



V-Doped CoP Nanosheet Arrays as Highly Efficient Electrocatalysts for Hydrogen Evolution Reaction in Both Acidic and Alkaline Solutions

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It is of significant necessity to explore inexpensive and high-active electrocatalysts toward hydrogen evolution reaction (HER) in both acidic and basic media. In this work, V-doped CoP nanosheet arrays supported on the carbon cloth (V-CoP/CC) are fabricated through a facile water-bath/phosphorization method. The nanoarray structure on the three-dimensional self-supporting electrode can provide a large electrochemical active surface area with more exposed active sites to accelerate the reaction kinetics. Furthermore, V doping is able to tune the electronic properties and thus enhance the intrinsic catalytic activity of CoP. Consequently, the V-CoP/CC electrode exhibits excellent electrocatalytic activities toward HER in both 0.5 M H₂SO₄ and 1 M KOH solutions with small overpotentials of 88 and 98 mV at a current density of 10 mA cm⁻², respectively. The present work will offer a feasible way to tailor the catalytic activity by hetero-atoms doping toward HER.

Keywords: hydrogen evolution reaction, V-doped CoP, acid and alkaline solutions, nanosheet arrays, water splitting

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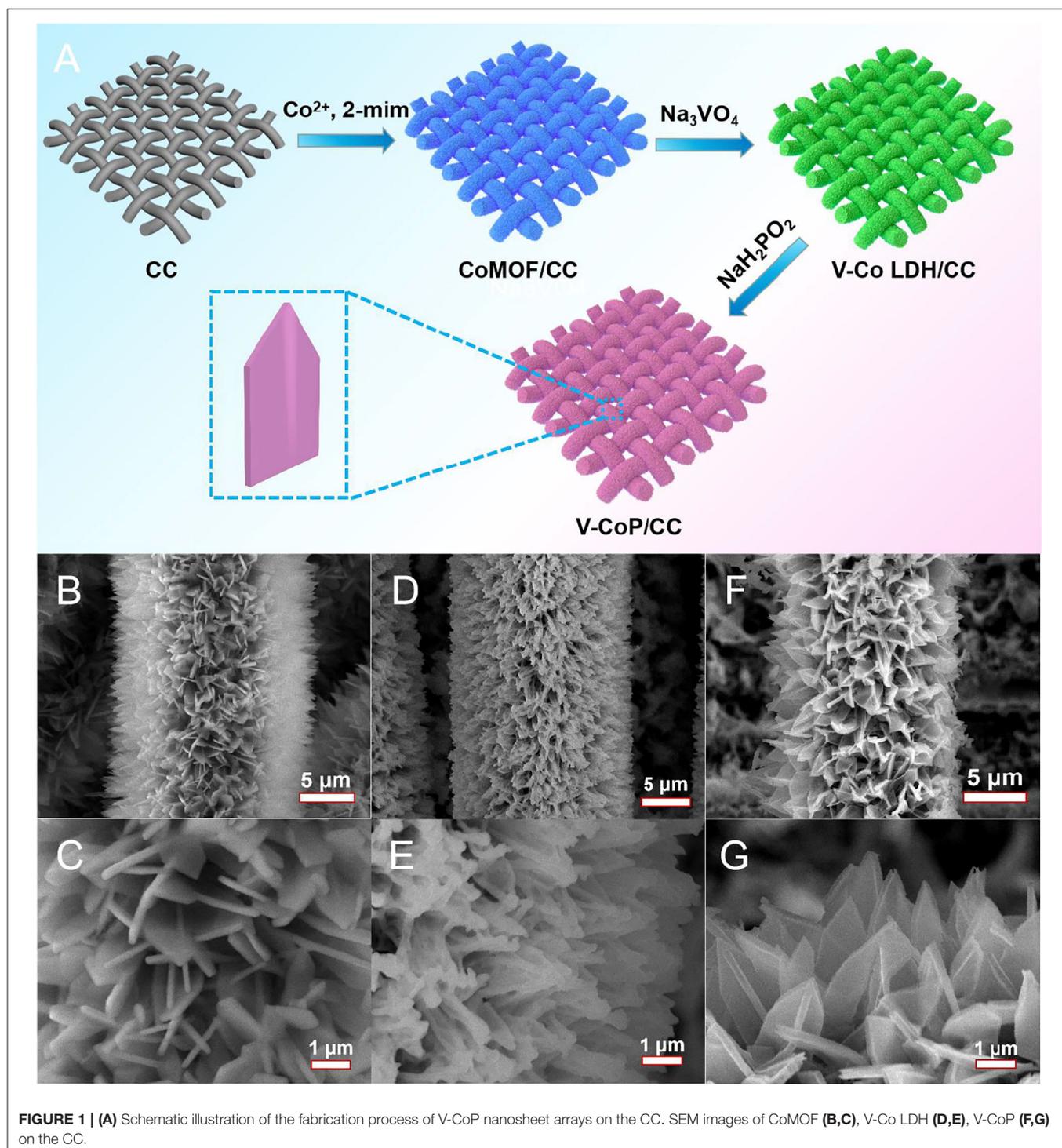
INTRODUCTION

Hydrogen is an effective energy carrier to solve the contemporary energy crisis and environmental pollution (Luo et al., 2014; Seh et al., 2017). Nowadays, hydrogen is still produced mainly from fossil fuels, which suffers from emission of large quantities of carbon dioxide (Zou and Zhang, 2015). Electrolysis of water based on renewable resources is considered as a practical method for producing hydrogen sustainability (Li and Zheng, 2017; Hua et al., 2020). By far, the state-of-the-art electrocatalysts for hydrogen evolution reaction (HER) are still precious Pt-based materials, the scale-up application of which, however, is restricted to their scarcity and high cost. Therefore, the development of low-cost and high-activity electrocatalysts for HER has attracted a wide spread attention.

The earth-abundant transitional metal-based materials, such as alloys (Zhang et al., 2017), oxides (Dong et al., 2019), sulfides (Chen et al., 2019), selenides (Liu et al., 2017), carbides (Lu et al., 2019), nitrides (Yao et al., 2019) and phosphides (Wang J. et al., 2018), have been proved as promising catalysts for HER. Of particular note, more efforts have been made in the design and preparation of transitional metal phosphides (TMPs) as HER catalysts owing to the excellent electrocatalytic performance and long stability in both acidic and alkaline media (Shi and Zhang, 2016; Wang Y. et al., 2017). However, the electrochemical activity of monophase TMPs needs to

be further improved compared with precious metal-based materials. HER occurs at the surfaces of electrocatalysts, hence, increasing the number of active sites is of great benefit in improving the catalytic performance. Notably, the array architecture combined with a bind-free three-dimensional (3D) self-supporting electrodes displays much better HER properties

than the planar electrodes due to the more accessible active sites (Wang Y. et al., 2018). Moreover, hetero-atom doping has been an effective method to improve the performance of electrocatalysts. For example, Pan et al. (2016) investigated the doping effect of Fe, Ni, and Cu elements on the catalytic properties of the Co_2P catalysts. Electrochemical results show



FEI Talos F200X) were used to study the morphology and structure of the as-synthesized samples. The phased structure was identified by X-ray diffraction (XRD, Shimadzu XRD-7000).

Electrochemical Evaluation

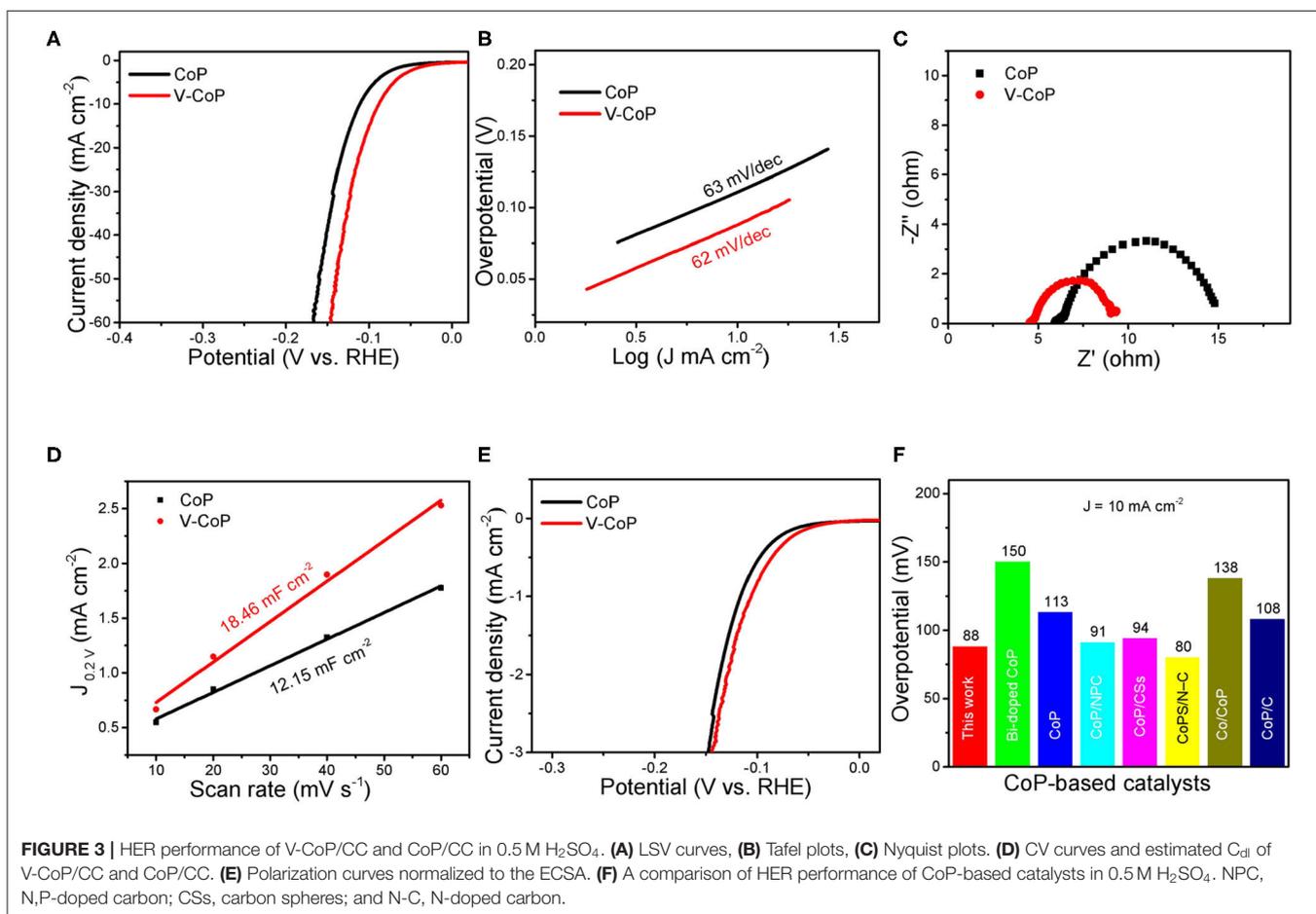
Electrochemical performance of the electrodes was tested on an electrochemical workstation (CHI 660E). The as-received samples and carbon rod were served as the working electrode and counter electrode, respectively. The reference electrodes were Hg/HgO electrode and saturated calomel electrode (SCE) in 1.0 M KOH (pH = 13.8) and 0.5 M H₂SO₄ (pH = 0.6), respectively. Polarization curves were tested by linear sweep voltammetry (LSV) at 2 mV s⁻¹, and the potential values were calibrated to reversible hydrogen electrodes (RHE) with IR-correction, $E_{RHE} = E_{Hg/HgO(SCE)} + 0.097 + 0.059 \text{ pH}$. The IR-correction was conducted by $E_{Corrected} = E_{Raw} - IR_s$, here, R_s corresponds to the series resistance, which can be obtained from the electrochemical impedance spectrum (EIS) measurements. The durability of the sample was studied by chronopotentiometry method at a constant current density of 10 mA cm⁻² and cyclic voltammetry (CV) at a scan rate of 50 mV s⁻¹ for 2,000 cycles. EIS was measured at -0.1 V vs. RHE in the frequency range between 0.1 Hz and 100 KHz with an AC amplitude of 5 mV. CV measurement was tested in the potential range from

0.15 to 0.25 V vs. RHE at various scan rates to estimate the electrochemical active surface area (ECSA).

RESULTS AND DISCUSSIONS

The preparation process of the V-CoP/CC electrode is schematically illustrated in **Figure 1A**. Firstly, CoMOF nanosheet arrays are uniformly grown on the surface of the carbon cloth via a simple aqueous solution reaction between Co²⁺ and 2-mim at room temperature (Fang et al., 2016). The SEM images (**Figures 1B,C**) show the uniform CoMOF nanosheet arrays supported on the CC. Secondly, the as-synthesized CoMOF precursor was immersed into a Na₃VO₄ solution. Owing to the hydrolysis of the solution, the hydrogen ions generated enhanced the etch of CoMOF and release Co ions, at the same time, the local pH increased, making V and Co precipitate on its surface to form V-Co LDH (**Figures 1D,E**). Finally, the V-CoP/CC was obtained through a typical phosphidation process. Remarkably, as shown in **Figures 1F,G**, the as-prepared V-CoP well-retain the nanoarray architecture on the CC. Similarly, CoP maintains the original morphology after phosphidation (**Supplementary Figures 1A,B**).

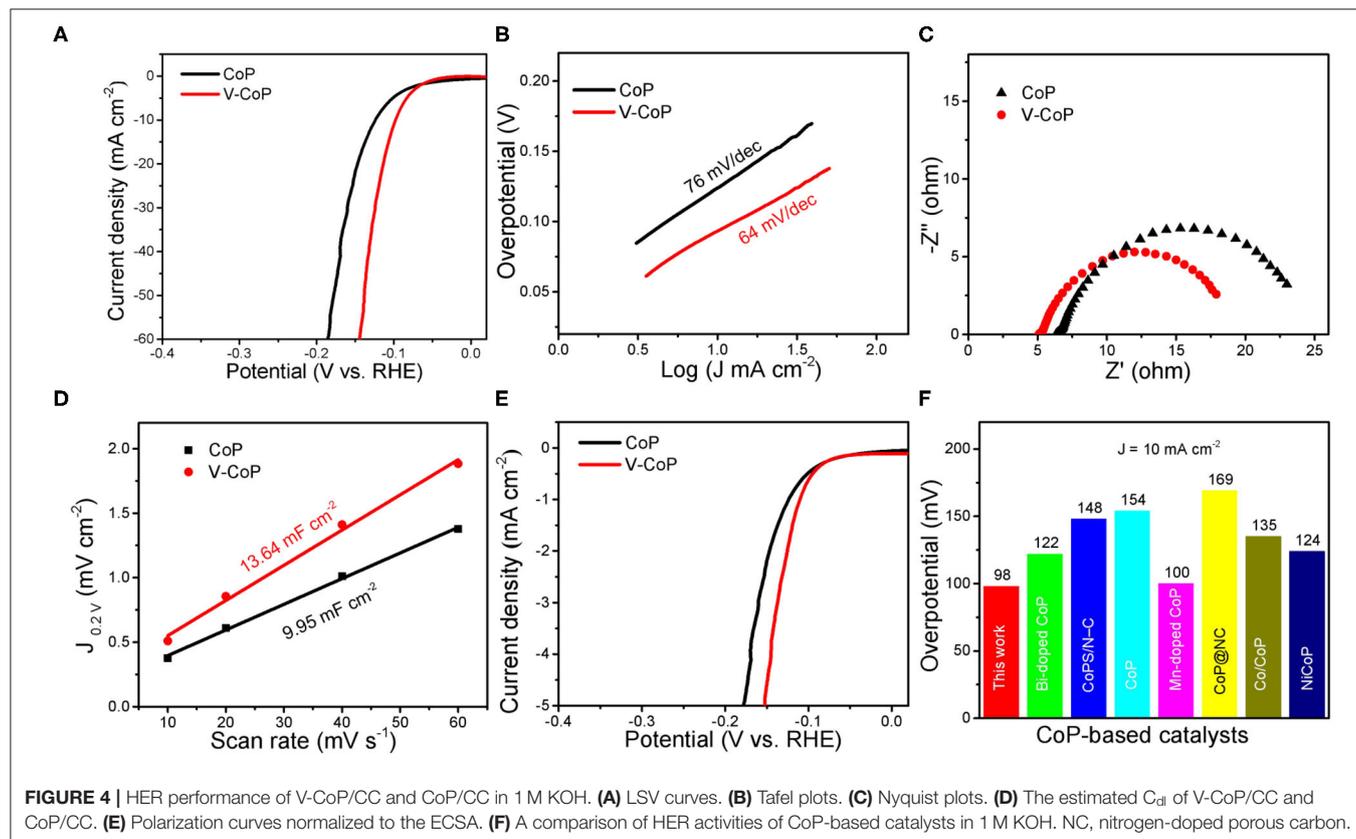
To further investigate the microstructure, the V-CoP nanosheets are characterized by TEM imaging. As displayed

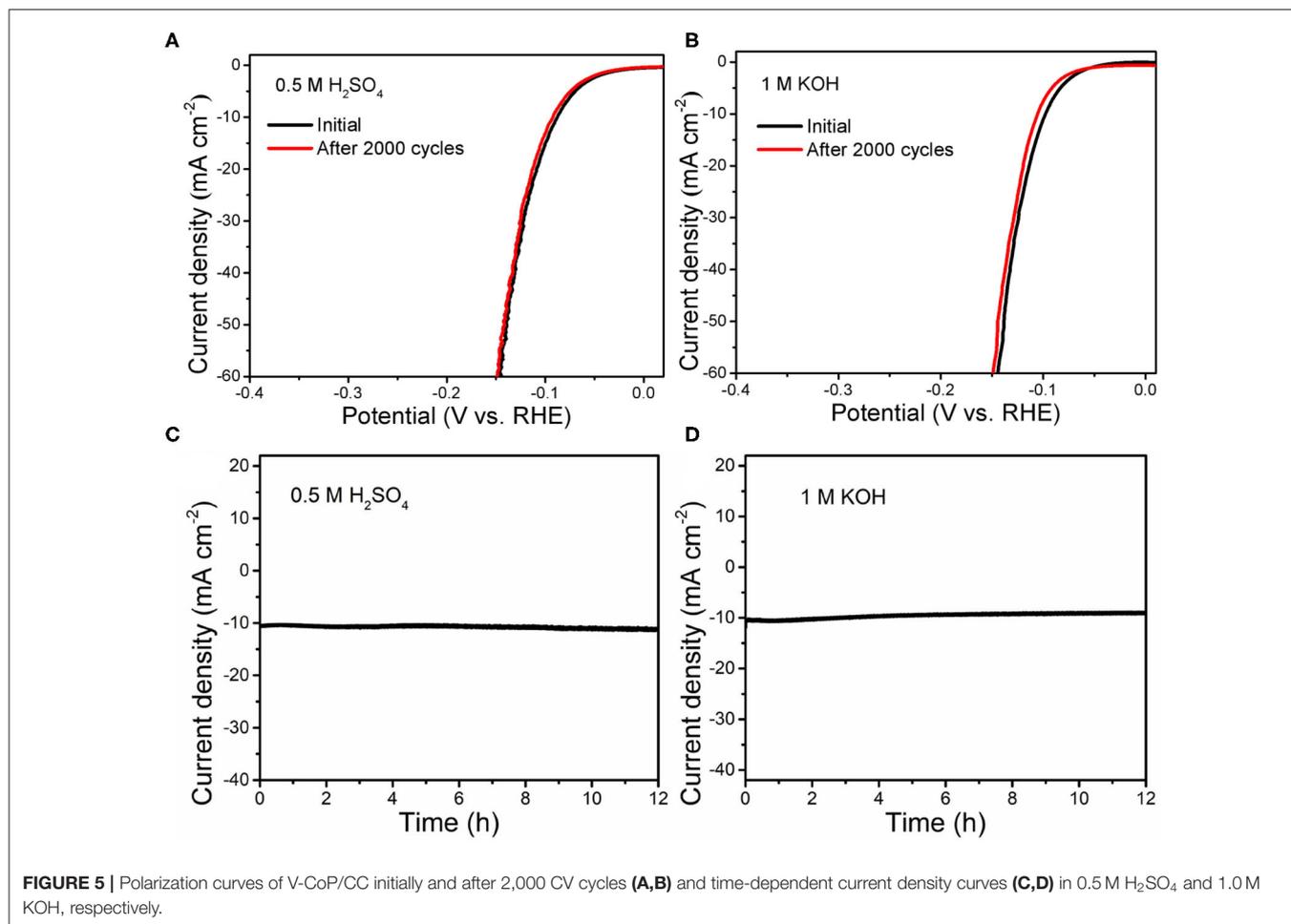


in **Figure 2A**, the V-CoP exhibits a thin nanosheet structure. **Figure 2B** reveals that the nanosheet is consisted of numerous ultrafine crystalline nanoparticles and amorphous components. The HRTEM image (**Figure 2C**) shows distinct crystal spacings of 0.25 nm and 0.19 nm on the nanoparticles, which are indexed to the (111) and (211) facets of CoP, respectively (Wang et al., 2019). Moreover, the specific feature of V-CoP nanosheet is further examined by HAADF-STEM and energy dispersive spectrometer (EDS) elemental mapping (**Figure 2D**). The EDS mapping result demonstrates the homogeneous distribution of Co, P and V elements, indicating that V element is uniformly doped in CoP and the atomic ratio of V:Co is determined to be about 0.23:1. The phase structures of the as-synthesized V-CoP/CC and CoP/CC are analyzed by XRD. As displayed in **Supplementary Figure 2**, apart from the two diffraction peaks corresponding to the CC substrate (Guan et al., 2017), there are no other distinct diffraction peaks. The phenomenon is consistent with the result of TEM that the sample is made up of ultrathin nanoparticles and amorphous components.

The results of the above characterization indicate that V-doped CoP nanosheet arrays on the CC are successfully prepared. The electrocatalytic HER performance of the sample in the acidic solution is first investigated. As displayed in **Figure 3A**, the CoP/CC requires an overpotential of 111 mV to afford the current density of 10 mA cm^{-2} , whereas V-CoP/CC only needs 88 mV to produce the same current density. The Tafel slopes are further calculated to study the HER mechanism on the

electrocatalysts (**Figure 3B**). The Tafel slopes of CoP/CC and V-CoP/CC are 62 and 63 mV/dec, respectively. The similar values indicate that the hydrogen evolution on the two samples follows the same Volmer-Heyrovsky mechanism. To study the kinetics of the catalysts, charge transfer resistances (R_{ct}) have been characterized by EIS at -0.1 V vs. RHE . As shown in **Figure 3C**, the V-CoP/CC manifests a smaller value of R_{ct} (4.6Ω) than that of CoP/CC (9Ω), indicating a faster reaction kinetics (Sun et al., 2020). To further understand the reason for the higher electrocatalytic activity of V-CoP/CC, the electrochemical double layer capacitances (C_{dl}) is measured by CVs with various scanning rates in the potential range between 0.15 and 0.25 V vs. RHE (**Supplementary Figures 3A,B**). As observed in **Figure 3D**, the V-CoP/CC electrode shows a bigger C_{dl} (18.46 mF cm^{-2}) than CoP/CC (12.15 mF cm^{-2}), suggesting that V-CoP/CC has higher ECSA and is able to expose more active sites during the reaction process. To investigate the intrinsic activity of V-CoP/CC, the polarization curves are further normalized to the ECSA (**Figure 3E**). Notably, the V-CoP/CC displays much higher current density than CoP/CC, indicating that V doping can improve the intrinsic catalytic activity of CoP (Liang et al., 2016). The aforementioned results show that V doping can not only increase the number active sites, but also optimize the electronic structure of CoP and improve the intrinsic catalytic activity, thus exhibiting the enhanced catalytic performance toward HER in acidic media. It is worth to note that the HER performance of the present V-CoP/CC electrode outperforms those of most reported





CoP-based catalysts in acidic solution, as shown in **Figure 3F** (Luo et al., 2017; Wang H. et al., 2017; Li H. et al., 2018; Li, Y et al., 2018; Gao et al., 2019; Huang et al., 2019).

The V-CoP/CC electrode has shown enhanced electrocatalytic performance for HER in acidic media. Meanwhile, water-alkali electrolyzer needs active and low-cost electrocatalysts that can work well in basic condition. As shown in **Figure 4A**, the V-CoP/CC also displays good catalytic performance toward HER in 1M KOH solution, reaching the current density of 10 mA cm⁻² with a small overpotential of 98 mV. By contrast, the CoP/CC electrode requires a higher overpotential of 124 mV to obtain the current density of 10 mA cm⁻². Tafel slopes are also employed to investigate the reaction kinetics in basic media. The Tafel slopes of V-CoP/CC and CoP/CC electrodes are 64 and 76 mV/dec, respectively (**Figure 4B**). The value of V-CoP/CC is similar with that of the electrode in acidic media, while CoP/CC exhibits higher Tafel slope in 1 M KOH, suggesting that V-doping can improve the water dissociation process and accelerate the reaction kinetics in alkaline condition. In line with this result, as displayed in **Figure 4C**, the V-CoP/CC shows a smaller R_{ct} (13.9 Ω) than CoP/CC (18.3 Ω). The CVs (**Supplementary Figures 4A,B**) in 0.15–0.25 V vs. RHE are also tested to calculate the C_{dl} (**Figure 4D**). The C_{dl} value

of V-CoP/CC is 13.64 mF cm⁻², which is higher than that of CoP/CC (9.96 mF cm⁻²). The current density is also normalized to the corresponding ECSA, the property of V-CoP/CC is still superior to CoP/CC (**Figure 4E**). It is worth to note that, when normalized to ECSA, the performance difference between CoP and V-CoP is larger in alkaline than in acidic electrolyte. HER in basic media is not only dominated by the binding energy of hydrogen, but also depends on the water dissociation step. The larger difference indicate that V doping can efficiently accelerate the water dissociation process, and thus V-CoP exhibits much better intrinsic catalytic activity. The result reveals that the V-CoP/CC electrode shows not only more active sites but also the higher intrinsic catalytic activity than CoP/CC. Remarkably, the present performance is at the top level among the previous reported CoP-based samples, as summarized in **Figure 4F** (Li et al., 2017; Ge et al., 2018).

To evaluate the stability of V-CoP/CC in both acidic and basic solutions, long-term CV scanning is performed for 2,000 cycles. As displayed in **Figure 5A**, the polarization curves of the electrodes before and after the cycling test are almost overlapped under the acidic condition. As for the alkaline solution, only 8 mV negative shift is observed

after the 2,000-cycling at the current density of 10 mA cm^{-2} (Figure 5B). In addition, the current density-time tests are carried out to explore the stability of the V-CoP/CC electrode. As shown in Figures 5C,D, the current density expresses a negligible decay during a 24-h durability test in 1 M KOH, while there is barely change in the current density during the measurement in 0.5M H_2SO_4 . The above results show that the material has excellent stability in acidic media, and the performance has only a small attenuation under alkaline condition, which is mainly due to the generated corresponding hydroxides on the surface (Zhang et al., 2018; Lwu et al., 2019).

CONCLUSIONS

In summary, a novel V-CoP nanosheet array grown on the CC skeleton has been successfully synthesized through a facile method. The V doping poses a positive effect on the electrocatalytic performance for HER under both acidic and alkaline conditions. The optimized electronic property by V doping is of great benefit in increasing the intrinsic catalytic activity of CoP. In addition, the nanoarray architecture is of great benefit for offering more accessible catalytic active sites. As a result, the V-CoP/CC electrode only requires small overpotentials of 88 and 98 mV to reach the current density of 10 mA cm^{-2} in acidic and basic media, respectively. The present hetero-atom doping strategy would offer a new window for rationally designing high active catalysts toward HER.

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DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/Supplementary Material.

AUTHOR CONTRIBUTIONS

WH carried out experiments and wrote the paper. HS performed and analyzed experimental results. LR carried out experiments. DN designed experiments and contributed to writing the paper. All authors contributed to the article and approved the submitted version.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2020.608133/full#supplementary-material>

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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