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Tungsten promoted nickel phosphide nanosheets supported on carbon cloth: An efficient and stable bifunctional electrocatalyst for overall water splitting



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HIGHLIGHTS

- W-Ni₂P NS/CC was prepared via hydrothermal and phosphorization method.
- W-Ni₂P NS/CC exhibits excellent HER and OER activity in 1 M KOH.
- It demands 1.55 and 1.64 V to deliver j_{20} and j_{50} , respectively.
- W-doping causes the phase structure of the catalyst to change.

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ABSTRACT

It is of great significance to develop a highly active, durable and inexpensive bifunctional electrocatalyst for both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Herein, we report a tungsten-doped nickel phosphide nanosheets based on carbon cloth (W–Ni₂P NS/CC) as an efficient bifunctional catalyst through simple hydrothermal and phosphorization for overall water splitting in 1 M KOH. The W–Ni₂P NS/CC exhibits excellent electrochemical performance with low overpotentials for HER ($\eta_{10} = 71 \text{ mV}, \eta_{50} = 160 \text{ mV}$) and OER ($\eta_{20} = 307 \text{ mV}, \eta_{50} = 382 \text{ mV}$) in 1 M KOH, as well as superior long-term stability. Moreover, W–Ni₂P NS/CC as a bifunctional catalyst reveals remarkable activity with a low voltage of 1.55 V to reach a current density of 20 mA cm⁻². This work provides a viable bifunctional catalyst for the overall water splitting.

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Introduction

With the consumption of fossil fuels and the intensification of environmental issues, exploring efficient and renewable energy sources has become a research hotspot [1,2]. Hydrogen energy has become the most promising candidate to replace fossil fuel due to its clean, renewable and high energy density [3,4]. Among many hydrogen production technologies, electrolysis of water is widely studied as convenient environmentally-friendly and efficient method for the hydrogen generation [5]. As we all know, hydrogen evolution

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reaction (HER) and oxygen evolution reaction (OER) are the main parts of reaction in the electrolysis of water process [6-8]. To promote the efficiency of water electrolysis, it is necessary to adopt high activity and robust stability electrocatalysts in HER and OER. Although Pt and RuO₂/IrO₂ are considered the best catalysts for HER and OER, respectively, the scarcity and the expensiveness have greatly hindered its large-scale industry applications [9–11]. Thus, it is of significance to find an efficient non-noble metal based electrocatalyst with abundant resources, inexpensive and long-term stability for HER and OER [12,13].

Currently, non-noble metal phosphides [14,15], carbides [16,17], nitrides [18,19] have been studied as HER catalysts in different electrolyte and metal oxides [20,21] or hydroxide [22,23] are widely investigated as electrocatalysts for OER in alkaline solutions. However, it is difficult to combine HER and OER in the same medium with good overall splitting performance owing to their incompatibility between activity and stability [24,25]. Transition metal phosphides (TMPs), such as CoP [26,27], Ni₂P [28,29], MoP [30,31] and FeP [32,33] have been regarded as the most promising electrocatalyst for HER or OER because of their good electrical conductivity, low cost and superior catalytic activity [34,35]. Nevertheless, the electrocatalytic activity of the TMPs, particularly Ni₂P, is still far from practical application owing to their relatively slow charge carrier migration rate and low electrocatalytic active surface [36]. Hence, improving the electrocatalytic performance of TMPs has become a challenging work for researchers.

Recently, heteroatom-doping has emerged as a promising way to adjust the electronic structure and optimize the electronic conductivity of TMPs for improved their activity and stability [37,38]. For instance, Wen et al. reported that V-doped Ni₂P nanosheet on carbon cloth (V–Ni₂P NS/CC) for the HER, which exhibited outstanding HER performance with a low overpotential of 85 mV to reach 10 mA cm⁻² [39]. Guan et al. reported a hollow Mo-doped CoP nanoarrays as a bifunctional catalyst for overall water splitting, which demonstrated highefficiency overall water splitting performance under alkaline media [40]. Zhang et al. studied a Mn-doped Ni₂P nanosheet array on nickel foam (Mn-Ni2P/NF) required only an overpotential of 103 mV to drive 20 mA cm^{-2} in 1.0 M KOH [41]. In spite of many studies have been carried out for the investigation of heteroatom-doped TMPs for the HER and OER, highly active and durable Ni₂P-based electrocatalysts suitable for both HER and OER in the same electrolyte for overall water splitting have rarely been reported. In recent years, many studies have shown that the introduction of W atom could increase the electrochemical conductivity and improve the adsorption energy of hydrogen intermediates [42-44]. Meanwhile, W element possessed high affinity for water [4] and W doping had been proven to improve the electronic structure of Ni center [38]. For example, Lu et al. reported a W-NiCoP/NF catalyst with outstanding water dissociation ability, which was attributed to the W and H atoms possessed moderate combination ability and W sites could effectively convert H_{ad} to H₂ so as to accelerate the HER rate [45]. Therefore, introducing W into nickel phosphide catalyst was an effective way to achieve excellent catalytic performance.

In this communication, we report a W-doped Ni₂P nanosheets on carbon cloth (W-Ni₂P NS/CC) through a simple hydrothermal and phosphating strategy, which behaves as an efficient and durable HER and OER electrocatalyst for overall water splitting in alkaline media. Its ample nanosheets provides abundant active sites and facilitates ions transport to benefit HER and OER. Moreover, tungsten doping could enhance electrochemical conductivity, improves the water adsorption and optimize the hydrogen adsorption energy to improve the catalytic activity of HER and OER [42,46]. Consequently, the W-Ni₂P NS/CC catalyst exhibits superior HER performance with a low overpotential of and 71 mV at a current density of 10 mA $\rm cm^{-2}$ and Tafel slope of 67.4 mV dec⁻¹ in 1 M NaOH. The W-Ni₂P NS/CC electrode also presents an excellent OER activity with a small overpotential of 307 mV at 20 mA $\rm cm^{-2}$ and Tafel slope of 192 mV dec⁻¹ in 1 M NaOH electrolyte. Besides, the high performance for overall water splitting with W- Ni₂P NS/CC as both the anode and the cathode, which achieve a current density of 20 mA $\rm cm^{-2}$ at operating potential of 1.55 V. This work provides a feasible strategy for exploring highly efficient electrocatalysts with low-cost and earth-abundant.

Experimental

Chemical reagents and materials

Ammonium metatungstate hydrate $((NH_4)_6H_2W_{12}O_{40} \cdot xH_2O)$ was supplied by Sigma Aldrich Fluke. Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) was purchased from Shanghai Maclin Biochemical Co., Ltd. Ammonium fluoride (H₄FN), Urea (CH₄N₂O) and Sodium hypophosphite (NaH₂PO₂) were all bought from Shanghai Aldrich Biochemical Technology Co., Ltd. Carbon cloth (CC, WOS1009 Hydrophilic) was obtained from Taiwan Carbon Energy Co., Ltd. Among the above materials, only CC needs hydrophilic treatment and further cleaning, other reagents were used without any purification treatment. All the electrochemical measurements were carried out at room temperature.

Synthesis of W-Ni LDH supported on carbon cloth

Carbon cloth (CC, $1.0 \times 4.0 \text{ cm}^2$) was treated with concentrated nitric acid, then ultrasonic cleaned with ethanol and deionized water in turn to further remove surface impurity. The W–Ni layer double hydroxide precursor on CC (W–Ni LDH/CC) was synthesized by a feasible hydrothermal method. Typically, urea (10 mmol), NH4F (6 mmol), Ni(NO₃)₂·6H₂O (2 mmol), and (NH₄)₆H₂W₁₂O₄₀·xH₂O (0.013 mmol, the molar amount of W is 0.16 mmol) were dissolved in 30 mL deionized water and stirred for 20 min to obtain a clear and uniform precursor solution. Then, the precursor solution and a piece of pretreated carbon cloth were transferred into 50 mL Teflon-line stainless-steel autoclave, and reacted at 120 °C for 6 h. Subsequently, the CC with intermediate material was taken out, cleaned with deionized water and dried in oven at 60 °C. This sample was named W–Ni LDH/CC.

Synthesis of W–Ni $_{2}\text{P}$ or Ni $_{2}\text{P}$ nanosheets supported on carbon cloth

Firstly, for the convenience of reading, we named W doping nickel phosphide and nickel phosphide as W-Ni₂P and Ni₂P, respectively. The preparation of W-Ni₂P and Ni₂P were carried out under low-temperature phosphating process. The above prepared W-Ni LDH/CC was placed at downstream side of porcelain boat and 0.4 g NaH₂PO₂ as a source of phosphorus putted at the upstream side. Afterwards, the porcelain boat was calcined in a tube furnace at 350 °C for 2 h with heating rate of 5 °C min⁻¹ and cooled to room temperature. The whole process was carried out in Ar flow. The final sample was named W-Ni₂P NS/CC. The mass of the prepared catalyst and CC ($1.0 \times 4.0 \text{ cm}^2$) were 0.0863 and 0.0525 g, respectively, so the mass loading of the active material could be obtained as 8.45 mg cm⁻². The fabrication of Ni₂P NS/CC was the same as the above hydrothermal and phosphating processes but without adding (NH₄)₆H₂W₁₂O₄₀·xH₂O. Besides, other samples with different tungsten doping molar ratios (4%, 6%, 10% correspond to the molar amount of W is 0.08, 0.12, 0.20 mmol, respectively) as well as a sample for comparison with 12% W (the molar amount of W is 0.24 mmol) usage were also prepared in the same way as above.

Materials characterization

The field-emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL, Japan) was used to observed morphological and microstructural characterization at 3 kV. The transmission electron microscope (TEM) images were obtained on transmission electron microscope (JSM-2100, JEOL, Japan) at 200 kV. The high-angle annular dark-field scanning

transmission electron microscopy (HAADF-STEM, Tecnai G2 F30 S-Twin, Philips-FEI) crystal structures and more detailed morphology information were examined by transmission electron microscope (TEM, JSM-2100, JEOL, Japan). The highangle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and STEM-EDX element mapping were characterized by a STEM (Tecnai G2 F30 S-Twin, Philips-FEI) at 300 kV. The phase component of the prepared materials were characterized by X-ray diffraction (XRD) patterns using a D8 DISCOVER X-ray diffractometer (Bruker AXS) at a scanning rate of 5° min⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were used for further analytical the elemental states of materials were recorded with a Kratos Axis Ultra DLD photoelectron spectrometer with an Al K_a radiation.

Electrochemical measurements

All electrochemical measurements were performed on an electrochemical workstation (CHI660E, Shanghai Chenhua) with standard three electrodes system. Working electrode, reference electrode and counter material were composed of synthesized materials, saturated calomel electrode (SEC) and graphite rod. The polarization curves of HER and OER were obtained by linear sweep voltammetry (LSV) with a scan rate of 1 mV s⁻¹. In overall water splitting system, synthesized materials served as cathode and anode at the same time. The potentials obtained in this work were calibrated with the reversible hydrogen electrode (RHE). The Tafel slope is based on polarization curve fitting with a Tafel equation: $\eta = a + b$ log |j|, where b is the Tafel slope. The electrochemical impedance (EIS) test was measured at the frequency ranging from 10 kHz to 0.01 Hz. The electrochemically active surface area (ECSA) values were generally estimated from



Fig. 1 – (a) Schematic illustration of the preparation of $W-Ni_2P$ nanosheets on carbon cloth. (b, c) XRD patterns of Ni_2P NS/CC, $W-Ni_2P$ NS/CC and $W-Ni_2P$ NS/CC with different W contents.

RESULTS AND DISCUSSION

electrochemically double layer capacitance (C_{dl}), while the C_{dl} was obtained by a series of CV tests with different sweep speeds in a non-Faradaic region for HER (10, 20, 40, 60, 80, 100 mV s⁻¹) in alkaline condition. The above test results were obtained at room temperature.

Results and discussion

The preparation process of W–Ni₂P NS/CC is schematically presented in Fig. 1a, which includes hydrothermal reaction and phosphorization process. Before morphology analysis, we utilize XRD images to compare the phase evolution of Ni₂P NS/ CC and W–Ni₂P NS/CC. As shown in Fig. 2b, we can clearly observed that the XRD patterns of Ni₂P NS/CC and W–Ni₂P NS/ CC match with Ni₅P₄ (JCPDS no. 18–0883) and Ni₂P (JCPDS no. 03–0953), respectively. The W–Ni₂P NS/CC exhibits diffraction peaks at 40.8, 44.6, 47.3, 54.2 and 74.7, which can be attributed to (111), (201), (210), (300) and (400) planes of Ni₂P (JCPDS no. 03–0953). Moreover, it can be clearly observed from Fig. 1c, the phase structure of the catalyst has been transformed into Ni₂P no matter when a small amount (W/Ni = 4%) or a large amount (W/Ni = 12%) of W is introduced. The above results reveal that W doping can cause the phase structure of the catalyst to change, which may be related to the different atomic size of W and Ni.

The morphology and nanostructure of the W–Ni₂P NS/CC is characterized by SEM, as shown in Fig. 2a and b. The SEM images show that W-Ni₂P is formed by cross-growing nanosheets, which structure is evenly distributed on the surface of the carbon cloth. The SEM images of W-Ni₂P LDH/CC (Fig. S1) prove that the nanosheets structure have been successfully grown in the hydrothermal process. Moreover, its morphology has not changed but the surface of the nanosheets is rougher than the original after phosphating. Compared with Ni₂P NS/ CC (Fig. S2), the size of nanosheets become smaller and the surface became more regular after W doping. TEM is used to further explore the morphology and lattice structure of W-Ni₂P NS/CC and presented in Fig. 2c-e. In Fig. 2c, TEM image with low magnification demonstrate that the nanosheets structure of W-Ni₂P NS/CC is composed of numerous nanoparticles. The high-resolution TEM images (Fig. 2d) of $W{-}Ni_2P$ NS/CC reveals interplane distance of 0.268 and 0.303 nm corresponding to the (2 2 0) and (3 1 1) facets of Ni_2P , respectively. This result is consistent with XRD pattern. Additionally, it is observed that the existence of lattice defects (Fig. 2e), which may be attributed to the W doping. The EDX mapping images are displaced in Fig. 2f, illustrating the



Fig. 2 – (a, b) SEM images of W–Ni₂P NS/CC with high and low resolution, respectively. (c) TEM images of W–Ni₂P NS/CC with low resolution, (d) HRTEM images of W–Ni₂P nanocrystal and (e) the partial enlarged figure of (d). (f) STEM-EDX elemental mapping of Ni, P and W for W– Ni₂P.



Fig. 3 – (a) XPS survey spectrum of Ni_2P NS/CC and W- Ni_2P NS/CC. (b) The XPS spectra of W in the W- Ni_2P NS/CC. The high-resolution XPS of (c) Ni and (d) P in the Ni_2P NS/CC and W- Ni_2P NS/CC.

homogeneous distribution of Ni, P and W in W–Ni₂P NS/CC. The above results indicate W–Ni₂P NS is successfully synthesized on carbon cloth.

The compositions and valence states of Ni₂P NS/CC and W-Ni₂P NS/CC are performed on X-ray photoelectron spectroscopy (XPS) spectrum and presented in Fig. 3. As shown in Fig. 3a, it indicates that the W, Ni, P, O, C elements are present on the catalyst, suggesting W is successfully doped into Ni₂P. In the high-resolution W 4f spectrum (Fig. 3b), two peaks at 36.5 eV and 38.7 eV can be ascribed to the W $4f_{7/2}$ and W $4f_{5/2}$, respectively. Moreover, the W $4f_{7/2}$ (36.5 eV) and W $4f_{5/2}$ (38.7 eV) can be attributed to W^{6+} formed by surface oxidation [47,48]. It can be observed from Fig. 3c, the high-resolution XPS spectrum of Ni 2p shows the peaks at 853.6 and 857.5 eV attribute to Ni $2p_{3/2}$, while 870.9 and 875.5 eV belong to Ni $2p_{1/2}$ [49]. The Ni^{2+} peaks at 857.5 and 875.5 eV as well as two satellite peaks at 862.4 eV and 880.0 eV can be assigned to NiO [41]. Moreover, the peaks at 853.6 and 870.9 eV correspond to the binding energy of Ni in Ni₂P [49]. Compared with the spectrum of Ni₂P/CC, the peaks of Ni 2p show the pair of peaks at 853.3 (Ni 2p_{3/2}) and 870.6 eV (Ni 2p_{1/2}) are assigned to the characteristic signals of $Ni^{\delta+}$ in Ni_5P_4 [50,51]. The binding energies at 856.9 and 875.0 eV as well as two satellite peaks belong to Ni oxide due to surface oxidation [52]. This change from Ni_4P_5 to Ni_2P is consistent with XRD result. Apparently, the Ni 2p peaks of W-Ni₂P/CC shifts to a higher binding energy, indicating that Ni has a partial positive charge [53]. From Fig. 3d, the binding energy of P 2p for W-Ni₂P NS/CC reveals that the metal phosphides can be detected at 129.8 and 130.7 eV, corresponding to P 2p_{3/2} and P 2p_{1/2}, respectively [45].

The broad peak at 134.8 eV belongs to P–O species because of partial oxidation [54]. Similar to the result of Ni 2p, P2p also shift to a higher binding energy compared to those in Ni₂P, demonstrating the increase in the electron density on the P element [55,56]. The above results illustrate that the introduction of tungsten could causes the change of electronic environment and electron density.

The catalytic activity of as-prepared materials are evaluated in alkaline electrolyte (1 M KOH) for the HER, OER and overall water splitting. The HER performance is characterized in a typical three-electrode system at a scanning rate of 1 mV s⁻¹. As depicted in Fig. 4, the bare CC shows almost no HER activity in 1 M KOH. As shown in Fig. 4a and b, the LSV curves of W-Ni LDH/CC and Ni₂P NS/CC exhibit poor catalytic performance with overpotentials of 363 and 127 mV at the current density of 10 mA cm⁻², respectively. Compared with W-Ni LDH/CC, Ni₂P NS/CC and Pt/C, the W doping into Ni₂P nanosheets (W-Ni₂P NS/CC) possesses excellent electrochemical property with overpotential of 71 mV at 10 mA cm^{-2} , closing to Pt/C (52 mV). The same advantage of activity can also be seen at the current density of 50 mA cm⁻², the overpotentials of W-Ni LDH/CC, Ni₂P NS/CC and W-Ni₂P NS/CC are 548, 222 and 160 mV, respectively (Fig. 4b). Additionally, we also test the overpotentials of different W doping ratios (W/ Ni = 4%, 6%, 10% and 12%) for HER in alkaline media. It can be observed that the overpotentials of other catalysts with different W doping ratios such as W_{0.04}-Ni₂P NS/CC, W_{0.06}-Ni₂P NS/CC, W_{0.10}-Ni₂P NS/CC and W_{0.12}-Ni₂P NS/CC are 97, 80, 89 and 96 mV to achieve the current density of 10 mA cm⁻², respectively (Figs. S3a-b). Thus, W-Ni₂P NS/CC with 8%



Fig. 4 – Electrochemical performance for HER in 1 M KOH: (a) LSV curves and (b) overpotentials ($\eta_{10 \text{ mA cm}-2}$ and $\eta_{50 \text{ mA cm}-2}$) of bare CC, Ni₂P NS/CC, W–Ni LDH/CC, W–Ni₂P NS/CC and Pt/C. (c) Tafel images. (d) Nyquist plots of bare CC, Ni₂P NS/CC, W–Ni LDH/CC and W–Ni₂P NS/CC. (e) Double layer capacitance (C_{dl}) for Ni₂P NS/CC, W–Ni LDH/CC and W–Ni₂P NS/CC obtained at –0.15 V (vs. RHE). (f) The polarized curves of W–Ni₂P NS/CC before and after long-term electrolysis; the inset in (f) is chronopotentiometric curves at η_{10} .

doping ratio has the best HER activity in this system. And the comparison of the overpotentials between W–Ni₂P NS/CC and the other catalytic materials in literatures are displayed in Table S1. To further investigate the HER kinetics, the corresponding Tafel slopes are shown in Fig. 4c. The Tafel slope of W–Ni₂P NS/CC is 67.4 mV dec⁻¹, which is obviously smaller than those of Ni₂P NS/CC (129.1 mV dec⁻¹), W–Ni LDH/CC (285.3 mV dec⁻¹) and CC (434.6 mV dec⁻¹) electrodes. Furthermore, it is only 16.3 mV dec⁻¹ higher than Pt/C (51.1 mV dec⁻¹). From the comparison of Tafel slope, it can be concluded that W–Ni₂P NS/CC has faster kinetics and its hydrogen evolution reaction via a Volmer-Heyrovsky path [57].

In addition, as an important indicator of electrochemical performance, electrochemical impedance spectroscopy (EIS) is utilized to analyze the charge transfer rate and conductivity of the different catalysts. As shown in Fig. 4d, the R_{ct} values for

W–Ni₂P NS/CC, Ni₂P NS/CC and W–Ni LDH/CC in alkaline solution are 11.9, 24.8 and 42.6 Ω , respectively, indicating best conductivity and the ability to transport charge faster for W–Ni₂P NS/CC during HER. The electrochemical active surface area (ESCA) is proportional to double-layer capacitance (C_{dl}), while double-layer capacitance (C_{dl}) is calculated from cycle voltammetry (CV) curves at different scan rates (Figs. S4a–c). The C_{dl} of W–Ni₂P NS/CC exhibits a value of 58.26 mF cm⁻², which is more than twice as much as Ni₂P NS/CC (16.44 mF cm⁻²) and outdistance W–Ni LDH/CC (1.10 mF cm⁻²) (Fig. 4e). This larger C_{dl} implies that the W doping into Ni₂P NS/CC as well as phosphorization can increase the active surface area, thereby exposing more active sites to facilitate the HER process. These results are consistent with SEM images analysis.

The stability is a crucial factor in estimating electrochemical performance. As shown in Fig. 4f, the LSV curve is no



Fig. 5 – Electrochemical performance for OER in 1 M KOH: (a) LSV curves and (b) overpotentials ($\eta_{20 \text{ mA cm-2}}$ and $\eta_{50 \text{ mA cm-2}}$) of Ni₂P NS/CC, W–Ni LDH/CC, W–Ni₂P NS/CC and Pt/C. (c) Tafel images. (d) Nyquist plots of Ni₂P NS/CC, W–Ni LDH/CC and W–Ni₂P NS/CC. (e) The polarized curves of W–Ni₂P NS/CC before and after long-term electrolysis; (f) is chronopotentiometric curves at η_{50} .

obvious recession after 2000 and 5000 cycles of CV. Moreover, the chronopotentiometry is also used to analyze the long-term stability of W–Ni₂P NS/CC and the corresponding curve demonstrate that catalytic activity can be maintained for at least 40 h in 1 M KOH electrolyte (inset in Fig. 4f). After stability tests, XRD and SEM images reveal that the phase structure and nanosheets morphology of W–Ni₂P NS/CC are well preserved (Figs. S5 and S6), which suggest its superb stability. It can be seen from these results that W–Ni₂P NS/CC possesses excellent catalytic performance and robust stability in 1 M KOH for HER.

To verify the application of as-prepared catalysts in the water splitting process, the electrochemistry measurement of OER is also carried out in the alkaline electrolyte (1 M KOH) and presented in Fig. 5. The polarization curve and corresponding potential value (Fig. 5a and b) of $W-Ni_2P$ NS/CC shows excellent OER activity with overpotentials of 307 and 382 mV to drive current density of 20 mA cm⁻² and

50 mA cm⁻², respectively, which outperforms those in Ni₂P NS/CC (η_{20} = 412 mV, η_{50} = 508 mV) and W–Ni LDH/CC $(\eta_{20} = 535 \text{ mV}, \eta_{50} = 631 \text{ mV})$. This reveals that the catalytic activity is significantly improved after the introduction of W and phosphating also provides a performance boost in OER process. From Figs. S3c-d, the polarization curve and corresponding overpotentials of $W_{0.04}$ -Ni₂P NS/CC ($\eta_{50} = 425$ mV), $W_{0.06}$ -Ni₂P NS/CC (η_{50} = 399 mV), $W_{0.08}$ -Ni₂P NS/CC ($\eta_{50} = 382 \text{ mV}$), $W_{0.10}$ -Ni₂P NS/CC ($\eta_{50} = 408 \text{ mV}$) and $W_{0.12}$ -Ni₂P NS/CC ($\eta_{50} = 420 \text{ mV}$) reveal that the W/Ni = 8% possesses the best performance. What's more, it can be seen from Fig. 5a that the CC substrate shows virtually no OER activity. The comparison of the OER performance between W-Ni₂P NS/CC and the catalytic materials in other literatures are presented in Table S1. The corresponding Tafel slopes are calculated from polarization curves and displaced in Fig. 5c, W-Ni₂P NS/ CC possesses a low Tafel slope with 192.0 mV dec^{-1} . Compared with Ni_2P NS/CC (284.3 mV dec⁻¹) and W–Ni LDH/



Fig. 6 – Overall water splitting in 1.0 M KOH: (a) Polarization curves of Ni₂P NS/CC and W–Ni₂P NS/CC. (b) Chronopotentiometry image of W–Ni₂P NS/CC.

CC (234.6 mV dec⁻¹), W-Ni₂P NS/CC exhibits faster electrocatalytic kinetics for oxygen evolution reaction. EIS measurements are preformed to further study the OER electrochemical property of catalysts. The results shown in Fig. 5d, the R_{ct} values of W-Ni₂P NS/CC, W-Ni LDH/CC and Ni_2P NS/CC electrodes are 1.1, 6.8 and 2.0 Ω , respectively, demonstrating the conductivity and charge transfer efficiency of W-Ni₂P NS/CC are better than others. Moreover, the stability of W-Ni₂P NS/CC is measured by CV cycle scan and chronopotentiometry. As shown in Fig. 5e, the polarization curve hardly change after 2000 and 5000 CV cycles. Moreover, W-Ni₂P NS/CC maintains catalytic activity for at least 40 h at a current density of 50 mA cm⁻² (Fig. 5f). These results indicate that W-Ni₂P NS/CC exhibits robust catalytic stability in 1 M KOH for OER. Meanwhile, its outstanding stability can be further proved in the XRD and SEM images (Figs. S5 and S7) of after I-T test. The above results reveal that the wonderful electrochemical performance of W-Ni₂P NS/CC can not only be applied to HER but also play a role in OER.

Based on the bifunctional feature of the as-prepared material, an overall water splitting device is constructed with W-Ni₂P NS/CC as both anode and cathode in 1 M KOH. The W-Ni₂P NS/CC bifunctional electrode only requires voltages of 1.55 and 1.64 V to achieve 20 and 50 mA $\rm cm^{-2}$ (Fig. 6a), respectively, which outperforms that of Ni₂P NS/CC as well as other reported bifunctional catalysts in overall water splitting (Table S2). Additionally, there is no significant voltage decay at 50 mA cm⁻² after overall water splitting for 40 h in Fig. 6b, demonstrating the outstanding durability. After long-term stability, the polarization curve is no obvious change compared to initial (Fig. S9). Finally, the SEM and XRD images of after I-T test are shown in Figs. S5 and S8, which further illustrate the excellent stability of W-Ni₂P NS/CC. Overall, as a bifuctional catalyst, W-Ni₂P NS/CC shows its superior activity in the processes of HER, OER and overall water splitting. This work provides a feasible strategy for bifunctional electrolysis water catalysts.

Conclusion

In summary, we have fabricated a W-doped Ni_2P nanosheets as an effective bifunctional catalyst for HER, OER and overall water splitting. The as-prepared W- Ni_2P NS/CC exhibited its low overpotentials and Tafel slopes in 1 M KOH for HER ($\eta_{10} = 71 \text{ mV}$, 67.4 mV dec⁻¹) and OER ($\eta_{20} = 307 \text{ mV}$, 192 mV dec⁻¹), as well as superior stability. Moreover, W–Ni₂P NS/CC also revealed prominent performance for overall water splitting, which displaced outstanding activity with 1.55 and 1.64 V voltage at 20 mA cm⁻² and 50 mA cm⁻². The above excellent performance can be attributed to the following advantages: (1) W doping modulates the electronic structure of Ni₂P for promoting inernal activity. (2) The rich cross-grown nanosheets structure provides abundant active sites. (3) The existence of defects on the nanosheet contributes to the catalytic reaction. This work provides a feasible pathway for the research of bifunctional catalysts.

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.ijhydene.2021.09.012.

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