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Yin-Yang Harmony: Metal and Non-metal Dual-Doping Boosts Electrocatalytic Activity for Alkaline Hydrogen Evolution

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ABSTRACT

The active site number, water dissociation and hydrogen adsorption free energy are the three main parameters for regulating the activity of electrocatalysts for hydrogen evolution reaction (HER) in alkaline media. However, at present, simultaneous modulations of these three parameters for alkaline HER still remain challenging. In this work, we take the CoP as the model material and demonstrate that metal and non-metal dual-doping strategy can achieve simultaneous modulation of these three parameters by inducing lattice irregularity and optimizing the electronic configuration in CoP nanomaterial. Benefiting from oxygen and copper dual-doping collective effect, the optimized O, Cu-CoP nanowire arrays electrode shows nearly 10-fold enhancement in their catalytic activity for alkaline HER compared to pure CoP nanowire electrode. Our work may provide a new concept to boost performance of non-precious metal electrocatalysts for alkaline HER.

TOC GRAPHICS

Developing clean, efficient and renewable energy source to mitigate the reliance on the combustion of traditional fossil fuels has triggered extensive attentions.¹ Hydrogen, as a central

energy carrier, has been widely regarded a key role player in the future energy era due to its high energy density and pollution-free feature.^{2, 3} Producing hydrogen by integrating the electrocatalytic water splitting and solar-energy conversion offers a potential way for sustainable energy conversion.⁴ It is therefore desirable to develop non-noble metal, highly efficient and cost-effective electrocatalysts for hydrogen evolution reactions (HER).

In the past few decades, owing to earth abundant nature and special d electronic configuration, considerable efforts have been devoted to study the HER properties of 3d transition metal-based compounds, spanning from carbide,⁵ nitride,^{6, 7} phosphides,⁸⁻¹⁰ sulfides¹¹⁻¹³ to selenides.¹⁴⁻¹⁶ To further improve the catalytic activity, metal doping engineering has been regarded as a promising strategy to modify these non-noble metal based electrocatalysts. In previous studies, metal doped HER electrocatalysts, such as Fe-doped CoP nanowire arrays¹⁷ and Mn-doped CoSe₂ ultrathin nanosheets,¹⁸ have shown outstanding activity to catalyze HER in acidic media. While the metal doping is effective in inducing additional active sites exposure and optimizing the free energy of hydrogen adsorption in acidic solution, their HER activity in alkaline media is still poor due to a large kinetic energy barrier for the initial Volmer step (metals are always not hydrophilic).¹⁹ Given that most of non-noble metal based OER catalysts, especially oxides, are unstable in acidic solution, it is therefore very necessary to develop non-noble based electrocatalysts with stable alkaline HER performance in order to achieve overall electrolysis of water in the same alkaline media.

In response to above problem, a few recent studies are undertaken to enhance the alkaline HER electrocatalytic activities by modifying the surface of non-noble metal based electrocatalysts to accelerate the prior Volmer step.^{20, 21} The general method is to introduce metal oxides on the surface of electrocatalysts, because the oxides can lower the energy barrier of water dissociation.^{22, 23} Although this method has been shown effective in enhancing the electrocatalytic activity, the improvement is still marginal probably because the surface oxide blocks active sites exposure and also cannot modulate the subsequent Herovskyy/Tafel step. Recently, anion doping, especially the hydrophilic oxygen doping, has been reported which can modulate both water dissociation and free energy of hydrogen adsorption, thus leading to enhanced alkaline HER activity.^{24, 25} However, it is still an open question whether the doping engineering technique can simultaneously influence the three important factors for alkaline HER: high active sites exposure, optimal water dissociation energy, and hydrogen adsorption energy.

In this work, we successfully achieved the modulation of the above three effects by oxygen and copper co-doping in CoP nanowire arrays, which leads to 10-fold enhancement of the electrocatalytic activity for HER in 1M KOH electrolyte. First, HRTEM unravels notable and massive lattice distortion in the O, Cu-CoP nanowires, which lead to more active sites exposure as evidenced by EDLC measurements. This is extrinsic enhancement. Moreover, density function theory (DFT) calculations verify intrinsic enhancement, that both the water activated and hydrogen adsorption free energy in the O, Cu co-doped CoP nanowire catalysts

are significantly lowered than the undoped sample. Our strategy of combining both metal and non-metal co-doping may open a promising route to boosting the performance of non-noble based electrocatalysts for HER in alkaline media.

Figure 1. (a) XRD patterns of CoP and O, Cu-CoP nanowire arrays. Inset: zoomed in view of the (211) peak. (b) and (c) Co 2p and P 2p XPS spectra of CoP and O, Cu-CoP-2 nanowire arrays. The pink labels correspond to Co-P, and the blue labels correspond to Co-O. The double arrows highlight the change in relative peak intensity as a result of O doping. S stands for satellite peaks. (d) Cu XPS spectra of O, Cu-CoP-2 nanowire arrays.

The O, Cu co-doped CoP nanowire arrays were prepared by a low-temperature phosphidation of Cu-Co₂(OH)₂CO₃ nanowire arrays precursor. In brief, the lower reagent demand of P source and Cu incorporation into the Co₂(OH)₂CO₃ precursor are both the prerequisite for the synthesis of O, Cu-CoP nanowire arrays (morphology of the Cu-Co₂(OH)₂CO₃ nanowire arrays can be seen from **Figure S1**). **As the P source decreases, the oxygen can be incorporated due to insufficient phosphidation, and the generated Co (Cu)-O bonds are inherited from the Cu-Co₂(OH)₂CO₃ precursor.** X-ray diffraction (XRD) characterization of the crystal structure (**Figure 1a**) reveals that both the pure and co-doped CoP nanowire arrays match well with the pure orthorhombic CoP phase (JCPDS Card No. 29-0497). The two broad peaks located at 25° and 44° are due to carbon cloth. There are no impurity peaks appearing in the XRD pattern of O, Cu-CoP, suggesting that the incorporation of both oxygen and copper atoms does not alter the orthorhombic-crystal structure of CoP. However, the diffraction peaks of O, Cu-CoP shift slightly to a higher angle direction compared to that of pure CoP (**Figure 1a inset**), suggesting the decreased lattice parameters in O, Cu-CoP caused by the smaller atomic sizes of Cu and O incorporation. In addition, X-ray photoelectron spectroscopy (XPS) was carried out to further investigate the possible change in chemical composition and chemical state. First, the XPS survey spectrum confirms the presence of O, Cu, Co and P in the sample (**Figure S2**). **Figure 1b** shows the comparative high-resolution Co 2p spectra of both array samples. It is noteworthy that surface oxidation is inevitable for the CoP array when it is exposed to air, leading to the presence of the Co(II)-O bond in CoP. Therefore, for careful

comparison, spectra due to CoP (pink spectra) and Co-O (blue spectra), either natural oxidation CoO_x or O doping, are both included. The Co 2p_{3/2} peak (~779.0 eV) and 2p_{1/2} (794.0 eV) match well with the electronic state of metallic Co (0) in CoP (**Note: CoP is an alloy compound**).^{22, 26} The peaks at ~782.2 and 798.4 eV are ascribed to Co-O bonds.²² By comparing to the Co 2p spectra, we notice that the intensity ratio of metallic Co(0) to Co(II)-O decreases with the O incorporation (when less P source is used), indicating the weakening of phosphidation in the O, Cu-CoP. As for the high-resolution P 2p spectra presented in **Figure 1c**, in addition to the characteristics peaks due to P 2p_{3/2} and P 2p_{1/2} in CoP, a broad peak located at 134.1 eV corresponding to P-O bonds due to natural oxidation are also observed.²⁷ Again, by comparing the intensity ratio of P-Co to P-O bonds, we can see the weaker phosphidation in O, Cu-CoP than CoP. Finally, the appearance of Cu (0) 2p doublets in the O, Cu-CoP product confirms the existence of Cu (0) in the co-doped nanowires (**Figure 1d**).²⁸ **Meanwhile, another two obvious Cu 2p peaks and satellite peaks in Cu XPS spectra are observed that correspond to the Cu-O bonds.²⁹ The Cu-O bonds is a result of weaker phosphidation in O, Cu-CoP (similar to the Co-O bonds inherited from the precursor).** Hence, the XRD and XPS results clearly demonstrate the successful incorporation of both O and Cu into the CoP nanowires.

The morphology and crystalline structure of the co-coped nanowires were further systematically characterized using electron microscopy techniques. The pristine Cu-Co₂(OH)₂CO₃ precursor nanowires fully cover the carbon fibers. After phosphidation, the array features of nanowires for both undoped, single O-doped, and Cu,O dual-doped samples

with different concentrations are preserved (**Figure S2** and **S5**), indicating strong adhesion of the nanowires to the carbon cloth. Transmission electron microscopy (TEM) image also illustrates that the O, Cu-CoP product have a quasi 1D morphology (**Figure 2b inset**). The nanowires have a width in the range of 80-200 nm and a length of a few micrometers. The characteristic lattice fringe of the (011) plane of orthorhombic CoP are presented in HRTEM images of both pure CoP and O, Cu-CoP nanowires (**Figure 2a** and **b**), implying that the oxygen and copper dual-incorporation does not alter the orthorhombic crystal phase, which is consistent with XRD results. However, in contrast

Figure 2. Morphology, structure and chemical composition analyses. (a) and (b) HRTEM images of CoP and O, Cu-CoP. Inset: Corresponding TEM images. The circles indicate the lattice distortion. (c) HAADF-STEM image of O, Cu-CoP. (d-f) HADDF line intensity profile. (g) Schematic illustration of ideal and real atomic location of Co atoms. (h-l) HAADF-STEM image and corresponding EDX mapping images of O, Cu-CoP.

to the relatively regular lattice structure in CoP, the lattices of the doped nanowire become curvy and locally distorted (marked in **Figure 2b**). Such lattice distortion would induce more exposure of active atom sites. To provide more evidence to the co-doping, high-angle annular dark field (HAADF) TEM investigation was also carried out to the O, Cu-CoP sample (**Figure 2c-g**). The incorporated of copper and oxygen atoms are pinpointed as outlined by the brown and orange balls, which are more directly confirmed from the corresponding profile lines. Furthermore, as measured from the HADDF image, the distance between Co-1 and Co-2 in Cu, O-CoP is about 0.33 nm, and that between Co-3 and Co-4 is about 0.29 nm (**Figure 2e and f**). For an ideal crystal structure of CoP, the distance between Co-1 and Co-2 is 0.376 nm, and that between Co-3 and Co-4 is about 0.26 nm. The deviation from the ideal Co sites give solid evidence to the structural distortion in the as-obtained Cu, O-CoP. The energy dispersive X-ray (EDX) elemental mapping analysis (**Figure 2h-l**) further confirms the existence of all the elements and their uniform spatial distributions in the O, Cu-CoP-2 nanowires (5.57 at% Cu according to ICP result). Other nanowire array samples with different Cu concentrations (O,

Cu-CoP-1, 3.11 at% Cu; and O, Cu-CoP-3, 6.42 at% Cu) have also been prepared and they exhibit similar structure feature (see data in **Figure S4** and **S5**). Taking the results above, it is concluded that copper and oxygen atoms are successfully incorporated into the CoP nanowires without changing the orthorhombic phase but with occurrence of obvious lattice distortion.

Figure 3. Electrochemical performance for alkaline HER. (a) IR-corrected polarization curves of O, Cu-CoP nanowire, O-CoP nanowire, CoP nanowire electrodes, and bare carbon cloth in 1M KOH electrolyte with Ag/AgCl as the reference electrode (RE) and a graphite bar as the counter electrode (CE). (b) HER performance comparison. (c) **Tafel plots**. (d) Nyquist plots. (e) Generated and theoretical volumes of H₂ as a function of time for O, Cu-CoP-2. (f) IR-corrected polarization curves of O, Cu-CoP-2 nanowire arrays before and after 5000 CV cycles. Inset: Chronopotentiometric curves the O, Cu-CoP-2 nanowire electrode at 10 and 50 mA/cm² over 24 h. Current densities are all calculated on the basis of electrode area.

To explore the effect of oxygen and copper dual doping to the HER catalytic activity of the CoP nanowire arrays in alkaline media, the electrocatalytic properties of the O, Cu-CoP nanowire array and pure CoP nanowire arrays were thoroughly characterized in 1M KOH solution using a standard three-electrode system using Ag/AgCl (3M KCl) electrode as the reference electrode and a graphite bar as counter electrode. O-CoP nanowire arrays and bare carbon cloth were also investigated for comparison. In order to illustrate the overall electrode performance, the currents are calibrated to the electrode area. Intrinsic catalytic property will be evaluated by calibrating currents to electrochemical surface areas (see below). As shown in **Figure 3a**, the O, Cu-CoP-2 (Cu 5.6 at% based on ICP measurement) shows the best catalytic activity among all the investigated samples, with a low overpotential of 72 mV to research the current density of 10 mA/cm². In comparison, the CoP, O-CoP, O, Cu-CoP-1 (Cu 3.1 at%) and O, Cu-CoP-3 (Cu 6.4 at%) nanowire array electrode require overpotentials of 137, 109, 91 and 85 mV to achieve the same HER current density, respectively. Additionally, at the overpotential of 150 mV, the HER current density of O, Cu-CoP-2 nanowire arrays is 145 mA/cm², nearly 10 times that of CoP nanowire arrays (**Figure 3b**). Note that carbon cloth substrate shows negligible catalytic activity for HER. Meanwhile, the Tafel slope value of the O-CoP-2 nanowire arrays is 57.6 mV/dec (**Figure 3c**), smaller than that of CoP nanowire arrays (76.8 mV/dec), O-CoP (71.3 mV/dec), O, Cu-CoP-1 (64 mV/dec) and O-CoP-3 (62.2 mV/dec), suggesting the better HER kinetic process of O, Cu-CoP-2 nanowire array electrode. Clearly,

both LSV and Tafel results show that the oxygen and copper dual incorporation with an appropriate level benefits the HER catalytic activity.

To further gain insight of the catalytic kinetics during the HER process, the electrochemical impedance spectroscopy (EIS) was performed (see data in **Figure 3d**). The impedance spectra were obtained at the overpotential of 0.2 V between 100 KHz and 0.1 Hz, and the corresponding amplitude of the applied voltage was 10 mV. Obviously, the charge transfer resistance of O, Cu-CoP is smaller than that of CoP. Moreover, the Faradic efficiency measurement was conducted by the water drainage method. As shown in **Figure 3e**, the amount of hydrogen matches well with the theoretical amount of hydrogen, suggesting a nearly 100% Faradic efficiency during the process of electrolysis. Furthermore, the accelerated degradation studies also reveal the good durability of O, Cu-CoP-2 nanowire arrays (**Figure 3f**), that the HER current density shows negligible decay even after 5000 CV cycles. The inset figure in **Figure 3f** also that the overpotentials of the electrode remain stable both at low (10 mA/cm²) and high (50 mA/cm²) current densities over 24 h. This further proves the long-term stability of our dual doped nanowire arrays.

Figure 4. (a) HER polarization curves normalized by the electrochemical double-layer capacitance. (b) The corresponding HER diagram on the (011) surface of clean CoP and oxygen and copper doped CoP. (c) Calculated structural model for free energies of *H-OH and *H adsorption. Color denotation: blue (Co), green (Cu), pink (P), red (O), and gray (H).

The electrocatalytic performance of an electrode is highly related to electrochemical active surface area. Hence, electrochemical double-layer capacitance (C_{dl}) measurements were performed (**Figure S6**) to check the difference in active surface areas between different nanowire arrays. The value of C_{dl} of O, Cu-CoP-2 nanowire arrays (9.14 mF/cm^2) is calculated to be 3.57 times larger than that of pure CoP nanowire arrays (2.56 mF/cm^2), confirming the lattice distortion induced by oxygen and copper dual incorporation can indeed increase active

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4 sites exposure. In order to reveal the intrinsic catalytic activity, the LSV curves of all
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6 investigated samples are also normalized to Cdl (**Figure 4a**). The C_{dl} -normalized results indicate
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8 that, in addition to higher active surface areas, the intrinsic alkaline HER catalytic activity of
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10 the O, Cu co-doped CoP nanowire is also higher than those of pure CoP and O-CoP. This
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12 suggests the enhancement of electrocatalytic performance not merely arises from the increased
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14 active sites exposure; there exist other factors.
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20 To understand the influence of oxygen and copper atoms on the intrinsic catalytic
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22 activity, the reaction coordinates on the CoP and O, Cu-CoP for HER in alkaline media were
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24 studied by density functional theory (DFT) calculations. As well known, HER in alkaline
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26 media occurs via two elementary steps – the initial water dissociation to generate co-adsorbed
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28 OH^* and H^* intermediates (Volmer step), and subsequent release of H^* to produce gaseous
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30 hydrogen (Heyrovsky step or Tafel step).^{30, 31} Based on the free energy diagram (**Figure 4b**),
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32 the adsorption energy of activated water ($\Delta G_{\text{H-OH}^*}$) on clean CoP is 0.62 eV, which is a high
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34 energy to initiate this reaction. By incorporating O and Cu onto the surface of CoP (011), the
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36 free energies for the rate-determining step ($* + \text{H}_2\text{O} \rightarrow \text{H-OH}^*$) are steadily decreased. On the
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38 optimal O, Cu-CoP-2 catalyst, $\Delta G_{\text{H-OH}^*}$ is reduced to 0.34 eV, which is almost half the value on
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40 clean CoP. The optimized $\Delta G_{\text{H-OH}^*}$ could facilitate the dissociation of water, resulting in
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42 accelerated initial HER kinetics. Furthermore, the Gibbs free energy of H^* intermediates
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44 (ΔG_{H^*}) is reduced from 0.65 for CoP to 0.04 eV for O, Cu-CoP-2, indicating the kinetics for the
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46 subsequent H_2 generation is also lifted (**Figure 4b**). Hence, we may infer that the higher
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intrinsic alkaline HER activity on the O, Cu co-doped CoP nanowire arrays than the pure CoP should be attributed to the optimized $\Delta G_{\text{H-OH}^*}$ and ΔG_{H^*} . It should be noted that if the Cu atom incorporation is insufficient or excessive, it will trigger a negative effect for HER. This is because it results in weak or strong binding abilities toward H- and O-containing intermediates, leading to a sluggish Volmer or Heyrovsky/Tafel step. Therefore, compared to O, Cu-CoP-1 and O, Cu-CoP-3, the O-CoP-2 shows the best HER catalytic activity due to optimized $\Delta G_{\text{H-OH}^*}$ and ΔG_{H^*} .

In summary, through both experiments and calculation, we have demonstrated that metal and non-metal dual doping can simultaneously modulate three important parameters (active site number, water dissociation and hydrogen adsorption free energy) of CoP nanowire array electrode for alkaline HER. The O, Cu co-doped CoP nanowire arrays with an optimized doping content exhibit nearly 10-fold enhancement in catalytic activity compared with undoped CoP nanowire arrays. As evidenced by HRTEM, EDLC measurements and DFT results, the enhancement is mainly due to the dual incorporation of oxygen and copper atoms in CoP, which result in increased active sites exposure, and optimization of activated water dissociation energy and binding free energy of H^* intermediates. Our metal and non-metal dual doping concept may provide new insights for enhancing the non-precious metal electrocatalysts to realize low-cost overall water splitting in alkaline media.

ASSOCIATED CONTENT

Supporting Information

Supporting Information Available: Detailed experimental methods for material synthesis and characterization, electrochemical tests, DFT calculation details; More SEM and XRD data of other control samples; **ICP results**, electrochemical double-layer capacitance measurements; **XRD, Raman, and XPS measurements of the samples after HER tests**. This material is available free of charge via ACS Publication website at <http://pubs.acs.org>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

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Notes

The authors declare no competing financial interests.

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