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Ni₂P@MoS₂/CC catalysts with heterogeneous structure are used for highly efficient electrolysis of water for hydrogen evolution



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ABSTRACT

Efficient and inexpensive electrocatalysts play an important role in electrolysis of water and hydrogen evolution reaction. The catalytic activity of electrocatalyst can be improved by adjusting the electronic structure and increasing the active center. In this study, Ni₂P nanosheets were grown on carbon cloth through straightforward solvothermal, and tiny MoS₂ nanosheets were uniformly covered on Ni₂P nanosheets by in-situ growth method to form heterogeneous electrocatalyst (Ni₂P @ MoS₂/CC). The results show that Ni₂P @ MoS₂/CC had more active sites than Ni₂P/CC and MoS₂/CC catalysts. In addition, the interface interaction based on heterogeneous structure promotes its charge transfer kinetics. In alkaline electrolyte, Ni₂P @ MoS₂/CC electrocatalyst had good HER performance. At a current density of 10 mA cm⁻², the overpotential was 99 mV, and the Tafel slope was 97 mV dec⁻¹. In addition, the catalyst showed excellent electrochemical stability, with no significant loss of activity after 2000 cyclic voltammetry tests and 50 h i-t tests.

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1. Introduction

The environmental pollution caused by the consumption of traditional fossil energy and its products has attracted much attention. It is extremely urgent to find clean and sustainable new energy to replace traditional fuel [1]. As a strategic reserve energy in the 21st century, hydrogen energy is favored for its zero pollution, recyclability and high energy density [2]. As one of the hydrogen production methods, water electrolysis has a very wide application prospect because of abundant raw materials, high product purity and easy control of reaction conditions [3,4]. There are two half reactions in the electrolytic water reaction: oxygen evolution (OER) at the anode and hydrogen evolution (HER) at the cathode [5.6]. OER is a four-electron proton coupling reaction, and HER is realized through two-electron transfer reaction [7,8]. Theoretically, the electrolysis voltage of water is 1.23 V, but the actual voltage is higher than 1.23 V due to low energy conversion rate and slow dynamics [9,10]. Pt/C and RuO₂/IrO₂ show the best performance of HER and OER, but their

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high price, lack of reserves and poor durability limited their application [11].

In order to reduce energy consumption and accelerate water decomposition efficiency, many works had been focused on the design of high-efficiency and cheap electrolytic water catalysts for a long time. In recent decades, transition metal compounds have attracted much attention because of particular electronic structure and abundant resource, include transition metal phosphates [12–15], sulfides [16,17], selenides [18] and oxides [19,20], which are expected to become an alternative to traditional noble metal catalysts [21–25]. Among these transition metal compounds, Ni Phosphides has attracted lots of attention due to its low price, particular electronic structure, outstanding chemical stability and solid HER properties [26–28]. Nevertheless, the HER performance of pure nickel phosphides is not very ideal in alkaline solution. The heterostructure strategy can effectively improve the electrocatalytic performance of nickel phosphating compounds [29,30]. For example, Xiao et al. achieved efficient water electrolysis by NiS/Ni₂P heterostructure engineering [31]. In addition, through a large number of experimental and theoretical studies, researchers have found that molybdenum disulfide (MoS₂) has electrocatalytic activity and good conductivity in Volmer reaction, with extremely low H adsorption free energy, similar to Pt electrode [32-34]. Reasonable heterostructure engineering, while retaining the inherent properties of

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each component, can also produce synergistic electrocatalytic effects among different components, which cannot be achieved by single component or simple physical mixing [20]. Therefore, rational design of nickel phosphide and MoS₂ to form heterogeneous catalyst can obtain more excellent HER performance.

Inspired by the above, herein, we synthesized a heterostructure catalyst by hydrothermal and phosphating methods. The catalyst consists of Ni₂P nanosheets grown directly on a flexible substrate of carbon cloth and in-situ growth MoS₂ nanosheets (hereinafter referred to as Ni₂P @ MoS₂/CC). Due to the heterogeneous interface between Ni₂P and MoS₂ as well as the nanosheet array, the Ni₂P @ MoS₂/CC catalyst formed had a larger specific surface area, exposed more active sites, improved electrical conductivity, and its hydrogen evolution performance was much better than that of the single component Ni₂P and MoS₂. Ni₂P @ MoS₂/CC showed satisfactory electrocatalytic HER performance in alkaline medium. At 10 mA cm⁻² current density, the overpotential of Ni₂P @ MoS₂/CC was 99 mV, and the corresponding Tafel slope was 97 mV dec⁻¹. In addition, its activity remained stable after 50 h of operation without significant change.

2. Experiments

2.1. Chemicals and materials

Carbon cloth (CC, WOS1009 Hydrophilic) was purchased from Taiwan Carbon Energy Co., Ltd. Ni $(NO_3)_2$.6 H₂O was provided by Shanghai Maclin Biochemical Co., Ltd. Urea (CH₄N₂O), ammonium fluoride (NH₄F), and sodium hypophosphite (NaH₂PO₂) were bought from Shanghai Aladdin Biochemical Technology Co., Ltd. Thiourea (CH₄N₂S) and ammonium molybdate (H₈MoN₂O₄) were purchased from Sinopharm Chemical Reagent Co. Ltd and Tianjin cameo chemical reagent co., LTD. The above materials can be used without further treatment except CC which needs further cleaning and hydrophilic treatment.

2.2. Synthesis of Ni₂P nanosheets arrays on carbon cloth (Ni₂P/CC)

First, the carbon cloth (CC, 1 cm × 4 cm) was soaked in concentrated nitric acid (HNO₃) at 90 °C for 2 h, cooled to room temperature, ultrasonic removal of surface impurities with ethanol and deionized water, finally dried at 60 °C for 6 h. The precursor of Ni₂P/ CC was prepared by hydrothermal method. 0.5816 g Ni(NO₃)₂.6 H₂O (2 mM), 0.6 g CH_4N_2O (10 mM) and 0.222 g NH_4F (6 mM) were dissolved in 30 mL DI water, then stirred for 20 min to formed a uniform solution. After that, the treated CC was placed in solution and transferred together to a stainless autoclave in the oven at 120 °C for 6 h. Cooling down to room temperature, the CC surface was washed by DI water, and then dried for 6 h at 60 °C in an oven to obtain the precursor. Phosphating treatment was to put the precursor and 0.5 g NaH₂PO₂ into two porcelain boats, respectively placed in the downstream and upstream of the tubular furnace, heated to 300 °C at a rate of 5 °C/min, and maintained for 2 h. Finally, Ni₂P/CC was obtained after cooling to room temperature.

2.3. Synthesis of Ni₂P @ MoS₂/CC

0.3 g CH₄N₂S and 0.3 g H₈MoN₂O₄ were added to 30 mL DI water and stirred for 20 min to obtain a uniform solution. The previously prepared Ni₂P/CC and the solution were then transferred to a stainless reactor and reacted at 210 °C for 12 h in the oven. After natural cooling to room temperature, the surface was washed with DI water, and finally dried at 60 °C for 6 h to obtain the product Ni₂P @ MoS₂/CC. In order to find the best dosage of CH₄N₂S and H₈MoN₂O₄, we chose 0.1 g, 0.2 g, 0.3 g, 0.4 g and 0.5 g (the amount of CH₄N₂S and H₈MoN₂O₄ was the same) to compare. The corresponding samples were denoted as $Ni_2P @ MoS_2-x/CC$ (x = 1,2,3,4 and 5).

2.4. Synthesis of MoS₂/CC

The preparation of MoS_2/CC is similar to that of $Ni_2P @ MoS_2/CC$. The Ni_2P/CC was replaced with bare CC. Herein, we controlled the dosage of CH_4N_2S and H_8MoN_2O at 0.3 g.

2.5. Material characterization

The Bruker AXS D8 Advance X-ray diffractometer with Cu Kαradiation (wavelength of 0.15406 nm) was served to measure Xray diffraction (XRD) results. The scanning range was 10-90°, and the scanning rate was 5° per minute. The operating voltage was 40 mV and operating current was 40 mA. The X-ray photoelectron spectra of the products were recorded using an X-ray photoelectron spectrometer (Kratos Axis Ultra DLD) with an Al (mono) Ka source (1486.6 eV). The Al K α source was operated at 15 kV and 10 mA. The field emission scanning electron microscope (FE-SEM, JSM-6700 F, JEOL, Japan) was used to observe the morphology and structural characteristics of the catalyst, and the acceleration voltage was 3 KV. Besides, 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) were used to examine the structures of crystal and detailed morphology information. Element distribution was obtained by Energy dispersive X-ray spectrometer (EDX) mapping, which was characterized by HAADF-STEM. X-ray photoelectron spectrometer (Kratos Axis Ultra DLD) was used to record X-ray photoelectron spectroscopy (XPS) measurements and investigate the valence states.

2.6. Electrochemical measurements

In 1 M KOH electrolyte, with a typical three-electrode configuration, all the electrochemical tests were carried out through the CHI660E electrochemical workstation (CH Instruments, Inc., Shanghai). Generally, the prepared catalyst, graphite rod and Hg/ HgO electrode were respectively served as the working electrode, the counter electrode and the reference electrode. The SCE reference electrode was pre-calibrated concerning a reversible hydrogen electrode (RHE) during all measurements. In addition, iR compensation was made for the performance of the working electrode to compensate for the ohmic voltage reduction between the working electrode and the reference electrode [35,36]. The actual working potential could obtain by the calculation: E(E vs. RHE) = E(vs. SCE)+ 0.098 ($E_{Hg/HgO}$)+ 0.0592 ×PH [37,38]. Linear sweep voltammetry (LSV) had recorded the polarization curve of prepared catalysts at scan rate of 1 mV s⁻¹. According to the Tafel equation ($\eta = b \log |j| + a$, where η is overpotential, *j* is current density and *b* is tafel slope), the corresponding Tafel curves were calculated through converting polarization curves. Within the frequency range of 10⁵-0.01 Hz, the electrochemical impedance spectrum (EIS) was used to test the interfacial charge transfer resistance. CVs were tested under sweep speeds of 1-10 mV s⁻¹.

3. Results and discussion

The preparation process of this experiment was illustrated in Fig. 1a, the heterogeneous catalysts prepared by hydrothermal, phosphating and in-situ growth processes. First, the crystal structure grown on the carbon cloth was analyzed by XRD. Fig. 1b showed the XRD pattern of Ni₂P/CC, the diffraction peaks at 40.80°, 44.60°, 47.31°, 54.23°, 54.94°and 74.68° is corresponding to the (111), (201), (210), (300), (211) and (400) planes, respectively, which fitted with



Fig. 1. (a) Schematic preparation of Ni₂P@MoS₂/CC. (b)The XRD pattern of Ni₂P/CC. (c) The XRD patterns of Ni₂P@MoS₂-3/CC.

the pattern of Ni₂P (PDF #03-0953). In addition, several diffraction peaks at 30° – 40° may be due to the by-product of phosphating reaction, forming Ni-P nanoparticles with different binding forms, such as Ni_5P_4 [39]. And the MoS₂/CC showed the diffraction peaks at 14.38°, 33.51°, 39.54°, 49.79°, 60.14° and 70.14°, which is corresponding to the (002), (101), (103), (105), (008) and (108) planes of MoS₂ (PDF#37-1492). This indicates that the prepared molybdenum disulfide belongs to 2 H phase MoS₂. In Fig. 1c, after in-situ growth processes on Ni₂P/CC, the peak intensity of Ni₂P of heterogeneous catalyst Ni₂P @ MoS₂-3/CC decreased after loading MoS₂ nanosheets, and only a few characteristic peaks can be observed. Other peaks with strong signals are all from the loaded MoS₂ nanosheets. This is because the surface of Ni₂P was wrapped by dense MoS₂, which weakens the peak intensity of Ni₂P and makes it difficult to observe. Besides, the elemental contents of Ni, Mo, P and S in Ni₂P/MoS₂-3/CC were tested by ICP. The content of P element is the lowest, which is 0.08%. And the content of Mo element is 44.298%. In addition, the mass percentage of Ni and S elements is 8.54% and 9.798%, respectively.

Fig. 2a and d show the SEM images of Ni₂P at different rates. The morphology of Ni₂P/CC nanosheets obtained by hydrothermal and phosphating reaction was relatively loose, and the size of the nanosheets was large, similar to petal shape. MoS₂ nanosheets (Fig. 2b and e) grown directly on carbon cloth are smaller in size and packed tightly. Fig. 2c and f are the SEM images of Ni₂P@MoS₂/CC at different rates. Ni₂P was loaded with many compact tiny nanosheets. It can be preliminarily confirmed that MoS₂ nanosheets had successfully grown on Ni₂P. High-resolution TEM (HRTEM) images further reveal the microstructure and composition of catalyst. In Fig. 2g, the lattice spacing of 0.223 nm and 0.305 nm corresponds to the (111) and (211) crystal planes of Ni₂P, respectively. And the HRTEM image of MoS₂/CC (Fig. 2h) showed that the lattice spacing of 0.216 nm and 0.575 nm corresponds to the (103) and (2011) crystal planes of MoS₂,

respectively. In Fig. 2i, the lattice spacing of Ni₂P @ MoS₂-3/CC are around 0.267 nm and 0.255 nm, corresponding to the (105) and (103) plane of MoS₂ crystals, which is in accord with the XRD result. This indicates that Ni₂P is completely covered by MoS₂ nanosheets. In addition, X-ray (EDX) elemental mapping images (Fig. 2j-n) were used for element mapping of selected regions in the nanosheet, and the results showed that Ni, P, Mo and S elements were all dispersed on the surface of Ni₂P @ MoS₂-3/CC.

The surface composition and chemical states of Ni₂P/CC, MoS₂/CC and Ni₂P@MoS₂-3/CC were further analyzed with X-ray photoelectron spectroscopy (XPS). In, Ni, P, C and O elements can be detected from the XPS survey spectra of Ni₂P/CC. According to the high-resolution P 2p spectra (Fig. 3a), the peaks that appeared at 129.2 and 129.9 eV are ascribed to P 2p_{3/2} and P 2p_{1/2}, respectively [40]. Furthermore, the peak at 133.5 eV was caused by oxidation of the sample exposed to air [41]. The shows that MoS_2/CC and $Ni_2P@$ MoS₂-3/CC have the similar diffraction pattern, which indicates that the surface composition and chemical state of the two are consistent. The surface of Ni₂P/CC was completely covered by MoS₂. And the C1s spectrum of Ni₂P@MoS₂-3/CC can be deconvoluted into C-C (284.8 eV), and C-O (286.3 eV) used as calibration standard [42]. There are three main peaks matched binding energies of 852.5, 855.9 and 861.6 eV in the high-resolution Ni 2p spectrum of pure Ni_2P/CC (Fig. 3b), which corresponding to Ni $2p_{3/2}$, Ni²⁺ oxidation states and the satellite peak, respectively; [43] and the other peaks at 873.7 and 879.3 eV are ascribed to Ni²⁺ oxidation states and the satellite peak [44]. After loading MoS₂ nanosheets, the intensity of XPS peak of Ni 2 P decreased compared with pure Ni₂P, which may be because Ni₂P nanosheets were completely covered by MoS₂. In addition, the peak position of Ni 2 P also shifted, especially the Ni²⁺ oxidation state peak at 855.9 eV and 873.7 eV shifted to lower energy after loading MoS₂. The offset of the peak position indicates that there is an electronic interaction between Ni₂P and MoS₂. The high-resolution



Fig. 2. Morphological characterization of the as-prepared Ni₂P/CC, MoS₂/CC and Ni₂P@MoS₂-3/CC. (a-c)Low range SEM images of Ni₂P/CC,MoS₂/CC and Ni₂P@MoS₂-3/CC. (d-f) High range SEM images of Ni₂P/CC,MoS₂/CC and Ni₂P@MoS₂-3/CC (g-i)TEMHAADF-STEM images of Ni₂P/CC,MoS₂/CC and Ni₂P@MoS₂-3/CC. (j-n)EDX elemental mapping of Ni₂P@MoS₂-3/CC.

Mo 3d spectrum of Ni₂P @ MoS₂-3/CC (Fig. 3c) can be well deconvoluted into two peaks of Mo⁴⁺ 3d_{5/2} (229.2 eV), Mo⁴⁺ 3d_{3/2} (232.3 eV),and the peak at 226.5 eV ascribes to S 2 s peak, which indicated the formation of Mo-S bond [45]. In addition, the binding energy of Mo 3d decreases slightly after the formation of Ni₂P/MoS₂ heterogeneous interface. These results show that the electron interaction between MoS₂ and Ni₂P structure exists due to the establishment of coupling interface [46]. From the Fig. 3d, the high-resolution spectrum of Ni₂P @ MoS₂-3/CC exhibits two predominant peaks of S 2p_{3/2} and S 2p_{1/2} at 162.1 and 163.4 eV, respectively. Similarly, compared with MoS₂/CC, the binding energy of S 2p decreases slightly after the formation of Ni₂P/MoS₂ heterogeneous interface, which further indicates the existence of electron interaction between Ni₂P and MoS₂ structure.

With a classical three-electrode system, the HER performance of different catalysts was tested in 1 M KOH solution. Hg/HgO electrode worked as the reference electrode, carbon rod worked as the contrast electrode and the prepared catalyst was used as the working electrode. Fig. 4a showed the iR compensation of linear scan voltammetry (LSV) curves for Pt/C, Ni₂P/CC, MoS₂/CC and Ni₂P@MoS₂-3/CC. No surprising, the Pt/C showed the best HER performance. Moreover, compared to Ni₂P/CC and MoS₂/CC, Ni₂P@MoS₂-3/CC showed more excellent electrocatalytic performance. It just needed

an overpotential of 99 mV to derived current density of 10 mA cm⁻², which was superior to Ni₂P/CC (157 mV) and MoS₂/CC (204 mV). Tafel slope is another crucial criterion to test HER dynamics. From the Fig. 4b, Ni₂P@MoS₂-3/CC possessed a smaller tafel slope of 97 mV dec⁻¹, which better than Ni₂P/CC (115 mV dec⁻¹) and MoS₂/CC (120 mV dec⁻¹). From electrochemical impedance spectroscopy (EIS), the kinetics and charge carrier migration resistance of different catalysts between the electrolyte and electrode interface can be investigated [47]. In the EIS test, smaller semicircles mean lower impedance, greater electrical conductivity, and higher electron transport efficiency, which ultimately leads to excellent catalytic performance [48]. Here, the relationship between electron transfer resistance and electrochemical activity was further illustrated by using EIS tests. In Fig. 4c, the EIS semicircle of Ni₂P@MoS₂-3/CC is smaller than that of Ni₂P/CC and MoS₂/CC, which means the faster electron conductivity of the former. Abundant electrochemically active sites and electron synergies between heterogeneous interfaces may enhance conductivity [49]. To further calculate the electrochemically active surface area (ECSA), the double-layer capacitance (C_{dl}) was measured at different scanning rates using cyclic voltammetry. Electrochemical active area (ECSA) is directly proportional to C_{dl} [50]. In Fig. 4d, the results showed that the value of C_{dl} of Ni₂P@MoS₂-3/CC (86.1 mF cm⁻²) was bigger than Ni₂P/CC



Fig. 3. XPS spectra of a) P 2p for Ni₂P/CC and b) Ni 2p for Ni₂P/CC and Ni₂P @ MoS₂-3/CC; c) XPS Mo 3d and d) XPS S 2p spectra for MoS₂/CC and Ni₂P @ MoS₂-3/CC, respectively.

 (3.5 mF cm^{-2}) and MoS₂/CC (14.8 mF cm⁻²), which means the Ni₂P @ MoS₂-3/CC had more active site. In addition, Ni₂P @ MoS₂/CC showed excellent HER performance in alkaline solution compared with other reported sulfide and phosphide-based catalysts.

In addition, the stability of catalyst is another standard to measure its performance. The HER stability of Ni₂P@MoS₂-3/CC in 1 M KOH was tested in Fig. 4e. The LSV curves of Ni₂P@MoS₂-3/CC was almost the same as the initial one after 2000 cycles of CV tests. And after the 2000 cycle test in 1 M KOH alkaline solution, the morphology of Ni₂P@MoS₂-3/CC was basically the same as the initial morphology before the test, heterogeneous structure was easy to be recognized, MoS₂ nanosheet was densely covered on Ni₂P. Furthermore, chronopotentiometry was used to test the long-term stability of the catalyst. In the Fig. 4f, the current density remains almost unchanged within 50 h. These results indicated that Ni₂P@MoS₂-3/CC had good stability.

In addition, because of the weak electrical conductivity of MoS_2 , the amount of MoS_2 will affect the electrical conductivity of the catalyst, thus affecting the overall catalytic performance. Different contents of ammonium molybdate and thiourea will affect the load of MoS_2 generated. Therefore, the contents of ammonium molybdate and thiourea were changed to 0.1 g, 0.2 g, 0.3 g, 0.4 g and 0.5 g at the same time to explore the specific influence of the content of MoS_2 generated on the catalytic performance of the electrocatalyst. The results showed that when the amount of thiourea and ammonium molybdate was 0.3 g, the prepared sample ($Ni_2P@MoS_2-3/CC$) had the best HER performance. In Fig. 5a, the $Ni_2P@MoS_2-3/CC$ had the

minimum required overpotential of 99 mV at a current density of 10 mA cm^{-2} , which was better than Ni₂P@MoS₂-1/CC (122 mV), Ni₂P@MoS₂-2/CC (116 mV), Ni₂P@MoS₂-4/CC (123 mV) and Ni₂P@ MoS₂-5/CC (137 mV). Besides, Ni₂P@MoS₂-3/CC showed a smaller Tafel slope of 97 mV dec⁻¹ the same as $Ni_2P@MoS_2-1/CC$ (Fig. 5b), and better than Ni₂P@MoS₂-2/CC (101 mV dec⁻¹), Ni₂P@MoS₂-4/CC $(107 \text{ mV dec}^{-1})$ and Ni₂P@MoS₂-5/CC (105 mv dec⁻¹). EIS testing further demonstrated the excellent performance of Ni₂P@MoS₂-3/ CC. In the Fig. 5c, Ni₂P@MoS₂-3/CC had the least resistance. In addition, there was little difference in the resistance of the other samples except Ni₂P@MoS₂-4/CC, which was particularly large. As shown in, 1 mV s⁻¹ to 10 mV s⁻¹ of CV curves were tested for catalysts with different contents of thiourea and ammonium molybdate. C_{dl} value can be obtained by further calculation (Fig. 5d). When the dosage of thiourea and ammonium molybdate was 0.3 g, the sample prepared Ni₂P@MoS₂-3/CC had the largest C_{dl} value of 86.1 mF cm⁻², which was better than $Ni_2P@MoS_2-1/CC$ (67.1 mF cm⁻²), $Ni_2P@$ MoS_2-2/CC (75.4 mF cm⁻²), $Ni_2P @ MoS_2-2/CC$ (77.0 mF cm⁻²) and Ni₂P@MoS₂-2/CC (39.1 mF cm⁻²). In addition, SEM images of Ni₂P@ MoS₂-x/CC showed that with the increase of thiourea and ammonium molybdate content, the denser MoS₂ grown on Ni₂P/CC nanosheets showed better HER performance, and the catalyst prepared with 0.3 g content had the best catalytic performance. However, when the amount of thiourea and ammonium molybdate continued to increase, MoS₂ will over accumulate on Ni₂P nanosheets and formed agglomeration, which will hinder electron transfer and lead



Fig. 4. Evaluation of HER performances of different samples in 1.0 M KOH. (a-d) LSV polarization curves, Tafel plots, Nyquist plots and the C_{d1} measurements of Ni₂P/CC, MoS₂/CC, MoS₂/CC, Ni₂P @ MoS₂-3/CC and Pt/C. (e) Polarization curves of Ni₂P @ MoS₂-3/CC at the first cycle and after 2000 cycles. (f) The chronopotentiometry curve with a constant current density of 10 mA cm⁻² for 50 h in 1 M KOH.

to the reduction of catalytic activity, which was consistent with the results of electrochemical performance test. Therefore, in this work, it was concluded that under the experimental conditions, when the content of ammonium molybdate and thiourea ranges from 0.1 g to 0.5 g, the heterostructure catalyst Ni₂P @ MoS₂/CC prepared at 0.3 g has the best HER performance. The heterostructure formed by the combination of MoS₂ and Ni₂P can promote electron transfer and enhance the overall conductivity of the catalyst. However, when MoS₂ load is too much, not only agglomeration will occur, but also its poor conductivity will hinder electron transmission and weaken the performance of the catalyst [42,51].

The heterogeneous composite catalyst Ni₂P@MoS₂/CC can improve HER performance for the following reasons: (1) The in situ growth of Ni₂P and MoS₂ nanosheets on carbon cloth can ensure the seamless interface contact between the components and the substrate, enhance the overall conductivity of the catalyst, and prevent the aggregation and stratification between the components; (2) the gap channel between Ni₂P and MoS₂ nanosheets is beneficial to electrolyte penetration, increase the active area, rapidly accumulate and release bubbles, and significantly accelerate the reaction kinetics; (3) the active component modified substrate can be used directly as a self-supporting and adhesive-free working electrode,



Fig. 5. The electrocatalytic measures of Ni₂P@MoS₂-x/CC (x = 1,2,3,4 and 5) in 1 M KOH. (a-d) LSV polarization curves, Tafel plots, Nyquist plots and the C_{dl} measurements.

making efficient use of the active site and greatly reducing resistance.

4. Conclusion

In summary, we synthesized a heterogeneous catalyst composed of Ni₂P nanosheets grown directly on CC substrate and densely packed MoS₂ nanosheets. Compared with Ni₂P and MoS₂ alone, the performance of HER was greatly improved. Thanks to the interface engineering between heterogeneous structures and nanosheet array structure, the prepared Ni₂P@MoS₂/CC electrode has rich active sites, the synergistic effect of electrons between different components and the fast electron transport channel, which enables it to show outstanding electrocatalytic performance for HER in alkaline medium, and the overpotential is 99 mV at 10 mA cm⁻². In addition, the catalyst also has good stability, and the performance of the catalyst has no obvious attenuation after running for 50 h under the condition of j_{10} . This work provides a kind of low cost, good performance and stable electrocatalyst material for electrolysis of water to produce hydrogen.

CRediT authorship contribution statement

Yinchen Dai: Conceptualization, Methodology, Formal analysis, Validation, Investigation, Data curation, Writing – original draft, Writing – review & editing. Wubing Chen: Validation, Investigation. Baochun Guo: Writing – original draft. Xiao Li: Writing – review & editing. Jibiao Guan: Resources. Lina Wang: Resources. Ming Zhang: Conceptualization, Methodology, Resources, Writing – review & editing, Supervision.

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.

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