

Communication

Two-dimensional ultrathin arrays of CoP: Electronic modulation toward high performance overall water splitting



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ABSTRACT

Transition metal phosphides (TMPs) have shown promising performance in electrocatalytic water splitting. However, the sluggish kinetic of oxygen evolution reaction (OER) process deteriorates their activity toward overall water splitting. To overcome this issue, two-dimensional (2D) ultrathin arrays of metal-doped CoP (MCoP; M = Fe, Ni, and Mg) were successfully prepared by using layered double hydroxides (LDHs) as precursors. The as-obtained 2D ultrathin arrays exhibit an outstanding electrocatalytic activity and long-term durability toward both half-reaction in overall water splitting. As a result, the electrolyzer assembled by FeCoP UNSAs consumes a cell potential as low as 1.60 V (at 10 mA cm⁻²). An experimental-theoretical combination study reveals that the electronic structure of Co is modulated via the incorporation of Fe, which benefits the adsorption of water molecule and the dissociation of OH group, accounting for the largely enhanced activity toward overall water splitting.

1. Introduction

The development of water splitting electrocatalysts for efficient anodic oxygen evolution reaction (OER) and cathodic hydrogen evolution reaction (HER) has been regarded as a promising approach for energy storage and conversion systems [1–6]. Up to date, a variety of materials have been robustly explored (e.g., metal alloys, transition metal nitrides, sulfides) for the purpose of decreasing the overpotential of water splitting [7–12]. First-row transition metal phosphides (TMPs) are a typical class of metalloid compounds with superior HER performance, which serves as a promising candidate for water splitting [13–22]. However, these materials still suffer from relatively large overpotential and sluggish reaction kinetics; in addition, their OER performances are rarely studied and demonstrated, which deteriorates their catalytic behavior toward overall water splitting. Therefore, how to obtain new types of TMPs with excellent overall water splitting performance *via* structure design and synthesis exploration is highly desirable and remains a challenge.

Recently, two-dimensional (2D) ultrathin nanosheets have been explored for high-performance electrocatalysts due to their increased number of active sites and enhanced electronic conductivity compared with bulk materials [23–27]. As a result of reduced thickness of 2D nanomaterials, more surfaces with low-coordinated steps, edges, and kinks are exposed, providing abundant active sites to mediate the electrocatalytic process. Moreover, *in situ* growth of ultrathin arrays on

conductive framework would avoid the poor interparticle electron migration between electroactive center and current collector, accelerating the kinetic property of water splitting reaction [28,29]. In addition, the well-organized ultrathin arrays facilitate the penetration of the electrolyte and provide an effective pathway for fast ions diffusion, which is conducive to the mass diffusion in the water splitting. Based on the above considerations, fabrication of 2D ultrathin arrays of TMPs within nanometer scale would be an effective strategy so as to achieve high performance water splitting.

Layered double hydroxides (LDHs), with unique 2D structure in which di- and tri-valence cations are dispersed within the brucitelike layers at an atomic level, have attracted considerable attention as catalysts or catalyst precursors [30–32]. By virtue of the so-called topological transformation property of LDHs materials, herein, we report the preparation of metal-doped CoP (CoMP; M = Fe, Ni and Mg) ultrathin nanosheets arrays (UNSAs) by using CoM-LDHs as precursors: well-defined CoM-LDHs UNSAs were firstly prepared *via* an ultrafast electrosynthesis method, followed by an *in situ* phosphidation transformation from CoM-LDHs to CoMP UNSAs. The resulting FeCoP UNSAs exhibit significantly promoted electrocatalytic activity toward both half-reaction in overall water splitting, with an overpotential of 330 mV and 160 mV for OER and HER (at a current density of 100 mA cm⁻²), respectively. As a result, the electrolyzer assembled by FeCoP UNSAs for water splitting only needs a cell potential of 1.60 V to drive the current density at 10 mA cm⁻², which is among the highest level of

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TMPs electrocatalysts ever reported. Density functional theory (DFT) calculations and experimental results reveal that the electronic structure of Co is modulated *via* the incorporation of Fe; this benefits the adsorption of water molecule and the dissociation of OH group, accounting for the largely enhanced overall water splitting activity. This work provides a facile strategy for the preparation of 2D ultrathin TMPs arrays, which can be extended to the synthesis of other ultrathin metallic phosphides with expected performance in electrocatalysis and energy storage.

2. Experimental section

2.1. Synthesis of 2D FeCoP ultrathin nanosheets array

2.1.1. Preparation of CoFe-LDH ultrathin nanosheets arrays (UNSAs)

CoFe-LDH UNSAs on Ni foam were synthesized *via* an electro-synthesis method. In a typical procedure, a piece of Ni foam ($2\text{ cm} \times 4\text{ cm}$) was pretreated with absolute ethanol, 2.0 M HCl solution and deionized water, respectively (each for 15 min), to ensure a clean surface. The as-obtained substrate was used as the working electrode and placed in an electrochemical cell which was assembled in a three-electrode configuration, by using platinum wire as the counter electrode and Ag/AgCl as the reference electrode. The electrolyte for electrosynthesis of CoFe-LDH UNSAs was obtained by dissolving Co ($(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.09 g), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.208 g) and LiNO_3 (0.78 g) in 50 mL of distilled water. The potentiostatic deposition was carried out at a potential of -1.0 V vs. Ag/AgCl. The resulting CoFe-LDH UNSAs on Ni foam were withdrawn and rinsed with distilled water. A green thin film on the Ni foam substrate was formed and gradually became yellow after exposed in air, which was subsequently dried at 60°C for 6 h. CoCo-LDH, CoMg-LDH, and CoNi-LDH UNSAs were prepared with a similar method.

2.1.2. Preparation of FeCoP UNSAs

The FeCoP UNSAs were prepared by an *in situ* phosphidation process of the CoFe-LDH UNSAs precursor. In a typical procedure, 0.02 g $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ was adopted as phosphorus precursor, which can break into reductive PH_3 . CoFe-LDH UNSAs were annealed in a N_2 stream at 300°C for 1 h, with an initial heating rate of 5°C min^{-1} . The phosphidation process results in the chemical transformation from LDHs to transition metal phosphides. The resulting product was slowly cooled to room temperature in a N_2 stream.

2.2. Characterization

X-ray diffraction patterns of samples were collected on a Shimadzu XRD-6000 diffractometer using a $\text{Cu K}\alpha$ source, with a scan step of 10°min^{-1} and a scan range between 3° and 70° . The morphology of the nanosheet was investigated using a scanning electron microscope (SEM);

Zeiss SUPRA 55) with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were recorded with Philips Tecnai 20 and JEOL JEM-2010 high-resolution transmission electron microscopes. The accelerating voltage was 200 kV in each case. High-resolution TEM (HRTEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images were collected on an FEI Tecnai G2 F20 S-Twin working at 200 kV. The relative energy-dispersive X-ray spectrometry (EDS) elemental mapping in the STEM were operated with a probe focused to 0.2 nm and camera length of 20 cm. X-ray photoelectron spectra (XPS) were performed on a Thermo VG ESCALAB 250 X-ray photoelectron spectrometer at a pressure of $\sim 2 \times 10^{-9}\text{ Pa}$ using Al $\text{K}\alpha$ X-rays as the excitation source.

2.3. Electrochemical measurements

Electrodes were tested on a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co., China) in a three-electrode electrochemical cell using a 1 M KOH aqueous solution as electrolyte at room temperature. A $1\text{ cm} \times 1\text{ cm}$ area of CoP or MCoP UNSAs on Ni foam was used directly as working electrode. A Pt wire and Ag/AgCl electrode were used as the counter and reference electrode, respectively. The distance between the working electrode and the counter electrode was 2 cm. In the OER and HER, cyclic voltammetry and linear sweep voltammetry at a scan rate of 10 mV s^{-1} were conducted in 1 M KOH solution. AC impedance measurements were carried out in the same configuration at -1.0 V vs. RHE from 10^{-1} to 10^6 Hz with an AC voltage of 5 mV.

2.4. DFT calculation

The first-principles calculations were carried out based on density functional theory with generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) function for exchange-correlation potential. The vacuum slabs of $15\text{ \AA}$ were used to avoid interactions between adjacent atom layers. A self-consistent field method was employed in conjunction with plane-wave basis sets of cutoff energy of 400 eV using ultrasoft pseudopotentials in reciprocal space. For the calculation of the density of states (DOS) of CoP and FeCoP, the Γ -point-centered k-point meshes used for the Brillouin zone integrations were $3 \times 3 \times 1$ k-points.

3. Results and discussion

3.1. Synthesis and characterizations

As a typical example, the well-defined ultrathin FeCoP UNSAs are fabricated *via* a topological transformation process using CoFe-LDH as precursor (Fig. 1a). The CoFe-LDH UNSAs on nickel foam substrate are prepared by using a fast electrosynthesis method, which is further

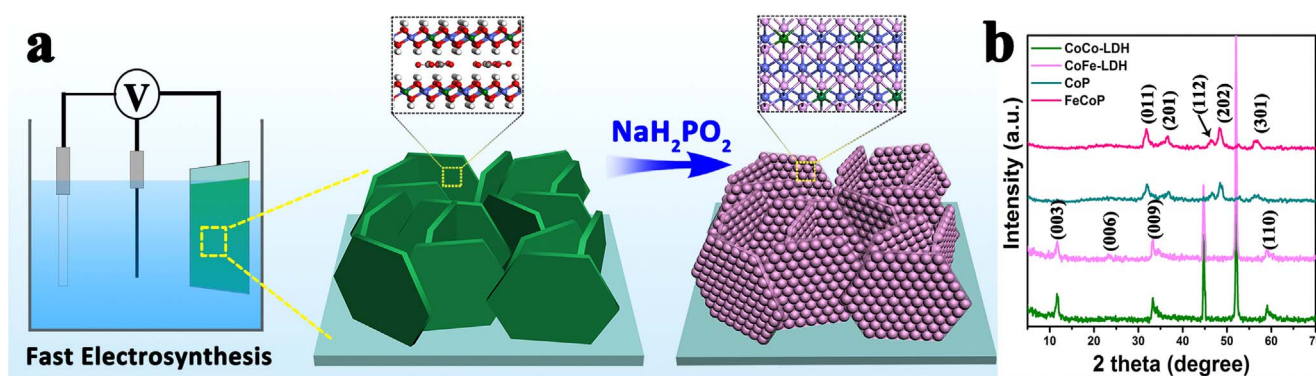


Fig. 1. (a) Schematic presentation for the synthesis of FeCoP; (b) XRD patterns of CoCo-LDH, CoFe-LDH, CoP and FeCoP.

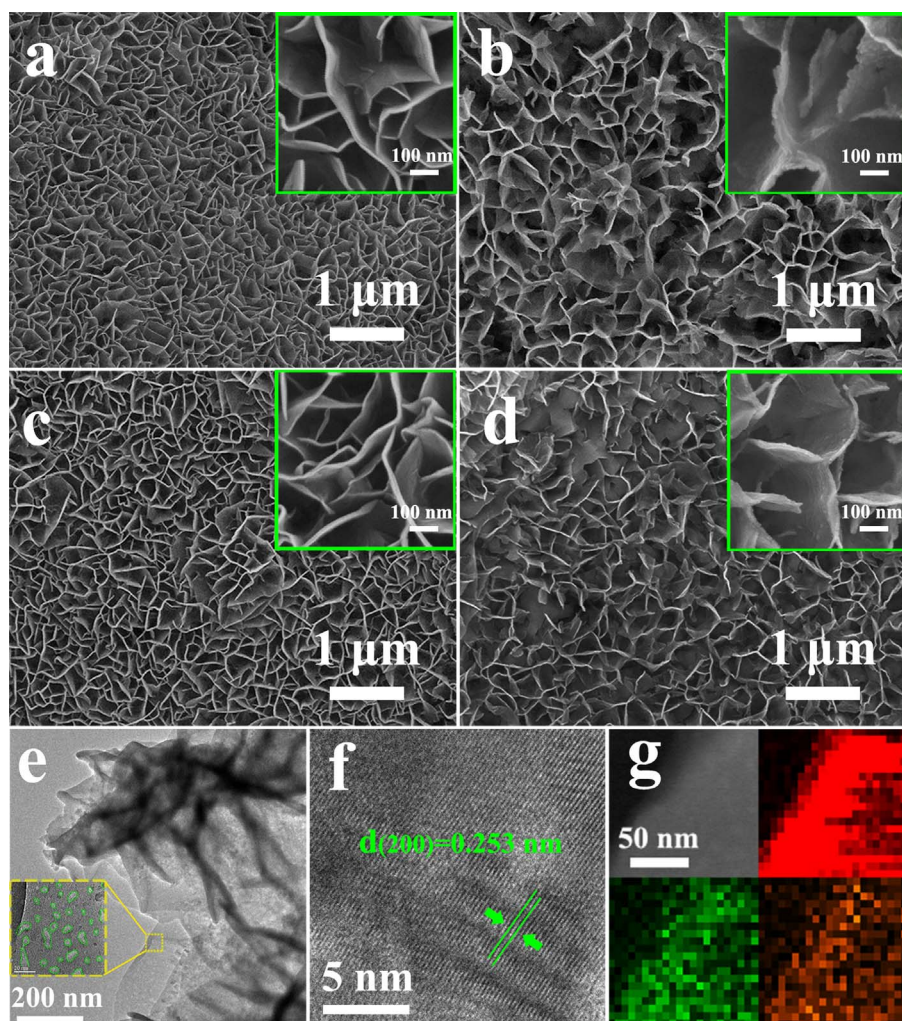


Fig. 2. SEM images of (a) CoCo-LDH, (b) CoP, (c) CoFe-LDH, and (d) FeCoP UNSAs; (e) TEM images, (f) HR-TEM image, (g) HAADF-STEM image and EDX mapping of FeCoP UNSAs.

transformed to FeCoP UNSAs by subsequent *in situ* phosphidation process (see the Experimental Section, [Supporting information](#)). The CoP UNSAs as a reference sample is prepared via a similar route by using CoCo-LDH precursor. Fig. 1b illustrates the X-ray diffraction (XRD) patterns of CoFe-LDH, CoCo-LDH and the corresponding phosphidated product (FeCoP and CoP UNSAs), respectively. The reflections of both two precursors are assigned to rhombohedral LDH phase with an interlayer distances (d_{003}) of 0.77 nm. After the phosphidation treatment, the as-obtained CoP and CoFeP UNSAs show diffraction peaks of (011), (201), (112), (202), (103) and (212), corresponding to the orthorhombic CoP (JCPDS No. 29-0497) [33]. No other crystalline phase is detected after the introduction of Fe, indicating that the incorporation of Fe does not change the crystal structure of CoP.

The low-magnification SEM images of CoCo-LDH and CoFe-LDH show uniform arrays with ultrathin nanosheets (Fig. 2a and b). The inset high-magnification SEM images further reveals that such nanosheets have a lateral size of ~ 500 nm. The thickness of CoCo-LDH and CoFe-LDH precursors is ~ 1.26 nm and ~ 1.05 nm, respectively, confirmed by atomic force microscopy measurements (AFM, Fig. S1). After phosphidation, the as-obtained CoP and FeCoP UNSAs inherit the morphology of their precursors (Fig. 2c and d). The ultrathin gauze-like nanosheets of FeCoP are displayed in Fig. 2e, which can be further revealed by atomic force microscopy (AFM) results with a thickness of about 1.1 nm (Fig. S2). The high-resolution TEM (HR-TEM) image (Fig. 2f) of FeCoP gives well-resolved lattice fringes with interplanar spacing of 0.253 nm, corresponding to the (200) plane. This is a little larger than that of pristine CoP (0.251 nm, Fig. S3), indicating a slight

expansion of lattice fringes after incorporation of Fe atoms into CoP. The typical high-angle annular dark-field scanning TEM (HAADF-STEM) image of an individual FeCoP nanosheet and corresponding energy-dispersive X-ray spectrometry (EDS) mapping analysis (Figs. 2g and S4) reveal the homogenous distribution of Fe, Co and P throughout the whole nanosheet, which further confirms the doping of Fe into CoP matrix. Furthermore, the specific composition determined with TEM-EDS measurements gives a Fe/Co/P ratio of about 1/5/5, as shown in Table S1. In addition, we also prepared Ni- or Mg-doped CoP UNSAs with a similar method (denoted as NiCoP and MgCoP UNSAs, respectively). The resulting NiCoP and MgCoP UNSAs display the same crystal structure (Fig. S5) and a similar architecture (Fig. S6), in comparison with FeCoP UNSAs.

3.2. Electrochemical performance

The electrocatalytic water splitting activities of MCoP ($M = \text{Fe, Ni, and Mg}$) UNSAs were further studied. The as-synthesized MCoP UNSAs were directly used as working electrode for OER and HER catalysis in 1.0 M KOH in a typical three-electrode setup at a scan rate of 10 mV s^{-1} . Considering that OER is the rate-determining step of water splitting due to its sluggish kinetics, the OER performance of the as-obtained electrodes was firstly examined. Linear sweep voltammetry (LSV) results (Fig. 3a) show both a largely enhanced current density and significantly reduced overpotential upon Fe incorporation into the CoP UNSAs. Typically, the FeCoP UNSAs display the lowest onset potential (1.48 V) compared with CoP (1.52 V), NiCoP (1.52 V), and

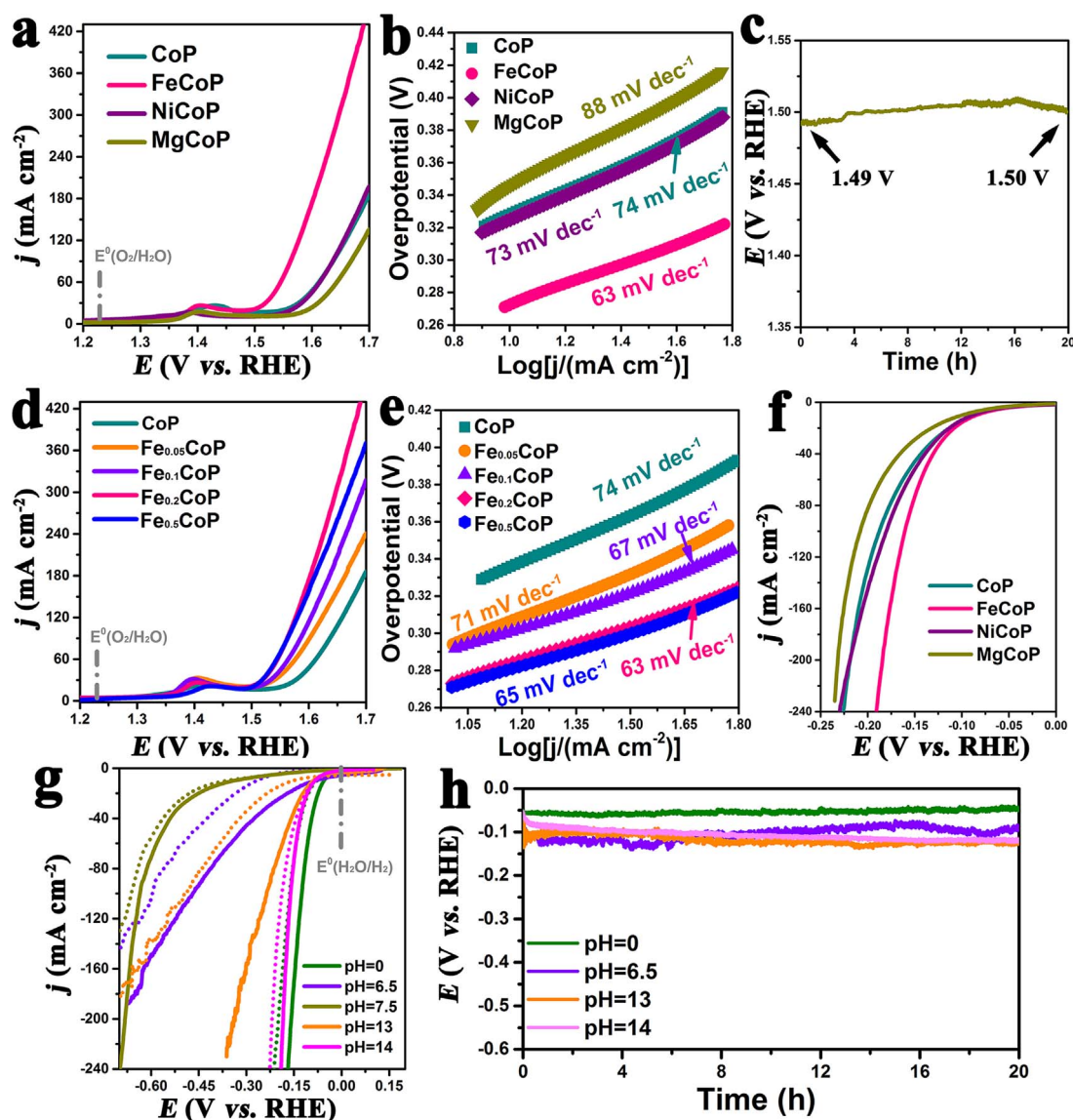


Fig. 3. (a) OER polarization curves and (b) corresponding Tafel plots of CoP, FeCoP, NiCoP, and MgCoP UNSAs; (c) stability test of FeCoP UNSAs in 1 M KOH; (d) OER polarization curves and (e) corresponding Tafel plots of FeCoP with various Fe doping; (f) HER polarization curves of CoP, FeCoP, NiCoP, MgCoP; (g) HER polarization curves and (h) long-term stability profiles of FeCoP in various pH electrolytes.

MgCoP (1.55 V) UNSAs, respectively. At a current density of 20 mA cm^{-2} , the as-prepared FeCoP UNSAs electrode requires an overpotential of 260 mV, which is 60, 60, and 100 mV less than that of CoP, NiCoP, and MgCoP UNSAs, respectively. The superior OER performance of FeCoP is also evident from the largest current density at a fixed potential. For instance, at a potential of 1.60 V (vs. RHE), FeCoP delivers a current density of 173.9 mA cm^{-2} , which is ~ 4 and 7 times higher than NiCoP and MgCoP, respectively. The cyclic voltammetry (CV) results show the similar conclusion according to Fig. S7. The enhanced OER performance of FeCoP is further confirmed by its Tafel slope of 63 mV dec^{-1} (Fig. 3b), which is much smaller than that of CoP, NiCoP, and MgCoP (74 , 74 , and 88 mV dec^{-1} , respectively). This suggests the more favorable reaction kinetics for Fe-doped CoP UNSAs compared with other control samples. In addition, when operating OER at a current density of 20 mA cm^{-2} , the potential of FeCoP UNSAs almost remains unchanged (with an overpotential change of $\sim 20 \text{ mV}$) during a 20 h continuous test, demonstrating an excellent stability of FeCoP UNSAs (Fig. 3c).

In order to investigate the influence of Fe content on the electrocatalytic activity, various molar ratio of Fe are introduced to obtained

Fe_xCoP UNSAs ($x = 0.05, 0.1, 0.2$, and 0.5 , respectively). The sample of $\text{Fe}_{0.2}\text{CoP}$ UNSAs manifests the highest current density at a given overpotential among these four electrocatalysts, indicating the lowest energy input to drive OER process (Fig. 3d). The Tafel slope decreases along with the increase of Fe content (Fig. 3e), which implies that the kinetic properties of OER activity are enhanced by Fe doping. However, the onset potential of FeCoP UNSAs with various Fe contents nearly remains constant, indicating the doping of Fe accelerates the OER kinetic process other than reduces the thermodynamic energy barrier of OER. Similar conclusion is also obtained according to the CV results displayed in Fig. S8.

Subsequently, the HER catalytic performances of these materials were investigated in a three-electrode setup (Fig. 3f). Remarkably, FeCoP UNSAs exhibits superior HER activity with the lowest onset potential ($\sim 45 \text{ mV}$), and only requires an overpotential of 188 mV to drive a current density of 100 mA cm^{-2} . The enhanced HER performance of FeCoP UNSAs is also evident in its Tafel slope of 76 mV dec^{-1} , much lower than CoP, NiCoP, and MgCoP (99 , 103 , and 110 mV dec^{-1} , respectively) (Fig. S9). These Tafel slope values suggest that HER occurs on MCoP via a Volmer–Heyrovsky mechanism ($\text{H}_2\text{O} + \text{e}^- = \text{H}_{\text{ads}} +$

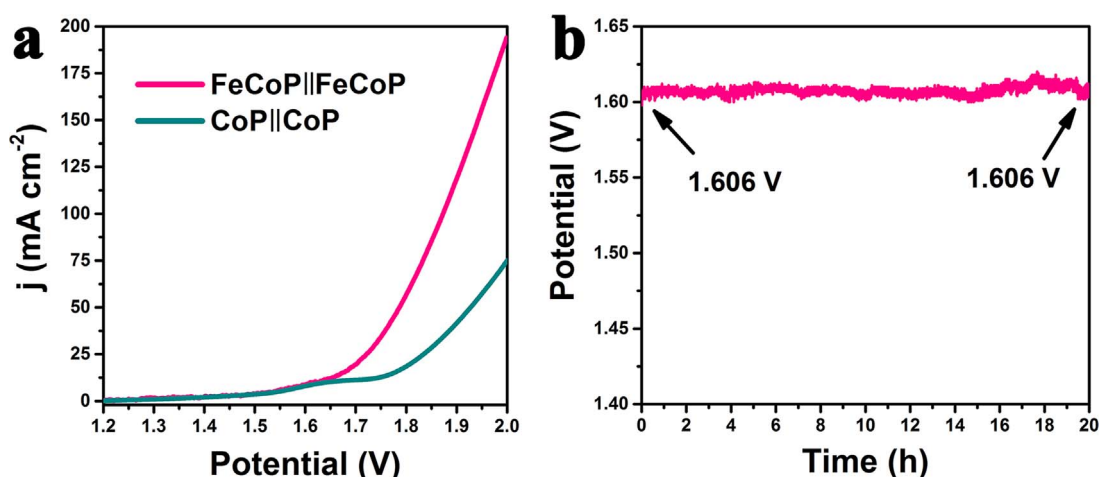


Fig. 4. (a) Polarization of CoP and FeCoP UNSAs served as both cathode and anode electrocatalyst in a two-electrode configuration at a scan rate of 10 mV s^{-1} in 1.0 M KOH and (b) corresponding chronopotentiometric curve at a current density of 10 mA cm^{-2} for 20 h.

OH^- and $\text{H}_2\text{O} + \text{e}^- + \text{H}_{\text{ads}} = \text{H}_2 + \text{OH}^-$ [34]. The lowest overpotential and smallest Tafel slope for FeCoP UNSAs indicate the positive effect of Fe doping toward HER activity. An examination on Co/Fe molar ratios shows that an optimal HER catalytic performance was achieved for $\text{Fe}_{0.2}\text{CoP}$ UNSAs with the lowest onset overpotential ($\sim 45 \text{ mV}$) and the fastest current enhancement upon increasing the biases (Fig. S10a). Moreover, the $\text{Fe}_{0.2}\text{CoP}$ UNSAs delivers the lowest Tafel slope of 76 mV dec^{-1} (Fig. S10b), implying an efficient mass and electron transfer during the HER process. In addition, the faraday efficiency of FeCoP UNSAs toward HER and OER at $j = 50 \text{ mA cm}^{-2}$ was measured to be $\sim 100\%$ and $\sim 99.8\%$, respectively (Fig. S11), indicating a rather high electron utilization efficiency. Based on the above results, we used the FeCoP UNSAs as a bifunctional electrocatalyst for overall water splitting in a two-electrode configuration (Fig. 4a). For the two-electrode electrolyzer based on FeCoP UNSAs, a cell voltage of 1.60 V is high enough to drive an overall water splitting to reach a current density of 10 mA cm^{-2} , which is much superior to that of pristine CoP UNSAs. Remarkably, it is dramatically lower than most of recently reported TMPs catalysts including Co-P films (1.64 V for 10 mA cm^{-2}), CoP nanosheets (1.64 V for 10 mA cm^{-2}), CoP/rGO (1.71 V for 10 mA cm^{-2}) and so on (Table S2). As shown in Fig. 4b, this current density (10 mA cm^{-2}) can be maintained with a negligible decrease over 20 h for FeCoP UNSAs electrode, demonstrating an excellent durability toward overall water splitting operated in alkaline electrolyte.

Although a high activity can be easily achieved in acid electrolyte, the HER performances of electrocatalysts in neutral and basic condition are also of great significance when applied in microbial electrolysis and proton exchange membrane-based electrolysis [35,36]. Accordingly, the design of an excellent pH-universal electrocatalyst with high-activity is extremely desired. Thus, the HER performance of FeCoP and CoP UNSAs in acid, basic, and neutral electrolyte were conducted (Fig. 3g). Surprisingly, the FeCoP UNSAs exhibits pretty prominent performance in each electrolyte compared with pristine CoP UNSAs, indicating a high hydrogen evolution activity at all pH values. Furthermore, long-term stability tests under various pH conditions show that the FeCoP UNSAs exhibits impressive durability on the catalytic performance and nanostructure (Fig. 3h). The chronoamperometry test demonstrates that FeCoP can keep working efficiently for $\sim 20 \text{ h}$ with rather little degradation at 10 mA cm^{-2} in every electrolyte. The used FeCoP electrocatalyst displays a well-preserved nanosheet morphology (Fig. S12). The results show that FeCoP UNSAs can serve as an excellent pH-universal HER electrocatalyst with both high-activity and long-term stability.

3.3. Mechanism investigation

Based on the results above, the Fe-doping into CoP UNSAs accelerates the activity of both OER and HER simultaneously. To further understand the improved electrocatalytic performance of FeCoP UNSAs, the electrochemical active surface area (ECSA) was estimated based on the electrochemical double-layer capacitance (C_{dl}) (Fig. S13). The calculated C_{dl} of FeCoP UNSAs is 13.30 mF cm^{-2} , showing a 113% increment compared with CoP UNSAs (6.24 mF cm^{-2}). For the purpose of excluding the improvement by ESCA, the OER performance normalized to ECSA was conducted (Fig. S13d). As a result, the FeCoP UNSAs still outperforms CoP UNSAs both in onset potential (1.48 vs. 1.52 V) and current density (13 vs. 6.7 mA cm^{-2}) at a fixed overpotential (1.6 V), suggesting that the improved ECSA is not the key factor for the Fe-doping enhanced OER performance. In addition, the Nyquist plots of FeCoP UNSAs electrode display a much smaller electron and charge transfer resistance relative to other control samples (Fig. S14), indicating an accelerated kinetics via Fe doping.

X-ray photoelectron spectroscopy (XPS) were employed to give a further insight into the change of electronic structure after incorporation of Fe atoms. The high-resolution Co 2p region (Fig. 5a) shows a complex structure broadened by multiplet splitting effects, resulting in two types of Co species: metallic Co (778.5 eV) and Co-P (781.6 eV), which is a typical situation for transition metal phosphides [37]. The incorporation of Fe leads to the shift of Co $2p_{1/2}$ and Co $2p_{3/2}$ to higher energy levels by 0.75 and 0.25 eV , respectively. In addition, the XPS spectra of MgCoP and NiCoP are displayed in Figs. S15 and S16. The Co 2p peaks of MgCoP slightly shift to lower binding energy and NiCoP remain almost unchanged, indicating the positively shifted and similar charged Co states, respectively, in line with their behavior of OER compared with CoP. In Fig. 5b, the P 2p spectra for pristine CoP show two peaks at 130.0 and 129.4 eV , which are assigned to $2p_{1/2}$ and $2p_{3/2}$ of phosphide. In addition, a broad peak at approximately 134.1 eV is due to oxidized P species arising from superficial oxidation [38]. After doping with Fe atoms, the P $2p_{1/2}$ and $2p_{3/2}$ move to higher binding energies by 0.20 and 0.24 eV , respectively. It should be noted that Fe 2p spectrum ascribed to FeP phase is not detected, further indicating the formation of Fe-doped CoP instead of a mixture of two solid phases (Fig. S15a). Based on the results above, the Co 2p and P 2p in FeCoP are unambiguously positively- and negatively-shifted compared with pristine CoP, suggesting that the introduction of Fe enhances the electron interaction between Co and P.

Density functional theory (DFT) calculations were carried out to understand the doping effect of Fe on the performance of FeCoP UNSAs toward overall water splitting. The model of FeCoP was built by a

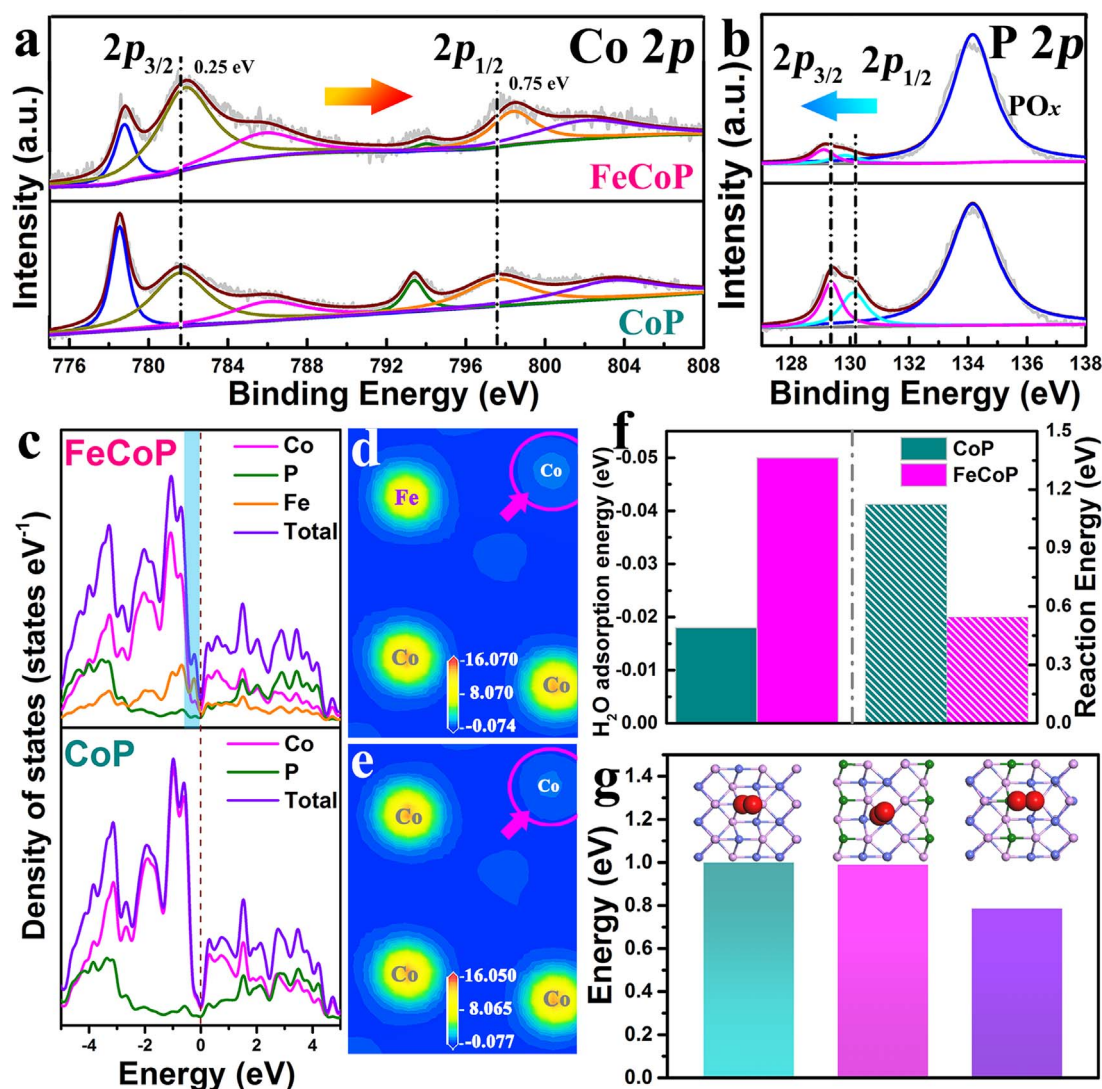


Fig. 5. (a) Co 2p and (b) Ni 2p orbital XPS spectra of FeCoP; (c) total and partial electronic density of states (TDOS and PDOS) calculated for CoP and FeCoP (the Fermi level is set at 0 eV); the charge density distributions of (d) FeCoP and (e) CoP; (f) adsorption energies of H₂O molecule, and the hydrogen dissociation energy on the surface of CoP and FeCoP; (g) desorption energy of oxygen molecule.

partial substitution of lattice Co atoms by Fe atoms in CoP structure (Fig. S17). Although previous DFT studies have reported that an improved electronic conductivity and a suitable hydrogen adsorption free energy account for the HER catalytic performance of TMPs, the OER performance is rarely mentioned and the catalytic mechanism is still unclear. To shed light on the OER process using TMPs catalysts, we calculated the density of states (DOS), charge density distributions and a series of adsorption energies. As shown in Fig. 5c, the DOS of FeCoP displays obviously increased charge density around the Fermi level with respect to that of the pristine CoP, which can provide more charge carriers for the oxidation reaction. It has been reported that metal and phosphorus in TMPs carry a partial positive (δ^+) and negative charge (δ^-), respectively, and positively-charged Co is favorable for OER process [39,40]. The DFT calculation indicates an enhanced electron transfer from Co to P in FeCoP system relative to CoP (Fig. 5d and e), in accordance with the XPS results. The more positive Co^{3+} in FeCoP is beneficial for the intermediate adsorption in OER process.

The adsorption behavior of H₂O on the electrocatalyst surface is a crucial factor for water splitting due to the same initial step for both OER and HER in basic electrolyte [41]. It is found that the adsorption energy of H₂O molecule on FeCoP (−0.05 eV) is much lower than that on CoP (−0.018 eV), implying a more thermodynamically favorable

H₂O adsorption on FeCoP (Fig. 5f). Furthermore, previous studies have shown that the rate-determining step is the second electron transfer step in OER when the Tafel slope is 60 mV dec^{−1} [42]. In this case, the Tafel slope for CoP and FeCoP are 63 and 74 mV dec^{−1}, respectively, indicating the removal of H from the adsorbed hydroxyl ($^*\text{OH} + \text{OH}^- \rightarrow ^*\text{O} + \text{H}_2\text{O} + \text{e}^-$) is the rate-determining step for OER. As displayed in Fig. 5f, the hydrogen dissociation energy of this elementary reaction on the surface of FeCoP (0.545 eV) is significantly less than that on CoP (1.125 eV), indicating a lower energy barrier for the dissociation of H from adsorbed OH in the former catalytic system. In addition, the rapid desorption of O₂ products can accelerate the OER process. It is assumed that O₂ products migrating to Fe sites to make desorption might occur due to the lower barrier on the Fe sites (Fig. 5g), which rapidly vacates the active site for the next OER cycle. It thus appears that the modification of electronic structure of the catalytic active center arising from the Fe-incorporation can modulate and facilitate the overall water splitting performances.

4. Conclusion

In summary, the well-uniformed ultrathin MCoP UNSAs have been synthesized via *in situ* transformation of CoM-LDHs UNSAs precursor.

The resulting FeCoP UNSAs display excellent electrocatalytic activity and robust durability for overall water splitting, compared with the pristine CoP, NiCoP and MgCoP UNSAs. The excellent performance of FeCoP UNSAs can be ascribed to the modified electronic structure of active sites, which gives improved H₂O adsorption and facile hydrogen dissociation on the surface of FeCoP. In addition, highly exposed active sites and ion transport in this ultrathin nanosheet arrays also contribute to the enhanced OER and HER activity. This study opens up an effective route to rational design and scalable fabrication of 2D ultrathin phosphide arrays with cost-effective, high-active, and long-term stability for energy storage and conversion applications.

Acknowledgements

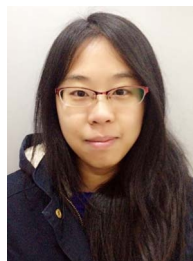
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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2017.10.009>.

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