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Review

Self-supported $Mo_{0.2}Co_{0.8}P$ nanowire arrays on carbon cloth as a high-performance and durable hydrogen evolution reaction electrocatalyst in wide-range pH



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ABSTRACT

Exploring an efficient non-noble metal catalyst for hydrogen production by electrolysis of water is one of the effective ways to solve energy shortage and environmental problems. Herein, we report a $M_{0.2}Co_{0.8}P$ nanowires based on carbon cloth ($M_{0.2}Co_{0.8}P$ NWAs/CC) as an efficient HER catalyst in wide-range pH, via facile hydrothermal and phosphorization methods. This $M_{0.2}Co_{0.8}P$ NWAs/CC exhibits the outstanding electrocatalytic performance with low overpotentials of 60 and 66 mV at 10 mA cm⁻² and small Tafel slopes of 69.5 and 78.3 mV dec⁻¹ in acidic and alkaline solution, respectively. Moreover, the long-term stability of $M_{0.2}Co_{0.8}P$ NWAs/CC also presents excellent for 50 h at η_{10} . The superior electrochemical properties of $M_{0.2}Co_{0.8}P$ NWAs/CC material are attributed to its smaller nanoscale, lattice defects and distortions, and strong synergistic effect between Co and Mo atoms. This work provides an effective electrocatalyst for the water electrolysis process.

Contents

		_
1.	Introduction	2
2.	Experimental section	2
	2.1. Chemical reagents and materials	2
	2.2. Synthesis of CoP and Mo _{0.2} Co _{0.8} -percursor on carbon cloth.	2
	2.3. Synthesis of CoP and Mo _{0.2} Co _{0.8} P nanowire arrays on carbon cloth	2
	2.4. Material characterization.	2
	2.5. Electrochemical measurements	3
3.	Results and discussion	3
4.	Conclusions	7
	Declaration of Competing Interest	7
	Appendix A. Supplementary data	7
	References	8

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1. Introduction

With the depletion of non-sustainable resources and the intensification of environmental pollution issues, the development of clean energy to replace fossil fuels has received extensive attention [1,2]. On account of its big superiorities of abundant reserves, non-pollution, and high calorific value of combustion, hydrogen energy has been recognized as the most promising alternative to traditional fossil fuels [3,4]. Electrocatalytic water splitting, consisting of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), is considered the most promising and efficient hydrogen production method at present [5-7]. Electrocatalysts, as the key role in the process of water electrolysis, should effectively reduce the overpotential of HER and OER and ensure its good stability [8]. To date, Pt and noble metal oxide (IrO2, RuO2) are still used as efficient electrocatalysts for HER and OER [9,10], yet the expensiveness and scarcity of Pt and RuO₂ hinder their widespread application in industry [11,12]. Therefore, it is worthy of research to develop a low cost and abundant storage electrocatalysts for HER or OER [13].

In recent years, transition metal-based catalysts such as sulfides [14], carbides [15], nitrides [16], oxides [17], selenides [18] phosphates [19] and alloys [20] have been extensively studied as effective electrocatalysts for HER. In particular, transition metal phosphides (TMPs) are highly valued due to its high activity and stability. Among these TMPs, cobalt phosphides (CoP) has attracted widespread attention of researchers because of its unique electronic structure, outstanding catalytic activity and extremely low price [21-28]. However, the performance of CoP in pH-universal remains to be improved so as to make the hydrolytic process more efficient. Heteroatom-doping has emerged as an effective way to regulate the internal electronic structure and optimize the external original morphology of CoP for improved its activity and stability [29-31]. For example, Wen et al. reported a Cu-CoP NRAs/CC as HER catalyst with overpotentials of 44, 81 and 137 mV at 10 mA cm⁻² in 0.5 M H_2SO_4 , 1 M KOH and 1 M PBS, respectively. The superior performance was benefitted from the strong heteroatomic interactions [32]. Du et al. reported that the urchin-like Co_{0.8}Mn_{0.2}P/CC possesses the overpotentials of 55 and 61 mV at η_{10} in acidic and alkaline electrolyte, which was attributed to the strong synergistic between bimetallic atoms [33]. Although numerous researches has been reported, it still demands in-depth studies in catalytic activity of cobalt phosphide (CoP) with lower overpotentials and faster reaction kinetics. As non-precious metal, molybdenum has been reported to be beneficial for the dissociation of water [34-37]. Furthermore, Mo-based catalysts have been widely studied as a substitute for HER catalytic materials because it can form a band that changes the structure of d band [38,39]. And many experiment results have demonstrated that Mo-P can provide highly active sites, thus it possesses excellent catalytic activity for HER [7,35]. In recent years, Mo and Co based catalysts have received extensive attention due to their potential high-efficiency activity for HER. For example, Jiang et al. reported a Co-Mo-P catalyst with the overpotential of 67.3 mV at 10 mA cm^{-2} in 1 M KOH, which excellent activity owing to abundant active sites could be obtained by tuning of the Co and Mo contents [40]. Zhang et al. designed a CoMoP NSs@NF as an electrocatalyst for overall water splitting and experiment indicated that Mo has important regulatory effect on the number of surface active sites, thus the catalytic activity has been improved [41]. It can be seen that Mo is vital for adjusting the active sites of transition metal-based catalysts. Therefore, the introduction of Mo into CoP to prepare binary transition metal catalyst may effectively improve the stability and HER process in acidic or alkali condition, which is rarely reported.

In this study, we adopted simple hydrothermal and low-temperature phosphorization process to prepare a self-supported $Mo_{0.2}Co_{0.8}P$ nanowire arrays based on flexible carbon cloth ($Mo_{0.2}Co_{0.8}P$ NWAs/CC). Simply, by calcining the corresponding Mo

and Co precursor to obtain a series of electrocatalytic materials. The $Mo_{0.2}Co_{0.8}P$ NWAs/CC exhibits the prominent electrochemical performance in both acidic and alkaline electrolytes with low overpotentials of 60 and 66 mV at 10 mA cm⁻² as well as small Tafel slopes of 69.5 and 78.3 mV dec⁻¹, respectively. Meanwhile, it can maintain its activity for 50 h without significant decline. The remarkable HER activity can be attributed to its smaller nanoscale, lattice defects and distortions, and strong synergistic effect between Co and Mo atoms.

2. Experimental section

2.1. Chemical reagents and materials

All the chemicals were bought from Shanghai Maclin Biochemical Co., Ltd or Shanghai Aldrich Biochemical Technology Co., Ltd, including cobalt nitrate ($Co(NO_3)_2$ · $6H_2O$), sodiummolybdate dihydrate (Na_2MoO_4 · $2H_2O$), ammonium fluoride (H_4FN), urea (CH_4N_2O) and sodium hypophosphite (NaH_2PO_2). The above chemicals are analytical grade and used without further purification. Platinum catalyst (20 wt% Pt/C) was supplied by Alfa Aesar. Carbon cloth (CC, WOS1009 Hydrophilic) was provided by Taiwan Carbon Energy Co., Ltd and needed further cleaning and hydrophilic treatment.

2.2. Synthesis of CoP and Mo_{0.2}Co_{0.8}-percursor on carbon cloth

Firstly, CC was cut into $1 \times 4 \text{ cm}^2$ and cleaned with concentrated nitric acid (HNO₃) for 2 h at 90 °C. Then, sonicated by deionized (DI) water and ethanol to further remove its surface impurity. The Mo_{0.2}-Co_{0.8}-precursor/CC were synthesized by hydrothermal reaction. Typically, Na₂MoO₄·2H₂O (0.4 mM), Co(NO₃)₂·6H₂O (1.6 mM) , urea (10 mM) and NH₄F (6 mM) were dissolved in 35 mL DI water under vigorous stirring for 30 min until form a homogeneous precursor solution. Then, the precursor solution and a piece of surface-cleaned CC were put into a Teflon-lined stainless autoclave and reacted at 120 °C for 6 h in an oven. After the above reaction, the CC with precursor washed with ethanol and deionized water several times, and then dried at 60 °C for 6 h.

2.3. Synthesis of CoP and Mo_{0.2}Co_{0.8}P nanowire arrays on carbon cloth

The low-temperature phosphating treatment is used to synthesize Mo_xCo_{1-x} -P nanowire arrays on carbon cloth. The $Mo_{0.2}Co_{0.8}$ -precursor/CC and NaH_2PO_2 (0.4 g) were placed on the downstream and upstream side of the porcelain boat. Then, the porcelain boat was putted into the tube furnace and heated to 350 °C for 2 h with a ramping rate of 5 °C min⁻¹. Finally, the furnace was naturally cooled down to room temperature and $Mo_{0.2}Co_{0.8}P$ NWAs/CC catalyst was successfully prepared. The above calcination process was all carried out under Ar flow. For comparison, CoP and other Mo_xCo_{1-x} -P (molar ratio of Co/Mo = 3:1, 5:1 and 6:1) nanowire arrays on carbon cloth were synthesized under the same condition and method.

2.4. Material characterization

X-ray diffraction (XRD) results were measured on a Bruker AXS GmbH X-ray diffractometer with Cu K_{α} radiation. The morphological and structural characterization were observed by field-emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL, Japan) at an accelerating voltage of 3 kV. The crystal structures and more detailed morphology information were examined by transmission electron microscope (TEM, JSM-2100, JEOL, Japan) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Tecnai G2 F30 S-Twin, Philips-FEI). Energy dispersive X-ray spectrometer (EDX) mapping were characterized by HAADF-STEM to obtain element distribution. X-ray photoelectron spectroscopy (XPS) measurements were recorded with an X-ray photoelectron spectrometer (Kratos Axis Ultra DLD) and to investigate the valence states.

2.5. Electrochemical measurements

All the electrochemical measurements were performed in the electrochemical workstation (CHI660E, Shanghai Chenhua). The prepared samples, graphite rod, saturated calomel electrode (SCE) were used as the working electrode, counter material and reference electrode in a standard three-electrode system, respectively. All electrodes were performed in aqueous solution of 0.5 M H₂SO₄ and 1 M NaOH. Linear sweep voltammetry (LSV) measurement was tested at a scan rate of 1 mV s⁻¹, and the obtained polarization curves was calibrated with the reversible hydrogen electrode (RHE) ($E_{RHE} = E_{SCE} + 0.244 +$ $0.0592 \times pH$). The Tafel slopes are calculated from the LSV curves and based on Tafel equation: $n = a + b \log |i|$. In this work, the electrochemical impedance (EIS) measurement was measured in the frequency range of 10-0.01 kHz. The cyclic voltammetry (CV) test is measured in acidic solution with a voltage range from -0.25 to -0.15 mV with a series of different scan rates (10–100 mV s⁻¹), while the voltage range in alkaline solution is -1.05 to -0.95 mV. The electrochemical active surface areas (ECSA) were estimated by electrochemical double layer capacitance (C_{dl}). The conversion formula was $ECSA = C_{dl}/C_{s}$, where C_{dl} represented the double-layer capacitor and $C_{\!s}$ as a fixed value. The CVs were measured at scan rates of 10, 20, 40, 60, 80 and 100 mV s⁻¹ in a non-Faradaic region. The above all measurements were performed at room temperature.

3. Results and discussion

Self-supported Mo_{0.2}Co_{0.8}P nanowire arrays on carbon cloth is prepared through a facile hydrothermal and phosphorization process, as shown in Fig. 1. The composition, structure and morphology of $Mo_{0.2}$ -Co_{0.8}P NWAs/CC were firstly characterized. The phase composition of Mo_{0.2}Co_{0.8}P NWAs/CC and CoP NWAs/CC are tested by X-ray diffraction (XRD) and presents in Fig. 2a. The XRD patterns of Mo_{0.2}Co_{0.8}P NWAs/CC and CoP NWAs/CC show the similar diffraction peaks at 31.60°, 36.70°, 46.23°, 48.40°, and 56.78°, which can be assigned to the (011), (102), (112), (202) and (301) facets of CoP (JCPDS no. 29-0497), respectively. This reveals that Mo has been simply incorporated into the lattice of CoP. Scanning electron microscope (SEM) images show the morphology of Mo_{0.2}Co_{0.8}P NWAs/CC. In Fig. 2b, we can clearly see that the Mo_{0.2}Co_{0.8}P are covered on the surface of the CC with uniform, highly density and large-scale nanowire arrays. Compared with the morphology of CoP NWAs/CC (Fig. S1a and b), Mo_{0.2}Co_{0.8}P covers on CC substrate with a smaller size and denser nanowire arrays, which is likely to expose more active sites for its electrochemical performance. In Fig. S2a-d, it shows the morphology of Mo_{0.25}Co_{0.75}P NWAs/CC, Mo_{0.17}Co_{0.83}P NWAs/CC and Mo_{0.14}Co_{0.86}P

NWAs/CC. Transmission electron microscopy (TEM) images prove the microscopic structure of Mo_{0.2}Co_{0.8}P NWAs/CC and its nanowire arrays structure (as shown in Fig. S3). It can be seen that the surface of Mo_{0.2}Co_{0.8}P NWAs/CC is rough and the diameter of the root of nanowire is about 60 nm (Fig. S3). In order to further observe the detailed microstructure of $Mo_{0.2}Co_{0.8}P$ NWAs/CC, the high-angle annular dark-field scanning TEM (HAADF-STEM) is performed. The image in Fig. 2e exhibit the interspacing of lattice fringes are 0.175 and 0.285 nm, corresponding to the (011) and (103) planes of CoP nanowire, respectively. Moreover, some defects and distortions can be clearly observed on the Mo_{0.2}Co_{0.8}P NWAs/CC surface (Fig. 2d). This phenomenon may be caused by the different radius of Co and Mo atoms. The relevant energy dispersive X-ray spectroscopy (EDX, Fig. 2f-i) mappings illustrates that Co, Mo and P elements are homogeneously distributed in Mo_{0.2}Co_{0.8}P NWAs/CC. Besides, HRTEM line scan test and surface scan test (Figs. S4 and S5) further prove above statement, consequently these results demonstrate that the atomic ratio of Mo/Co is close to 1:4.

The elements composition and valence state of CoP NWAs/CC and Mo_{0.2}Co_{0.8}P NWAs/CC catalyst are analyzed by X-ray photoelectron spectroscopy (XPS). Obviously, the Mo_{0.2}Co_{0.8}P NWAs/CC spectra displays an extra weak peak of Mo 3d (Fig. 3a), which demonstrates that Mo coexistence with Co, P, C, and O in Mo_{0.2}Co_{0.8}P NWAs/CC, and this result is consistent with EDX mappings. Besides, the peaks of oxygen are originate from surface oxidation [7]. Fig. 3b displays the binding energies of Mo 3d with two main peaks appear at 230.4 eV and 232.7 eV belongs to Mo^{4+} $3d_{5/2}$ and Mo^{4+} $3d_{3/2}$, respectively [42,43]. Additionally, the peaks at 235.2 eV can be assigned to Mo^{6+} because of inevitable surface oxidation to form MoO_3 [8,44]. The high-resolution XPS spectrum of Co 2p (Fig. 3c) exhibits the peaks at 778.2 eV and 781.6 eV with a satellite peak at 786.2 eV attributes to Co 2p3/2, and the others 793.2 eV and 797.6 eV accompanied by a satellite peak at 802.8 eV is corresponding to the Co $2p_{1/2}$ region [45]. The peaks of 778.2 eV and 797.6 eV belong to Co^{2+} , while the peak at 781.6 and 793.2 eV correspond to Co^{3+} [46]. Fig. 3d shows the main peaks of P 2p region spectrum, it can be clearly observed that the two peaks at 129.0 eV and 129.9 eV are belong to the P 2p_{3/2} and $2p_{1/2}$ region, respectively [47], and another oxidation peak (133.7 eV) is ascribed to P-O formed on the sample surface due to contact with air [48]. Compared with all the binding energy of CoP and Mo_{0.2}Co_{0.8}P, only Co has a slightly positive shift, it reveals that the introduction of Mo atom causes the change in the electronic structure of CoP [49].

The electrochemical performance of different electrodes towards HER is evaluated through a three-electrode working system in acid (0.5 M H₂SO₄) condition. As a comparison, Pt/C and CoP NWAs/CC exhibit their catalytic activity with overpotentials of 52 and 94 mV to reach 10 mA cm⁻², respectively, while bare CC showing almost no activity (Fig. 4a). Furthermore, a low overpotential of 60 mV to achieve 10 mA cm⁻² current density is required for Mo_{0.2}Co_{0.8}P



Fig. 1. Schematic preparation of Mo_xCo_{1-x}P NWAs/CC.



Fig. 2. (a) The XRD patterns of CoP NWAs/CC and Mo_{0.2}Co_{0.8}P NWAs/CC; (b) The SEM images of Mo_{0.2}Co_{0.8}P NWAs/CC; (c–e) The HAADF-STEM images of Mo_{0.2}Co_{0.8}P NWAs/CC; (f–i) The HAADF-STEM image and STEM-EDX elemental mapping of Mo_{0.2}Co_{0.8}P NWAs/CC.



Fig. 3. (a) XPS survey spectrum of CoP NWAs/CC and Mo_{0.2}Co_{0.8}P NWAs/CC; (b) The XPS spectra of Mo in Mo_{0.2}Co_{0.8}P NWAs/CC; (c) the Co 2p spectrum, and (d) the P 2p spectrum in the CoP NWAs/CC and Mo_{0.2}Co_{0.8}P NWAs/CC.



Fig. 4. (a) Polarized curves of CC, Pt/C, CoP NWAs/CC, and $M_{0.2}Co_{0.8}P$ NWAs/CC in 0.5 M H₂SO₄; (b) The Tafel slopes of all samples in 0.5 M H₂SO₄; (c) Cyclic voltammetry curves for $M_{0.2}Co_{0.8}P$ NWAs/CC at different scan rates (10, 20, 40, 60, 80, 100 mV/s) in 0.5 M H₂SO₄; (d) EIS of CoP NWAs/CC and $M_{0.2}Co_{0.8}P$ NWAs/CC; (e) C_{d1} for $M_{0.2}Co_{0.8}P$ NWAs/CC and CoP NWAs/CC obtained at -0.20 V (vs. RHE); (f) The time-dependent current density curve of $M_{0.2}Co_{0.8}P$ NWAs/CC in 0.5 M H₂SO₄. Insert is the polarized curves of $M_{0.2}Co_{0.8}P$ NWAs/CC at the first cycle, after 2000 cycles and 5000 cycles.

NWAs/CC, which is only 8 mV higher than Pt/C but 34 mV lower than CoP NWAs/CC. These results demonstrate that the HER electrocatalytic activity of the prepared sample is significantly improved after the Mo substitution for Co, which may be related to the synergistic effect between the molybdenum and the cobalt atoms. Generally speaking, the reaction process of HER is accompanied by a two-electron transfer process. Moreover, the electrolysis of water follows different paths in different electrolytes. The abundant protons in acidic electrolytes can be used to HER reaction, while HER requires extra energy to split water molecules to produce protons in alkaline media [50,51]. Therefore, the reaction kinetics is more sluggish in alkali. The different paths of HER process can be divided into the following steps [52,53]. Volmer reaction: $H^+ + e^- \rightarrow H_{ads}$ (Acidic solution); $H_2O~+~e^- \rightarrow H_{ads}~+~OH^-$ (Alkaline solution). Heyrovsky reaction: $H_{ads} + H^+ + e^- \rightarrow H_2$ (Acidic solution); $H_{ads} + H_2O + e^- \rightarrow H_2 + OH^-$ (Alkaline solution). To understand the HER mechanism of electrocatalysts, the Tafel slopes are used to further explore the catalytic mechanism of as-synthesized samples and can be calculated from the corresponding LSV curves, as shown in Fig. 4b. The Tafel slope of the $Mo_{0.2}Co_{0.8}P$ NWAs/CC catalyst is only 69.5 mV dec⁻¹, which is smaller than that of CoP NWAs/CC catalyst (124.1 mV dec⁻¹) and close to Pt/C catalyst (65.5 mV dec⁻¹). These value of the Tafel slope indicate that the Volmer-Heyrovsky mechanism is applicable to the hydrogen evolution reaction process [54].

Electrochemical impedance spectroscopy (EIS) is applied to examine the electrochemical kinetics and charges carrier migration resistance of the $Mo_{0.2}Co_{0.8}P$ NWAs/CC (Fig. 4d). Moreover, the measured semicircle pattern is inversely proportional to the electric conductivity of the electrode, which means that the smaller the radius, the better the conductivity. $Mo_{0.2}Co_{0.8}P$ NWAs/CC shows a smaller semicircle than CoP NWAs/CC, suggesting the lower impedance, better conductivity and faster electron transfer efficiency. Additionally, electrochemical active surface area (ECSA) is also a non-negligible factor for testing the HER activity, and it is proportional to the electrochemical double-layer capacitance (C_{dl}). Fig. 4c reveals the cycle voltammetry (CV) curves of $Mo_{0.2}Co_{0.8}P$ NWAs/CC at a series of different scan rates, and the voltage range is -0.25 to -0.15 mV. In Fig. 4e, the calculated C_{dl} value of $Mo_{0.2}Co_{0.8}P$ NWAs/CC is 103.3 mF cm⁻², which is a triple higher than CoP NWAs/CC (31.3 mF cm⁻²). The higher Cdl of Mo0.2Co0.8P NWAs/CC means the larger electrochemical active surface area (ECSA) and expose more active sites. This is because that Mo_{0.2}Co_{0.8}P NWAs/CC possesses smaller size and denser nanowire arrays. Another important factor of excellent performance is reflected at long-term stability. The durability of Mo_{0.2}Co_{0.8}P NWAs/CC is measured by cyclic CV with a scan rate of 100 mV s⁻¹. After 2000 or even 5000 cycles of CV, the polarization curves of Mo_{0.2}Co_{0.8}P NWAs/CC only shows a negligible change (insert in Fig. 4f). Meanwhile, the chronopotentiometric method used to further examine the durability of Mo_{0.2}Co_{0.8}P NWAs/CC. In Fig. 4f, the I-T test curve could be maintained for at least 50 h at η_{10} in acidic solution. The SEM images (Fig. S6a, b) and XRD pattern (Fig. S7a) after cyclic test and I-T test show that the catalyst maintains the original morphology and phase structure. Therefore, the above results further confirm that Mo_{0.2}Co_{0.8}P NWAs/CC has excellent stability.

In order to make the application of electrocatalytic water splitting more extensive, we further explored the activity and stability of the prepared samples in a lkaline condition (1.0 M KOH). Significantly, Mo_{0.2}Co_{0.8}P NWAs/CC exhibits outstanding catalytic performance and excellent durability. As shown in Fig. 5a, Mo_{0.2}Co_{0.8}P NWAs/CC presents an overpotential of 67 mV to achieve a current density of 10 mA cm⁻², which is slightly higher than Pt/C (52 mV) and much lower than CoP NWAs/CC (92 mV). In addition, the corresponding Tafel slopes of CoP NWAs/CC, Mo_{0.2}Co_{0.8}P NWAs/CC and Pt/C are 116.2, 78.3 and 68.7 mV dec⁻¹, respectively (Fig. 5b). These results illustrate that Mo_{0.2}Co_{0.8}P NWAs/CC still maintains its superior activity in alkaline condition. In Fig. 5d, the EIS measurements display that the resistance of Mo_{0.2}Co_{0.8}P NWAs/CC is smaller than CoP NWAs/CC, revealing that Mo_{0.2}Co_{0.8}P NWAs/CC possesses the lower electrochemical impedance and higher electron conductivity. The results in Fig. 5e show that Mo_{0.2}Co_{0.8}P NWAs/CC has a larger C_{d1} value of 79.1 mF cm⁻² than CoP NWAs/CC (34.9 mF cm⁻²), proving the larger ECSA and more active sites of Mo_{0.2}Co_{0.8}P NWAs/CC. Additionally, after 2000 cycles or even 5000 cycles cycling test (insert in Fig. 5f) and I-T test for 50 h at 10 mA cm⁻² (Fig. 5f) prove its excellent long-term stability. As shown in Figs. S6c, d and S7b, the SEM images and XRD pattern reveal that Mo_{0.2}Co_{0.8}P NWAs/CC could maintains



Fig. 5. (a) HER polarized curves of CC, Pt/CC, CoP NWAs/CC, and $M_{0.2}Co_{0.8}P$ NWAs/CC in 1 M KOH; (b) The Tafel slopes of all samples in 1 M KOH; (c) Cyclic voltammetry curves for $M_{0.2}Co_{0.8}P$ NWAs/CC at different scan rates (10, 20, 40, 60, 80, 100 mV/s) in 1 M KOH; (d) EIS of CoP NWAs/CC and $M_{0.2}Co_{0.8}P$ NWAs/CC (e) C_{dl} for $M_{0.2}Co_{0.8}P$ NWAs/CC and CoP NWAs/CC obtained at -1.00 V (vs. RHE); (f) The time-dependent current density curve of $M_{0.2}Co_{0.8}P$ NWAs/CC in 1 M KOH. Insert is polarized curves of $M_{0.2}Co_{0.8}P$ NWAs/CC at the first cycle, after 2000 cycles and 5000 cycles.



Fig. 6. (a) HER polarization curves of a series of $Mo_xCo_{1-x}P$ NWAs/CC in 0.5 M H₂SO₄; (b) The overpotentials at η_{10} with different HER catalysts in 0.5 M H₂SO₄; (c) HER polarization curves of a series of $Mo_xCo_{1-x}P$ NWAs/CC in 1 M KOH; (d) The overpotentials at η_{10} with different HER catalysts in 1 M KOH.

the nanowire structure and phase structure. The above results suggest the outstanding HER electrocatalytic activity and robust durability of $Mo_{0.2}Co_{0.8}P$ NWAs/CC in both acid and alkaline condition.

The electrocatalytic performance of CoP NWAs/CC and Mo_xCo_{1-x}P NWAs/CC (Mo/Co = 1:3, 1:4, 1:5, 1:6) towards the HER are tested in acidic and alkaline media. In addition, its LSV curves and the corresponding overpotentials are shown in Fig. 6. The HER activity of catalysts can be significantly improved by the introduction of Mo. The overpotentials of CoP NWAs/CC, Mo_{0.25}Co_{0.75}P NWAs/CC, Mo_{0.2}Co_{0.8}P NWAs/CC, Mo_{0.17}Co_{0.83}P NWAs/CC and Mo_{0.14}Co_{0.86}P NWAs/CC are 93, 113, 60, 97 and 102 mV at η_{10} , respectively (Fig. 6b). Obviously, Mo_{0.2}Co_{0.8}P NWAs/CC exhibits the best HER performance among all samples in acid media. Meanwhile, it can be seen that Mo_{0.2}Co_{0.8}P NWAs/CC also shows the best catalytic activity compared to other prepared catalysts in alkaline media (Fig. 6c). In Fig. 6d, the overpotentials of CoP NWAs/CC, Mo_{0.25}Co_{0.75}P NWAs/CC, $Mo_{0.2}Co_{0.8}P$ NWAs/CC, $Mo_{0.17}Co_{0.83}P$ NWAs/CC and $Mo_{0.14}Co_{0.86}P$ NWAs/CC are 92, 81, 66, 74 and 87 mV, respectively. Moreover, the comparison of the HER performance between Mo_{0.2}Co_{0.8}P/CC prepared in this paper and the other hydrogen evolution catalysts were shown in the followed Table S1. These results indicate that the Mo_{0.2}Co_{0.8}P NWAs/CC catalytic material can be applied in acid and alkaline conditions with excellent HER catalytic activity. From the above results, it can be proved that the best feeding ratio of Mo/Co is 1:4. Furthermore, the superior electrocatalytic performance of Mo_{0.2}Co_{0.8}P NWAs/CC electrode for HER can be attributed to the following reasons: (1) the smaller nanoscale of Mo_{0.2}Co_{0.8}P NWAs/CC provides a larger surface area, which can expose more efficient active sites; (2) there are crystal defects and distortions exist on the Mo_{0.2}Co_{0.8}P NWAs/CC surface; (3) the strong synergistic effect between Co and Mo atoms modifies the electronic structure. Indeed,

the superiority of the $Mo_{0.2}Co_{0.8}P$ NWAs/CC is ascribed to the result of all the above factors.

4. Conclusions

In summary, we successfully synthesized a self-supported $Mo_{0.2}$ - $Co_{0.8}P$ NWAs/CC as a superior activity electrocatalyst for HER through a facile hydrothermal and low-temperature phosphorization processes. On the account of its smaller nanoscale, lattice defects and distortions as well as strong synergistic effect between Co and Mo atoms, more efficient active sites are exposed and the electronic structure is further modified for HER process. Therefore, the obtained $Mo_{0.2}Co_{0.8}P$ NWAs/CC exhibits excellent catalytic activity in the both acidic and alkaline electrolytes with low overpotentials of 60 and 66 mV at 10 mA cm⁻² and small Tafel slopes of 69.5 and 78.3 mV dec⁻¹, respectively. Meanwhile, its long-term stability also shows outstanding performance. This work provides an eco-friendly and efficient electrocatalyst toward electrochemical water splitting.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jelechem.2021.115201.

S. Li et al.

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