ORIGINAL RESEARCH

A Highly Active and Robust CoP/CoS₂-Based Electrocatalyst Toward Overall Water Splitting

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Abstract



The development of low-cost, highly active, and robust electrocatalysts for catalyzing the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) holds a pivotal role in electrocatalytic water splitting. Herein, a two-step method was presented to synthesize CoS_2/CoP heterostructures grown on carbon cloth ($CoS_2/CoP/CC$). The precursor Co(OH)F/CC synthesized through the hydrothermal process can be successfully converted into $CoS_2/CoP/CC$ catalyst via gas-phase phosphorization and sulfurization. The as-obtained $CoS_2/CoP/CC$ exhibited promising performances for HER and OER with low overpotentials of 90 and 334 mV at a current density of 10 mA cm⁻² in 1.0 M KOH, respectively. The improved electrocatalytic performance of the $CoS_2/CoP/CC$ can be attributed to the strong electron interactions and synergistic efforts between CoS_2 and CoP, abundant active sites of the heterostructures, and enhanced smaller charge-transfer resistance.

Keywords CoS₂/CoP · Electrocatalysis · Hydrogen evolution reaction · Materials chemistry

Introduction

Due to the increasing demand for energy and the rise of concern about the environment, much more attention has been focused on developing a green renewable energy resource [1]. Hydrogen (H₂), as a clean energy carrier with high energy density, is one of the promising substitutions for fossil fuel that has the potential to alleviate the global energy crisis [2, 3]. It can be conveniently achieved from electroreduction of water $(2H_2O \rightarrow 2H_2 + O_2)$. However, water electrolysis requires highly active and robust catalysts to reduce the excess potential (also known as overpotential, η) so as to diminish energy consumption [4]. The Pt can be regarded as the best

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Ming Zhang zhangming@zstu.edu.cn electrocatalyst for hydrogen evolution reaction (HER) and RuO_2 is considered as the best oxygen evolution reaction (OER) catalysts, which are both restricted by their scarcities and high costs for large-scale applications [5–7].

Recently, earth-abundant non-noble metal compounds have emerged as novel electrocatalysts to accelerate water splitting. Transition metal sulfides [8, 9], selenides [10, 11], carbides [12], oxides [13, 14], hydroxides [15], and perovskite oxides [16] are potential low-cost alternatives to precious metal in electrolyzing water efficiently. Among various kinds of catalysts, transition metal dichalcogenides (TMDs), such as CoS_2 [17], MoS_2 [18], Ni_3S_2 [19], and WS_2 [20], have been extensively demonstrated as alternative electrocatalysts for hydrogen production owing to their high catalytic activity, low cost, and easy preparation. TMDs can be classified into two categories. One is the well-known two-dimensional (2D) layered metal dichalcogenide materials (e.g., MoS₂ and WS₂), which have a drawback of their relatively poor electrical conductivity [21]. The other is non-layered metal dichalcogenides (e.g., CoS₂ and NiS₂), owning cubic pyrite-type or orthorhombic marcasite-type structures [22–24], which possess an evident advantage over 2D layered TMDs owing to their intrinsic metallic and conductive properties. In particular, cobalt-based dichalcogenides have been proved as high-efficiency electrocatalysts due to their low-energy barrier for the adsorption of hydrogen atoms on cobalt atoms [25–27]. Transition

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metal phosphides (TMPs), generally considered as efficient catalysts for hydrodesulfurization (HDS) reactions [28, 29], which reacts relying on the reversible binding of catalysts and hydrogen (similarly to the process hydrogen produced in the HER). Actually, many of TMPs have been demonstrated to have the prominent catalytic performance for the HER, such as CoP [30-32], MoP [33], NiP [34], and FeP [35]. Nevertheless, the catalytic activity of the above catalysts still lower than those of Pt-based catalysts restricted by the reactivity and density of active sites. Thus, various methods have been employed to improve catalytic performance of electrocatalysts, mainly the structural adjustment and surface modification of catalysts, including creating porous structure [36], constructing active site-rich nanosheets [37], and doping heteroatoms [38]. In addition, the hybrid materials with two or more components via chemical combination or interface engineering can often be found to have better catalytic performance than any one of them. For example, Hou et al. prepared oxygenated-CoS₂-MoS₂ heteronanosheets grown on carbon fiber cloth through the hydrothermal process and found that the exposed heterointerfaces, the abundant active sites, and the interface synergistic effect of the heterostructures play crucial roles in increasing HER and OER activity [39]. There are many electrocatalysts of mixed transition metal compounds demonstrated to have superior catalytic performance, such as CoS₂/WS₂ [40], Ni₂P/CoP [41], CoP/CeO₂ [42], CoS₂/TiO₂ [43], MoS₂/NiS/MoO₃ [44], MoS₂/Ni₃S₂ [45], and NiS₂/ MoS₂ [46]. Furthermore, carbon cloth (CC), a threedimensional conductive substrate, could not only offer strong adhesion and reduced interfacial impedance to promote the electrochemical activity of catalysts, but also provide flexible substrates on which catalysts grown as flexible electrodes, which are important for the development of portable hydrogen devices.

On the basis of the analysis above, it can thus be concluded that engineering novel heterostructures is a sure way to raise the catalysts activity. Meanwhile, Co-based phosphides and sulfides have been proved highly active and earth-abundant catalysts for the HER and OER. Herein, we report a two-step method for the fabrication of CoS₂/CoP heterostructure anchored on carbon cloth (denoted as CoS₂/CoP/CC). In comparison to CoS₂/CC and CoP/CC, the as-prepared CoS₂/CoP/ CC presented lower overpotentials of 90 mV and 334 mV to reach 10 mA cm⁻² in 1 M KOH electrolyte media for the HER and OER, respectively.

The two-step approach for the preparation of CoS_2/CC is depicted in Scheme 1. First, Co(OH)F nanoclusters were uniformly distributed in CC fibers after the hydrothermal reaction at 120 °C. The second step through a solid-/gas-phase reaction in high temperature is to introduce P and S to synthesize $CoS_2/$ CoP/CC composite. After the phosphorization and sulfurization, the CoS₂ and CoP are integrated into thin layers which are considered as heterointerfaces. In addition, the heterogeneous interfaces of CoS2/CoP layers can provide synergetic effects of these two compounds to boost electrochemical activity, which can further enrich active edge sites and structural defects to contribute to higher catalytic performance, compared to the single component (CoS₂ and CoP). Furthermore, the nanoclusters inside of CoS2/CoP with a relatively high conductivity which can serve as the electron "highway" to guarantee the fast ion/electron transfer between the CoS₂/CoP and the CC. Certainly, there are numerous nanoclusters attaching to the carbon fibers, making more abundant CoS₂/CoP catalysts grown on a single fiber. And the porosity of the nanoclusters could also expose more active sites, allowing electrolyte to diffuse easily into all the pores to facilitate reactants reacting with these abundant active sites [47]. Besides, carbon cloth as a three-dimensional substrate is capable to get the generated bubbles evolving and releasing more easily.

Experimental Section

Materials

Cobalt nitrate hexahydrate (AR 99%) was purchased from Shanghai Macklin Biochemical Co., Ltd. Ammonium fluoride (ACS 98%) and sodium hypophosphite (AR 99.0%) were both obtained from Aladdin Industrial Corporation (Shanghai, China). Urea was purchased from Wuxi Zhanwang Chemical Reagent Co., Ltd. Sulfur sublimed (chemically pure) was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. The carbon cloth (WOS1002) was purchased from CeTech Co., Ltd.

Material Synthesis

In the first step, the Co(OH)F/CC was prepared through a hydrothermal process similar to the means reported in the literature [47]. Briefly, 3 mmol cobalt nitrate, 8 mmol urea, and 15 mmol ammonium fluoride were dissolved in 30 mL deionized water under steady stirring for 30 min. Then, the above solution was transferred into a Teflon-lined stainless-steel autoclave (50 mL), and a piece of cleaned CC (2 cm \times 2 cm) was immersed in the solution. Afterwards, the autoclave was sealed and placed in an electric oven maintained at 120 °C for 6 h. Thereafter, the Co(OH)F/CC was obtained and rinsed with deionized water and then dried at 60 °C.

In the second step, the $CoS_2/CoP/CC$ was fabricated via chemical vapor deposition (CVD) method. The prepared Co(OH)F/CC was placed in a ceramic boat and put at the center of the tube furnace. In addition, the sodium hypophosphite (0.5 g) was put next to the Co(OH)F/CC at the upstream side of the furnace, while sublimed sulfur powders (0.25 g) were put into a heating zone at upstream side out



of the furnace. Before the heating program started, argon gas was flowed through the tube under 150 sccm for 30 min to remove residual oxygen. Subsequently, the Co(OH)F/CC was annealed at 350 °C for 1 h under 150 sccm Ar gas flow at a heating speed of 5 °C min⁻¹ to obtain CoP/CC. Then, the temperature of the furnace was raised to 550 °C; meanwhile, the heating zone (S powders) reached 150 °C rapidly and both retained 3 h in Ar atmosphere. After the phosphorization and sulfurization, the CoS₂/CoP/CC was fabricated completely without any further operation. As the contrast, the CoP/CC and CoS₂/CC are obtained just through only one process of phosphorization or sulfurization under the same conditions.

Characterization

X-ray diffraction (XRD) patterns of the samples were recorded with an X-ray diffractometer (Bruker AXS D8 DISCOVER) by Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) at room temperature. X-ray photoelectron spectroscopy (XPS) measurements were performed on an X-ray photoelectron spectrometer (Kratos Axis Ultra DLD) by using monochromatic Al $K\alpha$ radiation as the exciting source (1486.6 eV) which was operated at 15 kV and 10 mA. The morphologies of the samples were captured by using JSM-2100 transmission electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV and JSM-6700 field-emission scanning electron microscope (JEOL, Japan) with an acceleration voltage of 3 kV.

Electrochemical Characterization

All electrochemical performance tests were carried out with a standard three-electrode system using a CHI660E electrochemical workstation (Shanghai Chenhua), taking the asfabricated catalyst as the working electrode, a graphite rod as the counter electrode, a saturated calomel electrode (SCE), as the reference electrode. For the HER performance, linear sweep voltammetry (LSV) was conducted with a scan

rate of 1 mV/s in alkaline medium. In 1.0 M KOH, E(RHE) = E(SCE) + 1.068. All electrochemical measurement of catalysts was tested at 25 °C.

Results and Discussion

Field-emission scanning electron microscopy (FESEM) images in Fig. S1 revealed that the Co(OH)F small flowers comprised of nanoclusters with an average thickness of about 300 nm were uniformly covered on CC substrate. After reacting with PH₃, there is no significant change in morphology of CoP/CC (Fig. S2), but its surface became rather rougher than that of the precursor Co(OH)F/CC nanoclusters. Figure 1 a depicts the corresponding low-magnification SEM image of prepared CoS2/CoP/CC with clear carbon fibers grown dense nanoclusters which covered by thin $CoS_2/$ CoP coating. After the subsequent sulfurization process, the nanoflowers exhibit distinct rough surface (Fig. 1b). Obviously, it can be observed that the nanoclusters were covered by some thin layers and became a little thicker, the peripheries of which were multilayered CoS₂/CoP heterostructure layers with high-density active sites. As a contrast, the SEM image of CoS₂/CC in Fig. S3 shows that there is no nanoclusters found in CoS2/CC and its morphology is quite different from that of CoP/CC. In conclusion, the CoS₂/ CoP/CC hybrid exhibited a hierarchical structure attributed to the different experimental treatment. First, the hydrothermal treatment generated the nanoclusters of Co(OH)F fully anchored on carbon cloth fibers. Then, the phosphorization process produced CoP grown on nanoclusters without much difference in morphology compared to the precursor Co(OH)F. Through the sulfurization, the reactant CoP/Co(OH)F converted into CoS₂/CoP hybrid with a rougher surface of nanoclusters and finally, the hierarchical structure of CC-CoP/CoS₂ came into being. A further detailed inspection of the surface structures and crystalline orientation of the as**Fig. 1 a**, **b** Low- and highmagnification SEM image of CoS₂/CoP/CC. **c** TEM image of CoS₂/CoP nanocluster. **d** Highresolution TEM image of CoS₂/ CoP nanocluster. **e** STEM-EDX elemental mapping of the CoS₂/ CoP nanocluster representing the homogeneous distribution of Co, P, and S elements over the marked detection range on a single nanocluster



prepared samples was obtained by TEM characterization (Fig. 1c, d). From the HRTEM image (Fig. 1d), various lattices could be clearly seen with diverse fringe spacings, which are indexed to CoS_2 and CoP, respectively. The lattice distance of 0.277 nm corresponds to the (200) crystal plane of CoS_2 , while 0.283 and 0.247 nm are attributed to the (011) and (111) crystal planes of CoP. Furthermore, STEM and energy-dispersive X-ray (EDX) elemental mapping show the homogeneous distribution of Co, P, and S elements over the marked detection range on a single nanocluster (Fig. 1e), which offers the coexistence possibility of CoS_2 and CoP on the product.

The crystal structures of the as-fabricated CoS₂/CoP/ CC composite, single-component CoS₂/CC, and CoP/CC were characterized by the XRD technique. Figure S4 reveals that Co(OH)F/CC was obtained through the hydrothermal process [47] (JCPDS no. 74-2075). As a contrast, after the treatment of phosphorization or sulfurization, the XRD patterns (Fig. 2a) of the as-obtained products indicate that all diffraction peaks, which can be indexed to CoS₂ (JCPDS no. 41-1471) and CoP (JCPDS no. 29-0497), respectively, suggesting successful conversion of Co(OH)F into CoS₂ or CoP. Additionally, while the precursor Co(OH)F/CC was treated by phosphorization and sulfurization successively, the corresponding XRD pattern in Fig. 3 a confirms the coexistence of CoS_2 and CoP. The peaks at $2\theta = 31.60^{\circ}$ and 48.13° are assigned to (011) and (211) plane of CoP, while the peaks marked with green triangles are consistent with CoS₂, indicating the formation of the CoS₂-CoP hybrid in comparison to the XRD pattern of single-phase CoS₂ and CoP. All XRD characterizations are in agreement with the analysis of TEM images for the CoS₂/CoP/CC.

Furthermore, X-ray photoelectron spectroscopy (XPS) characterization was employed to investigate the surface chemical states and composition of the catalysts. As shown in the corresponding Co 2p spectrum (Fig. 2b), two distinct peaks located at binding energies of 779.2 and 781.7 eV are both assigned to Co $2p_{3/2}$ orbital, while the other two peaks at 794.1 and 798.3 eV are attributable to the Co $2p_{1/2}$ core levels of Co²⁺ species [48–50]. The remaining two peaks observed at 787.5 and 803.8 eV are identified as satellite peaks [51]. Multiple peaks exist due to the existence of different Co species in the composite. It can be observed in Fig. 2 b that the peaks of Co $2p_{3/2}$ (781.7 eV) and Co $2p_{1/2}$ (798.3 eV) in CoS₂/ CoP exhibit a positive shift compared to that of CoP and a negative shift compared to that of CoS2. The shift of peaks due to the interfacial charge redistribution between CoS₂ and CoP, indicating the electronic structure of CoS2/CoP/CC has changed. Different electronic structure of the catalysts may result in a significant change in catalytic properties. Therefore, the charge redistribution of the CoS₂/CoP/CC hybrid would be an essential factor for the enhanced catalytic activity. The presence of S in the CoS₂/CoP/CC composite can further be confirmed by the high-resolution S 2p spectrum (Fig. 2c), which could be deconvoluted into doublet peaks at 163.7 and 162.6 eV, referring to S $2p_{1/2}$ and S $2p_{3/2}$ of the divalent sulfide ions (S²⁻), respectively [52]. Another S 2p peak can be divided into 169.6 and 168.6 eV, which are probably ascribed to C-SO_x-C groups [50]. High-resolution XPS results of the P 2p region are presented in Fig. 2 d, in which there are three decomposed components located at 129.4, 130.2, and 134.1 eV, reflecting the binding energies of the P 2p_{3/2}, P 2p_{1/2} in CoP, and oxidized P species, respectively [42, 48].



Fig. 2 a XRD patterns of CoS₂/CC, CoP/CC, and CoS₂/CoP/CC. b High-resolution XPS spectra of Co 2p of CoS₂/CoP/CC, CoS2, and CoP. c–d High-resolution XPS spectra of S 2p and P 2p in CoS₂/CoP/CC

To assess the electrocatalytic activities of the prepared CoS₂/CoP/CC catalysts, the HER performances were carried out in 1 M KOH solution with a three-electrode system. For comparison, catalytic activities of CoP/CC, CoS₂/CC, Co(OH)F/CC, and Pt/C were also tested. As depicted in Fig. 3 a, it can be seen obviously that Pt/C catalyst exhibits the most outstanding HER activity with an overpotential of 51 mV at 10 mA cm⁻² and Co(OH)F/CC shows a poor performance with an onset overpotential of ~295 mV. Besides, the CoP/CC and CoS₂/CC reach a current density of 10 mA cm⁻² at overpotentials of 129 and 184 mV, respectively. Compared with CoP/CC and CoS₂/CC, the CoS₂/CoP/CC exhibits a much lower overpotential, that is, only 90 mV at 10 mA cm^{-2} . Moreover, the CoS₂/CoP/CC has a much larger current density than CoS₂/CC and CoP/CC at all potentials for the HER depicted in Fig. 3 a, revealing the $CoS_2/CoP/CC$ has the optimal catalytic activity among all three catalysts for the HER.

Moreover, the Tafel slope is a significant indicator to get a deeper understanding of HER catalytic mechanism and HER kinetics of different catalysts. The Tafel slope is derived from the Tafel equation: $\eta = a + b\log|j|$; where *b* is the Tafel slope and is determined by electrode material, temperature, and property of electrolyte. In alkaline medium, CoS₂/CoP/CC electrode delivers a low Tafel slope (b) of 91.2 mV dec⁻¹ (Fig. 3b), which is smaller than that of CoP/CC electrode (113.1 mV dec⁻¹) and CoS₂/CC electrode (134.7 mV dec^{-1}), indicating faster kinetics and a higher rate of hydrogen generation with applied overpotential. The low Tafel slope plainly declares that the CoS₂/CoP/CC electrocatalysts delivered a faster HER than other catalyst. The Tafel plot is a critical indicator to determine the kinetics and mechanism of HER for the catalyst. Catalysts are involved with several pathways through a complete HER process in an alkaline electrolyte. First, H₂O molecules are attached to the surface of the catalyst getting electronic to generate H_{ads}. This pathway would be followed by the direct bonding of two H_{ads} to produce a H₂ molecule or by the reaction of H_{ads} with another H₂O molecules and electrons to release hydrogen. The former we called Volmer-Tafel pathway (Eq. 1), the latter we called Volmer-Heyrovsky pathway (Eq. 2). In this paper, the Tafel slope for the CoS₂/CoP/CC catalyst is 91.2 mV dec⁻¹ lied in the range of 40–120 mV dec⁻¹, demonstrating CoS2/CoP/CC catalyst proceeds via the Volmer-Heyrovsky pathway while the Heyrovsky reaction (H_{ads} + $e^- + H_2O \rightarrow OH^- + H_2)$ is the rate-determining step in the whole HER process [53, 54].

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Fig. 3 a Polarization curves of CoS2/CoP/CC, CoP/CC, CoS2/CC, Co(OH)F/CC, and Pt/C for HER. b Polarization curve-derived Tafel plots of the corresponding electrocatalysts. c Nyquist plot of various catalysts

$$\begin{array}{ll} H_2O + e^- {\rightarrow} H_{ads} + OH^- & Volmer \\ H_{ads} + H_{ads} {\rightarrow} H_2 & Tafel \end{array} \tag{1}$$

Furthermore, electrochemical impedance spectroscopy (EIS) analyses were conducted to measure the electron- and charge-transfer ability in the HER process. And an equivalent electrical circuit presented in the inset of Fig. 3 c was used to describe the HER kinetic processes of the catalysts. In the equivalent circuit, R_s denotes the electrolyte resistance, while $R_{\rm ct}$ is referred to the charge-transfer resistance which usually assesses the HER kinetic processes at the electrode/electrolyte interface. The Nyquist plots (Fig. 3c) demonstrated that CoS₂/ CoP/CC has a smaller charge-transfer resistance (6.247 Ω) compared to CoP/CC (8.086 Ω), CoS₂/CC (18.58 Ω), indicating CoS₂/CoP/CC has a higher conductivity with a faster electrochemical reaction rate. This result is consistent with the small Tafel slope of CoS₂/CoP/CC. Electrochemical stability is another important indicator to measure the quality of catalysts. The long-term stability of CoS2/CoP/CC was examined by constant voltage chronoamperometry in alkaline solution, and it tested over 24 h with higher stability without a distinct

at - 0.2 V vs RHE in 1 M KOH. d Chronopotentiometry measurement of CoS2/CoP/CC for HER at a constant potential of -0.1 V vs RHE

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15 Time (h)

.4 0.8 log(|j|/mA cm⁻²)

CoS₂/CoP/CC

0.4

CoP/CC

CoS₂/CC

Pt/C

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decline of current density except for a small initial drop (Fig. 3d). We further tested the durability of $CoS_2/CoP/CC$. After 5000 cycles of continuous CV scanning at a scan of 2 mV s^{-1} in 1 M KOH solution, the polarization curve of CoS₂/CoP/CC is similar to the initial one with a negligible loss of current density confirmed that it has satisfactory durability (Fig. S5). Figure S6 exhibits the amount of H₂ released over CoS2/CoP/CC in 1 M KOH for 60 min, and the catalyst afforded a stable H₂ evolution rate of 6.0 mmol h^{-1} . Note that the measured value matched well with the theoretical H₂ amount, indicating CoS₂/CoP/CC presents a ~ 100% faradaic efficiency for the HER while the side reactions are negligible.

The electrocatalytic activity of CoS₂/CoP/CC for the OER was further evaluated systematically using the typical threeelectrode system in alkaline electrolyte, with CoS2/CC and CoP/CC under the same condition for comparison. As depicted in Fig. 4 a, CoS₂/CoP/CC with prominent OER activity exhibited a low overpotential of 334 mV to deliver a current density of 10 mA cm^{-2} . This value is less than those of CoS_2/CC (374 mA at 10 mA cm⁻²) and CoP/CC (401 mA at 10 mA cm⁻²), strongly confirming the great enhancement of OER performance achieved with the CoS2/CoP/CC composite, which may be chiefly attributed to the synergistic effects of CoS₂/CoP heterostructures.



Fig. 4 a Polarization curves of CoS₂/CoP/CC, CoP/CC, and CoS₂/CC for OER. b Polarization curve-derived Tafel plots of the corresponding electrocatalysts. c Nyquist plot of various catalysts at 1.50 V vs RHE in

Moreover, to evaluate the OER kinetics, Tafel plots were further obtained in an alkaline electrolyte (Fig. 4b). The CoS₂/CoP/CC electrode delivers a relatively low Tafel slope of 105.7 mV dec $^{-1}$, which is small than those of CoS_2/CC (109.4 mV dec⁻¹) and CoP/CC $(130.5 \text{ mV dec}^{-1})$, demonstrating favorable kinetics for OER on CoS₂/CoP/CC catalyst. In the alkaline medium, the following four reaction steps were generally proposed as the mechanism for the OER process [55]: $M + OH^- \rightarrow$ M-OH_{ads}* + e^{-} (R1); M-OH_{ads}* \rightarrow M-OH_{ads} (R2); M- $OH_{ads} + OH^- \rightarrow M-O_{ads} + H_2O + e^- (R3); M-O_{ads} \rightarrow M +$ $1/2O_2$ (R4). When the Tafel slope is ca. 120, 60, 40, or 30, the rate-determining step of the OER correspond to the pathway of R1, R2, R3, or R4, respectively. The Tafel slope of $CoS_2/CoP/CC$ was measured to be 105.7 mV dec $^{-1}$, indicating the rate-determining step at this catalyst is R2.

Similarly, to the HER, the charge-transfer resistance (R_{ct}) of CoS₂/CoP/CC during the OER showing a much smaller semicircle depicted in the Nyquist plots (Fig. 4c), indicating its higher electron transfer properties compared with CoS₂/CC and CoP/CC. Notably, the long-term stability under OER condition is an important indicator for evaluating the performance of electrocatalysts. The durability of the CoS₂/CoP/CC

1 M KOH. d Chronopotentiometry measurement of CoS2/CoP/CC for OER at a constant potential of 1.55 V vs RHE

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catalyst was examined by a 24-h chronoamperometric test, which proved to be highly stable with $\sim 85\%$ retention of initial current density (Fig. 4d).

The high catalytic activity of CoS₂/CoP/CC for the HER and OER may be attributed to the following points: (a) the drastic electron interactions and synergistic effects of CoS₂/ CoP heterointerfaces can raise the catalyst activity; (b) the CC as the substrate cannot only improve the conductivity of the hybrid materials, but also provide the porous structures and open space between nanoclusters will accelerate the diffusion of active reactants and reaction products; (c) the 3D configuration of nanoclusters with rough textures and increased surface area could expose more active sites and could serve as the electron "highway" to improve charge-transfer efficiency.

Conclusion

In summary, a novel flexible CoS2/CoP/CC cathode was designed and fabricated. Vertically aligned CoS₂/CoP heteronanoclusters anchored on flexible and conductive carbon cloth have been prepared by a simple two-step method. The CoS₂/CoP/CC served as an outstanding binder-free cathode electrode for the HER and OER exhibiting low

overpotentials and excellent durability. The improved electrochemical activity could be attributed to strong electron interactions and synergistic efforts between CoS_2 and CoP, abundant active sites of the heterostructures, and enhanced smaller charge-transfer resistance. This work represents a simple and feasible method to design and explore effective non-noble metal hybrid materials as efficient catalysts for the practical application in renewable energy conversion and storage.

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