantial charge transfer between CoP and Ni3P in Ni-Co20-P@NF composite. The H2 generation by catalytic NaBH4 hydrolysis shows that the optimized Ni-Co20-P@NF catalyst has a higher H2 evolution rate (4323.0 mL g−1 h−1) and is higher than most of the previously reported non-precious metal catalysts. Besides, the Ni-Co20-P@NF catalyst also demonstrates excellent electrocatalytic H2 production capacity with low overpotential (65 mV) to reach 10 mA cm−2, small Tafel slope (42.7 mV dec−1), and high double-layer capacitance (476.9 mF cm−2). Also, the Ni-Co20-P@NF catalyst exhibits excellent reusability and long-term stability, presenting a potential commercial application.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests.
interests or personal relationships that could have influenced the results reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at https://doi.org/10.1016/j.apcatb.2019.118584.

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