Electronic Structure Modulation of Nanoporous Cobalt Phosphide by Carbon Doping for Alkaline Hydrogen Evolution Reaction

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Seawater electrolysis under alkaline conditions presents an attractive alternative to traditional freshwater electrolysis for mass sustainable high-purity hydrogen production. However, the lack of active and robust electrocatalysts severely impedes the industrial application of this technology. Herein, carbon-doped nanoporous cobalt phosphide (C-Co₂P) prepared by electrochemical dealloying is reported as an electrocatalyst for hydrogen evolution reaction (HER). The C-Co₂P achieves an overpotential of 30 mV at a current density of 10 mA cm⁻² in 1 M KOH, along with impressive catalytic activity and stability at large current densities in artificial alkaline seawater electrolyte containing mixed chlorides of NaCl, MgCl₂, and CaCl₂. Experimental analysis and density functional theory calculations reveal that the C atom with strong electronegativity and small atomic radius can tailor the electronic structure of Co₂P, leading to weakened Co-H bonding toward promoted HER kinetics. Moreover, the C doping introduces a two-stepped H delivery pathway by forming C-H_{ad} intermediate, thus reducing the energy barrier of water dissociation. This study offers a new vision toward the development of seawater electrolysis for large-scale hydrogen production.

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1. Introduction

Water electrolysis powered by renewable electricity has been considered as one of the most feasible strategy to achieve scalable high-purity hydrogen production.^[1] For the purpose of electrolytic hydrogen production, tremendous efforts have been devoted to developing the electrolyzer, such as the liquid-electrolyte alkaline electrolysis, the high-temperature solid oxide electrolysis, the proton exchange membrane electrolysis and the anion exchange membrane electrolysis.^[2] However, the shortage of freshwater may become a bottleneck for the application of freshwater electrolysis at an industrial level.^[3] Direct electrolysis of seawater would be a good candidate to replace freshwater for the mass production of H_2 due to the almost unlimited resource.^[4] However, the hypochlorite

and chlorine generated from the competing chlorine evolution reaction (CER) against oxygen evolution reaction (OER) at anode can hinder the hydrogen evolution reaction (HER) and cause electrode corrosion.^[5] The competing chloride oxidations are thermodynamically unfavorable compared with the OER under high alkaline conditions, which guarantees a 480 mV kinetic overpotential without interfering chlorine chemistry.^[6] Thus, an alkaline environment is more favorable for the implementation of industrial hydrogen production under seawater electrolysis. However, it is extremely challenging to develop high-performance seawater HER electrocatalysts with low corrosivity, high conductivity and high poisoning resistance of saline seawater since the active sites of the conventional noble metal electrocatalysts can be blocked by the cation ions and attacked by the hypochlorite generated at the counter electrode in CER.^[7]

Recent studies have witnessed breakthrough to develop various cost-effective electrocatalysts with excellent catalytic activities in alkaline seawater electrolytes.^[7,8] Among these electrocatalysts, transition metal phosphides with excellent electrical conductivity and corrosion resistance have been demonstrated as attractive electrocatalysts for seawater splitting in alkaline freshwater and seawater electrolytes.^[5b,9] The metal concentration in metal phosphide is diluted by the introduction of phosphorus, which makes the phosphides behave like the hydrogenase rather than the neat metal surface.^[10] Additionally, the negatively charged P atoms can draw electrons from metal



atoms and act as Lewis bases to trap the protons, endowing moderate kinetics of hydrogen activation.^[11] However, the development of metal phosphides for alkaline HER is still challenging due to the high energy barrier for water dissociation and the unsatisfactory hydrogen desorption.^[12] Therefore, synergistically tuning the binding energies of water adsorption and dissociation is the key for boosting the intrinsic properties of electrocatalysts for alkaline HER.

Heteroatom doping represents a promising strategy to improve the HER activity as electronic structure of catalysts can be tuned by introducing charge redistribution and enabling energetically favorable water dissociation and hydrogen desorption.^[13] To date, doping a variety of metal elements has been evidenced to enhance electrocatalytic performance of metal phosphides.^[14] On the other hand, nonmetal heteroatom dopants may effectively modulate electronic structure, accelerate charge transfer and activate surface sites of the catalysts.^[15] The P species can be stabilized by sharing electrons with high-electronegative nonmetal atoms, contributing to improved intrinsic activity of metal phosphides.^[16] For instance, nitrogen-doped Co₂P nanorod arrays exhibit superior catalytic activity for HER in neutral medium due to the tailored electronic structure of Co₂P by N doping.^[17] Additionally, oxygen-incorporated Co₂P is demonstrated as an efficient HER electrocatalyst in alkaline condition since the water dissociation and hydrogen adsorption are optimized simultaneously after oxygen incorporation.^[18] Moreover, the nonmetal sites in transition metal based catalysts such as single atom nickel iodide can accelerate the dissociative adsorption of water by forming the I-H_{ads} intermediate, leading to superb electrocatalytic activity in alkaline media for the HER.^[19] Considering smaller atomic radius, higher electronegativity and less valence electrons of carbon than phosphorus, it is expected to boost the catalytic performance of phosphoruscontained materials via enhancing the hydrogen delivery and modulating the bonding of HER intermediates with carbon dopant. Wang et al. have demonstrated that C-doping can endow semiconducting NiPS3 with metallic nature and activate surface sites for hydrogen adsorption by pushing unfilled states to filled lower-Hubbard band above Ni-S bonding band.^[20] Despite the benefit of C doping verified in the cases of trichalcogenidophosphates^[20] and sulfides,^[21] there has been scarce report^[22] on carbon-doped phosphides for HER, which remains uninvestigated in seawater so far.

Herein, nanoporous C-doped Co₂P (C-Co₂P) prepared by dealloving method is proposed as an efficient electrocatalyst for HER in both alkaline freshwater and simulated seawater electrolytes. The C-Co₂P displays an overpotential of 30 mV at 10 mA cm⁻² in alkaline condition, outperforming that of the benchmark Pt/C catalyst. In addition, it also shows outstanding catalytic activity and stability at high current densities in artificial seawater electrolyte containing 1 м KOH, 0.5 м NaCl, 41.2×10^{-3} м MgCl₂, and 12.5×10^{-3} M CaCl₂. Due to the stronger electronegativity and appropriate atomic radius of C, the substitution of C for P can tune the electronic structure and lower the d-band center of Co. Moreover, the in situ Raman spectroscopy reveals the formation of C-H_{ad} intermediate, which promotes the HER process. Density functional theoretical (DFT) analysis indicates carbon doping improves the charge density and electronic states of Co₂P, which gives rise to a reduction of the energy barriers of water adsorption and dissociation. This work would enlighten the development of efficient HER catalysts for both seawater splitting and large-scale H_2 generation.

2. Results and Discussion

As shown in Figure 1a, nanoporous C-Co₂P material is fabricated via selective phase corrosion of the Co-P-C precursor alloy. Hexagonal-close-packed Co and orthorhombic Co₂P phase can be detected in the precursor alloy, which can be identified by the X-ray diffraction (XRD) pattern (Figure S1, Supporting Information). During dealloying, the Co phase is etched, leaving Co₂P phase to form interconnected nanostructure.^[23] Scanning electron microscopy (SEM) images show that bicontinuous nanostructure distributes uniformly with interconnected nanopore channels and C-Co₂P ligaments (Figure 1b). No obvious solid alloy can be seen after dealloying, demonstrating the cobalt phase is completely etched (Figure 1c). In addition, no obvious corrosion current is detected at the end of dealloying, verifying the complete dissolution of the Co phase (Figure S2, Supporting Information). Different from the conventional spinodal decomposition mechanism, well-interconnected and crack-free nanoporous structure is preformed in precursor alloy, thus the formation of broken and dangled ligaments can be avoided during dealloying, indicating good mechanical property of the nanoporous C-Co2P electrode.[24] As evidenced in Figure S4 (Supporting Information), the C-Co₂P electrode preserves the similar shape of the precursor ribbon, demonstrating the potential application of C-Co₂P as the binder-free electrocatalyst.

Figure 1d displays the transmission electron microscopy (TEM) image of C-Co₂P catalyst, further confirming the size of the isotropic nanopore and ligament about 20 nm. The high resolution TEM (HRTEM) image exhibits well-resolved lattice fringes, where the interplanar spacing of 0.201 nm can be indexed as the (211) plane of Co₂P (Figure 1e). The selected area electron diffraction (SAED, inset in Figure 1e) further suggests polycrystallinity ligaments that are composed of small orthorhombic Co₂P nanocrystals. It is worth mentioning that no obvious carbon coating is observed on the surface of C-Co₂P, suggesting possible carbon doping in the Co₂P. In addition, the TEM image and the corresponding energy-dispersive X-ray spectroscopy (EDS) mapping images (Figure 1f) indicate homogenous distribution of Co, P and C atoms. To certify the enhancement of HER activity by C doping, nanoporous Co₂P and C-Co₂P with various C:P ratios are prepared as the counterparts. Figure S5 and Table S1 (Supporting Information) shows the SEM images and compositions of the synthesized nanoporous Co₂P and C-Co₂P with different C:P ratios, demonstrating similar bicontinuous nanostructure of the batch of catalysts.

XRD was carried out to confirm the crystal structure of the as-prepared C-Co₂P and Co₂P catalysts. As displayed in **Figure 2a** and Figure S6 (Supporting Information), the diffraction peak at 40.8°, 43.4°, 52.5°, and 55.8° in XRD pattern can be indexed as the (201), (211), (002), and (040) planes of Co₂P phase, respectively. No Co phase can be detected after dealloying, verifying the complete dissolution of the Co phase. In addition, the C-Co₂P and Co₂P show similar orthorhombic phosphide structure, while the diffraction peaks of the C-Co₂P



Figure 1. a) Schematic of the preparation of nanoporous $C-Co_2P$ electrocatalysts. SEM images of b) the surface, c) cross-section, d) TEM image, e) HRTEM image, and f) the element distribution of nanoporous $C-Co_2P$. The inset in (c) and (e) are the enlarged cross-section SEM image and SAED pattern, respectively.

shift slightly to the higher angle region, indicating the introduction of C leads to the slightly compressed lattice distortion without altering the bulk crystal structure. Moreover, the lattice parameter of (211) plane decreases with the increase of C:P ratio, verifying the compressed lattice distortion caused by the C doping (Figure S7, Supporting Information).

X-ray photoelectron spectroscopy (XPS) is carried out to probe localized electronic states of the C-Co₂P and Co₂P catalysts. As evidenced in Figure 2b and Figure S8 (Supporting Information), the fitting peaks at 778.2, 778.8, and 781.2 eV suggest three states of Co–P, Co–C, and Co–O on the surface, respectively.^[25] The C:P ratio in the C-Co₂P catalysts are further determined from the areal ratio of fitted Co-P and Co-C peaks in the XPS spectra, which are similar to those of the EDS results (Table S2, Supporting Information).^[21] In addition, the C 1s spectrum of C-Co₂P (Figure S9, Supporting Information) also supports the existence of Co–C bond (284.2 eV) in C-Co₂P, which confirms successful doping of carbon atoms into the Co₂P lattices.^[26] Meanwhile, the appearing P 2p peaks (Figure 2c) can be deconvoluted into a pair of peaks at 129.6 and 130.4 eV, which correspond to the typical Co–P states of cobalt phosphide.^[27] In addition, the positive shift of Co 2p spectrum of C-Co₂P relative to Co₂P indicates the reduction of electrons around Co and thus an enhanced electron transfer.^[28] Such variation can be ascribed to the stronger electronegativity of C than P that enhances electron transfer,^[29] as further confirmed by the shift of the P 2p peaks to lower binding energies in C-Co₂P.

Previous works have proved that the nonmetal dopants can adjust the hydrogen adsorption by tuning the electronic structure and distorting the lattices of the parent compounds.^[15a,30] ADVANCED SCIENCE NEWS_____



Figure 2. a) XRD patterns of the Co_2P and $C-Co_2P$ electrocatalysts. XPS spectra of b) Co 2p and c) P 2p of $C-Co_2P$ and Co_2P . d) UPS spectra of the C-Co₂P and Co₂P.

Thus, the modulated electronic effect of C doping is further investigated by the ultraviolet photoelectron spectroscopy (UPS). Figure 2d shows the UPS valence band spectra of the Co_2P and $C-Co_2P$ catalysts. The valence band maximum value is determined as 3.81 eV for $C-Co_2P$, which is 0.31 eV away from Fermi level as compared with Co_2P , implying the shift of d-band center of $C-Co_2P$.^[31]

The electrocatalytic activities of the prepared samples were first evaluated in 1 м KOH freshwater electrolytes. Figure S10 (Supporting Information) shows the polarization curves of the precursor alloy and C-Co₂P with various loadings up to 2.18 mg cm⁻². The enhancement of catalytic performance with the increase of C-Co₂P loading indicates that the nanoporous C-Co₂P is the active material for HER. According to polarization curves (Figure 3a), the C-Co₂P catalyst exhibits an overpotential of 30 mV to achieve a geometric current density of 10 mA cm⁻² (η_{10}). The η_{10} of C-Co₂P is smaller than those of the commercial Pt/C catalyst (34 mV) and counterpart Co₂P (58 mV), demonstrating the promotion role of C dopants in HER activity (Figure 3b). To probe the effects of carbon contents, the HER catalytic activities of C-Co₂P with various C:P ratios were further tested. With the increase of C:P ratio, the catalytic activity of C-Co₂P increases and reaches the highest at the C:P ratio of 0.29 (Figure S11, Supporting Information). The HER kinetics are further evaluated by the Tafel slope, exchange current density (j_0) and HER rate constant (k^0) . The as-obtained C-Co₂P possesses a Tafel slope of 36.9 mV dec⁻¹, lower than those of Pt/C (37.5 mV dec⁻¹) and Co₂P (45.1 mV dec⁻¹), indicating promoted water dissociation kinetics with the Heyrovsky

process as the rate-determining step (Figure 3c; Figure S12, Supporting Information).^[32] The j_0 and corresponding k^0 of C-Co₂P are 1.79 mA cm⁻² and 1.7×10^{-7} cm⁻² s⁻¹, which are 2.81 times higher than that of Co₂P (Table S5, Supporting Information). In addition, the electrochemical impedance spectroscopy (Figure S13 and Table S6, Supporting Information) results further reveal lower charge transfer resistance (R_{ct}) of C-Co₂P (34.9 Ω cm⁻²) in comparison with Co₂P (108.2 Ω cm⁻²), suggesting enhanced charge transfer kinetics during HER.^[33] Note that excess C doping in Co₂P results in higher R_{ct} value and implies hindered HER kinetics. The improved charge transfer is relative to the electronic modulation by appropriate C doping for the C-Co₂P catalyst to lower the kinetic energy barriers of the catalytic processes.^[28,34] Furthermore, Figure 3d and Table S4 (Supporting Information) summarize the HER performance of C-Co₂P and reported electrocatalysts in 1 м KOH. The HER activity of C-Co₂P is comparable to that of the best nonnoble-metal catalysts in alkaline conditions.

The intrinsic catalytic activities of the as-prepared catalysts are further measured by turnover frequency (TOF). To evaluate TOF, the number of active sites is first measured according to the electrochemical active surface area (ECSA). The ECSA of C-Co₂P material is 1.9 times higher than that of Co₂P (Figures S14 and S15, Supporting Information). The carbon dopant might increase the disorder to form active sites for HER, as confirmed by ECSA.^[35] The TOF values of the as-prepared materials are plotted in Figure S16 (Supporting Information). At an overpotential of 100 mV, the C-Co₂P exhibits a TOF value of 0.14 s⁻¹, revealing a superior intrinsic catalytic activity than SCIENCE NEWS ______ www.advancedsciencenews.com

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Figure 3. a) Polarization curves, b) overpotential comparison and c) Tafel plots of the C-Co₂P, Co₂P and Pt/C catalysts in 1 KOH. d) Performance comparison of C-Co₂P with the ever-reported transition metal-based catalysts in alkaline condition. e) Polarization curves and f) galvanostatic curves of the as-prepared catalysts in simulated alkaline seawater containing 1 KOH, 0.5 M NaCl, 41.2 10⁻³ MgCl₂ and 12.5 10⁻³ M CaCl₂.

 Co_2P (0.04 s⁻¹). To identify the catalytic active sites of the asprepared phosphide catalysts, thiocyanate ions with strong metal bonding ability were introduced into the electrolyte.^[36] As shown in Figure S17 (Supporting Information), the current densities of the C-Co₂P and Co₂P decrease obviously in the presence of thiocyanate ions, suggesting that Co atoms are the feasible active sites of the phosphide catalysts. Based on above results, the improved catalytic activity can be attributed to decreased charge-transfer resistance, increased amount of active sites and enhanced intrinsic catalytic activity caused by tailored electronic structure of Co via C doping.

Motivated by the high activity of C-Co₂P in freshwater, the HER performance is further evaluated in simulated alkaline seawater electrolyte. The influence of Ca and Mg ions on the HER performance was first evaluated in electrolytes with different concentrations of Ca and Mg ions. As shown in Figure S18 (Supporting Information), the HER activity of C-Co₂P decreases with the increase of the concentrations of Mg and Ca ions. The decrease in activity may be attributed to the obstruction of active sites and surface poisoning by ions and insoluble precipitates.^[8a] Even so, the C-Co₂P exhibits much higher catalytic activity compared with CoP and Pt/C catalysts in the alkaline electrolyte with similar ion concentrations to natural seawater (Figure 3e). More remarkably, the C-Co₂P catalyst delivers an overpotential of 192 mV to reach a current density of 1000 mA cm⁻², which is superior to the commercial Pt/C catalyst, demonstrating the potentiality of C-Co₂P for industrial applications. Besides the high HER activity, the C-Co₂P electrode exhibits outstanding stability during a long-term measurement operated at various current densities. The C-Co2P delivers slight potential decay of 0.2, 0.6, and 0.8 mV h⁻¹ at current densities of 10, 100, and 1000 mA cm⁻², respectively

(Figure 3f). In addition, no obvious structural degradation is detected for C-Co₂P, demonstrating its high durability for HER in simulated alkaline seawater (Figures S19 and S20, Supporting Information). Moreover, only slight decrease of Mg and Ca concentration is detected, which also confirms good stability and selectivity of the C-Co₂P catalyst (Table S7, Supporting Information). These results indicate respectable activity and stability of nanoporous C-Co₂P in simulated seawater electrolyte.

Considering the favorable catalytic activity of C-Co₂P catalyst, the overall seawater splitting performance is measured by using a two-electrode electrolyzer in which C-Co₂P is employed as both the anode and cathode in artificial seawater electrolyte. As displayed in Figure S21 (Supporting Information), the electrolyzer with C-Co₂P requires an overpotential of 449 mV to produce a current density of 100 mA cm⁻², which is lower than that of the Co₂P catalyst and comparable to those of the previous reports in an alkaline simulated seawater electrolyte (Table S8, Supporting Information). In addition, the electrolyzer operates stably with only slight degradation over 60 h at a constant current density from 10 to 1000 mA cm⁻², verifying the superior durability of C-Co₂P catalyst in water splitting devices.

To further investigate the reaction intermediates and possible role of carbon dopant on C-Co₂P during HER, in situ Raman spectroscopy was applied under various potentials. As displayed in Figure S22 (Supporting Information), no peaks are detected on either Co₂P or C-Co₂P at open circuit potentials and potential above 0 V versus RHE. Interestingly, a peak at 2445 cm⁻¹ is observed on C-Co₂P at a potential of -50 mV versus RHE, which is attributed to the C–H_{ad} vibrational band.^[19,37] In addition, the peak intensity increases when more negative potentials are applied from -50 to -200 mV, demonstrating the formation of C–H_{ad} intermediate during HER. However, no

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such peak is observed when potential was applied for Co_2P . The above results suggest that the water dissociation and H adsorption kinetics are accelerated by carbon doping through the generation of $C-H_{ad}$ intermediates.

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To get further insight into the HER mechanism on C-Co₂P, DFT calculations were performed using the models shown in Figures S23-S26 and Table S9 (Supporting Information). Selected adsorption sites of H* and the corresponding adsorption free energies (ΔG_{H^*}) are shown in **Figure 4**a. Basically, a good HER catalyst should possess the thermoneutral nature for the adsorption and desorption of H with ΔG_{H^*} around zero, which could facilitate the charge transfer processes for both H* intermediate and H2 formation.^[38] The Co sites on both C-Co₂P and Co₂P surfaces exhibit the lowest $|\Delta G_{H^*}|$ value (Table S10, Supporting Information), which suggests that the Co atoms are the preferred HER sites and accords with the electrochemical measurements. In addition, Co sites on C-Co₂P have a more favorable ΔG_{H^*} value (-0.09 eV) compared with Co₂P (-0.15 eV), accounting for much superior catalytic activity toward the HER.

The hydrogen source in alkaline condition comes from the dissociation of H_2O molecule because of low proton concentration. Therefore, the energy barriers of the dissociation of water to form adsorbed H^* and OH^- are discussed and compared on Co_2P and C-Co₂P. Moreover, the in situ Raman results have demonstrated that the C atoms act as hydrogen deliverer that provides moderate bonding to the reaction intermediates involved in the HER. Thus, two water dissociation pathways including direct dissociation pathway (Figures S28 and S29, Supporting Information) and proton-delivery pathway (Figure 4b) are proposed to study the reaction intermediates involved in the HER. The energy barriers of water dissociation step in proton-deliver pathway are lower than those in direct dissociation pathway for both Co₂P (1.26 vs 1.61 eV) and C-Co₂P (1.00 vs 1.51 eV), suggesting preferable proton-delivery pathway. Furthermore, the C site on C-Co₂P gives a much lower energy barrier of water dissociation (1.00 eV) than P site on Co₂P (1.26 eV). As such, the C atoms can expedite water dissociation and H adsorption through C–H_{ads} bond formation, thereby resulting in enhanced HER activity.

The d-band center is used as the descriptor of the adsorbate–metal interaction to further investigate the improvement mechanism for C-Co₂P. As displayed in Figure 4c and Figure S30 (Supporting Information), the projected density of states (pDOS) reveals the orbital hybridization between Co 3d orbital and C 2p orbital of C-Co₂P, which indicates the effective optimization of d-electrons dominated Co atoms. Significantly, the d-band centers of active Co atoms on C-Co₂P and Co₂P surfaces are calculated as -1.615 and -1.567 eV, respectively. This calculation illustrates lowered antibonding energy states after C doping, in agreement with the UPS results. As a result, the d-band center shifts away from the Fermi level



Figure 4. a) The free-energy diagram for HER on $Co_2P(211)$ and $C-Co_2P(211)$ surfaces. b) The relative energy diagram along the proton-deliver pathway on Co_2P and $C-Co_2P$ surfaces. The key structures of intermediates of H₂O splitting on $C-Co_2P(211)$ were shown in pictures. c) The pDOS of Co 3d orbital for active sites on Co_2P and $C-Co_2P$. d) The charge density contour plot of the Co active sites on Co_2P and $C-Co_2P$. The unit is e Bohr⁻³. e) The schematic of enhanced water dissociation and hydrogen desorption ability for $C-Co_2P$ based on the DFT calculation results. Blue, silver, brown, red and white balls represent Co, P, C, O, and H atoms, respectively.





and the interaction between the adsorbate and Co site is weakened, leading to fast HER kinetics.^[39] Further insights can be gained from the charge density contour plots of H* on C-Co₂P and Co₂P surfaces (Figure 4d). The electron density distribution in Co-C region on C-Co₂P shifts closer to C atom than that in Co-P region on Co₂P, which is attributed to the stronger electronegativity and smaller atomic radius of C atom than P atom. As a result, fewer electrons in Co active site can be transferred to interact with H*, resulting in weakened adsorption of H* intermediate. On the other hand, the enlarged Co-H bond length in C-Co₂P also suggests the weaker binding interaction between Co and H after C doping. These results indicate that the modulation of electronic structure of Co atoms by C doping would improve H₂O dissociation and H₂ formation, leading to facilitated HER process in alkaline media. Therefore, it is reasonable to propose efficient dissociative adsorption of water by forming preferred C-H_{ads} intermediates in view of the higher electronegativity of C compared with P (Figure 4e). Subsequently, H* adsorbates combine with H₂O to form molecular hydrogen on Co site. Additionally, the Co site possesses a moderate positive charge state, leading to the accelerated hydrogen desorption.

Benefiting from the chemical stability of cobalt phosphide, the less stable cobalt phase in the precursor Co-P based alloy can be dissolved in the selective dealloying process, forming the 3D nanoporous skeletons.^[23] The present dealloying strategy can be easily extended to prepare other nonmetal-doped cobalt phosphides by predoping desired nonmetal atoms into a precursor alloy. As displayed in Figure S31 (Supporting Information), the nanoporous nitrogen-doped Co₂P (N-Co₂P) possesses similar bicontinuous nanostructure and orthorhombic phosphide phase to nanoporous Co₂P. Remarkably, the synthesized N-Co₂P exhibits lower η_{10} (46 mV) and smaller Tafel slope (39.8 mV dec⁻¹) compared with Co₂P, again verifying that the HER catalytic activity of Co₂P can be enhanced by doping elements with higher electronegativity (Figure S32, Supporting Information).

3. Conclusion

In summary, carbon-doped nanoporous cobalt phosphide prepared by dealloying enables advances in alkaline water electrolysis. The synthesized nanoporous C-Co₂P exhibits an overpotential of 30 mV at 10 mA cm⁻² in 1 \times KOH and good stability at large current densities in artificial alkaline seawater electrolyte. Combining experimental analysis and DFT calculations, C doping can tailor the electronic structure of Co₂P and form C–H_{ad} intermediate through H delivery pathway, which eventually facilitates the HER by facilitating water dissociation and hydrogen desorption. This nonmetal doping strategy can generally boost the HER electrocatalysis for a variety of metal phosphides that are promising non-noble metal catalysts for industrial seawater electrolysis.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

cobalt phosphide, dealloying, electrocatalysis, hydrogen evolution reaction

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