

Vanadium doped cobalt phosphide nanorods array as a bifunctional electrode catalyst for efficient and stable overall water splitting



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HIGHLIGHTS

- V-CoP NRs/CC was prepared via hydrothermal and phosphating process.
- It demands 1.491 and 1.606 V to deliver j_{10} and j_{50} , respectively.
- V–CoP NRs/CC possesses strong stability for more than 40 h at *j*₅₀.
- V-doping leads defects and distortions on the material surface.

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GRAPHICAL ABSTRACT



ABSTRACT

For the sake of sustainable development, water splitting without other pollutants has been a candidate technology in green energy. Due to the low efficiency of water splitting, innovative breakthroughs are desirable to improve efficiency significantly. Nowadays, the rational design of non-precious metal-based robust bifunctional catalysts is considered to be a feasible way to promote both the cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER). Herein, we proposed a vanadium doped CoP nanorods array catalyst grown on carbon cloth (V–CoP NRs/CC) as a bifunctional electrode material. When V–CoP NRs/CC employed as both anode and cathode materials, it only demands low cell voltages of 1.491 V and 1.606 V to drive a current density of 10 mA cm⁻² (j_{10}) and 50 mA cm⁻² (j_{50}) in 1 M KOH alkaline electrolyte. Especially, V–CoP NRs/CC can maintain its outstanding electrocatalytic performance for more than 40 h at j_{50} in overall water splitting.

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Introduction

At present, to solve pressing problems of modern society, that is, the shortage of fossil energy and the deterioration of the ecological environment, overall water decomposition technology has become a hotspot for researchers [1,2]. Overall water splitting consists of two half-reactions in alkaline electrolyte: the HER for cathodic and the OER for anodic [3]. The HER can be achieved by two electrons transfer reaction while the OER is a four electron-proton coupling reaction [4,5]. However, the sluggish kinetics leads to low energy conversion efficiency, and for which reason, the practical potential of overall water splitting is higher than the theoretical voltage (1.23 V) [2,6]. Thus, to accelerate the decomposition of water molecules and reduce power consumption, researchers are committed to designing efficient and inexpensive catalysts for water splitting.

Currently, Pt-based materials with negligible overpotential are state-of-the-art catalysts to the HER [7] and IrO₂ and RuO₂ are considered to be the best two catalysts for the OER [8,9]. But their universal applications are hindered by limited crustal storage and exorbitant price. Over the past decades, a massive number of articles about outstanding electrocatalysts derived from earth-enriched elements for the HER and the OER have been published [2,10], such as phosphides [11,12], sulfides [13-15], selenides [16], oxides [17,18], layered double hydroxides [19], etc. Among them, cobalt phosphide with excellent catalytic performance has been studied extensively. For instance, Cheng et al. synthesized a multifunctional carbon cloth supported cobalt phosphide electrocatalyst (CoP@CC) that demands a low cell voltage of 1.68 V to drive j_{10} when applied as both anode and cathode materials, making this catalyst a potential candidate in industrial application [20]. However, researchers are not satisfied with the results that have been achieved, and they are looking for a way to further improve the performance of catalytic materials. Based on recent researches, a strategy for producing defects through heteroatom doping has been extensively studied [21,22]. Reported defects include anions and cations vacancies, inherent defects, dislocation, etc [23]. The increase in defects will change the performance of electronic and surface materials, usually resulting in enhanced electrocatalytic performance [24]. Qu et al. reported a one-step hydrothermal method to synthesize V-doped Ni₃S₂ nanowire arrays directly grown on nickel foam [25]. They found that V-doping leads to a large number of free carriers around the Fermi level, which contributes to an elevated charge transfer efficiency of V-doped Ni₃S₂ nanowires in the HER.

In this article, we design a V–CoP NRs/CC electrocatalyst for overall water splitting, which was produced *via* the hydrothermal and phosphating process. The obtained V–CoP NRs/CC shows superior catalytic activity toward the HER with a low overpotential of 63 mV at -10 mA cm⁻² in 1 M KOH alkaline media. Besides, it also capable of catalyzing the OER with high efficiency achieved an overpotential of 222 mV. As a bifunctional electrocatalyst, when used as both the cathode and anode for overall water splitting, V–CoP NRs/CC requires a cell voltage as low as 1.491 and 1.606 V to achieve j_{10} and j_{50} in 1 M KOH. Furthermore, V–CoP NRs/CC can maintain its outstanding electrocatalytic performance for more than 40 h at j_{50} in overall water splitting. Besides, we expect that this work can guide researchers to create outstanding catalysts at the technical level.

Experimental methods

Chemicals and materials

Carbon cloth (CC, WOS1009) was purchased from CeTech Co., Ltd. Vanadium(III) chloride (VCl₃) was bought from Saan Chemical Technology (Shanghai) Co., Ltd. Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O) was provided by Shanghai Maclin Biochemical Co., Ltd. Urea (CH₄N₂O), ammonium fluoride (H₄FN), and sodium hypophosphite (NaH₂PO₂) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. CC needs further cleaning and hydrophilic treatment, while others can be used without further treatment.

Fabrication a series of V_x-CoP/CC

CC (1 cm \times 4 cm) was treated with concentrated nitric acid at 90 °C for 2 h, then ultrasonicated with ethanol and water for 10 min, respectively. In this work, V_x -CoP/CC was synthesized by hydrothermal phosphating strategy. In a typical synthesis, 0.06 mM, 0.08 mM, 0.10 mM, 0.12 mM (different vanadium doping levels: 3%, 4%, 5%, 6%) VCl₃, 2 mM Co(NO₃)₂·6H₂O, 6 mM H₄FN, and 10 mM Co(NH₂)₂ were dissolved in 30 mL deionized water to obtain the precursor solution in 50 mL polytetrafluoroethylene liner. The prepared precursor and one piece of treated CC were transferred into a 50 mL Teflon-lined stainless-steel autoclave, after which the autoclave was heated to 120 °C and maintained for 6 h. The next step was the low-temperature phosphating treatment, which is calcination in a tube furnace: 0.5 g NaH₂PO₂ and post-hydrothermal CC were placed on the upstream and downstream of a porcelain boat, respectively. This phase was carried out at 400 $^\circ\text{C}$ for 2 h and the shielding gas was argon (Ar) at a heating rate of 5 $^\circ$ C min^{-1} to protect the whole reactions. Finally, a series of $V_{0.03}\text{-}CoP/CC,\,V_{0.04}\text{-}CoP/CC,\,V_{0.05}\text{-}CoP/CC,\,and\,V_{0.06}\text{-}CoP/CC$ nano-catalyst materials grown on carbon cloth were prepared.

Fabrication of CoP NWs/CC

Firstly, 2 mM $Co(NO_3)_2 \cdot 6H_2O$, 6 mM H_4FN , and 10 $Co(NH_2)_2$ carbamide were dissolved in 30 mL deionized water to obtain the precursor solution in 50 mL polytetrafluoroethylene liner. The hydrothermal and phosphating processes of CoP NWs/CC are the same as V–CoP NRs/CC.

Fabrication of Pt/C catalyst

Pt/C (4 mg cm⁻²) electrode was prepared as follows. Typically, 10 mg of 20 wt% Pt/C powder was added in 1 mL solution containing 50 μ L of 0.5 wt% Nafion and 0.95 mL of ethanol, then ultrasonicated for 20min. Finally, the mixture solution was transferred onto the surface of CC several times.

Material characterization

X-ray diffraction (XRD, Bruker AXS GmbH, Germany) test was conducted at an angle range of $10-80^{\circ}$ with a working voltage of 40 kV. The morphology of prepared samples was characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6700, JEOL, Japan). The crystal structures were observed by transmission electron microscopy (TEM, JSM-2100, JEOL, Japan) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Tecnai G2 F30S-Twin, Philips-FEI). Energy dispersive spectrometer (EDS) mappings were analyzed by HAADF-STEM at an acceleration voltage of 300 kV. X-ray photoelectron spectroscopy (XPS) was conducted on a Kratos Axis Ultra DLD with an Al (mono) K_{α} source (1486.6 eV).

Electrochemical measurements

All the electrochemical tests were performed on a CHI660E electrochemical workstation (CH Instruments, Inc., Shanghai) via a typical three-electrode configuration in 1 M KOH electrolyte. Generally, the prepared samples, Hg/HgCl electrode, and a graphite rod were used as the working electrode, reference electrode, and counter electrode, respectively. Especially, in overall water splitting tests, the prepared samples were used as both anode and cathode materials. During all measurements, the SCE reference electrode was precalibrated concerning a reversible hydrogen electrode (RHE). To compensate for the decline of ohmic voltage between the working electrode and the reference electrode, iR compensation is necessary for the performance of working electrodes [26,27]. The real working potential was obtained by the calculation: E (E vs. RHE) = E(vs. SCE) + 0.242 ($E_{H\sigma/H\sigmaC}$)-+ 0.0592 × PH [28,29].

The polarization curve of prepared catalysts was recorded by linear sweep voltammetry (LSV) with a scan rate of 1 mV s⁻¹. The corresponding Tafel curves were obtained by converting polarization curves according to the Tafel equation $(\eta = b \log |j| + a, where \eta$ is overpotential, *j* is current density, and b is Tafel slope). The electrochemical impedance spectrum (EIS) was used to determine the interfacial chargetransfer resistance within the frequency range of 10^5 –0.01 Hz. CVs were tested under a series of sweep speeds (20–180 mV s⁻¹). The scan rate for the 2000 and 5000 cycling tests was set to 100 mV s⁻¹. The time-dependent current density curve for the V–CoP NRs/CC electrode was measured under a constant current density of *j*₅₀ for 40 h.

Results and discussion

The preparation process of the nano-catalytic material grown on carbon cloth in this study is schematically illustrated in Fig. 1, including two steps: hydrothermal and phosphating. The morphology and structure of $V_{0.05}$ -CoP/CC can be observed in Fig. 2, which is a vanadium-doped cobalt phosphide nanorod array structure grown on carbon cloth (V–CoP NRs/CC). As shown in Fig. 2a, as-prepared V–CoP NRs/CC and CoP NWs/CC are well fitted with the pattern of CoP (PDF #29-0497), with diffraction peaks at 31.6°, 36.3°, 46.2°, 48.1°, and 56.8°, corresponding to the (011), (111), (112), (211), and (301) planes, respectively. The SEM images (Fig. 2b–d and Fig. S1) demonstrate that the synthesized V doped CoP nanorods array is growing uniformly on CC. Especially in Fig. S2, we can clearly observe the CoP without V-doping is nanowires array structure. Moreover, compared to CoP NWs/CC, the diameter of V–CoP NRs is smaller and the surface is bumpier (Figs. S3 and S4).

As shown in Fig. 2e and f, the HAADF-STEM images indicate that the surface of V–CoP NRs/CC shows abundant crystal defects and distortions, which indicated that V-doping can cause structural changes in the surface of nano-catalyst materials. Normally, defects are caused by the lattice mismatch and unsaturated or imperfect bonding in each phase [30]. Moreover, the morphology, crystal structure, and the electronic environment of V–CoP NRs/CC was be reformed, which can result in an increase in the accessible internal surface area and exposure of more active edge sites, accelerating electron transfer between the surface of the catalytic material and the electrolyte [31].

In Fig. 2g, the lattice spacing of V—CoP NRs/CC is around 0.254 nm, corresponding to the (112) plane of CoP crystals (CoP, PDF # 29-0497), which is in line with the XRD result. The TEM-EDX images of V—CoP NRs/CC (Fig. S5 and Table 1) further confirm the successful doping of vanadium. The elemental mappings of the selected area in a nanorod were carried out by the STEM-EDX (Fig. 2h—k). The mappings show that V, Co, and P elements are distributed uniformly on the surface of V—CoP NRs/CC.

The chemical compositions and elemental bonding configurations on the surface can be found in the X-ray photoelectron spectra (XPS) test. As presented in Fig. 3a, both CoP NWs/CC and V–CoP NRs/CC exhibit similar XPS survey spectra except that a weak peak is attributed to the V 2p in the V–CoP NRs/CC spectra, which indicated the existence of V atoms. Additionally, C and O were caused by the contamination and the surface oxidation of the catalytic materials [11]. Fig. 3b shows the high-resolution V 2p XPS spectrum of V–CoP NRs/CC. Two peaks located at 517.06 and 524.66 eV can be attributed to the V 2p_{3/2} and 2p_{1/2} states of the V–P bond [32].

The high-resolution XPS of Co 2p regions of as-prepared catalysts is demonstrated in Fig. 3c. The peaks of Co $2p_{3/2}$ (778.7 and 782 eV) and $2p_{1/2}$ (793.6 and 798.2 eV) of V–CoP NRs/ CC are attributed to Co²⁺ with a shift to higher binding energy when compared with those of CoP NWs/CC. The Co 2p binding energy of V-CoP NRs/CC shifts to larger binding energy, implying that the Co carries a partially positive charge [20]. V-CoP NRs/CC (785.8 and 802.8 eV) and CoP NWs/CC (785 and 802.5 eV) are shaky satellite peaks, which may be attributed to excited electron and valence electron collision [33]. As shown in Fig. 4d, the P 2p peaks of V-CoP NRs/CC located at 129.45 and 130.3 eV are attributed to the P³⁻ of the metal-phosphorus bond, which may be a potential electrocatalytic active center, and the peak at 134.2 eV is assigned to oxidized P (PO_4^{3-}) species arising from superficial oxidation of CoP due to air exposure [34]. Similar to the result of the Co element, the peaks of P 2p of V-CoP NRs/CC also shift to a higher energy than those of CoP NWs/CC, indicating the increase in the electron density on the P element and the improvement of electron transfer rate for Co and P [35-37].



Fig. 1 - Schematic preparation of V-CoP NRs/CC.



Fig. 2 – (a) The XRD patterns of CoP NWs/CC and V–CoP NRs/CC. (b–d) The SEM images of V–CoP NRs/CC. (e–g) The HAADF-STEM images of V–CoP NRs/CC. (h–k) The HAADF-STEM image (h) and STEM-EDX elemental mapping (i–k) of V–CoP NRs/ CC.

Finally, according to the XPS analysis results, it can be concluded that V-doping will reshape the electron density and electron transfer on the surface of the material, resulting in a large number of uncoordinated metal ions and P ions, which ultimately leads to the formation of a large quantity of catalytic active center.

The HER performance of as-prepared samples was tested through electrochemical tests in 1 M KOH alkaline electrolyte. Fig. 4a shows the linear scan voltammetry (LSV) curves with iR compensation for V–CoP NRs/CC, Pt/C, and CoP NWs/CC with a scan rate of 1 mV s⁻¹. As expected, the Pt/C possesses the highest HER electrocatalytic performance. Compared to CoP

NWs/CC, V–CoP NRs/CC exhibits remarkably enhanced electrocatalytic performances. The considerably higher catalytic activity exhibited by V–CoP NRs/CC toward the HER can be attributed mainly to the presence of crystal defects and distortions. The formation of defects will cause the generation of holes with unsaturated bonds, followed by the transfer of excess electrons to P atoms, which can reduce the conversation barriers for the transformation of H⁺ ions into H₂ [38].

HER consists of two-electron transfer and it detailed reaction mechanism in alkaline media are as follows: 1) Volmer reaction ($H_2O + e^- \rightarrow H^* + OH^-$), 2) for the second step, there are two possibilities: one is the Heyrovsky reaction



Fig. 3 – (a) The XPS survey spectra of CoP NWs/CC and V–CoP NRs/CC. (b) The XPS spectra of V in V–CoP NRs/CC. The highresolution XPS spectra of Co (c) and P (d) in CoP NWs/CC and V–CoP NRs/CC.

 $(H_2O + e^- + H^* \rightarrow H_2 + OH^-)$ and the other is the Tafel reaction (2 H* → H₂) [21]. Tafel slope of samples is calculated to reflect the mechanism of the reaction, which suggested the potential reaction paths [39]. In Fig. 4b, the Tafel slopes of CoP NWs/CC, V–CoP NRs/CC, and Pt/C are 121.5, 55.2, and 40.2 mV dec⁻¹, respectively. The corresponding HER mechanism of V–CoP NRs/CC and Pt/C is the Heyrovsky-Volmer mechanism [40]. The presence of surface defects in the catalytic material will lead to an improvement in the electronic environment and the production of more electrochemical active centers, which will accelerate the reaction rate of the Heyrovsky step and the Tafel step.

EIS is employed to investigate the kinetics and charge carrier migration resistance of different catalysts at the electrolyte/electrode interface [31]. Nyquist plots in Fig. 5a were fitted by the equivalent circuit, which consists of two pathways: CPE1-Rct for charge-transfer and CPE2-Rp for surface porosity, and the Rc and Rs represent the contact resistance among catalyst layers and the solution resistance, respectively [41]. In the EIS test, a larger semicircle means greater impedance, worse conductivity, and lower electron transmission efficiency, which eventually causes inferior catalytic performance [42]. In Fig. 4c, the EIS semicircle of V–CoP NRs/ CC is smaller than that of CoP NWs/CC, indicating the stronger electron conductivity of the former. The electron-rich character of the defective structures, which could contribute to high electrical conductivity [43].

Moreover, we further compared the HER activity of prepared catalysts, as shown in Fig. 4d and e. In Fig. 4d, when given the potential of -100 mV, CoP NWs/CC, V–CoP NRs/CC, and Pt/C deliver $j_{.14.16}$, $j_{.34.27}$, and $j_{.65.51}$, respectively; similarly, when given the potential of -150 mV, they achieve $j_{.31.91}$, $j_{.77.65}$, and $j_{.132.6}$, respectively. As shown in Fig. 4e, the potentials of CoP NWs/CC, V–CoP NRs/CC, and Pt/C arrived at $j_{.10}$ are 84, 63, and 52 mV, respectively; moreover, they only require 195, 119, and 89 mV to reach $j_{.50}$, respectively. Besides, Fig. S6 shows the CVs test of V–CoP NRs/CC and CoP NWs/CC with a scan rate ranging from 20 to 180 mV s⁻¹. According to the calculation formula (ECSA = C_{dl} /Cs, C_{dl} is the double-layer capacitor, and Cs is the fixed value), electrochemical active area (ECSA) and C_{dl} have a proportional relationship, that is, a larger C_{dl} represents a larger ECSA and a larger ECSA indicates a higher catalytic activity [23]. As exhibited in Fig. 4f, the values of C_{dl} of V–CoP NRs/CC (128.7 mF cm⁻²) is bigger than that of CoP NWs/CC (71.9 mF cm⁻²), which can indirectly prove the larger ECSA after V-doping.

In addition to excellent catalytic performance, an ideal catalyst should also possess strong stability. The HER durability of V–CoP NRs/CC in 1 M KOH is proved in Fig. 4g. After 2000 and 5000 cycles of CV tests, the LSV curves exhibit negligible decline. Moreover, in Fig. 4h, the chronoamperometric test demonstrated that V–CoP NRs/CC can maintain its j_{-50} catalytic performance for at least 40 h without an obvious decrease. The above results reveal that V–CoP NRs/CC has outstanding catalytic performance and stability beyond most reported non-noble-metal based materials, and it possesses huge potential for universal application [44–47].

In addition to the excellent HER performance, we also found that V–CoP NRs/CC has highly active towards OER in the same electrolyte. Fig. 5a shows the LSV curves of V–CoP NRs/CC and CoP NWs/CC catalysts. The existence of oxidation peaks in the LSV curve may be related to the oxidation



Fig. 4 – The electrocatalytic measures of the HER. (a) The LSV curves of CoP NWs/CC, V–CoP NRs/CC, and Pt/C. (b) Corresponding Tafel plots of catalysts. (c) Nyquist plots of CoP NWs/CC and V–CoP NRs/CC. (d, e) Comparisons of samples: (d) current densities delivered at -100 mV and -150 mV, (e) potentials required at j_{-10} and j_{-50} . (f) The C_{dl} measurements of CoP NWs/CC and V–CoP NRs/CC. (g) The LSV curves of V–CoP NRs/CC before and after 2000 and 5000 cycling tests. (h) I-t curve of V–CoP NRs/CC at j_{-50} for 40 h. Electrolyte: 1 M KOH.

reaction on the catalyst surface [48]. The obtained V–CoP NRs/ CC product exhibit an oxygen-defect-enriched structure with fast charge transferability, which helped to assimilate the conversion rate of OH^- ions to O_2 and thus led to outstanding OER catalytic performance [49,50].

The OER reaction is more complex with a four-electron transport process. In alkaline electrolytes, hydroxide ions are oxidized into water and oxygen, involving three adsorption intermediates OH*, O*, and OOH* on the surface of the catalytic material. The OER process under alkaline conditions involves the following steps: 1) $OH^- + * \rightarrow HO^* + e^-$; 2) $HO^* + OH^- \rightarrow O^* + H_2O + e^-$; 3) $O^* + OH^- \rightarrow HOO^* + e^-$; 4) $HOO^* \rightarrow * + O_2 + H_2O + e^-$; 39]. With the increase of defects and the improvement of the electronic environment, the conversion rate of OH⁻ to O_2 is accelerated [51–53]. In Fig. 5b, V–CoP NRs/CC has a low Tafel slope of 166.2 mV dec⁻¹, which is 89.8 mV dec⁻¹ smaller than that of CoP NWs/CC (256.0 mV dec⁻¹).

Fig. 5c and d compare the OER performance of as-prepared catalysts in 1 M KOH alkaline media, which demonstrates the improvement of OER catalytic activity after V-doping. When

given potentials of 400 and 500 mV (Fig. 5c), V-CoP NRs/CC reached $j_{56.07}$ and $j_{136.33}$, which is 42.82 and 88.92 mA cm⁻² higher than those of CoP NWs/CC ($j_{13.25}$ and $j_{47.41}$). Moreover, we can see from Fig. 5d, V-CoP NRs/CC only requires potentials of 222 and 391 mV to deliver j_{10} and j_{50} , which is 158 and 114 mV less than those of CoP NWs/CC catalyst (380 and 505 mV). The OER performance of V-CoP NRs/CC is better than most other non-noble based catalysts [54,55]. The durability of V-CoP NRs/CC in the OER was tested by continuous CV sweeps at a scan rate of 100 mV s $^{-1}$ for 2000 and 5000 cycles and 40 h I-T test. From Fig. 5e we can observe that the LSV curves demonstrate negligible decay after 2000 and 5000 CV cycling tests, suggesting its excellent durability. Moreover, as demonstrated in Fig. 5f, the 40 h I-T curve for V-CoP NRs/CC at i_{50} exhibits no significant change, suggesting its long-term stability. All of these results establish the high catalytic activity and strong durability of V-CoP NRs/CC catalyst for OER in alkaline electrolyte.

We further utilized the prepared V–CoP NRs/CC bifunctional catalyst as both anode and cathode in a two-electrode configuration for overall water splitting in the same



Fig. 5 – The electrocatalytic tests about OER. (a) The LSV curves of V–CoP NRs/CC and CoP NWs/CC. (b) Corresponding Tafel plots of catalysts. (c, d) Comparisons of samples: (c) current densities delivered at 400 mV and 500 mV, (d) potentials required at j_{10} and j_{50} . (e) The LSV curves of V–CoP NRs/CC before and after 2000 and 5000 cycles. (e) I-T curve for V–CoP NRs/CC at j_{50} for 40 h. Electrolyte: 1 M KOH.

electrolyte. Overall water splitting includes two half-cell reactions. The total reaction: $2H_2O \rightarrow 2H_2 + O_2$. In the alkaline electrolyte, cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$; anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ [39]. The theoretical decomposition voltage of water is 1.23 V. However, in practice, the actual voltage is usually higher than the theoretical voltage, due to the obstruction of electrochemical kinetics [56,57].

As shown in Fig. 6a, V–CoP NRs/CC delivers a bigger current density than that of CoP NWs/CC in the same cell voltages for the overall water splitting test, indicating that the prepared V-doped nanomaterials have better catalytic performance. The Tafel slopes of V–CoP NRs/CC (179.9 mV dec⁻¹) is lower than that of CoP NWs/CC of 226.1 mV dec⁻¹ (Fig. 5b), suggesting that it has a faster reaction kinetics. Fig. 6c illustrates that when given cell voltages of 1.6 and 1.7 V, V–CoP NRs/CC delivers $j_{46.93}$ and $j_{110.58}$, which is 36.63 and 69.85 mA cm⁻² higher than those of CoP NWs/CC ($j_{10.60}$ and $j_{40.73}$). In contrast, Fig. 6d shows that the cell voltages of catalysts to achieve current densities of j_{10} and j_{50} , V–CoP NRs/CC is as low as 1.491

and 1.606 V, which is 0.106 and 0.116 V lower than those of CoP NWs/CC catalyst (1.597 and 1.722 V). Furthermore, we tested the long-term stability of V–CoP NRs/CC catalyst. In Fig. 6e, the LSV curves of V–CoP NRs/CC show negligible decay after 2000 and 5000 CV cycling test. In the 40 h I-T test at j_{50} (Fig. 6f), V–CoP NRs/CC demonstrates a negligible decline, which further proves its strong stability.

Besides, we also created a series of V_x -CoP/CC on CC with different amounts of V-doping (3%, 4%, 5%, and 6%), and it comes out that the 5% is optimal content for V-doping. More details can be found in Fig. S8.

According to the above result and discussion, this work demonstrated the detailed reason for such outstanding HER, OER performance of V–CoP NRs/CC. Firstly, the *in-situ* growth of V–CoP on CC makes catalysts possess abundant contact interfaces for facilitating their charge carrier migration. Based on the SEM images and C_{dl} values, it can be concluded that V–CoP NRs/CC nanorods array has a larger electrochemical surface area, which is beneficial to enhancing the surface-



Fig. 6 – The overall water splitting activity tests. (a) The LSV curves of V–CoP NRs/CC and CoP NWs/CC catalysts. (b) Corresponding Tafel plots of catalysts. (c, d) Bar charts of comparisons of samples: (c) Current densities delivered at 1.6 and 1.7 V Cell voltage. (d) Potentials required at j_{10} and j_{50} . (e) The LSV curves of V–CoP NRs/CC before and after 2000 and 5000 cycling tests. (f) I-T curve for V–CoP NRs/CC at j_{50} for 40 h. Electrolyte: 1 M KOH.

active sites of the HER and the OER. Furthermore, the electronic structures and the morphology of prepared catalysts can be reformed after V-doping, and the formation of defects and distortions leads to the generation of many uncoordinated bonds and vacancy defects, which can reduce the conversation barriers for the transformation of H⁺ ions into H₂. The oxygen-rich-defects structure of V–CoP NRs/CC exhibits fast charge transferability, which helped to assimilate the conversion rate of OH⁻ ions to O₂ and thus led to outstanding OER catalytic performance.

Conclusions

In summary, we synthesized a V—CoP NRs catalyst supported on CC via the V-doping strategy and hydrothermal phosphating method, which is proved to be an excellent bifunctional electrochemical catalyst in 1 M KOH alkaline electrolyte. Regarding the potential mechanism, we have made a summary from three aspects: defect mechanism research, electrolysis mechanism research, and XPS analysis. The obtained V–CoP NRs/CC shows superior catalytic activity toward the HER and OER with a low overpotential of 63 and 222 mV at -10 mA cm⁻² in 1 M KOH alkaline media, respectively. As a non-noble-metal electrocatalyst, V–CoP NRs/CC demands very low cell voltages of 1.491 and 1.606 V to deliver j_{10} and j_{50} , respectively, and possesses strong stability for more than 40 h without significant decay during the test of overall water splitting at j_{50} . This work affords a cost-effective and excellent bifunctional electrocatalyst material for overall water splitting in the field of hydrogen production.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2020.09.242.

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