Electron Redistributed S-Doped Nickel Iron Phosphides Derived from One-Step Phosphatization of MOFs for Significantly Boosting Electrochemical Water Splitting

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1. Introduction

Electrocatalytic water splitting technology represents a promising method for energy conversion and storage due to its potential large-scale production, readily available reactant and environmental-friendly approach.[8] Currently, the state-of-art catalysts for electrocatalytic water splitting are Pt and Ir (or Ru)-based nanocrystals for cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER), respectively.[9] Their large scale industrial applications are hampered by their high cost, scarcity, and unsatisfactory durability.[10] It is imperative to develop high efficiency non-noble metal catalysts as alternatives.[4] Tremendous research efforts have been made in the past decades in improving electrocatalytic performance and stability of non-noble metal based catalysts. For example, transition metal based sulfides (TMSs), phosphides (TMPs), and nitrides (TMNs) have been actively
investigated as electrocatalytic materials for water oxidation and reduction. As reported in literature, transition metal phosphides especially Fe, Co, Ni-based phosphides exhibited superior electrical conductivity and higher electron density near the Fermi level, leading to the enhancement of the intrinsic conductivity of bulk materials. As a result, the materials can achieve higher charge carrier transfer efficiency and higher catalytic activity in the electrocatalytic process. To be specific, for metal phosphides, the negatively charged P sites with moderate electronegativity can act as Lewis bases to effectively capture protons and promote the production of $H_2$. In some cases, it could potentially endow the TMPs with a Gibbs free energy of adsorbed H ($H_{ad}$) approximate to zero. Moreover, the P-H$_2$ bonds are easily to form on the surface of electrocatalysts during the electrocatalytic process, which means it is in favor of the adsorption of H species. Actually, the over-strong interaction between P and adsorbed $H_{ad}$ usually leads to the result that $H_{ad}$ is hard to desorb to form $H_2$. According to the previous reports, the $H_{ad}$ on metal phosphides would further decrease, which is caused by the gradually saturated coordination state during the process of hydrogen evolution reaction.

Recently, bimetallic transition-metal phosphides have attracted substantial research attention as HER and OER catalysts. For example, Hu et al developed a strategy to simultaneously boost the HER activity and durability of CoS$_2$ by fabricating polycrystalline nanowire (PCNW) arrays with dual doping of Fe and P. As a result, Fe/P-CoS$_2$ PCNW exhibits excellent HER performance with a low overpotential of 80 mV at 10 mA cm$^{-2}$ and robust durability in acidic media. Kim et al have successfully developed a facile strategy to fabricate self-assembled 3D architectures for a (Co$_{1-x}$Ni$_x$)(S$_{1-y}$P$_y$)$_2$/G bifunctional electrocatalyst through structural and compositional engineering. In the half-cell evaluation, (Co$_{1-x}$Ni$_x$)(S$_{1-y}$P$_y$)$_2$/G exhibited superior electrocatalytic HER and OER performances. Through rationally regulating the electronic density of catalytic sites and optimization the electronic structures to reduce the energy barriers, these bimetallic transition-metal phosphides could be potentially utilized effectively to boost the electrocatalytic activity during catalytic activity. For HER and OER in water splitting, the four-electron-transfer process involved in the OER has sluggish reaction kinetics and higher overpotential, which is the bottleneck of the water splitting reaction. Rational design of high efficient electrocatalysts for OER grasps the key in enlarging its wide applications. Notably, in the system of metal phosphides, the positively charged metal cations may serve as the hydroxyl receptors, while the negatively charged phosphorous active sites play vital role in facilitating the desorption of O$_2$ molecules. Similarly, as for OER, modifying the metal centers by introducing the secondary metal could also benefit materials' electrocatalytic properties by increasing the number of active sites, optimizing the electronic charge transfer path, and modulating the electronic structure as well. With respect to the sulfide doped metal phosphides for OER process, the metal sulfides and phosphides tend to transfer into metal hydroxides, which could show superior electrocatalytic performance than that of the bare metal oxides or hydroxides synthesized by the direct synthetic approach.

In a bid to tackle the challenges associated with the synthesis of homogeneous bimetallic or polymetallic phosphides and to control the stoichiometric ratios, metal organic framework (MOF) with different metal centers shed a light on solving this problem. MOFs are a family of porous coordination polymers constructed by metal centers and organic ligands through coordination bonds. MOFs have been recognized as one of the most promising electrocatalytic materials due to their tunable porosity, large surface area, flexibility to be functionalized with various ligands and metal centers and uniformly distributed metal centers or metal clusters through the frameworks. It is reported that the metal centers that exist in the framework can be regarded as the quantum dots, so it can greatly reduce the diffusion distance of the charge transfer in the process of electrocatalysis. Furthermore, these functionalized MOFs also can be applied as the outstanding precursors to fabricate metal phosphides, sulfides or other derived materials with rich morphological structures and versatile properties. Recently, tremendous research endeavors have been devoted to exploring MOFs as precursors and templates to synthesize bimetallic MOF derived metal phosphides for efficient overall water splitting. However, the electrocatalytic performance and long-term stability of metal phosphides are still far from satisfactory. Indeed, guidelines are offered for judiciously engineering the electronic structure of metal phosphide to regulate the electrocatalytically active sites by heteroatom doping, which is verified as a powerful strategy to further boost the intrinsic performance of transition metallic phosphides (TPMs) catalysts. The incorporation of the heteroatom with different atomic radii and electronegativities into the lattice of metal phosphides is another strategy to increase the materials' electrocatalytic activity by enhancing the amount of active sites, optimize the formation energy of intermediates as well as redistributing the electron structures. This could also provide opportunities for understanding how the changes in electronic structure at the atomic level impact the materials' properties by experimental analysis coupled with theoretical DFT calculations. For instance, B, N, and S tri-doped CoP composites and S-doped CoP electrocatalyst directly grew on highly porous and conductive carbon cloth and nickel foam exhibited superior electrocatalytic performance. Inspired by the aforementioned design rationales, here we report a feasible conversion strategy for the fabrication of MOF derived S-doped bimetallic phosphate based electrocatalytic materials for highly efficient overall water splitting. The materials are synthesized by using porous and conductive carbon cloth (CC) as the substrate, and MOFs containing S elements (CPM-443-SH) as precursor. The CPM-443-SH was grown in situ on CC to form CC-CPM-443-SH. The structure of the CPM-443-SH was the same as CPM-443 that our group synthesized before with SH inserted into the structure and pore channels. The synthesized CC-CPM-443-SH composites were transformed into the S-doped NiFeP (S-NiFeP-x. x = 0, 5, 10, 20, 30) upon a one-step mild phosphatization treatment. The structure of S-NiFeP was characterized by XRD, XPS, and XAS techniques. Density functional theory (DFT) calculations suggested that the presence of the S doping resulted in metal-sulfur bonds formation. The formed metal-sulfur bonds played an important role in tuning the electronic structure of the catalysts, leading to the decrease of the energy barrier during the process of adsorption and reaction pathway of HER and OER. Moreover, S doping plays a crucial role in facilitating the formation of OOH$^-$ and further releasing O$_2$ during OER process. Impressively, the
as-prepared S-NiFeP-10 sample exhibited superior OER performance and excellent durability in 1.0 m KOH electrolyte. It yields the highest OER activity with an overpotential of 201 mV at the current density of 10 mA cm\(^{-2}\) without \(iR\)-compensation. For HER, the sample of S-NiFeP-20 showed slightly higher overpotential (56 mV) than the state-of-art catalyst of Pt/C (48 mV) at a current density of 10 mA cm\(^{-2}\). More notably, the S-NiFeP-20\| S-NiFeP-10 couple delivered remarkable electrocatalytic overall water splitting activity with a very low cell voltage of only 1.5 V at 10 mA cm\(^{-2}\). In addition, the couple showed excellent stability with negligible polarization curve shift after 1000 cycles and longtime \(i-t\) tests. The work highlighted the importance of tuning the electronic structure by introducing S into the 3D NiFeP structure. The synthesized materials showed impressive hydrogen and oxygen catalytic activities for the development of high-performance water splitting devices.

2. Results and Discussion

2.1. Morphology and Microstructure Characterization

The fabrication process for the CCS-NiFeP composites is illustrated in Scheme 1.\(^{[25–26]}\) Before synthesize MOFs, it is necessary to activate the raw carbon cloth with a mild chemical oxidation in mixed acid (\(\text{H}_2\text{SO}_4 + \text{HNO}_3\)) aqueous solution at 70 °C to obtain CC-A, and next calcine the as-prepared CC-A in an air atmosphere at 500 °C for 2 h, eventually obtain CC-AC, which is depicted in Figure S1 in the Supporting Information. The Fourier transform infrared spectroscopy (FTIR) was used to investigate the surface compositional and chemical state of the carbon cloth. As shown in Figure S2 in the Supporting Information, both CC-A and CC-AC show a broad peak between 3000 and 3800 cm\(^{-1}\), which is attributed to the stretching vibration of the hydroxyl groups presented on the surface of carbon cloth.\(^{[27]}\) The peak around 1600 cm\(^{-1}\) could be assigned to the stretching vibrations of carboxylate ions COO\(^{-}\).\(^{[28]}\) Both COO\(^{-}\) and -OH peaks become stronger in CC-AC than that in CC-A, which means that after the mild acid oxidation and air calcination process, the commercial carbon cloth generates hydrophilic surface with optimized oxygen-rich functional groups. These oxygen-rich functional groups could have a positive effect on the absorption of metal ions and make the in-situ growth of MOF on the surface of carbon substrate easily.

As shown in Scheme 1, CPM-443-SH were grown on the CC-AC by a simple hydrothermal process. The synthetic procedure, as described in SI, was similar as the synthesis of CPM-443 with 3-Mercapto-1, 2, 4-triazole replaced 1, 2, 4-triazole in CPM-443. The scanning electron microscopy (SEM) (Figure S3a, Supporting Information) of CC-CPM-443-SH shows that the surface of carbon was fully covered by MOF crystals, the morphology of the crystals looks similar as that of CPM-443.\(^{[25]}\) The XRD confirms that the structure is the same as CPM-443 (Figure S3b, Supporting Information). The typical diffraction peaks of CPM-443-SH are consistent with that of CPM-443. Following the formula of CPM-443, the formula of CPM-443-SH can be written as \([\left[M_1\right]_3O-(L_1)_3][\left[M_2\right]_2(L_2)_3X_6]\) (X = \(\text{H}_2\text{O}\) or \(\text{Cl}\)), where \([M_1\] is the formula of acs net, and \([M_2\](\(L_2\))\(X_6\)) is the formula of triazolate dimer. Here the M\(_1\) is either Fe ion only or the combination Fe and Ni metal ions, \(L_2\) is 2-Hydroxyterephthalic acid. In the triazolate dimer, \(M_2\) can be either the single Ni ions or combination of Ni and Fe ions. The \(L_2\) here in CPM-443-SH is strz (3-Mercapto-1, 2, 4-triazole), which is the derivatives of 1, 2, 4-triazole (trz). The atom ratios of Fe, Ni, and S is nearly 2.3: 1.5: 1, which is detected from the EDX of CPM-443-SH (Figure S3c, Supporting Information).

After the mild phosphorization treatment of CC-CPM-443-SH by using Na\(_2\)H\(_2\)PO\(_4\) as phosphorous source, according to Scheme 1, upon heating to 300 °C, Na\(_2\)H\(_2\)PO\(_4\) would thermally decompose to generate PH\(_3\) gas and convert CC-CPM-443-SH precursor to CCS-NiFeP-x (x = 0, 5, 10, 20, 30) under different Na\(_2\)H\(_2\)PO\(_4\) content.\(^{[29]}\) here x represents the added mass ratio of Na\(_2\)H\(_2\)PO\(_4\) to CC-CPM-443-SH. The color of CC-CPM-443-SH changed from brick red to black through the phosphorization process. As shown in Figures S5a and S6a in the Supporting Information, the morphologies of CCS-NiFeP-10 and CCS-NiFeP-20 are similar to CC-CPM-443-SH, excepting for the rough surfaces. As the content of Na\(_2\)H\(_2\)PO\(_4\) increases, under the condition...
of the same amount of CC-CPM-443-SH, the S content is lower in the synthesized CCS-NiFeP-\(x\) samples, and the actual atomic ratio of P/S could be quantified by inductively coupled plasma-optical emission spectrometer (ICP-OES) and EDX characterizations. (Table S1, Supporting Information). Notably, XRD patterns taken on the CCS-NiFeP-20 (Figure 1c) and CCS-NiFeP-10 (Figure S8c, Supporting Information) are closely similar to the crystal structure of FeP (No. 78-1443) without showing peaks of nickel phosphides or other impurities, indicating that pure CC-CPM-443-SH precursors are totally transformed into metal phosphides, and also demonstrating formation of alloyed Fe-Ni-P as well.\(^{[30]}\) However, the main diffraction peaks are slightly shifted toward the lower 2\(\theta\), which indicates that fringe lattice distance of CCS-NiFeP-\(x\) are larger than FeP owing to the disparity in the atomic radii of Fe and Ni.\(^{[31]}\) As can be detected in the Figure 1c and Figure S8b (Supporting Information), the lattice distance of CCS-NiFeP-\(x\) (\(x=20,\ 10\), respectively) (011) and (211) are 0.275 and 0.19 nm, respectively, while the corresponding lattice distance of FeP are smaller, which are 0.273 and 0.188 nm, respectively, the result is consistent with XRD characterizations.

To further gain insight of the surface chemical states and compositions, the as-prepared samples are characterized by X-ray photoelectron spectroscopy (XPS). Figure S10 (Supporting Information) and Figure S11 (Supporting Information) display the high-resolution spectra of Fe 2p, Ni 2p, P 2p, and S 2p over the sample of CCS-NiFeP-20 and CCS-NiFeP-10. In XPS spectrum of Fe 2p in Figure S11a in the Supporting Information, the binding energies of Fe 2p peaks located around 707.8 and 720.5 eV can be assigned to Fe 2p \(3/2\) and 2p \(1/2\) of Fe-P species in the sample of CCS-NiFeP-10, respectively.\(^{[31]}\) Notably, the peak at 713.6 eV in Fe 2p coupling with 164 eV in S 2p is the typical character of Fe-S bond.\(^{[34]}\) Integrating with the results of XRD and HRTEM indicates that fraction of S atoms has substituted P to form Fe-S in the as-prepared samples. However, peaks of Fe 2p \(3/2\) and 2p \(1/2\) in Fe-P species are shifted to the higher binding energy relative to the pure NiFeP (707.5 and 720.3 eV), which is due to higher electronegativity of S (2.44) than Fe (1.83), Ni (1.91) and P (2.19), the S doping induces more positive charges on Fe, Ni, and P. Interestingly, the similar phenomenon can be observed in the spectra of Ni 2p as well. It shows that the S doping upward shifts the binding energy of Ni 2p \(3/2\) from 853.1 eV to 853.7 eV in Ni-P species. It also agrees well with the P 2p spectra in Figure S11c (Supporting Information), the peak at about 130 eV can be fitted into the P 2p \(3/2\) (129.5 eV) and P 2p \(1/2\) (130.5 eV) signals of Metal-P bonds, and the signals also show the same tendency of shifting to the higher binding energy results from partially lose charges as compared to the metal-P species.\(^{[23b]}\) While the bonding of S and metal (Ni or Fe) can be proven by the peak locates at 164 eV in the spectrum of S 2p (Figure S11d, Supporting Information).\(^{[33]}\) As for high-resolution XPS spectra of CCS-NiFeP-20 in Figure S10 (Supporting Information), due to the relative lower content of S than that of CCS-NiFeP-10, the binding energies of Fe 2p (Fe 2p \(3/2\) and 2p \(1/2\), Ni 2p \(3/2\) and P 2p also slightly shift positively in comparison to pure NiFeP. Thus, more electronegative S withdraws electron density from the less electronegative Ni, Fe, and P, which result in inducing more positive charges on Fe and Ni and then back-donating by overlapping of S 3p orbitals with P 3p and Ni, Fe 3d in S-NiFeP-\(x\).\(^{[34]}\) Interestingly, the highly positively charged Ni and Fe tend to coordinate with the lone pair electrons of O in H\(_2\)O, which facilitates the dissociation of -O-H bond by releasing adsorbed H to relative higher electronegative atoms P or S. Meanwhile, P/S can form hydrogen bonding with H of H\(_2\)O by contributing excess electron density and promote the adjacent metal ions to interact with H from H\(_2\)O molecules.\(^{[34]}\)

In order to further confirm the structure of S-NiFeP, we carried out X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra to provide further insights into the electronic structure and coordination environment of the Ni and Fe atoms in S-NiFeP catalyst (Figure 2a–d).\(^{[35]}\) The analysis of the XANES region can provide

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**Figure 1.** Morphology and structure characterizations of CCS-NiFeP-20 (particles ultrasonic stripped from carbon cloth). a) TEM and b) HRTEM images of as-prepared CCS-NiFeP-20. The insert red and yellow rectangles in (b) shows the different crystal plane of CCS-NiFeP-20. c) XRD pattern of CCS-NiFeP-20. d–f) Elemental mappings of Fe, Ni, P, and S.
information on the symmetry and the oxidation state of the Ni and Fe atoms. It can be seen that the Fe and Ni K-edge XANES of S-NiFeP is almost the same as that in NiFeP sample, which indicates that S doping induces almost no change of NiFeP structures, and the result is consistent with the XRD and XPS characterizations. Compared with NiFeP, a substantial shift of Ni and Fe K-edge XANES peaks to the higher energy are displayed in Figure 2a,c. The increase in edge position and intensity indicates an increase in unoccupied states of d-orbital, hence inducing positive charges on both of the Fe and Ni metal centers and thus causing the higher oxidation state.\[36\] The more obvious shift in Ni K-edge absorption than the counterpart of Fe K-edge can be attributed to the reason that S dopants have a stronger electronic interaction with the Ni species, which was verified by the following density of states (DOS) analysis. Considering the more unoccupied states can provide more charge transfer channels that increase the Ni(Fe)–P hybridization, simultaneously, modifying atomic and electronic structure in metal phosphides through coordination of S with Ni (Fe), it is believed to be an efficient way to impact the OER performance remarkably. This X-ray absorption spectroscopy (XAS) result also can be detected in the XPS results, which is introduced by the higher electronegativity S doping. The peaks at 1.8 Å and 2.3 Å in NiFeP and S-NiFeP (Figure 2b,d) catalysts are Fe-P (Ni-P) and Fe-Fe (Ni-Ni) coordination shells, respectively.\[37\] However, the coordination numbers of Ni (4.6) and Fe (1.9) in S-NiFeP are larger than that of NiFeP ($NaNi−P=2.8, NaFe−P=1.3$, respectively). Because P and S have a close scattering radius, so it is very hard to distinguish the metal whether coordinated with P or with S. From the fitting result, the larger coordination numbers of Ni-P and Fe-P in S-NiFeP might be account of Ni and Fe exhibiting strong ability of coordinating with S. The fitting results also confirm that the substitution of P by S weakens the Fe-Fe and Ni-Ni interactions and increases the degree of disorder in the S-NiFeP structure.\[38\]

2.2. Electrocatalytic HER Activity and Mechanism Discussion

The HER activities of the as-prepared electrocatalysts were investigated in 1.0 m KOH solution and without iR-correction. For comparison, the electrocatalytic activity of 20 wt% Pt/C was also measured and investigated as the benchmark catalyst. The liner sweep voltammetric (LSV) curves of all samples are illustrated in Figure 3a. Unquestionably, Pt/C is still the best HER catalysts in the basic electrolyte, it could reach a current density of 10 mA cm$^{-2}$ at an overpotential of 48.4 mV. Remarkably, among all as-prepared samples, CCS-NiFeP-20 electrode shows
Pt-like HER activity reaching 10 mA cm\(^{-2}\) at the overpotential of 56 mV, which is much lower than 407, 126, 100, 108, 103, and 64 mV of bare CC, CCS-NiFeP-5, CCS-NiFeP-10, CCS-NiFeP-30, CC-443 P-10, and CC-443 P-20 samples, respectively. It also shows excellent properties than most of metal phosphides as well as that applied overall water splitting electrodes (Table S3, Supporting Information). Moreover, the value of \(\eta_{50}\) (when \(i = 50\) mA cm\(^{-2}\)) and \(\eta_{100}\) (when \(i = 100\) mA cm\(^{-2}\)) are 125 and 161 mV, respectively, achieved by the CCS-NiFeP-20 electrode, indicating its excellent potential as a HER electrocatalyst for commercial electrolyzers. The HER kinetic characteristics of CCS-NiFeP-20 and other comparison samples were also investigated by Tafel plots as shown in Figure 3c. The CCS-NiFeP-20 shows the smallest Tafel slope of 38 mV dec\(^{-1}\), which is not only lower than those of other CCS-NiFeP-x and CC-443 P-y catalysts, but also significantly lower than most the previously reported metal phosphides electrocatalysts that used CC as conductive substrate (Table S3, Supporting Information). EIS is an outstanding means to further study the kinetic characteristics of electrodes. As shown in Figure S15 (Supporting Information), EIS was conducted at the frequency between 100 kHz and 1 Hz with an applied voltage amplitude of 5 mV in 1.0 m KOH electrolyte and was fitted with an equivalent circuit model. The electrocatalyst of CCS-NiFeP-20 owns the smallest radius because of its smallest charge transfer resistance \((R_{ct})\). The charge transfer resistance of CC-443 P-20 is much larger than CCS-NiFeP-20, which is attributed to the reduced energy barrier for HER due to the S-doping. The impact of S-doping for HER will be discussed in more detail via the DFT calculation. In addition, because the electrolytes can act as capacitors at the film/electrolyte interface,\(^{[39]}\) so it is an effective way to measure the value of the double-layer capacitance \((C_{dl})\) to obtain the electrochemically active surface areas (ESCA), which is generally proportional to the value of \(C_{dl}\). As shown in Figure 3d, the ESCA of CCS-NiFeP-x and CC-443 P-y are determined by the \(C_{dl}\). The \(C_{dl}\) of CCS-NiFeP-20 is 31.9 mF cm\(^{-2}\) that is larger than those of CC-443 P-y, CCS-NiFeP-0, and CCS-NiFeP-10, suggesting the more HER electrochemical active sites for CCS-NiFeP-20. It also proves that the CCS-NiFeP-20 has the highest intrinsic activity among the tested samples. To investigate the intrinsic activity of the catalyst, the TOF was also calculated. The TOF value for CC-NiFeP-20 is obtained to be 3.6 s\(^{-1}\) (\(\eta = 100\) mV), which is higher than those of CC-443 P-20 (2.3 s\(^{-1}\)), CC-NiFeP-10 (1.0 s\(^{-1}\)), and 443 P-10 (1.2 s\(^{-1}\)).

To elucidate the intrinsic influence of S dopants on the electronic structure of CCS-NiFeP-x and provide new insight into the electrocatalytic active centers, the theoretic DFT calculations were performed on the as-prepared samples. The detailed information of DFT calculations was illustrated in the Supporting Information. The DFT calculations showed that the S-NiFeP possesses a larger H\(_2\)O adsorption energy (−0.49 eV) than that of NiFeP species (−0.41 eV) (Figure 4c) when the Ni sites are used as the active sites. The active sites are labeled with the green circle in Figure 4a,b. The result means that the S-doping is favorable for adsorbing H\(_2\)O molecules and it also shed a light on elucidating the reason that introducing the S in the lattice of NiFeP is contributed to boosting the electrocatalytic activity.\(^{[33]}\) DOS that obtained by DFT calculation is a powerful evidence to further understand why S doping leads to the best HER performance and how S doping changes the electronic structure of...
NiFeP. As shown in Figure 4d,e, either for NiFeP or S-NiFeP, the Fe-3d orbitals show a stronger degree of spin splitting compared to the Ni-3d orbitals, which was revealed by the larger difference between spin-up orbitals and spin-down orbitals. The results indicate the Fe sites should be more spin polarized than Ni sites, that is Fe sites should have more eg electrons. This would weaken the bonding ability of H2O molecules on Fe sites due to the higher σ* orbital occupation arising from more eg electrons. The conclusions were also consistent with the following Crystal Field Theory discussions. In addition, there is a distinct orbital hybridization between 3d electronic orbitals of Ni, Fe and 2p orbitals of S for both NiFeP and S-NiFeP samples. Moreover, the orbital hybridization is more evident between Ni-3d and S-2p orbitals. The results indicate that the S dopants play a vital role in tailoring the electronic structure of metal sites, especially for Ni species. Moreover, the non-zero DOS at the Fermi level (EF) confirms the metallic property of both S-NiFeP and NiFeP, which means that both of them show excellent electronic conductivity as most reported metal phosphides. However, the intensity of DOS for S-NiFeP (6.73) at the Fermi level is much lower than NiFeP (7.24), which corroborates that hydride acceptor and proton acceptor properties are enhanced by S-doping as confirmed by XPS.

Based on the Crystal Field Theory, the valence electron configuration of Fe 3+ is 3d5 with high-spin state (Figure 5), so it has unpaired electrons in the π-symmetry (t2g) d-orbitals, theoretically, it interacts with the P 3– via π-donation. While, e–1 e–1 repulsion is the major interactions between Ni 2+ in Ni 2+/3+ species and P 3– because t2g d-orbitals of Ni 2+ in low-spin state are fully occupied by electrons. After the coupling between the Fe 3+ and Ni 2+, the π-donation via Fe-P can be enhanced by e–1 e–1 repulsion between Ni 3d and P 3– which accelerate the electrons transfer from Ni 2+ to Fe 3+ via P 3–, which can also be detected by the XPS technique. Correspondingly, DFT results clearly show that Ni possess fewer unfilled 3d eg states comparing with Fe, indicating that Ni both in NiFeP and S-NiFeP species are more active to interact with the OER intermediates. Figure 4f,g shows the 3D charge density differences of S-NiFeP and NiFeP calculated by DFT along c-axis and b-axis, respectively. (Cyan: loss electrons, Yellow: obtain electrons).
previously occupy the P 3p orbitals (Figure 4g) are more inclined to redistribute and accumulate around S atoms and less around P atoms (Figure 4f) because of the larger electronegativity of S, which induces the electrons redistribution. Consequently, this property can induce the high valence state of metallic atoms and contribute to the better overall water splitting activity.

In addition, the electrons that aggregate around non-metallic elements could in favor for HER reaction. So, in comparison with mono-metallic based catalysts, the efficient electrons transfer between different metals in the bimetallic structures could lead to the enhancement of HER and OER activities. Furthermore, the free energy of hydrogen adsorption ($\Delta G_{H^*}$) is a reasonable descriptor for explaining the adsorption/desorption of H species on different catalysts in the alkaline electrolyte, which also is a key to explain the mechanism of HER process.\[43\] Herein, to uncover the intrinsic influence of S doping on HER properties of NiFeP sample, the $\Delta G_{H^*}$ on different element doping and $d$-band center were calculated based on DFT calculation as displayed in Figure 6a,b. What’s more, the smaller $|\Delta G_{H^*}|$ enables a better activity toward HER, indicating that a catalyst giving absolute value of $\Delta G_{H^*} = 0$ eV is considered to be an excellent candidate for HER.\[45\] Thereinto, the negative and positive value correspond to the adsorption and desorption ability of water or intermediate $H^*$. As shown in Figure 6a, the $\Delta G_{H^*}$ of S-NiFeP is about 0.028 eV, the absolute value is smaller than NiFeP (0.03 eV) and FeP (−0.04 eV), notably, it is much smaller than the benchmark catalyst Pt, suggesting that S doping could facilitate the hydrogen adsorption/desorption process. The density of the states near the Fermi level that mainly originate from the $d$ state is also a descriptor to further investigate the electron interaction between adsorbate and NiFeP before and after S doping (Figure 6b). The $d$-band center ($E_d$) of NiFeP and S-NiFeP relative to the Fermi level are calculated to be −3.09 and −3.2 eV, respectively, which means that the $d$-band center is far away from the Fermi level after S doping. According to the frontier orbital theory, as left shift of $d$-band electron, the catalyst is less active to generate the chemical bonds with adsorbed $H^*$ species, leading to the decreased $|\Delta G_{H^*}|$ value.\[45\] These studies

Figure 5. Schematic representation of the electronic coupling between Fe and Ni in S-NiFeP.

Figure 6. a) The free energy diagram (FED) for HER on FeP, NiFeP, S-NiFeP, and Pt. b) Calculated $d$-band center position of NiFeP and S-NiFeP.
provide the intrinsic elucidation that the downshift of d-band center decreases the adsorption energy of H and accelerates desorption of H from catalyst surface for HER, which imply that S doping could benefit the HER catalysis of NiFeP.\cite{46}

In addition to the excellent activity, good stability is also of great significance for energy conversion. As display in Figure S16a in the Supporting Information, after 1000 voltammetry cycles, the polarization curve of CCS-NiFeP-20 exhibits almost the same as the original. The long-term stability (Figure S16b, Supporting Information) is investigated by i-t measurement with a continuous electrolysis at the overpotential of 136 mV, the CCS-NiFeP-20 shows excellent stability, and it clearly indicates that almost no significant activity degradation is detected after 24 h. Moreover, XRD images, FT-IR, and XPS spectra of CCS-NiFeP-20 after 24 h stability are shown in Figures S17 and S18 (Supporting Information), respectively, exhibiting that the structure and chemical state of CCS-NiFeP-20 are just with only a little change after the reaction for 24 h. Therefore, in contrast with NiFeP, MOF derived CCS-NiFeP-20 shows higher HER activity and rapid HER kinetics. In addition, the S doping in CCS-NiFeP-20 further improves the HER activity.

2.3. Electrocatalytic OER Activity and Mechanism Discussion

The S-doping also has a profound promotional effect on oxygen evolution reaction (OER) in 1.0 m KOH electrolyte. The commercial IrO$_2$ was also assessed as the benchmark with the overpotential of 295 mV to reach the current density of 10 mA cm$^{-2}$. As depicted in Figure 7a,b, the LSV curves of different as-prepared samples are investigated. Interestingly, CCS-NiFeP-10 presents the best OER performance, which exhibits the lowest overpotential of 201 mV to achieve the current density of 10 mA cm$^{-2}$, while CC-443 P-10, CCS-NiFeP-5, and CCS-NiFeP-20 require larger overpotentials of 225, 220, and 213 mV, respectively. Figure 7c implies that the Tafel slope of CCS-NiFeP-10 is about 41.2 mV dec$^{-1}$, which is smaller than those of CC-443 P-10 (74.9 mV dec$^{-1}$), CCS-NiFeP-5 (43.1 mV dec$^{-1}$), and CCS-NiFeP-20 (104.5 mV dec$^{-1}$), demonstrating the kinetic merits of the CCS-NiFeP-10 for water oxidation. Evidently, as for CCS-NiFeP-x (x = 5, 10, 20, 30), the moderate content of S doping plays a significant role in boosting OER process and decreasing the energy barriers. Electrochemical impedance spectroscopy was carried out to detect the charge transfer resistance in OER.

As shown in Figure S20 (Supporting Information), CCS-NiFeP-10 possesses the smallest charge transfer resistance among all as-prepared samples. Moreover, the electrochemical surface areas (ECSA) (Figure 7d) of various catalysts were calculated via scan CV curves (Figure S19, Supporting Information) under different scan rates. The double layer capacitance ($C_{dl}$) values were collected by measuring the current density change within the potential range that without Faradaic process. The $C_{dl}$ of CCS-NiFeP-10 (4.07 mF cm$^{-2}$) is higher than CC-443 P-0 (1.12 mF cm$^{-2}$), CC-443 P-10 (2.41 mF cm$^{-2}$), CCS-NiFeP-0 (1.68 mF cm$^{-2}$), and CCS-NiFeP-20 (1.93 mF cm$^{-2}$), indicating that proper S doping could be favorable for exposing more active sites in OER process. Furthermore, benefiting from the MOF derived 3D skeleton with plenty of micropores and mesopores that provide transfer pathway for electrons mass transfer.\cite{47} As evidenced by the almost overlapped LSV curves before and after continuous 1000 cycles in the insert image in

Figure 7. Catalytic performances of prepared samples. (where CC, 443 P-0, 443 P-10, P-0, P-10, P-20, P-30, and IrO$_2$ are short for carbon cloth, CC-443 P-0, CC-443 P-10, CCS-NiFeP-0, CCS-NiFeP-10, CCS-NiFeP-20, CCS-NiFeP-30, respectively.) a) LSV curves of obtained catalysts for OER tests in 1.0 m KOH aqueous solution. b) The overpotential required for a cathodic current of 10 mA cm$^{-2}$. c) Corresponding Tafel plots obtained from (a). d) The current density against scan rates of obtained catalysts for estimating $C_{dl}$ values.
Figure 8. a) The calculated free energies diagram for OER of NiFeP (Ni$^\text{II}$) and S-NiFeP (Ni$^\text{II}$) at different potential $U$ values and the bottom image is the most probable OER mechanisms on S-NiFeP with Ni atom as active adsorption site; b) The geometries of S-NiFeP and its 3D charge density differences (cyan: lose electrons, yellow: obtain electrons) calculated by DFT, the bottom image and table are the Bader charge numbers of atoms in S-NiFeP intermediates with OOH$^\ast$. (Negative value: lose electrons, Positive value: obtain electrons).

Figure S21 (Supporting Information), CCS-NiFeP-10 also presents a superior long-term electrochemical OER stability, which can be further corroborated by the stable i-t curve conducted at 1.52 V for at least 24 h. However, the FT-IR (Figure S22, Supporting Information), XRD (Figure S23, Supporting Information), and XPS (Figure S24, Supporting Information) results indicate that the sample surface is partially oxidized into the metal hydroxides under the strong oxidizing condition after 24 h, forming the S-NiFeP/NiFeOOH heterostructures as the actual catalytically active sites for OER.$^{[29a,48]}$

DFT calculations were employed to elucidate the detailed effects of S doping on S-NiFeP by performed OH$^\ast$, O$^\ast$, OOH$^\ast$ adsorption free energies in the elementary steps of NiFeP and S-NiFeP models. The possible active sites of Ni and Fe in the diverse sites in the models were evaluated and compared. Ultimately, we can conclude that the Ni replacing Fe in the discrete units should be the active sites, which is also consistent with the experimental results. The images on the bottom of Figure 8a and the Figure S25 (Supporting Information) display the optimized geometry models of S-NiFeP and NiFeP while processing the water oxidation reaction, which are the typical four-electron sequential steps. In the OER mechanism, the adsorption energy of oxygen-based intermediates is an objective parameter to understand the activity over the whole process. Notably, the energy barrier ($\Delta G$) is inversely related to the adsorption ability of OER intermediates. Figure 8a displays

Figure 9. Overall-water-splitting performance CCS-NiFeP-10|CCS-NiFeP-20. a) Polarization curves of CCS-NiFeP-10||CCS-NiFeP-20 and IrO$_2$||Pt/C for overall water splitting in 1.0 m KOH solution at a scan rate of 5 mV s$^{-1}$. b) Time-dependent current curves (i-t curve) under static overpotential of 1.5 V in 1.0 m KOH of CCS-NiFeP-10||CCS-NiFeP-20. The insert is polarization curves of CCS-NiFeP-10||CCS-NiFeP-20 before and after 1000 cycles CV.
the energy barriers of four steps under different potential U. It can be clearly seen that comparing with the pristine NiFeP, S introducing could effectively tune the ΔG values of the four steps. Also the absorption ability of OH* and O* has been dramatically improved for its lower ΔG value when applied potential is 1.23 V. The rate-determining step (RDS) of NiFeP is the third step that is the conversion of O* to OOH* with a considerable high energy barrier of 3.04 eV, which is caused by the weak adsorption ability of OOH* intermediate on the Ni sites. However, as for S-NiFeP, the energy barrier of RDS reduces to 2.86 eV, indicating that the S doping can effectively strengthen the OOH* adsorption and lower the energy barrier. Our calculations show that S doping can successfully tune the ΔG value for intermediates formation on Ni atoms to a suitable value and exhibit an improved the OER performance, which is in an agreement with the experimental results. To better understand the change of the electronic distribution degree on the interface between the Ni sites and OER intermediates during OER process, the 3D charge density difference and Bader charge numbers of atoms in S-NiFeP intermediates with OH* (Figure S26a, Supporting Information), O* (Figure S26b, Supporting Information), and OOH* (Figure 8b) are calculated. Since the OOH* is the rate-determining step for O₂ evolution, so it is vital to detect the electron transfer direction to understand the OER mechanism theoretically. The electronegativities of S and P are larger than Ni and Fe, thus electrons prefer to transfer from Ni and Fe to S and P atoms when they coordinate. This phenomenon also can be verified by the 3D charge density difference in Figure 8b, because the charge values of S and P atoms are positive, which means S and P can capture electrons during OER process. Meanwhile, partial electrons transfer from the metallic atoms to adsorbed OOH*, so in the case of S doping, more electrons will lose from metal active sites and induce more high valence state metal atoms to act as active sites to accelerate O₂ production.

2.4. Electrocatalytic Overall Water Splitting Activity

To investigate the S doped NiFeP in overall water splitting ability, a two-electrode electrolyser (CCS-NiFeP-10|CCS-NiFeP-20) was assembled by using CCS-NiFeP-10 and CCS-NiFeP-20 as an anode and cathode, respectively and the test was measured in 1.0 M KOH electrolyte. In addition, as comparison, the same mass loading of Pt/C and IrO₂ (IrO₂|Pt/C) were also assembled and tested under the same condition. As illustrated in Figure 9a, the voltage is 1.51 V of reference couple (IrO₂|Pt/C) to achieve 10 mA cm⁻². As for S-NiFeP-20|S-NiFeP-10, 1.5 V is required to offer the same current density, which exhibits similar or slightly better performance than that of the benchmark couple. The stability of CCS-NiFeP-10|CCS-NiFeP-20 is shown in Figure 9b, after 1000 cycles of samples, the LSV curves could not overlapped with before. However, after metal phosphides was converted into M-OOH, the long-time stability of samples got significant promotion which could be corroborated by the stable amperometric i-t curve conducted at 1.5 V for 24 h (Figure S21, Supporting Information). Figure S27 in the Supporting Information is an image to illustrate the overall water-splitting reaction over the couple of CCS-NiFeP-10|CCS-NiFeP-20, it shows the promising in the practical application in the field of energy storage and conversion.

3. Conclusions

In this work, CCS-NiFeP-x catalysts were successfully prepared by a simple phosphorization method of S doped NiFe-MOFs (CPM-443-SH). CCS-NiFeP-10 exhibited high intrinsic activity toward OER activity, and the sample of S-NiFeP-20 reveled superior HER performance. For HER, the CCS-NiFeP-20 allows the Gibbs free energy of atomic hydrogen binding to be close to zero, leading to excellent electrochemical hydrogen evolution activity compared to the CC-NiFeP species. While in OER, the S doping can successfully tune the ΔG values for intermediates formation in Ni atoms to a suitable value and exhibit a pronouncedly improved the OER performance under electrochemical conditions. In the view of the excellent performance in overall water splitting by using CCS-NiFeP-10 as anode and CCS-NiFeP-20 as cathode, the synthesized materials have great potential in building an overall water splitting device. The fabricated water splitting electrolysis cell exhibit excellent catalytic activity and stability. This strategy opens up a new pathway for designing and synthesizing of cost-effective and highly efficient multifunctional electrocatalysts for energy storage and conversion.

4. Experimental Section

Experimental details see Supporting Information.

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.
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