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Interface engineering of hierarchical P-doped NiSe/2H-MoSe₂ nanorod arrays for efficient hydrogen evolution†

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Developing non-noble metal-based electrocatalysts with excellent activity and stability for the hydrogen evolution reaction (HER) is crucial for the efficient electrolysis of water. Herein, self-supported three-dimensional (3D) P-doped NiSe/2H-MoSe₂ nanorod arrays (denoted as P-NiSe/MoSe₂) were fabricated by a hydrothermal reaction and subsequent selenization and phosphorization processes. Benefiting from P doping, the synergistic effect of the heterostructures, and abundant active sites, the P-NiSe/MoSe₂ electrocatalyst exhibits excellent alkaline HER performance, with only 43 mV required to achieve 10 mA cm⁻² with a Tafel slope of 93.1 mV dec⁻¹, even remaining stable at 10 mA cm⁻² for 30 hours. In addition, theoretical calculations show that the formation of the heterostructure and P doping optimize the H atom adsorption energies and accelerate electron transport, thus improving its performance in the HER. This work offers a hopeful route for the development of low-cost and efficient electrocatalysts through the simultaneous application of heterostructure engineering and heteroatom doping as well as a 3D structure.

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Introduction

The electrolysis of water has gained a lot of interest as a power conversion process for the efficient generation of H₂ from water or seawater to fulfil the energy demand and decrease carbon emissions due to the excessive usage of fossil fuels.^{1–3} Unfortunately, the sluggish kinetics of water electrolysis requires the use of precious metal-based electrocatalysts such as Pt and Ru/IrO₂. However, they cannot be applied in the industry on a large scale because of their low availability, high cost, and poor long-term stability.^{4–6} Therefore, oxides,⁷ carbides,⁸ nitrides,⁹ phosphides,¹⁰ sulfides,¹¹ and selenides¹² containing transition metal elements have been extensively investigated as alternatives to noble metal electrocatalysts. Among them, transition metal selenides (TMSes) are prospective electrocatalysts because their special electronic structure facilitates electron transport and reaction occurrence.^{12,13}

In recent years, various strategies have been used to prepare electrocatalysts with efficient electrocatalytic performance, such as heteroatom doping, interface engineering, phase engineering, defect engineering, and morphology control.^{14,15} Heteroatom doping can improve the chemical environment of the active sites and the electronic state of the catalyst.^{16–18} Zhu *et al.* prepared P-doped bimetallic NiSe₂-MoSe₂ grown on carbon cloth, which exhibited outstanding HER activity due to P doping, which modulates the electronic structure and promotes charge accumulation and consumption.¹⁶ In addition, the different components in a heterogeneous structure constructed by interface engineering can exhibit synergistic effects to enhance chemisorption and desorption at the interface.^{8,19,20} A new heterostructure containing crystalline NiSe and amorphous MoSe_x was developed by Feng *et al.* with increased electrical conductivity, improved multiphase balance, and enhanced stability through interface engineering.²⁰ However, the improvement of catalysts using only a single strategy is very limited, and therefore multiple strategies have been used to enhance the catalytic activity together. For example, Zhang *et al.* used interface engineering and heteroatom doping to prepare the Mo-NiS/Ni(OH)₂ bifunctional electrocatalyst with a heterogeneous structure,²¹ Li *et al.* prepared the Au@MoS₂ heterogeneous structure with a unique wing shape *via* morphology modulation and interface engineering,²² and Ma *et al.* used metal atom doping and phase engineering to prepare Mo₂C catalysts with Co doping and Mo defects at the same time, which exhibited excellent HER performance.²³

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Inspired by the above-mentioned research, we combined heteroatom doping and interface engineering to design the P-doped NiSe/2H-MoSe₂ electrocatalyst on NF with the structure of nanoparticles on nanorods. The obtained P-NiSe/MoSe₂ presents three advantages that favor electrocatalytic reactions. First, the three-dimensional (3D) hierarchical structure on nickel foam improves electrical conductivity, promotes the breakdown of small bubbles, and provides more active sites. Secondly, P doping modulates the electronic structures of both NiSe and 2H-MoSe₂, which improves the electronic conductivity of the electrocatalyst. Finally, the heterostructure containing NiSe and 2H-MoSe₂ can promote the synergetic effect among the components and optimize the interfacial charge transport. Benefiting from P doping and heterostructure construction, P-NiSe/MoSe₂ exhibits excellent HER performance, with overpotentials of 43 mV and 182 mV at 10 mA cm⁻² and 100 mA cm⁻², respectively, under alkaline conditions, exceeding the performance of most previously reported TMSes. This comprehensive strategy could encourage the development of new catalysts for the efficient hydrogen evolution reaction.

Results and discussion

Characterization of the electrocatalysts

P-NiSe/MoSe₂@NF was synthesized in two steps (Fig. 1a), starting with the hydrothermal reaction of nickel foam, followed by selenization and P doping. Digital images of the pre-

pared samples are shown in Fig. S1,[†] demonstrating the color change in the P-NiSe/MoSe₂@NF electrocatalyst from silver-white NF to green NiMoO₄@NF to black P-NiSe/MoSe₂@NF. SEM was used to investigate the microstructure and geometric morphologies of the as-synthesized materials. As shown in Fig. 1b and S2,[†] after hydrothermal treatment, the original smooth surface of NF was decorated with densely and uniformly distributed NiMoO₄ nanorods grown *in situ*. After selenization and P doping, the P-NiSe/MoSe₂@NF catalyst still maintains the uniformly distributed nanorods in its structure (Fig. 1c and d), and it is worth noting that many nanoparticles appear on the nanorods compared to the smooth nanorods of the NiMoO₄ precursor. Fig. S3[†] shows the SEM images and EDS results of samples with different phosphorus doping amounts, while Table S1[†] presents the phosphorus doping amounts in the different samples. Compared with the uneven morphological structure of Ni_xSe_y@NF (Fig. S4[†]), the unique structure of nanorod arrays with nanoparticles has a larger specific surface area, thus allowing more active sites to be involved in the reaction. In addition, the wettability of P-NiSe/MoSe₂@NF was examined by contact angle measurement. The drop stood stably over the face of NF, as seen in Fig. S5a,[†] but the drop rapidly penetrates P-NiSe/MoSe₂@NF (Fig. S5b[†]), which indicates its superhydrophilicity. This superior structure of P-NiSe/MoSe₂@NF not only brings the active surface sites in full contact with the electrolyte but also accelerates the detachment of bubbles, which facilitates the catalytic reaction.

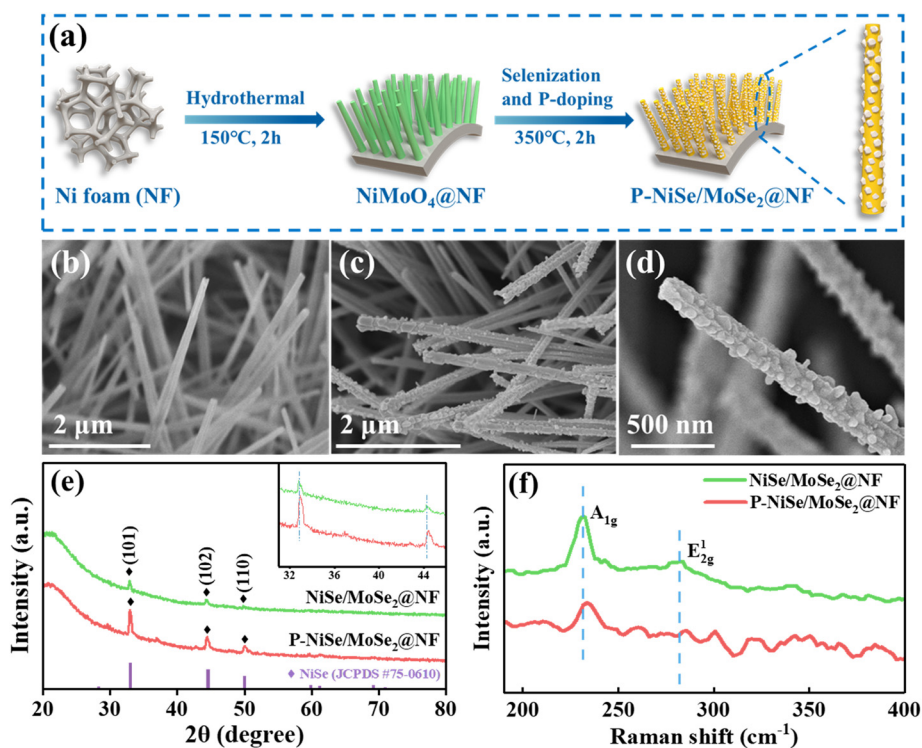


Fig. 1 (a) Schematic of the synthesis of the P-NiSe/MoSe₂@NF electrode. SEM images of (b) NiMoO₄@NF and (c and d) P-NiSe/MoSe₂@NF. (e) XRD patterns and (f) Raman spectra of NiSe/MoSe₂@NF and P-NiSe/MoSe₂@NF.

The phases of the samples were investigated by X-ray diffraction (XRD). The diffraction peaks of the as-prepared precursors match well with the standard XRD patterns of $\text{NiMoO}_4 \cdot x\text{H}_2\text{O}$ and $\text{Ni}(\text{OH})_2$ (Fig. S6[†]). As shown in Fig. 1e, the three peaks at 32.8° , 44.3° , and 49.7° in the diffraction pattern of $\text{NiSe}/\text{MoSe}_2@\text{NF}$ correspond to the (101), (102), and (110) planes of NiSe (JCPDS 75-0610). Similarly, the apparent peaks in $\text{P-NiSe}/\text{MoSe}_2@\text{NF}$ can be indexed to NiSe (JCPDS 75-0610). Notably, the diffraction peaks of $\text{P-NiSe}/\text{MoSe}_2@\text{NF}$ shift to a higher angle, indicating that P doping decreases the lattice parameters of $\text{P-NiSe}/\text{MoSe}_2@\text{NF}$.^{18,24} The lack of diffraction peaks related to the molybdenum phase is due to the poor crystallinity of MoSe_2 , which can be explained by Raman spectroscopy.²⁵ According to the Raman data (Fig. 1f), $\text{NiSe}/\text{MoSe}_2@\text{NF}$ and $\text{P-NiSe}/\text{MoSe}_2$ show characteristic peaks at 231 and 282 cm^{-1} , respectively belonging to the vibration of A_{1g} and E_{2g}^1 of 2H- MoSe_2 .^{26,27} Therefore, we can reasonably conjecture that $\text{NiSe}/\text{MoSe}_2@\text{NF}$ and $\text{P-NiSe}/\text{MoSe}_2@\text{NF}$ contain the NiSe and 2H- MoSe_2 phases, which was confirmed by the subsequent TEM characterization. In comparison, the pattern of $\text{Ni}_x\text{Se}_y@\text{NF}$ has several peaks that can be well-indexed to NiSe (JCPDS 75-0610), Ni_3Se_2 (JCPDS 85-0754), and Ni (JCPDS 04-0850) (Fig. S7[†]). To observe the morphological details of the $\text{P-NiSe}/\text{MoSe}_2@\text{NF}$ heterostructure, transmission electron microscopy (TEM) was used. It is observed that the $\text{P-NiSe}/\text{MoSe}_2@\text{NF}$ catalyst is composed of nanorods with a diameter of about 131 nm that have many nanoparticles on their surface (Fig. 2a and b). As shown in Fig. 2c and d, it is observed that the (002) plane of 2H- MoSe_2 (JCPDS 29-0914) has lattice fringes of 0.643 nm and 0.646 nm, and the lattice

fringes of 0.260 nm and 0.165 nm belong to the (102) and (110) planes of 2H- MoSe_2 (JCPDS 29-0914), while the lattice fringes of 0.201 nm and 0.185 nm belong to the (102) and (110) planes of NiSe (JCPDS 75-0610). The selected area electron diffraction (SAED) image of $\text{P-NiSe}/\text{MoSe}_2@\text{NF}$ shows the indexes for NiSe (100), NiSe (102), and 2H- MoSe_2 (103) (Fig. 2e). Moreover, energy dispersive spectroscopy (EDS) mapping shows the uniform distribution of the elements Ni, Mo, Se, and P (Fig. 2f–j). According to the XRD, Raman, and TEM results, the heterostructure of $\text{NiSe}/2\text{H-MoSe}_2$ has been formed successfully, which may provide more active sites and further improve the HER performance.^{19,21}

X-ray photoelectron spectroscopy (XPS) was used to further investigate the elemental composition and atomic valence of the materials. The doping of different elements changes the coordination environment of the host elements, leading to a change in binding energy.²⁸ Therefore, we hope to obtain information on the electronic structural evolution of the material after P doping from the XPS data. As shown in Fig. 3a, the peaks at 855.8 and 873.7 eV in the Ni 2p region of $\text{NiSe}/\text{MoSe}_2@\text{NF}$ could be indexed to the Ni 2p_{3/2} and Ni 2p_{1/2} of Ni²⁺ in NiSe,^{29,30} while the other two peaks at 861.4 and 879.5 eV were attributed to satellite peaks.^{31,32} In addition, the binding energy peaks at 853.2 and 870.5 eV belong to metallic Ni,³³ which is generally ascribed to the exposed nickel foam. It is worth noting that the binding energies of Ni²⁺ 2p exhibit a positive shift of about 0.3 eV after P substitution, indicating that P doping modulates the electronic structure of $\text{P-NiSe}/\text{MoSe}_2@\text{NF}$, causing the electron density around the nickel atom to decrease.^{34,35} In the Mo 3d spectra in Fig. 3b, the peaks at 229 and 232.2 eV correspond to



Fig. 2 (a and b) TEM images, (c and d) HRTEM images, (e) SAED image, and (f–j) elemental mapping of $\text{P-NiSe}/\text{MoSe}_2@\text{NF}$.

the Mo 3d_{5/2} and Mo 3d_{3/2} of Mo⁴⁺, respectively, confirming the presence of 2H-MoSe₂.³⁶ Meanwhile, the peaks at 232.8 and 235.8 eV represent the appearance of Mo⁶⁺, which is due to partial oxidization in the air.³⁷ The other peak located at 229.9 eV is ascribed to the Se 3s of MoSe₂.³⁸ It is found that in P-NiSe/MoSe₂@NF, the binding energies of Mo⁴⁺ 3d exhibit a negative shift by ~0.2 eV, indicating that P doping reduces the electron density on Mo.^{39,40} In the case of the Se 3d spectrum (Fig. 3c), the two peaks of Se 3d_{5/2} (54.5 eV) and Se 3d_{3/2} (55.3 eV) reveal the presence of Se²⁻ in NiSe and 2H-MoSe₂,^{29,41} while the peak located at 59 eV indicates the surface oxidation state of selenium.³⁸ For P-NiSe/MoSe₂@NF, the two peaks of Se 3d show a negative shift of about 0.2 eV, suggesting an increase in electron occupation around the Se atom, resulting in an enhanced ability to provide electrons.⁴² Furthermore, the peak at 133.7 eV in the P 2p spectrum (Fig. 3d) indicates the existence of P=O bonding, which may be caused by the inevitable contact of the sample with air.^{43,44}

These results suggest that P doping can modulate the electronic structure and ionization state of the material, changing the electron density around Ni, Mo, and Se. These changes may optimize proton adsorption and increase the actual acceptor sites during the HER process, thus accelerating the catalytic reaction.^{45,46}

Electrocatalytic performance

In order to investigate the optimal amount of phosphorus doping, LSV tests were performed on the samples with different phosphorus doping amounts, and the results in Fig. S8† show that the best HER performance was achieved when the amount of sodium hypophosphite used was 20 mg.

The HER electrocatalytic performance of pure NF, NiMoO₄@NF, Ni_xSe_y@NF, NiSe/MoSe₂@NF, and P-NiSe/MoSe₂@NF was evaluated. From the LSV curves (Fig. 4a), it is evident that Ni_xSe_y@NF, NiSe/MoSe₂@NF, and P-NiSe/MoSe₂@NF show better HER catalytic activity than the precursors NiMoO₄@NF and pure NF. Obviously, P-NiSe/MoSe₂@NF exhibits excellent HER electrocatalytic performance. P-NiSe/MoSe₂@NF requires only 43 mV to reach 10 mA cm⁻², a better result than those of Ni_xSe_y@NF (135 mV) and NiSe/MoSe₂@NF (94 mV). This demonstrates the effective enhancement in HER performance *via* the combined effect of heteroatom doping and interface engineering. As seen in the quantitative bar chart (Fig. 4b), P-NiSe/MoSe₂@NF needs only 182 mV to reach 100 mA cm⁻², which is much better than most previously reported TMSes, as compared in Fig. 4c and Table S1.† The same result is obtained for the Tafel slopes (Fig. 4d), in which P-NiSe/MoSe₂@NF exhibits a Tafel slope of 93.1 mV dec⁻¹, smaller than those of pure NF (180.2 mV dec⁻¹), NiMoO₄@NF (161.9 mV dec⁻¹), Ni_xSe_y@NF (145.3 mV dec⁻¹), and NiSe/MoSe₂@NF (114.4 mV dec⁻¹), suggesting that the course of the HER in P-NiSe/MoSe₂@NF is the Volmer–Heyrovsky mechanism.⁴⁷ The values of the exchange current density (*j*₀) are obtained from the Tafel slopes (Fig. S9†). The *j*₀ value of P-NiSe/MoSe₂@NF (3.549 mA cm⁻²) is higher than those of NiSe/MoSe₂@NF (1.541 mA cm⁻²) and Ni_xSe_y@NF (1.195 mA cm⁻²). The Nyquist plots and the fitted results of all electrocatalysts (Fig. 5e and f) provide the solution resistance and charge transfer resistance of the electrocatalysts. The charge transfer resistance (*R*_{ct}) value of P-NiSe/MoSe₂@NF (3.11 Ω) is lower than those of pure NF (28.38 Ω), NiMoO₄@NF (23.15 Ω), Ni_xSe_y@NF (10.71 Ω), and NiSe/MoSe₂@NF (3.76 Ω), resulting

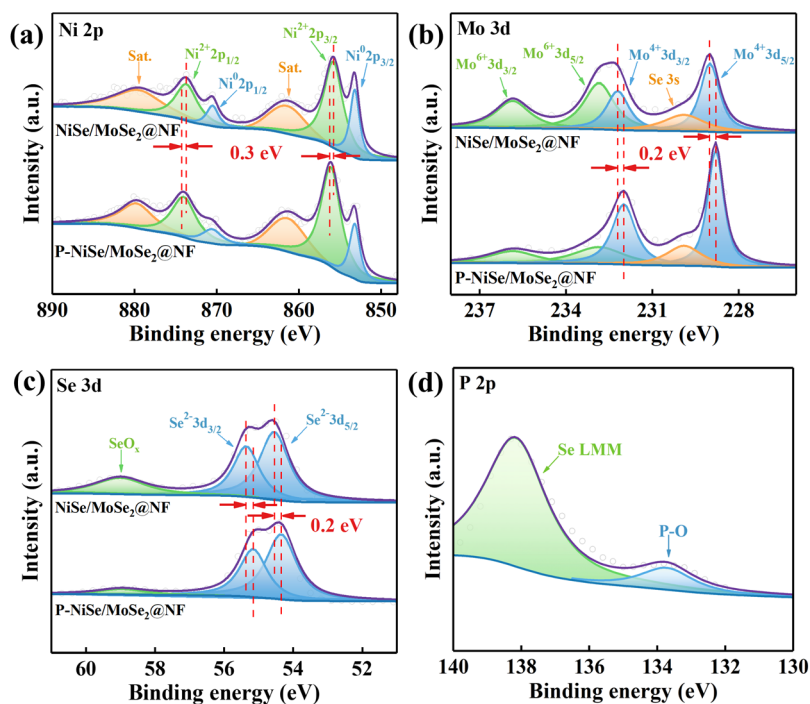


Fig. 3 XPS spectra of (a) Ni 2p, (b) Mo 3d, (c) Se 3d in NiSe/MoSe₂@NF and P-NiSe/MoSe₂@NF. (d) XPS spectrum of P 2p in P-NiSe/MoSe₂@NF.

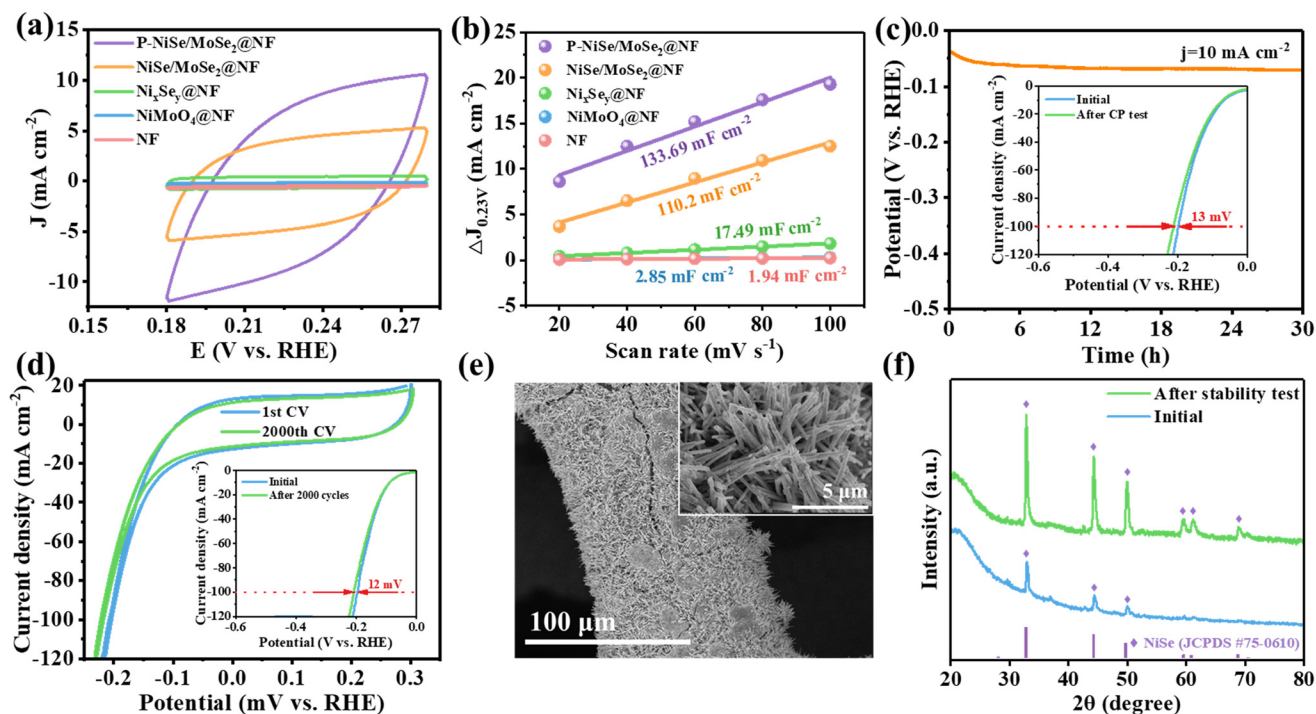


Fig. 5 (a) CV curves of the catalysts at a scan rate of 60 mV s^{-1} (b) The approximate C_{dl} obtained by calculating the current density change at 0.23 V with different scan rates. (c) Chronopotentiometric curve of P-NiSe/MoSe₂@NF for 30 h at 10 mA cm^{-2} (inset: polarization curves after the CP test). (d) The first CV cycle curve and 2000th CV cycle curve of the P-NiSe/MoSe₂@NF catalyst (inset: polarization curves after CV for 2000 cycles). (e) SEM images and (f) XRD patterns of the P-NiSe/MoSe₂@NF catalyst after the stability test.

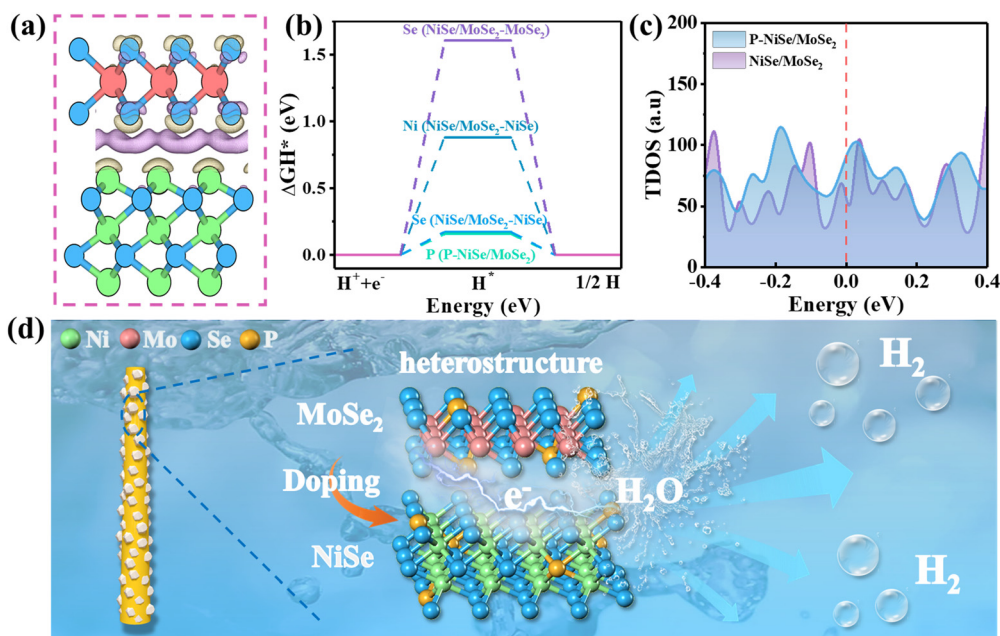


Fig. 6 (a) Charge density difference at the interface of the NiSe/MoSe₂ heterostructure. (b) Gibbs free-energy diagrams of NiSe/MoSe₂ and P-NiSe/MoSe₂ for H adsorption (H^*). (c) The calculated total electronic density of states (TDOS) of NiSe/MoSe₂ and P-NiSe/MoSe₂. The Fermi level is set at 0 eV as a reference. (d) Hydrogen production from the P-NiSe/MoSe₂@NF catalyst promoted by the comprehensive strategy of preparing a heterostructure and P doping.

adsorbed H atom.^{50,51} As observed in Fig. 6c, the total density of states of P-NiSe/MoSe₂ is significantly higher than that of NiSe/MoSe₂, which indicates that P doping accelerates electron transport and thus favors the charge transfer capability of the electrocatalyst in the HER process.

The HER performance of the material can be improved by using a combined strategy of interface engineering and heteroatom doping, as shown in Fig. 6e. The special morphology of nanoparticles on nanorods can increase the specific surface area, expose more active sites and promote bubble dissociation. *In situ* selenization on the precursor NiMoO₄ generates the NiSe and 2H-MoSe₂ heterostructure with rich interfaces, while P doping optimizes the hydrogen adsorption energy and accelerates electron transport, thus promoting catalytic reactions. The synergistic effect generated by interface engineering and P doping endows P-NiSe/MoSe₂@NF with excellent HER performance, which is consistent with the results of the TEM, DFT, and XPS studies.

Conclusions

In summary, we report P-doped NiSe/2H-MoSe₂ nanorod arrays obtained by the strategy of interface engineering and P doping with a special structure of nanoparticles on nanorods, which effectively accelerates hydrogen production under alkaline conditions. Benefiting from the exposure of more active sites, rapid charge transfer, and the interfacial effects arising from the interfaces between NiSe and 2H-MoSe₂ in the heterostructure, as well as the optimized electronic structure and hydrogen adsorption energy achieved by P doping, the prepared P-NiSe/MoSe₂@NF possesses better HER performance than many recently reported TMSe catalysts under alkaline conditions. Specifically, P-NiSe/MoSe₂@NF requires η_{10} and η_{100} values of 43 mV and 182 mV, respectively, for the HER and exhibits durability for over 30 h. This work provides a hopeful approach for the rational preparation of catalysts with multi-interface heterostructures and better electronic structures.

Experimental

Chemicals

All chemicals were not purified further and were used in their raw state. Nickel(II) nitrate hexahydrate [Ni(NO₃)₂·6H₂O, Guangzhou Chemical Reagent Factory Co. Ltd]; sodium molybdate dihydrate (Na₂MoO₄·2H₂O, Shanghai Aladdin Biochemical Technology Co. Ltd); selenium powder (Se, Shanghai Aladdin Biochemical Technology Co. Ltd); sodium hypophosphite (NaH₂PO₂, Macklin Ltd); hydrochloric acid (HCl, 36.0%, Guangzhou Chemical Reagent Factory Co. Ltd); potassium hydroxide (KOH, Shanghai Aladdin Biochemical Technology Co. Ltd); and Ni foam (NF, areal density 320 g cm⁻², pore density 110 PPI, Suzhou Taili Material Technology Co. Ltd) were used as received. Ultrapure water with resistivity >18 MΩ cm⁻¹ was used throughout the experiments.

Synthesis of the NiMoO₄@NF and Ni(OH)₂@NF precursors

To remove the surface oxides, bare NF (2 cm × 3 cm) was first ultrasonicated in hydrochloric acid (6 M) and then cleaned multiple times with ethanol and DI water. In a 50 mL Teflon autoclave, the purged NF was immersed in a 20 mL solution containing 290.8 mg Ni(NO₃)₂·6H₂O and 121 mg Na₂MoO₄·2H₂O, and then hydrothermally treated at 150 °C for 2 h. The Ni(OH)₂@NF precursors were synthesized by the same procedure without Na₂MoO₄·2H₂O.

Synthesis of P-NiSe/MoSe₂@NF and the other contrast catalysts

Mixed powder containing 200 mg selenium powder and 20 mg NaH₂PO₂ and the NiMoO₄@NF precursor were positioned upstream and downstream of the porcelain boat, respectively. After that, the porcelain boat was positioned at the center of a tube furnace, heated to 350 °C at a heating rate of 5 °C min⁻¹ and then held for 2 hours. A 5% H₂-Ar reduction gas was used throughout the process, and P-NiSe/MoSe₂@NF was obtained after naturally cooling to room temperature in the tube furnace. To investigate the optimal amount of phosphorus doping, 10 mg, 20 mg, and 30 mg NaH₂PO₂ were used, and the prepared samples were named P-NiSe/MoSe₂@NF-1, P-NiSe/MoSe₂@NF-2, and P-NiSe/MoSe₂@NF-3, respectively. For comparison, NiSe/MoSe₂@NF was synthesized in a similar way as P-NiSe/MoSe₂@NF but without the use of NaH₂PO₂ during the annealing process. Ni_xSe_y/NF was synthesized in the same way as NiSe/MoSe₂@NF, using the precursor but without adding molybdenum sources.

Electrochemical measurements

Electrocatalytic performance tests were performed on an electrochemical workstation (Ivium V89105 and CHI 660E) using a three-electrode system in a 1.0 M KOH solution. The working electrode, counter electrode, and reference electrode were the prepared catalyst material, carbon rod, and mercuric oxide electrode, respectively. All potentials were further corrected with 80% *iR* correction and converted using the following equation:

$$E_{\text{RHE}} = 0.098 + 0.059 \times \text{pH} + E_{\text{Hg}/\text{HgO}}$$

The double layer capacitance (C_{dl}) was acquired by processing the cyclic voltammetry (CV) curves at various scan rates (20, 40, 60, 80, 100 mV s⁻¹) over a potential range of 0.18–0.28 V (*vs.* RHE). Electrochemical impedance spectroscopy (EIS) was performed at an overpotential of 600 mV in a frequency range of 10⁵–10⁻² Hz. The long-term durability was tested by chronopotentiometry (CP) measurements.

Characterization

The phase composition was studied with a Japan X-ray diffractometer (XRD, Rigaku, D/Max-III) equipped with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Scanning electron microscopy (SEM) was carried out on a HITACHI SU8010 field emission scanning electron microscope (FESEM). The Raman spectra were exam-

ined on a Renishaw inVia Qontor with a 532 nm laser as the excitation light source. X-ray photoelectron spectroscopy (XPS) was conducted using a SHIMADZU AXIS SUPRA with a monochromatic Al K α source. Transmission electron microscopy (TEM) was performed on an FEL Tecnai F30 apparatus. Elemental mapping was performed with an energy-dispersive X-ray spectrometer (EDX) attached to the FEL Tecnai F30 instrument.

Theoretical calculations

All the density functional theory (DFT) calculations were performed with the Vienna *ab initio* simulation package (VASP).^{52,53} The electron exchange–correlation was described by the generalized gradient approximation (GGA)⁵⁴ of the Perdew–Burke–Ernzerhof (PBE) functional.⁵⁵ Hubbard-*U* corrections were employed to calculate the on-site Coulomb repulsion for the Ni 3d electrons with $U = 3.0$ eV.⁵⁶ The cut-off energy for the plane wave basis was fixed at 450 eV. A vacuum larger than 15 Å was applied to remove the adjacent image interactions. Grimme's DFT-D3 method was applied to modify the van der Waals (vdW) interaction between NiSe and MoSe₂. Brillouin zone integration was conducted using a $4 \times 4 \times 1$ *k*-point mesh for free-energy calculations. During the calculations of all the surfaces and slabs, all the structures were totally relaxed, with an energy tolerance of 0.03 eV Å⁻¹ on each atom. Dipole correction was employed.^{57,58} The convergence tolerances for energy and force were 0.0005 eV and 0.03 eV Å⁻¹, respectively.

Conflicts of interest

There are no conflicts to declare.

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