Fluorine-induced dual defects in cobalt phosphide nanosheets enhance hydrogen evolution reaction activity

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ABSTRACT

Introduction of defects in a controllable way is important to modulate the electronic structure of catalysts towards enhancement of electrocatalytic activity. Herein, we report that fluorine incorporation into cobalt phosphide alloy has a unique effect – it creates both F-anion doping and P vacancy, which results in nearly 15-fold enhancement in catalytic activity for hydrogen evolution reaction (HER) in neutral solution. The existence of dual defects in CoP is confirmed by extended X-ray absorption fine structure (EXAFS) curve fitting results and density functional theory calculation. We show that the dual-defect feature is beneficial to increasing the

active site exposure, tuning the surface wettability and optimizing the electronic configuration of CoP for HER. Our fluorine-based modulation protocol may be applicable to other metal alloy electrocatalysts towards more efficient energy conversion reactions.

TOC GRAPHICS

Among the various new and sustainable energy systems, electrolysis of water is considered as a promising technology to generate hydrogen which is regarded as a potential alternative to fossil fuels.¹⁻³

Electrolysis of water involves two fundamental half-reactions: hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode.⁴⁻⁶ While typical precious metal based HER electrocatalysts are efficient and stable in acidic electrolytes, most of the non-noble-based OER electrocatalysts are inefficient and unstable in acidic electrolytes. It is therefore urgently needed to develop highly active and earth abundant based HER electrocatalysts in non-acidic media in order to realize overall water splitting.

During the past few years, numerous metal alloy-based compounds, including metal borides,^{7, 8} carbides,^{9, 10} metal nitrides,¹¹⁻¹³ and metal phosphides¹⁴⁻²¹ have been widely investigated as electrocatalysts for HER. Among those nonprecious HER electrocatalysts, metal phosphides are promising candidates due to their similarity with hydrogenase and suitable d-electron configuration.^{22, 23} Currently, to identify the actual active sites without double metal interference, nonmetal doping (e.g., B, N, and O) has become popular to regulate the electronic configuration of metal phosphides in order to optimize the adsorption energy of reaction intermediates.^{24, 25} For example, it has been demonstrated that oxygen doping can optimize the free energy of water dissociation and

hydrogen adsorption of Co_2P to improve the alkaline HER catalytic activity.²⁶ Moreover, boron doping has also been recently reported to promote HER performance of CoP in a wide pH range.²⁷ However, the most common nonmetal dopings (B, N, and O) are still not effective in increasing active site numbers, which may impede the further enhancement of the catalytic activity of metal phosphide for non-acidic HER.^{28, 29} Thus, it is expected that the incorporation of a special nonmetal element that can simultaneously increase the active site number and modulate the electronic structure of metal phosphide should be able to further boost the catalytic activity.

Lattice vacancies can provide additional active sites to promote enhanced catalytic performance.^{30, 31} The hydrogen/ NaBH_4 reduction is the most used strategy to generate vacancies in the crystal structure of metal oxide/chalcogenides.^{32, 33} However, this method is not very effective to generate vacancies in metal phosphide compounds because of the following reason. The electronegativity of the oxygen group element is much higher than that of 3d transition metals. For example, the electronegativity of O, S and Se is 3.44, 2.58 and 2.55, respectively; and that of Fe, Co and Ni is 1.83, 1.88 and 1.92, respectively. Thus, the electron transfer from metal to oxygen/sulfur/selenium will form ionic metal-O/S/Se bonds due to coulombic attraction. A strong reducing reagent can easily break the metal-O/S/Se ionic bonds and produce anion vacancies in

the compounds. However, the metal-P bonds are covalent bonds in nature as metal and phosphorus atoms have similar electronegativities (2.19 for P). The covalent bonds by electron clouds sharing are very hard to break. Hence, a new method is needed to create vacancies in metal phosphide alloys to boost their HER catalytic activity.

Fluorine is the element with largest electronegativity in the periodic table, and may induce more evident alteration to the electronic structure compared to other nonmetal elements (e.g., B, N, and O). Inspired by this, in this work, we demonstrate that incorporation of fluorine into CoP can uniquely induce dual defects (namely, F dopant and P vacancy) that coexist in the structure of CoP, which results in up to 15-fold enhancement of catalytic performance for HER in neutral media. The extended X-ray absorption fine structure (EXAFS) curve fitting results and density functional theory (DFT) analysis verify the coexistence of F-anion doping and generation of P vacancy. The effect of dual defects in modulating the electronic structure and surface properties of CoP will be elaborated. This is a new and more efficient doping strategy to boost the catalyst performance of metal alloy compounds in water splitting reactions.

Figure 1. Phase and composition analyses of the F-CoP-Vp nanosheets. (a) XRD pattern and (b) SEM image of the nanosheets grown on carbon cloth. (c) TEM image of the nanosheets. (d) HRTEM image showing the lattice of (211) planes. (e) The HAADF-STEM image and corresponding EDX elemental mappings, and (f) line-scan profile of the elemental distributions of Co, P, and F in the F-CoP-Vp-2 sample.

The dual-defect CoP (F-CoP-Vp) nanosheet arrays were synthesized by phosphidation of CoF_2 nanosheet (the process is schematically shown in **Figure S1**). Different fluorine concentrations are realized by controlling the degree of phosphidation

of the precursors. All the doped samples are named as F-CoP-Vp-X NSs, where X denotes the hour of phosphidation (e.g., F-CoP-Vp -1, F-CoP-Vp -2, and F-CoP-Vp-3). X-ray diffraction (XRD) was first used to investigate the possible change in crystal phase before and after F incorporation. **Figure 1a** show that, except for two broad peaks around 25° and 44° caused by the carbon cloth, all the diffraction peaks of F-CoP-Vp NSs are indexed to the orthorhombic cobalt phosphide phase (JCPDS Card No. 29-0497). The scanning electron microscopy (SEM) image unravel that the nanosheets are composed of a large number of nanowires (**Figure 1b**), which can also be seen from transmission electron microscopy (TEM) image (**Figure 1c**). The high-resolution TEM (HRTEM) image in **Figure 1d** shows the lattice spacing of 0.184 nm that corresponds to the (211) plane of orthorhombic CoP. This suggests the F-CoP-Vp still maintains an orthorhombic crystal phase, which agrees well with the XRD result. Furthermore, HAADF-STEM elemental mappings and line scan of F-CoP-Vp (**Figure 1e, f**) confirm that the fluorine has been successfully incorporated, and the Co, F, and P elements are homogeneously distributed in the entire nanosheet.

Figure 2. Confirmation of fluorine incorporation and dual defects. (a-c) In-situ depth XPS spectra of F-CoP-Vp-2 nanosheets. (a) Co 2p, (b) P 2p, and (c) F 1s. The Ar-ion-etching time from 0 to 15 min corresponds to different depth below the top surface. (d, e) Co K-edge XANES spectra, (f) FT-EXAFS curves.

X-ray photoelectron spectroscopy (XPS) was carried out to further study the composition and chemical state information of F-CoP-Vp. The transformation of XPS spectra and elemental contents at different depths in F-CoP-Vp were also detected under the assistant of Ar ions etching. As shown in **Figure 2a**, two peaks located ~778.6 and 793.9 eV are assigned to Co (0) 2p_{3/2}

and Co(0) $2p_{1/2}$, matching well with the electronic state of covalent Co (0)-P bonds in CoP.³⁴⁻³⁶ The peaks ~ 782.3 and 798.4 eV are ascribed to Co (II) peaks which come from the ionic Co (II)-F and Co (II)-O bonds (Note: the existence of Co-O bonds in CoP due to the surface oxidation when exposed to air).^{14, 37-39} The peaks at ~ 786.6 and 803.5 eV are ascribed to the satellite peaks. The ratio of the peak intensity of Co-P/Co-O (Co-F) gradually increases with continuous Ar ions etching, corresponding to more exposure of the 'bulk' Co-P bonds. **Figure 2b** shows the high-resolution P 2p spectra, where two high-resolution peaks at 129.9 and 130.6 eV can be ascribed to the P $2p_{3/2}$ and P $2p_{1/2}$ in CoP.^{14, 34} The peaks located at 134.5 eV can be assigned to P-O bonds due to surface oxidation.^{14, 34} Similar to the Co 2p spectrum, the intensity ratio of Co-P/P-O increases with the extension of etching time (**Figure 2b**). However, in the region of the high-resolution F 1s spectrum (**Figure 2c**), the appearance of F-Co bonds (about 685.5 eV) indicates the successful incorporation of F atoms into the CoP lattice.³⁷ It is noteworthy that the peak intensity of the F-Co bond distinctly decreases with Ar ions etching time. This implies that the degree of F doping in the F-CoP-Vp structure is depth-dependent.

To investigate the local structure of F-CoP-Vp, X-ray absorption near-edge structure (XANES) measurements were carried out. The pure CoP was also studied for comparison. In **Figure 2d**, both of CoP and F-CoP-Vp XANES profiles show a pre-edge peak, which is the characteristic peak of cobalt phosphide alloy.⁴⁰ The absorption edge of F-CoP-Vp shifts slightly to a higher energy compared with that of CoP (**Figure 2e**), indicating the increased average valence state of Co in F-CoP-Vp caused by the most electronegative F atoms incorporation (Note that only Co (0) exists in CoP alloy compound. But there will be Co (II)-F bonds existing in F-CoP-Vp). The Fourier transformation of the k^3 - weighted EXAFS oscillations (FT-EXAFS) at the Co K-edge of CoP and F-CoP-Vp are shown in **Figure 2f**. Both of F-CoP-Vp and CoP show the main peak at around 1.6 Å, which is ascribed to the Co-P bonds. In the doped sample, the Co-P bond length slightly decreases, corroborating the successful incorporation of F atoms in the F-CoP-Vp.⁴¹ Moreover, the fits resulting demonstrate the coordination number of Co-P in the F-CoP-Vp decreased to 3.6 from 6.2 for the pure CoP sample (**Table S2**). The fitting results clearly demonstrate the structure of F-CoP-Vp has been disordered with P vacancies formation

resultant of F incorporation. As well known, lattice vacancy is usually beneficial for electrocatalysis as it provides more active sites. Hence, the depth-dependent XPS in combination with XANES results unambiguously confirm the dual defects of F dopant and P vacancy that coexist in F-CoP-Vp.

Figure 3. Electrocatalysis of the HER in neutral solution. (a) IR-corrected polarization curves of various nanosheet electrodes and Pt/C in 1M PBS electrolyte with Ag/AgCl as reference electrode and a graphite bar as the counter electrode. (b) HER performance comparison. Note that the CoF_2 is assumed to be CoP with F 100% atom. (c) Tafel plots. (d) Nyquist plots. Inset: equivalent electric circuit used for fitting. (e) Generated and theoretical volumes of H_2 over time for F-CoP-Vp-2 nanosheet electrode. (f) IR-corrected

polarization curves of the F-CoP-Vp-2 nanosheet electrode before and after the 3500 CV cycles. Inset: stability test (current density versus time) of the F-CoP-Vp -2 nanosheet electrode at an overpotential of 120 mV over 20 h.

To evaluate the non-acidic HER electrocatalytic activity of the F-CoP-Vp NSs, the catalysts were firstly performed in a three-electrode configuration in 1.0 M PBS solution by linear scan voltammetry (LSV). Pure CoP NSs, CoF₂ NSs and Pt/C were also investigated for comparison. Noting that all as-measured steady-state LSV curves presented were recorded after iR compensation. As presented in **Figure 3a**, the F-CoP-Vp-2 (F 7.61% atom was calculated from XPS measurement) exhibits the best catalytic performance among all of the CoP and F-CoP-Vp samples, with a small overpotential of 108 mV to achieve a geometric current of 10 mA/cm². In contrast, the CoF₂, CoP, F-CoP-Vp-1 (F 13.6% atom) and F-CoP-Vp-3 (F 2.92% atom) NSs electrodes need overpotentials of 258, 215, 169, and 147 mV to reach the same HER current density, respectively. Moreover, the HER current density for the F-CoP-Vp -2 at an overpotential of 200 mV is 110.2 mA/cm², which is nearly 14.8 times that of pure CoP NSs. Note that

the measured activity exhibits a volcano-like dependence on the F content in the investigated catalysts (**Figure 3b**). Meanwhile, the reaction kinetics of the electrodes can be compared by evaluating the Tafel slope and electrochemical impedance. **Figure 3c** shows that the Tafel slope of F-CoP-Vp-2 is 88.9 mV/dec, obviously lower than that of CoF₂ (136.1 mV/dec), CoP (123.2 mV/dec), F-CoP-Vp-1 (109.4 mV/dec), and F-CoP-Vp-3 (94.6 mV/dec). From the electrochemical impedance spectroscopy (EIS) measurements (**Figure 3d**), we can see that the charge transfer resistance (R_{ct}) value of the F-CoP-Vp-2 NSs electrode is much lower than other investigated electrodes, corresponding to most rapid electron transfer and catalytic kinetics during the neutral HER process. Moreover, a nearly 100% Faradaic yield for the F-CoP-Vp-2 NSs electrode during the process of neutral HER process has been determined (**Figure 3e**). Another critical parameter to an HER catalyst is long-term stability. **Figure 3f** shows the result of the accelerated degradation study. The F-CoP-Vp-2 NSs electrode exhibits a fairly stable HER performance with a negligible loss of current after 3500 cycles. The inset in **Figure 3f** displays the chronoamperometry curve of the F-CoP-Vp-2 NSs array under a constant overpotential of 120 mV. Notably, the

stabilized HER current density shows no obvious degradation during the 20 h test. The sample after the durability test was further characterized using XRD, XPS, HRTEM, SEM and elements mapping (**Figure S9**). It is found that the 3D nanosheet network structure, surface chemical composition, and crystal phase of the electrode were all well preserved without obvious change. This further implies the good long-term durability of the F-CoP-Vp NSs electrode for neutral HER.

Figure 4. Mechanism analysis. (a) The C_{dl} linear fitting and calculation. (b) HER polarization curves normalized by the C_{dl} . (c) Static water contact angle measurements. (d) Calculated water adsorption energy. (e) HER reaction pathways on the (211) surface of CoP and F-CoP-Vp. (f) Charge density distribution of CoP (top) and F-CoP-Vp (bottom). (g) Calculated structure model. Color denotation: blue (Co), purple (P), cyan (fluorine), red (O), and white (H). The red circle represents P vacancy.

In the following, we discuss the intrinsic mechanism to the catalysis enhancement.

First, the HER currents were also calibrated to the electrochemical active surface areas (ECSA). Herein, electrochemical double-layer capacitance is evaluated since it is linear proportional to ECSA (**Figure S10, 4a**).²⁸ The calculated value of C_{dl} of F-CoP-Vp-2 NSs (2.34 mF/cm²) is approximately 4.2

times higher than that of pure CoP NSs (0.56 mF/cm^2). This increase is more likely related to vacancy formation instead of the nanosheet morphology. When normalized to the EDLC, the F-CoP-Vp-2 NSs still has the better HER activity than that of pure CoP NSs (**Figure 4b**), indicating the high intrinsic activity of F-CoP-Vp-2 NSs.

The second check is the surface hydrophilicity. For this, contact angle measurements were carried out to both CoP and F-CoP-Vp-2 NSs electrode (**Figure 4c**). It is observed that the pure CoP NSs electrode has a very large contact angle ($\sim 103.2^\circ$) because of the intrinsic hydrophobic surface of the CoP alloy. In contrast, after F incorporation, which dominates on the surface according to the depth-dependent XPS analysis in **Figure 2c**, the sample has a significantly reduced contact angle of $\sim 46.1^\circ$, suggesting its hydrophilic surface. This transformation could be ascribed to the strong hydrogen bonding between fluorine and water. Indeed a hydrophilic surface is desirable because it can facilitate the initial adsorption of water (reactants) on the electrode surface and promote the detachment of evolved H_2 bubbles, which is beneficial to the HER catalytic kinetics.^{42, 43}

To further get insight into the intrinsic mechanism for the catalytic performance enhancement due to dual defects, DFT calculations of a model of orthorhombic CoP with and without substitution of P by F were carried out. Interestingly, it is noted that when we construct the model by substituting P with F, the F atom will not occupy the original position of P, but will migrate to a new position and be surrounded by two cobalt atoms. This means it not only provides F doping but also simultaneously creates P vacancy. This unique configuration should be correlated to the strongest electronegativity of F element compared to other common non-metal dopants such as O, S, N, and P. The F-CoP-Vp structural characteristic with dual defects matches well with the XAFS fitting results. Based on the optimized model, the surface adsorption energies are calculated. In general, a typical non-acidic HER process involves H₂O adsorption, activation, and H₂ desorption. **Figure 4d** shows the calculated adsorption energy of water molecules on CoP and F-CoP-Vp surfaces. The water adsorption energy of CoP decreases after F incorporation, from -0.84 to -1.06 eV, indicating an easier adsorption of water molecular on the F-CoP-Vp electrode surface at the initial step. Then, we further calculated the change in Gibbs free energy for adsorption of activated water

($\Delta G_{\text{H-OH}^*}$) and for adsorption of H^* intermediates (ΔG_{H^*}). As shown in **Figure 4e**, both of the adsorption energies for F-CoP-Vp are significantly reduced closer to zero compared to the pure CoP. A decrease in adsorption energy of activated water will accelerate the initial kinetics of water dissociation. The optimized adsorption of H^* will facilitate the kinetics process of H_2 generation in the last step. Hence, the calculated result may account for the observed obvious reduction in the Tafel slope after F incorporation (**Figure 3c**). It needs to be noted that both the water molecular and hydrogen are adsorbed at the Co-Co bridge site for pristine CoP (**Figure 4g**). However, for F-CoP-Vp, the initial water molecule and hydrogen adsorption sites move to the Co and Co-P bridge near the P vacancy and F dopant sites, respectively. Hence, the calculation result also reveals that the dual defects (P vacancy and F dopant) strongly regulate the electronic structure of the CoP, which leads to a positive effect for HER catalysis. Meanwhile, it is noted that fluorine modification in CoP triggers localization of charge density distribution (**Figure 4f**) and thus may induce a decrease in electrical conductivity, which is a negative effect for the electrocatalytic process. Hence, it is expected that an optimized content of fluorine in cobalt phosphide should be able to enhance the HER catalytic performance.

Finally, to explore whether the dual defects is effective for promoting HER activity in alkaline environments, the HER measurements were also repeated in 1M KOH electrolyte. The results are presented in **Figure S11**. Similar to the neutral solution, the F-CoP-Vp-2 nanosheet arrays electrode also has a much smaller η_{10} than those of other control samples (see **Figure S11a**). This is also the case for the Tafel slope; The F-CoP-Vp-2 electrode has a Tafel slope of 81.2 mV/dec, which is much smaller than that of pure CoP (130.3 mV/dec), indicating its superior HER kinetics in alkaline media (**Figure S11b**). The electrode is equally stable in the strong base environment, as seen from the nearly unchanged LSV curve after 3000 cycles (**Figure S12**). After the alkaline HER test, we carried out thorough characterizations to the F-CoP-Vp electrodes, including XRD, XPS, HRTEM, SEM and elements mapping (see **Figure S13**). These results confirm the phase structure, bulk composition, and morphology of the nanosheet arrays remained almost unchanged, which corroborates the good long-term stability of the F-CoP-Vp NSs electrode for alkaline HER. Taking altogether the electrochemical results above, it is inferred that the dual defect strategy by fluorine incorporation is very effective to enhance the HER catalytic activity of CoP alloy NSs in a non-acidic media.

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4 In summary, we have demonstrated that fluorine doping has a unique effect
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7 compared to commonly employed nonmetal (e.g., O, S, N, and P) dopants in metal alloy
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10 electrocatalyst materials for HER. As exemplified by CoP nanosheets array, it is
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13 established unambiguously that the incorporation of fluorine can induce dual defects of
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16 F-anion doping and P vacancies in CoP. The dual defects provide beneficial effects
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19 including increased active sites, surface hydrophilicity, and optimization of electronic
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22 configuration. As a result, the optimized nanosheets array exhibits greatly enhanced HER
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25 catalytic activity in a non-acidic electrolyte. Our study may provide better understanding
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44 ASSOCIATED CONTENT

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Supporting Information Available: The characterizations of controlled samples and detailed experimental methods. This material is available free of charge via ACS

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The authors declare no competing financial interests.

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