Electronic modulation of Ni₂P through anion and cation substitution toward highly efficient oxygen evolution

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ABSTRACT Rationally designed oxygen evolution reaction (OER) catalysts with structural and compositional superiorities are essential for energy-related electrocatalytic techniques. Transition-metal phosphides have been used as promising electrocatalysts for OER. Incorporating heteroatoms into the lattice can induce lattice distortion and redistribution of electron density, consequently modifying the electronic structure and improving catalytic performance. Herein, Fe- and S-substituted Ni₂P uniformly dispersed throughout porous carbon substrate (Ni-Fe-P-S@C) was rationally designed through transformation from the pre-synthesized NiFe-metal organic frameworks (NiFe-MOFs) by partial sulfurization and subsequent phosphorization process. Experimental results and density functional theory calculations showed that Fe and S incorporation could modulate the electronic structure of Ni₂P and alter the adsorption free energies of reaction intermediates, contributing to admirable electrocatalytic activity and stability toward OER. Notably, the *in-situ* formed partially oxidized surface was vital to further improve the local environment. This proposed cation- and anion-substitution strategy will bring new inspiration to boost the electrocatalytic performance of transition-metal-based electrocatalysts for energy conversion applications.

Keywords: oxygen evolution reaction, electrocatalysis, transition-metal phosphide, cation- and anion-substitution, electronic modulation

INTRODUCTION

Electrochemical water splitting is a promising approach for producing high-energy-density, carbon-neutral, and environmentally friendly hydrogen energy, which can reduce our reliance on conventional fossil fuels and mitigate the impact on climate change [1]. However, its application is greatly hindered by the sluggish anodic oxygen evolution reaction (OER), which involves more complex multistep electron transfer steps as well as oxygen–oxygen bond formation compared with the cathodic hydrogen evolution reaction (HER) [2,3]. Although noble metal-based catalysts with high activity are regarded as the benchmark catalysts for OER, their scarcity and high cost greatly impede prevailing implementation, particularly in industrial mass production [4–6]. In this regard, it is highly urgent but challenging to develop cost-effective and efficient non-noble metal-based

alternatives for OER.

Transition-metal phosphides (TMPs) have attracted extensive research interests for application in OER by virtue of their natural abundance, low cost, remarkable activities, and simple preparation process [7]. Nevertheless, their catalytic performance is still far from satisfactory. Modulating their intrinsic electronic properties and increasing the exposed active sites are two powerful strategies for regulating their surface properties and electronic structures and influencing mass transfer, which can further improve the OER performance of TMP catalysts [8]. Incorporating heteroatoms with different atomic radii and electronegativities into the lattice of TMPs can induce lattice distortion and redistribution of electron density, consequently modifying the electronic structure and improving catalytic performance [9]. For example, the extraordinary OER activity of Ni_{0.6}Co_{1.4}P was verified by both density functional theory (DFT) simulations and experimental studies [10]. Compared with Ni₂P, Co substitution could increase the density of states (DOS) at the Fermi level and make d-states closer to the Fermi level, resulting in high charge carrier density and low intermediate adsorption energy. Appropriate O incorporation into CoP nanosheets could dramatically improve the electrical conductivity and optimize the adsorption energy of reaction intermediates through electronic structure modification [11]. Additionally, nanostructured OER catalysts with hierarchical pores can not only increase the surface area and expose a high density of active surface sites but also effectively reduce the ion diffusion pathways and increase the contact with electrolyte for mass transportation. Lou and coworkers [8] designed porous Fe–Co–P nanoboxes. The structural advantages and effective electronic coupling between Fe and Co were responsible for the superior OER activity. Yu and coworkers [12] constructed ternary Ni_{0.1}Co_{0.9}P porous nanosheets with large electrolyte-accessible surface and abundant mass diffusion pathways. This ternary structure with porous surfaces and favorable electronic states resulting from the synergistic interaction between Ni and Co exhibited high electrocatalytic activity and excellent stability. Based on the above considerations, we are motivated to incorporate composition modulation and morphological control into TMP catalyst design to fully exploit their respective advantages for OER.

Herein, we developed a novel strategy for preparing Fe- and S-substituted Ni₂P uniformly dispersed throughout porous carbon substrate (Ni-Fe-P-S@C) through structural and compositional engineering using NiFe-based bimetallic metal-organic frame-

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works (NiFe-MOFs) as the sacrificial template. Experimental characterizations and DFT calculations verified the modulation of electronic structure within the whole structure as a result of Fe and S substitution, which further tuned the adsorption behavior of oxygen-containing intermediates. Postelectrolysis characterizations further revealed that although Ni-Fe-P-S@C was mostly retained after the OER process, the surface was partially oxidized, which served as actual OER active site with high activity. Besides, such a hierarchical porous structure could expose more accessible active sites and benefit mass transportation of ions/gas. Compared with unsubstituted Ni₂P@C and Fe-substituted Ni₂P (Ni-Fe-P@C), Ni-Fe-P-S@C demonstrated excellent OER activity with an overpotential of 247 mV to drive 20 mA cm⁻². Our findings suggest that the cation- and anion-substitution strategy for electronic modulation provides a new pathway to rationally design efficient and low-cost electrocatalysts for OER.

EXPERIMENTAL SECTION

Chemicals

Nickel acetate tetrahydrate (Ni(OAc)₂·4H₂O), iron sulfate heptahydrate (FeSO₄·7H₂O), terephthalic acid (1,4-H₂BDC), *N,N*-dimethylacetamide (DMAC), thioacetamide (TAA), sodium hypophosphite monohydrate (NaH₂PO₂·H₂O), and ethanol (CH₃CH₂OH) were purchased from commercial suppliers and used without further purification.

Synthesis of NiFe-MOFs

NiFe-MOFs were prepared in a solvent mixture of DMAC and water. Typically, 0.5 mmol (0.124 g) of Ni(OAc)₂·4H₂O and 0.15 mmol (0.0417 g) of FeSO₄·7H₂O were dissolved in 30 mL of water. And 0.25 mmol (0.0415 g) of 1,4-H₂BDC was dissolved in 30 mL of DMAC. These two solutions were then thoroughly mixed before being transferred to a Teflon-lined stainless-steel autoclave (100 mL) and heated at 150°C for 3 h. The products were collected *via* centrifugation, washed with water and ethanol six times, and dried in a vacuum oven at 60°C for 12 h. For the preparation of Ni-MOFs, the synthesis method was the same as that of NiFe-MOFs except without the addition of FeSO₄·7H₂O.

Synthesis of partially sulfurized NiFe-MOFs (PS-NiFe-MOFs)

TAA was used for the synthesis of PS-NiFe-MOFs. First, 2 g of TAA was dissolved in 50 mL of ethanol. Next, 50 mg of NiFe-MOFs was immersed into the above TAA solution, and the entire solution was transferred to a Teflon-lined stainless-steel autoclave (100 mL) and heated at 90°C for 12 h. The resulting products were collected through filtration, washed with ethanol and water several times, and dried in a vacuum oven at 60°C for 12 h.

Synthesis of Ni-Fe-P-S@C

Ni-Fe-P-S@C was synthesized by the phosphorization of PS-NiFe-MOFs using NaH₂PO₂ as the phosphorus source. Typically, 20 mg of PS-NiFe-MOFs was placed in a small crucible, which was then placed into a big crucible containing 400 mg of NaH₂PO₂·H₂O. These two crucibles were placed in a tube furnace and kept at 350°C (2°C min⁻¹ ramping up to 350°C) for 2 h under Ar atmosphere, and were naturally cooled down to room temperature. The final product Ni-Fe-P-S@C was obtained and directly used without any further treatments.

Synthesis of Ni-Fe-P@C

For the preparation of Ni-Fe-P@C, the synthesis method was the same as that of Ni-Fe-P-S@C except that NiFe-MOFs rather than PS-NiFe-MOFs were used as precursors.

Synthesis of Ni₂P@C

For the preparation of Ni₂P@C, the synthesis method was the same as that of Ni-Fe-P@C except that Ni-MOFs rather than NiFe-MOFs were used as precursors.

Characterization

The crystallographic structures of the materials were determined using a Rigaku Corporation SmartLab 9 kW diffractometer at 45 kV and 200 mA with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The surface characterization of elemental electronic states was measured by an X-ray photoelectron spectrometer (XPS; Axis Ultra imaging photoelectron spectrometer with the monochromatic Al K α as source of X-ray). Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images and energy dispersive spectroscopy (EDS) elemental mapping images were collected by an FEI Tecnai F30 microscope. Raman analysis was performed on a Renishaw RM 1000 spectromicroscopy system ($\sim 2 \text{ \mu m}$ spot size) with a 20 $\times$ objective optical microscope. An Ar laser with a 488 nm wavelength was used for the excitation of the Raman signal with a total power of 10 mW.

Electrochemical measurements

The electrochemical measurements were carried out on a CHI 760E electrochemical workstation using a standard three-electrode system with catalyst-modified glassy carbon electrode (GCE), Hg/HgO (1 mol L⁻¹ KOH, aqueous), and Pt foil as the working electrode, reference electrode, and counter electrode, respectively. To prepare the working electrode, 4 mg of catalyst containing 2 mg of the as-prepared catalyst and 2 mg of Super P was ultrasonically dispersed in 1020 μ L of the solution containing 500 μ L of ethanol, 500 μ L of deionized water, and 20 μ L of Nafion (5 wt%) solution to form an ink. Next, the ink (10 μ L) was drop-casted onto the polished GCE (5 mm in diameter) with a mass loading of 0.2 mg cm⁻² and dried at room temperature to produce a thin-film electrode. The potentials in this paper were referred to reversible hydrogen electrode (RHE) using $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 \text{ V} + 0.059\text{pH}$. The catalyst-coated working electrode was subjected to cyclic voltammetry (CV) measurements with a scan rate of 50 mV s⁻¹ to activate the catalysts, and linear sweep voltammetry (LSV) polarization curves were obtained at a scan rate of 10 mV s⁻¹ with an electrode rotation rate of 1600 r min⁻¹. All data were corrected for *i*R loss unless otherwise noted. For rotating ring-disk electrode (RRDE) measurements, RRDE with glassy carbon disk and Pt ring (PINE E6 RRDE) was used. To investigate the OER mechanism, Pt ring potential was set at 1.5 V for the detection of H₂O₂ oxidation in O₂-saturated 1.0 mol L⁻¹ KOH, and disk potential ranged from 1.0 to 1.6 V. Besides, LSV curves of Pt ring were also collected with disk potentials of 0 and 1.7 V. When disk potential was set at 1.7 V, the current response at Pt ring corresponded to oxygen reduction reaction with oxygen generated from the catalyst-modified disk, while negligible current should be detected at Pt ring when disk potential was set at 0 V, confirming the exclusive O₂ generation by the catalyst. The stability tests were performed by chronopotentiometry at current densities of 10 and 50 mA cm⁻² under the same

experimental setup without iR drop compensation. The accelerated durability test was performed by potential cycling between 1.15 and 1.65 V with a scan rate of 100 mV s^{-1} for 1000 cycles. After the cycles were completed, the electrode was used for testing the polarization curve with a scan rate of 10 mV s^{-1} . Electrochemically active surface areas (ECSAs) were estimated by electrochemical double-layer capacitance C_{dl} , which was determined from CV curves measured in a non-Faradaic region at different scan rates ($\nu = 10, 20, 30, 40$, and 50 mV s^{-1}) in the potential range from 0.92 to 1.02 V. The differences in current density between anodic and cathodic sweeps at 0.97 V against scan rates were fitted to obtain C_{dl} ($C_{dl} = (j_A - j_C)/2\nu$), where j_A and j_C correspond to anodic and cathodic current densities, respectively.

RESULTS AND DISCUSSION

Ni-Fe-P-S@C was fabricated through transformation from the pre-synthesized NiFe-MOFs by partial sulfurization and subsequent phosphorization, as illustrated in Fig. 1. First, NiFe-MOFs were fabricated *via* a reported bottom-up solvothermal method [13]. X-ray diffraction (XRD) pattern (Fig. S1) corroborated the successful formation of NiFe-MOFs, which had a similar crystal structure to $[\text{Ni}_3(\text{OH})_2(1,4\text{-BDC})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ (CCDC No. 638866). Representative scanning electron microscopy (SEM) and TEM images (Fig. S2) revealed the flexible ultrathin morphology of the resulting NiFe-MOFs with spontaneously curly surfaces. Then, TAA was used during the following sulfurization of NiFe-MOFs. Notably, although the smooth and sheet-like morphology of NiFe-MOFs became porous and rough upon sulfurization (Fig. S3), the XRD pattern of sulfurized NiFe-MOFs still retained the characteristic peaks of pristine NiFe-MOFs but with decreased intensity (Fig. S4). Besides, no obvious sulfide phase was observed owing to its low amount and weak diffraction peak intensity compared with that of NiFe-MOFs. However, the crystal plane of $(\text{Fe,Ni})\text{S}_2$ could be observed in HRTEM images (Fig. S5), and the digital images in Fig. S6 showed the color of the sample transformed from dark yellow to dark gray after sulfurization. All the preceding findings suggested that NiFe-MOFs were partially sulfurized (the derived composite was denoted as PS-NiFe-MOFs). It should be noted

Figure 1 Schematic illustration of the synthesis of Ni-Fe-P-S@C.

that increasing the sulfurization temperature to 120°C could completely convert NiFe-MOFs into $(\text{Fe,Ni})\text{S}_2$ (Fig. S7). Afterwards, the subsequent low-temperature phosphorization treatment was performed. As shown in the XRD pattern (Fig. 2a), all reflected peaks matched well with Ni_2P (PDF #03-0953) without any peaks related to sulfide phase, confirming the sulfurized NiFe-MOFs were completely transformed into phosphide (Ni-Fe-P-S) with P sites partially substituted by S. In view of morphology, although Ni-Fe-P-S@C displayed a deformation after phosphorization, it possessed a three-dimensional (3D) porous architectural morphology with uniformly distributed phosphide nanoparticles on carbon substrate (Fig. 2b). Upon closer observation, hierarchical pores could also be observed within Ni-Fe-P-S@C (Fig. 2c), which were conducive to shortening the mass transport pathway of electrons/ions and evolved gas during electrocatalysis [14]. The HRTEM image in Fig. 2d revealed two sets of distinct lattice fringes with d -spacing of 0.203 and 0.221 nm corresponding to the (201) and (111) planes of Ni_2P , which was consistent with the XRD result. EDS elemental mapping images (Fig. 2e) showed homogeneous dis-

Figure 2 (a) XRD pattern, (b, c) TEM images, (d) HRTEM image, and (e) the corresponding EDS elemental mapping images of Ni-Fe-P-S@C.

tribution of Ni, Fe, P, S, and C throughout the whole architecture.

To investigate the effects of cation and anion substitutions, Fe-substituted Ni_2P (Ni-Fe-P@C) and unsubstituted $\text{Ni}_2\text{P@C}$ were synthesized. Ni-Fe-P@C was obtained by the one-step phosphorization process. As shown in Figs S8 and S9, without the sulfurization process, the hierarchical 3D structures of NiFe-MOFs were partially preserved, and many Fe-substituted Ni_2P nanoparticles could be observed on the porous carbon substrate. In contrast, in the absence of Fe^{2+} addition, the morphology of Ni-MOFs was different from that of NiFe-MOFs, which exhibited 2D ultrathin smooth features (Fig. S10). Although $\text{Ni}_2\text{P@C}$ maintained 2D structures after phosphorization, a slight contraction appeared and Ni_2P nanoparticles were distributed on the surface of porous carbon substrates (Fig. S11).

XPS was used to reveal the surface chemical states of Ni-Fe-P-S. The existence of Ni, Fe, P, S in Ni-Fe-P-S was confirmed by the XPS survey spectrum, while the completely phosphorized Ni-Fe-P@C and unsubstituted $\text{Ni}_2\text{P@C}$ showed the absence of S and Fe/S, respectively (Fig. 3a). Notably, the peak positions of Ni 2p and Fe 2p of Ni-Fe-P-S@C shifted to higher binding energy than the corresponding peaks in Ni-Fe-P@C and $\text{Ni}_2\text{P@C}$, which could be attributed to the stronger electronegativity of S in comparison with P (Fig. 3b, c) [15]. In P 2p spectra (Fig. 3d), a predominant peak of oxidized phosphorus species locating at the binding energy of 133.7 eV was observed due to air exposure [16]. Besides, although the characteristic peaks of S 2p could be observed in Ni-Fe-P-S@C, the peak intensity was much lower than that of the completely sulfurized Ni-Fe-S@C (Fig. S12).

Meanwhile, although peaks of sulfate in S 2p spectra resulting from exposure to air could be observed in both Ni-Fe-P-S@C and Ni-Fe-S@C, the peak intensity of sulfate relative to sulfide decreased after phosphorization (Fig. S12). This suggested that a small amount of S substitution in P sites could alleviate oxidation upon air exposure, which could improve the stability of Ni-Fe-P-S@C [17,18]. All abovementioned conclusions confirmed the successful incorporation of Fe and S into Ni_2P lattice.

The electrocatalytic activities of all samples for OER were evaluated using a three-electrode configuration cell in alkaline electrolyte ($1 \text{ mol L}^{-1} \text{ KOH}$) at room temperature. All LSV curves were corrected with 95% iR compensation, and all potentials were referenced to the RHE. Commercial RuO_2 and IrO_2 nanoparticles were used as reference materials to evaluate the OER performance of samples. LSV curves were tested at a rotation rate of 1600 r min^{-1} and normalized by the geometrical area of electrode for comparison. The oxidation of low-valence metal ions normally happens prior to oxygen evolution [19]. Hence, to avoid the influence of anodic oxidation peak on polarization curves, the overpotential at 20 mA cm^{-2} was used to assess the OER activity. As shown in Fig. 4a and Fig. S13, Ni-Fe-P-S@C showed a robust OER performance on GCE with a small overpotential of 247 mV required to afford $20 \text{ mA cm}^{-2}_{\text{disk}}$ (η_{20}). This value was lower than that of Ni-Fe-P@C (265 mV), $\text{Ni}_2\text{P@C}$ (286 mV), Ni-Fe-S@C (260 mV), and PS-NiFe-MOFs (258 mV) when reaching the same current density. It is also worth noting that a sharp increment in anodic current density was observed for Ni-Fe-P-S@C after 1.5 V, which even outperformed that of commercial RuO_2 and IrO_2 , further demon-

Figure 3 (a) XPS survey spectra and high-resolution XPS spectra of (b) Ni 2p and (c) Fe 2p of Ni-Fe-P-S@C, Ni-Fe-P@C, and $\text{Ni}_2\text{P@C}$. (d) High-resolution XPS spectra of P 2p of Ni-Fe-P-S@C.

Figure 4 (a) LSV polarization curves of the catalysts. (b) Difference in current density at 0.97 V as a function of scan rate for different catalysts to obtain the electrical double-layer capacitance. (c) RRDE voltammogram of Ni-Fe-P-S@C obtained in O₂-saturated 1.0 mol L⁻¹ KOH. The inset shows the corresponding electron transfer number (*n*) as a function of applied potential. (d) LSV polarization curves of Ni-Fe-P-S@C at Pt ring at disk potentials of 0 and 1.7 V, respectively. (e) LSV polarization curves of Ni-Fe-P-S@C before and after CV cycling between 1.15 and 1.65 V for 1000 cycles. (f) Chronopotentiometric curves of Ni-Fe-P-S@C and IrO₂ at a constant current density of 10 mA cm⁻².

strating its exceptional OER activity. Tafel plots were also studied to obtain the kinetic information on OER process. The corresponding Tafel plots in Fig. S14 revealed that Ni-Fe-P-S@C possessed the smallest Tafel value of 51.9 mV dec⁻¹, indicating its obviously boosted kinetics for OER. The superior OER performance of Ni-Fe-P-S@C was comparable to that of other TMPs, as listed in Table S1. To further help understand the observed differences in OER performance, the ECSAs of all materials were evaluated by *C_{dl}* via CV scanned at different rates in the non-Faradaic potential region without any redox processes (0.92 to 1.02 V vs. RHE, Fig. S15). As seen in Fig. 4b, although the *C_{dl}* of Ni-Fe-P-S@C was small, the improved electrocatalytic performance confirmed its activity enhancement should be attributed to the increase of intrinsic activity of active sites by electronic modulation. The superb OER performance reflected that the precise cation- and anion-substitution strategy successfully constructed optimized electronic structures of active sites for OER. To investigate the OER mechanism of Ni-Fe-P-S@C, RRDE measurements at a rotation rate of 1600 r min⁻¹ were then used to check the electron transfer number and intermediates of OER process. First, as shown in Fig. 4c, when the potential on Pt ring was set at 1.5 V to ensure the complete oxidation of any generated peroxide intermediates on disk electrode, negligible current density on ring electrode was observed although a relatively high current density was obtained at disk, revealing a desirable four-electron pathway on Ni-Fe-P-S@C for water oxidation ($4\text{OH}^- = \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$) [20]. Then, LSV polarization curves of the ring electrode were collected by setting the disk potential at 0 and 1.7 V, respectively. At a disk potential of 1.7 V, the current response of the ring corresponding to oxygen reduction reaction with oxygen generated from the disk electrode, while negligible current response was

detected at ring when the disk potential of 0 V was applied, demonstrating the observed catalytic current exclusively originated from water oxidation by Ni-Fe-P-S@C (Fig. 4d) [21]. More importantly, Ni-Fe-P-S@C also displayed robust stability during the OER process. Continuous CV cycling was conducted at a scan rate of 100 mV s⁻¹ between 1.15 and 1.65 V. Compared with the initial state, Ni-Fe-P-S@C exhibited a negligible shift of polarization curve after 1000 cycles (Fig. 4e). The stability of Ni-Fe-P-S@C was further confirmed by chronopotentiometry measurements. Exceptionally, Ni-Fe-P-S@C showed stable potential curve during continuous O₂ production at a constant current density of 10 mA cm⁻², while IrO₂ showed severe activity loss with a potential shift of over 300 mV after 5 h (Fig. 4f). Besides, when a larger current density of 50 mA cm⁻² was applied, Ni-Fe-P-S@C could also stably perform under intense O₂ production for 12 h (Fig. S16). Based on the above stability test results, it can be inferred that Ni-Fe-P-S@C is a highly active and stable OER electrocatalyst.

Actually, the outstanding activity of TMPs as electrocatalysts for OER can be attributed to their natural properties [22]. It has been reported that real OER active species in TMPs are ascribed to the gradually formed metal oxide/hydroxide phases on the surface, while the inner TMP core may serve as the conductive scaffold, and the synergetic effect between oxidized species and phosphide may promote the OER kinetics [23]. In this case, TMPs are regarded as “pre-catalysts”. To investigate the surface composition changes of Ni-Fe-P-S@C with the ongoing OER process, SEM, TEM, XRD, and XPS measurements were carried out after chronopotentiometry measurements. SEM images in Fig. S17 showed the morphology of Ni-Fe-P-S@C did not change obviously except the surface became rougher after the test. To characterize the structure and morphology more clearly,

TEM images were collected. It can be observed that although the porous morphology and phosphide phase were well preserved after the OER measurement, and a large number of phosphide nanoparticles still uniformly dispersed throughout the whole structure, the size of nanoparticles was slightly smaller than that before the stability test (Fig. S18a, b). Besides, a thin layer of amorphous oxidized species was formed on most of the surface of Ni-Fe-P-S@C (Fig. S18c). EDS elemental mapping images further demonstrated the existence and uniform distribution of Ni, Fe, P, S, and O, and P and S elements in the catalyst were largely dissolved, and the O content was greatly increased after long-term OER operation (Fig. S18d and Table S2). XRD analysis also confirmed the formation of α -Ni(OH)₂, in addition to a small amount of Ni₂P remnant that was not oxidized inside (Fig. S19). As revealed in the high-resolution XPS spectrum of Ni 2p (Fig. S20), the characteristic peaks of Ni²⁺ disappeared (853.0 and 870.3 eV), and two peaks at 855.8 and 873.6 eV could be assigned to oxidized nickel species, indicating the oxidation of Ni-Fe-P-S@C after the chronopotentiometry test [24]. For P 2p spectrum (Fig. S21), the emergence of P-O signal at 133.7 eV and the disappearance of Ni-P signal at 132.1 eV confirmed the surface oxidation of phosphides according to the previous reports [14,25]. Moreover, compared with Fe 2p spectrum before the chronopotentiometry measurement, the peaks of Fe²⁺ (711.6 and 724.2 eV) could not be observed, and the appearance of strong peaks at 714.5 and 724.8 eV indicated the exclusive existence of Fe³⁺ after long-term OER test (Fig. S22) [26–28]. We also found that the peak area ratio of S₂²⁻/SO₄²⁻ was extremely low compared with that of pristine Ni-Fe-P-S@C due to the surface oxidation (Fig. S23) [29]. Based on the above experimental observations, Ni-Fe-P-S possessed higher Ni and Fe average valence along with the oxidation after chronopotentiometry operation, which arose from the self-adaptive

surface reconfiguration during the harsh OER process.

The pre-oxidation process of phosphides to form partially oxidized phosphides is essential for OER performance improvement of phosphides in alkaline solution [30,31]. Thus, to further investigate the structural/compositional evolution of Ni-Fe-P-S@C during the OER process, CV curves of Ni-Fe-P-S@C within the pre-OER region (prior to oxygen evolution) and OER region, and their corresponding XPS signals were tested. A pair of redox peaks between 1.30 and 1.50 V in CV curves could be clearly observed, which resulted from Ni^{II}/Ni^{III} redox reaction, demonstrating the surface of Ni-Fe-P-S@C was oxidized within the pre-OER potential region (Fig. 5a) [27,32]. Then, this *in-situ* formed oxidized species could serve as the active sites for the subsequent OER process. To explore whether Ni-Fe-P-S@C was partially or completely oxidized under this condition, argon ion sputtering was applied to remove the oxidized surface of Ni-Fe-P-S@C, and then XPS signals of O 1s, P 2p, S 2p, Fe 2p, and Ni 2p were measured. After ion sputtering, it was evident that O signals weakened (Fig. 5b), and the peak intensity of P-Ni relative to P-O enhanced (Fig. 5c). Additionally, although the main region of Ni 2p could be separated into six peaks corresponding to the existence of Ni²⁺ and Ni³⁺ in both Ni 2p spectra before and after ion sputtering, the peak intensity of Ni²⁺ appeared to be enhanced after ion sputtering, indicating the increased content of Ni²⁺ (Fig. 5d). The same phenomenon could be observed in Fe and S spectra, where the peak area ratios of Fe²⁺/Fe³⁺ and S₂²⁻/SO₄²⁻ increased after ion sputtering (Fig. 5e, f). These results verified the partially oxidized surface/phosphide core structure was formed during OER. Furthermore, as a powerful technique sensitive to changes in composition or structure, Raman spectroscopy was used to probe the evolution of catalyst structure during the OER process [33]. The pristine Ni-Fe-P-S@C showed two distinct peaks at 283 and 439 cm⁻¹

Figure 5 (a) CV curves of the first ten cycles of Ni-Fe-P-S@C within the OER region. The inset shows the CV curves of the first ten cycles of Ni-Fe-P-S@C within the pre-OER region. High-resolution XPS spectra of (b) O 1s, (c) P 2p, (d) Ni 2p, (e) Fe 2p, and (f) S 2p of Ni-Fe-P-S@C before and after argon ion sputtering.

attributed to in-plane E_g vibrational mode and out-of-plane A_g vibrational mode in phosphide or sulfide (Fig. S24) [34–38]. However, after experiencing OER CV cycling, the peaks of phosphide faded away, and new peaks appearing at 450 and 539 cm^{-1} could be attributed to the stretching mode of Ni–OH and Ni–O [27,39,40]. Raman analysis again verified the catalyst surface was oxidized *in-situ* during the OER process, which should be responsible for the improvement of OER performance.

DFT calculations were then performed to elucidate the origin of the excellent OER activity of Ni–Fe–P–S@C in alkaline solution *via* the adsorption Gibbs free energy (ΔG) profiles of elementary steps. Under alkaline conditions, OER typically takes four elementary steps: (i) OH^- firstly adsorbs onto the catalyst surface *via* a one-electron oxidation process to form adsorbed $^*\text{OH}$ at the metal site; (ii) $^*\text{OH}$ then reacts with OH^- to form $^*\text{O}$, releasing one H_2O molecule and one electron; (iii) $^*\text{O}$ further associates with one OH^- , forming $^*\text{OOH}$ by losing a third electron; (iv) $^*\text{OOH}$ reacts with the fourth OH^- and is finally oxidized by a one-electron transfer process to release O_2 and H_2O [9,41,42]. Given the fact that the catalyst surface underwent partial oxidation during OER, partial surface oxidation was introduced into the lattice configuration to explore the OER process more accurately. Thus, Ni–Fe–P–S, Ni–Fe–P, and Ni_2P with corresponding oxygen-modified surfaces were selected for modeling the elementary steps of OER. Detailed calculations

revealed that oxygen intermediates preferred to adsorb on the triangular vacancy sites surrounded by nickel and iron atoms. Fig. 6a–c showed the structure models of OER intermediates adsorbed on surface-oxidized Ni–Fe–P–S, Ni–Fe–P, and Ni_2P , and the corresponding free energy diagrams were displayed in Fig. 6d. Interestingly, for Ni_2P , the rate-determining step (RDS) was the O_2 formation step ($^*\text{OOH} \rightarrow \text{O}_2$) with a high reaction free energy change of 3.10 eV, while for Ni–Fe–P and Ni–Fe–P–S, the third elementary step for $^*\text{O}$ formation ($^*\text{O} \rightarrow ^*\text{OOH}$) became the RDS. Specifically, the free energy change of the RDS (ΔG_3) of Ni–Fe–P (2.98 eV) decreased in the presence of Fe, and that of Ni–Fe–P–S further decreased to 2.91 eV, manifesting the incorporation of Fe and S into Ni_2P lattice might help enhance its OER performance, which was consistent with the experimental results. As shown in Fig. S25, although the RDS was still from $^*\text{O}$ to $^*\text{OOH}$ on unoxidized Ni–Fe–P–S, the ΔG_3 was larger than that on its corresponding oxygen-modified surfaces, indicating the compositional/structural evolution of Ni–Fe–P–S into partially oxidized Ni–Fe–P–S played an important role in its desirable OER performance [43,44]. Moreover, total and projected charge DOS for partially oxidized Ni–Fe–P–S, Ni–Fe–P, and Ni_2P were calculated. An obvious increase in DOS around the Fermi level for partially oxidized Ni–Fe–P–S suggested its higher charge carrier density and favorable charge transfer during the electrocatalytic process (Fig. 6e) [22,45]. Overall, the above DFT calculations demonstrated the incorporation of Fe

Figure 6 Top views of the geometric configurations of $^*\text{OH}$, $^*\text{O}$, and $^*\text{OOH}$ intermediates adsorbed on the (a) oxidized Ni_2P surface and (b) oxidized Ni–Fe–P surface. (c) Reaction pathways and the corresponding geometric configurations of $^*\text{OH}$, $^*\text{O}$, and $^*\text{OOH}$ intermediates adsorbed on the oxidized Ni–Fe–P–S surface. The active adsorption sites are circled by the green dotted circles. (d) Free-energy diagrams at potential $U = 0$ V for OER on the oxidized Ni–Fe–P–S, Ni–Fe–P, and Ni_2P . (e) Calculated total and projected DOS of the oxidized Ni–Fe–P–S, Ni–Fe–P, and Ni_2P with the Fermi level aligned at 0 eV. The blue, green, pink, yellow, red, and white balls represent Ni, Fe, P, S, O, and H atoms, respectively.

and S into Ni₂P could provide new catalytic active sites, and the existence of partially oxidized surface could efficiently lower the free energy barrier for RDS and promote OER.

The outstanding OER performance of Ni-Fe-P-S@C could be attributed to the following factors. Heteroatom incorporation and the synergistic effect could generate new active sites and reduce the oxygen intermediate adsorption energy. Besides, increased charge density around the Fermi level could also be realized, resulting in favorable charge transfer during OER. The compositional/structural evolution of Ni-Fe-P-S into partially oxidized Ni-Fe-P-S also played an important role for its desirable OER performance, which resulted in a decreased free energy change of RDS. Although the composition and morphology of Ni-Fe-P-S@C had partially changed, long-term stability tests revealed the excellent OER activity of the material was still maintained. Therefore, we suggested both the phosphide core and *in-situ* formed oxidized surface contributed to the excellent OER activity and stability of our catalyst. Furthermore, the porous structure of Ni-Fe-P-S@C could expose more active sites and accelerate the mass/electron transfer.

CONCLUSIONS

In summary, Fe- and S-substituted Ni₂P uniformly dispersed throughout porous carbon substrate (Ni-Fe-P-S@C) was fabricated through transformation from the pre-synthesized NiFe-MOFs by partial sulfurization and subsequent phosphorization process. Ni-Fe-P-S@C with a porous architecture exhibited superior electrocatalytic activity, stability, and a desirable four-electron pathway for oxygen evolution. DFT calculations revealed that Fe and S incorporation into Ni₂P as well as the partial oxidation process played crucial roles for the improved OER properties. Such a cation- and anion-substitution strategy provides a new avenue for the rational design and preparation of a series of other efficient electrocatalysts for energy storage and conversion applications.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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通过阴、阳离子取代调控Ni₂P的电子结构用于高效氧析出反应

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摘要 合理设计具有结构和组分优势的氧析出反应(OER)催化剂对电催化能源转换技术至关重要。过渡金属磷化物是较有前景的OER催化剂。将杂原子引入过渡金属磷化物的晶格可以引起晶格畸变和电子密度的重新分布,从而改变电子结构,提高催化性能。在此基础上,本文通过部分硫化 and 随后的磷化过程,将预先合成的镍铁金属有机框架(NiFe-MOFs)转化为均匀分散在多孔碳基底上的Fe和S取代的Ni₂P(Ni-Fe-P-S@C)。实验结果和密度泛函理论计算表明,Fe和S的掺入可以调节Ni₂P的电子结构,改变反应中间体的吸附自由能,使得Ni-Fe-P-S@C具有良好的OER催化活性和稳定性。值得注意的是,原位形成的部分氧化的表面对改善局部环境并进一步提升催化活性至关重要。本文提出的阴、阳离子取代策略为提高过渡金属基催化剂的电催化性能带来了新的启示。