

# Oxygen-deficient $\text{MoO}_x/\text{Ni}_3\text{S}_2$ heterostructure grown on nickel foam as efficient and durable self-supported electrocatalysts for hydrogen evolution reaction

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**Abstract** High-performance and ultra-durable electrocatalysts are vital for hydrogen evolution reaction (HER) during water splitting. Herein, by one-pot solvothermal method,  $\text{MoO}_x/\text{Ni}_3\text{S}_2$  spheres comprising  $\text{Ni}_3\text{S}_2$  nanoparticles inside and oxygen-deficient amorphous  $\text{MoO}_x$  outside *in situ* grow on Ni foam (NF), to assembly the heterostructure composites of  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF}$ . By adjusting volume ratio of the solvents of ethanol to water, the optimized  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF}$ -11 exhibits the best HER performance, requiring an extremely low overpotential of 76 mV to achieve the current density of  $10 \text{ mA}\cdot\text{cm}^{-2}$  ( $\eta_{10} = 76 \text{ mV}$ ) and an ultra-small Tafel slope of  $46 \text{ mV}\cdot\text{dec}^{-1}$  in  $0.5 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$ . More importantly, the catalyst shows prominent high catalytic stability for HER ( $> 100 \text{ h}$ ). The acid-resistant  $\text{MoO}_x$  wraps the inside  $\text{Ni}_3\text{S}_2/\text{NF}$  to ensure the high stability of the catalyst under acidic conditions. Density functional theory calculations confirm that the existing oxygen vacancy and  $\text{MoO}_x/\text{Ni}_3\text{S}_2$  heterostructure are both beneficial to the reduced Gibbs free energy of hydrogen adsorption ( $|\Delta G_{\text{H}^*}|$ ) over Mo sites, which act as main active sites. The heterostructure effectively decreases the formation energy of O vacancy, leading to surface reconstruction of the catalyst, further improving HER performance. The  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF}$  is promising to serve as a highly effective and durable electrocatalyst toward HER.

**Keywords** molybdenum oxides, oxygen vacancies, heterostructure, electrocatalysts, hydrogen evolution reaction

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## 1 Introduction

With the fast growth of energy demands and deterioration of environment, it is necessary to develop renewable and clean energy [1]. Hydrogen ( $\text{H}_2$ ), thanks to its environmental friendliness and high energy density, has attracted great attention [2]. Electrocatalytic water splitting has been considered as the most eco-friendly and economical route to produce  $\text{H}_2$ , because water is an abundant and renewable source [3]. However, the hydrogen evolution reaction (HER) during water electrolysis suffers from large overpotential and slow kinetics [4]. To speed up the HER kinetics, highly active and durable electrocatalysts are applied to lower the dynamic overpotentials [5]. Pt-based compounds have been considered as the most efficient electrocatalysts toward HER, but the preciousness and scarcity of Pt seriously restrict its practical utilization in water electrolysis [6]. Thus, it is vital to explore low-cost while high-efficiency electrocatalysts to replace Pt-based materials.

Nonprecious metal materials, such as Mo-based sulfides [7], oxides [8], phosphides [9], and carbides [10], have been investigated as potential HER catalysts. Compared with molybdenum sulfides, molybdenum oxides are highly stable and readily available in large scale and can also show acceptable HER property [11].  $\text{MoO}_3$  ( $\alpha\text{-MoO}_3$ ), as a low-price and nontoxic material, has been reported to be widely applied in HER, exhibiting an overpotential of 112 mV achieving the current density of  $10 \text{ mA}\cdot\text{cm}^{-2}$  ( $\eta_{10} = 112 \text{ mV}$ ) in acid media [12]. However, because of the less active sites and poor conductivity of intrinsic  $\text{MoO}_3$ , its catalytic performance

has been reported to be much lower than that of Pt-based materials [13]. If the  $\text{MoO}_3$  is combined with other substances to fabricate certain active interfaces, the active sites of  $\text{MoO}_3$  may be exposed as much as possible [14]. Zhang's group [15] coupled  $\text{MoO}_3$  with 1T'- $\text{MoS}_2$  to assembly 1T'- $\text{MoS}_2/\text{MoO}_3$  heterostructure nanosheets, in which the  $\text{MoS}_2/\text{MoO}_3$  interfaces can facilitate electron transfer and surface hydrogen generation, leading to the improvement of electrocatalytic performance. Besides, loading P element onto  $\text{MoO}_3$  nanosheets can also improve the HER catalytic performance [16], for which the P component can boost the adsorption/desorption of proton and afterwards increase electrocatalytic performance. A composite electrocatalyst comprising  $\text{RuO}_2$  supported on  $\text{MoO}_3$  nanosheets was investigated as an HER electrocatalyst, in which the synergetic effect created through interaction between  $\text{MoO}_3$  and  $\text{RuO}_2$  led to the enhancement of catalytic activity [17]. Nevertheless, their HER performance is still inferior to that of precious metals. In addition, the oxygen vacancy in  $\text{MoO}_3$  may not only produce greater conductivity, but also act as HER active site [13]. For example,  $\text{MoO}_{3-x}$  with oxygen vacancies depicted higher HER catalytic activity than com- $\text{MoO}_3$  [13]. Density functional theory (DFT) calculation revealed that the oxygen vacancy prominently reduces the adsorption energy of  $\text{H}_2\text{O}$  and then improves the catalytic activity. Thus, fabricating oxygen vacancies and active interfaces into molybdenum oxides may be effective ways to enhance the HER performance of molybdenum oxides. The known researches on molybdenum oxides with oxygen vacancy are all about crystalline  $\text{MoO}_3$ , but there are lack of reports focused on amorphous  $\text{MoO}_x$  with oxygen vacancy.

Meanwhile, Ni-based materials have shown a big potential for using as HER catalysts [18].  $\text{Ni}_3\text{S}_2$ , because of the existence of Ni–Ni networks throughout its crystal structure, exhibits good metallic conductivity [19]. So far, many studies revealed that  $\text{Ni}_3\text{S}_2$  owns HER activity [20], while its catalytic activity and stability are still less competitive relative to noble-metal catalysts. On the other hand, self-supported catalysts, compared to powdery ones, avoid the addition of polymer binder. Meanwhile, the introduction of substrates in self-supporting catalysts can raise electrochemical active areas. The three-dimensional nickel foam (NF) is a low-cost template with large surface area, and is normally used as a conductive substrate to host electrocatalyst materials [21]. Using thiourea,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and NF as reactants,  $\text{Ni}_3\text{S}_2/\text{NF}$  was fabricated to depict high HER activity and good durability in basic and neutral conditions [22]. Hybridizing  $\text{Ni}_3\text{S}_2$  with other electrocatalysts such as  $\text{MoS}_2$  [23] and/or  $\text{Co}_9\text{S}_8/\text{MoS}_2$  [24] is also a commonly employed method to augment the catalytic activity. Moreover,  $\text{Ni}_3\text{S}_2$  is generally combined with other sulfides, while the integration of  $\text{Ni}_3\text{S}_2$  with amorphous  $\text{MoO}_x$  is rarely reported. As known,  $\text{Ni}_3\text{S}_2$  and NF matrix are unstable in

acidic solutions, while  $\text{MoO}_3$  or  $\text{MoO}_x$  is acid-resistant. Therefore, if NF and the *in situ* grown  $\text{Ni}_3\text{S}_2$  are wrapped by dense layers of  $\text{MoO}_x$ , it is expected to improve the acid resistance of the integrated electrocatalysts.

Herein, via a facile solvothermal method, we fabricate  $\text{MoO}_x/\text{Ni}_3\text{S}_2$  spheres which consist of dispersed  $\text{Ni}_3\text{S}_2$  nanoparticles and amorphous  $\text{MoO}_x$  wrapped outside. By adjusting ratios of water/ethanol solvents, the as-prepared  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF}$ -11 (volume ratio of ethanol:water is 1:1) exhibits optimum HER performance, requiring an extremely low overpotential ( $\eta_{10} = 76$  mV) and a much low Tafel slope of  $46$  mV $\cdot\text{dec}^{-1}$  in  $0.5$  mol $\cdot\text{L}^{-1}$   $\text{H}_2\text{SO}_4$ . Benefiting from the existing oxygen vacancy and formed heterojunction, Mo atoms are exposed as much as possible to exhibit reduced Gibbs free energy of hydrogen adsorption ( $\Delta G_{\text{H}^*}$ ) and act as active-sites. Additionally, the stability of the catalyst under acidic conditions is greatly improved because the acid-resistant amorphous  $\text{MoO}_x$  layer is wrapped around  $\text{Ni}_3\text{S}_2/\text{NF}$ . The  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF}$ -11 displays extremely high stability ( $\geq 100$  h at  $23.5$  mA $\cdot\text{cm}^{-2}$ ). This study would give a novel perspective on the fabrication of amorphous molybdenum oxides or oxygen-deficient materials with excellent HER performance.

## 2 Experimental

### 2.1 Synthesis of $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF}$ composites

A series of  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF}$  composites (labeled as  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF}$ -*mn*, where *m* and *n* are volume ratios of ethanol:water) were synthesized via a one-pot solvothermal reaction. Typically, two pieces of commercial NF (1 cm  $\times$  2 cm) were first immersed in an acid solution (1 mol $\cdot\text{L}^{-1}$  HCl) for 20 min, to remove the oxides on the surface of NF. Then the NF was washed using acetone, water and ethanol in turn, and then was dried in vacuum at  $45$  °C, followed by weighing. Meanwhile, 2 mmol of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  was dissolved in 30 mL of ethanol:water mixture solvents. After stirred for 30 min, 10 mmol of thiourea was dissolved in the solutions. The abovementioned solutions and pre-treated NF were simultaneously transferred to a Teflon-lined autoclave (50 mL) and reacted at  $140$  °C for 18 h. After cooled, the obtained  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF}$ -*mn* products were washed with excess deionized water and ethanol several times, and then dried in vacuum at  $45$  °C overnight.

### 2.2 Electrochemical measurements

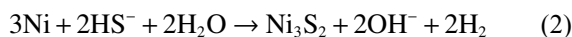
The electrochemical tests were conducted in a three-electrode cell in a  $0.5$  mol $\cdot\text{L}^{-1}$   $\text{H}_2\text{SO}_4$  solution. Ag/AgCl (saturated KCl) electrode and a graphite rod electrode worked as reference and counter electrodes, respectively.

The as-prepared samples were used directly as working electrodes. For a reliable comparison, we loaded Pt–C and commercial MoO<sub>3</sub> (com-MoO<sub>3</sub>) on NF with the same mass loading as MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11. Table S1 (cf. Electronic Supplementary Material, ESM) listed the mass loading of all catalysts. The details of electrochemical measurements are shown in ESM.

### 3 Results and discussion

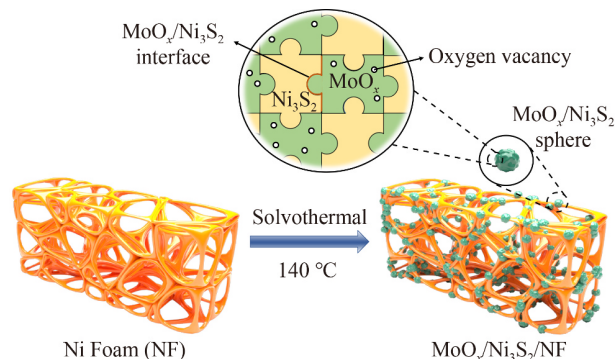
#### 3.1 Material characterization

The fabrication procedure of the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF composites is described in Scheme 1. In the solvothermal reaction, the thiourea may break down to release HS<sup>-</sup> ions (Eq. (1)); meantime, the NF can release Ni<sup>2+</sup> into the solution, and the Ni<sup>2+</sup> would react with the active HS<sup>-</sup> to generate the Ni<sub>3</sub>S<sub>2</sub> particles (Eq. (2)) [24]:

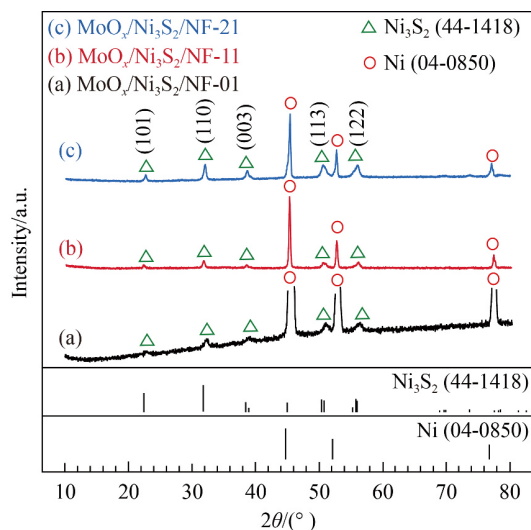


The structures of the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-*mn* were studied firstly by X-ray diffraction (XRD) measurements. As shown in Fig. 1, for all samples, there appeared diffraction peaks at 21.7°, 31.1°, 37.8°, 49.7° and 55.2° respectively assigned to the (101), (110), (003), (113) and (122) planes of hexagonal Ni<sub>3</sub>S<sub>2</sub> (JCPDS no. 44-1418) [25]. This indicates that the partial NF surface was converted to Ni<sub>3</sub>S<sub>2</sub> under the solvothermal conditions. Three strong diffraction peaks of Ni were derived from the NF substrate. However, no distinguishable diffractions related to MoO<sub>x</sub> were found, suggesting that if there is certain MoO<sub>x</sub> phase, it would exist in amorphous form. The transmission electron microscope (TEM) characterization discussed below with the absence of lattice fringes would provide important evidence of the amorphous characteristic.

The morphologies of NF (Fig. S1, cf. ESM) and MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-*mn* (Fig. 2) were characterized by

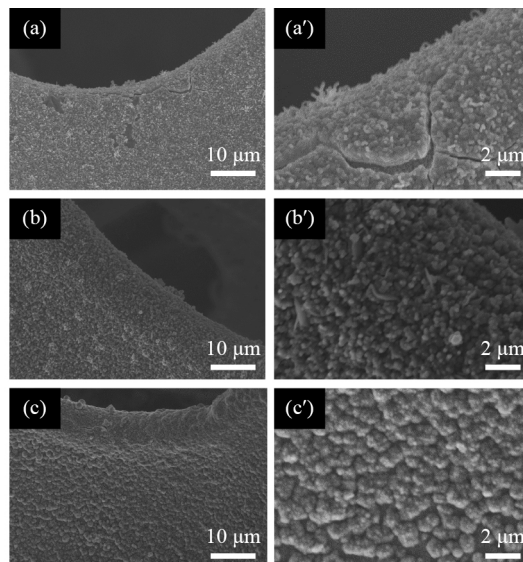


**Scheme 1** Schematic illustration of formation of oxygen-deficient MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF composites.



**Fig. 1** XRD patterns of (a) MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-01, (b) MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 and (c) MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-21.

scanning electron microscopy (SEM). Figure S1(a) shows the 3D porous characteristic of NF, and at higher magnification, the surface of NF can be observed to be very smooth (Fig. S1(a')). The special skeleton of NF provides large surface area and ideal mechanical stability. As seen in Fig. 2, the entire NF surface is tightly covered by the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>. When ethanol solvent was absent in the reaction (no ethanol), the resulting product of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-01 (Figs. 2(a) and 2(a')) has some cracks on its surface, which may reduce the conductivity of the catalyst [26]. At the ethanol:water ratio of 1:1, the as-formed MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 presents irregular small spheres grown on the substrate (Figs. 2(b) and 2(b')). In addition, it can be seen from Fig. 2(b) that there is no



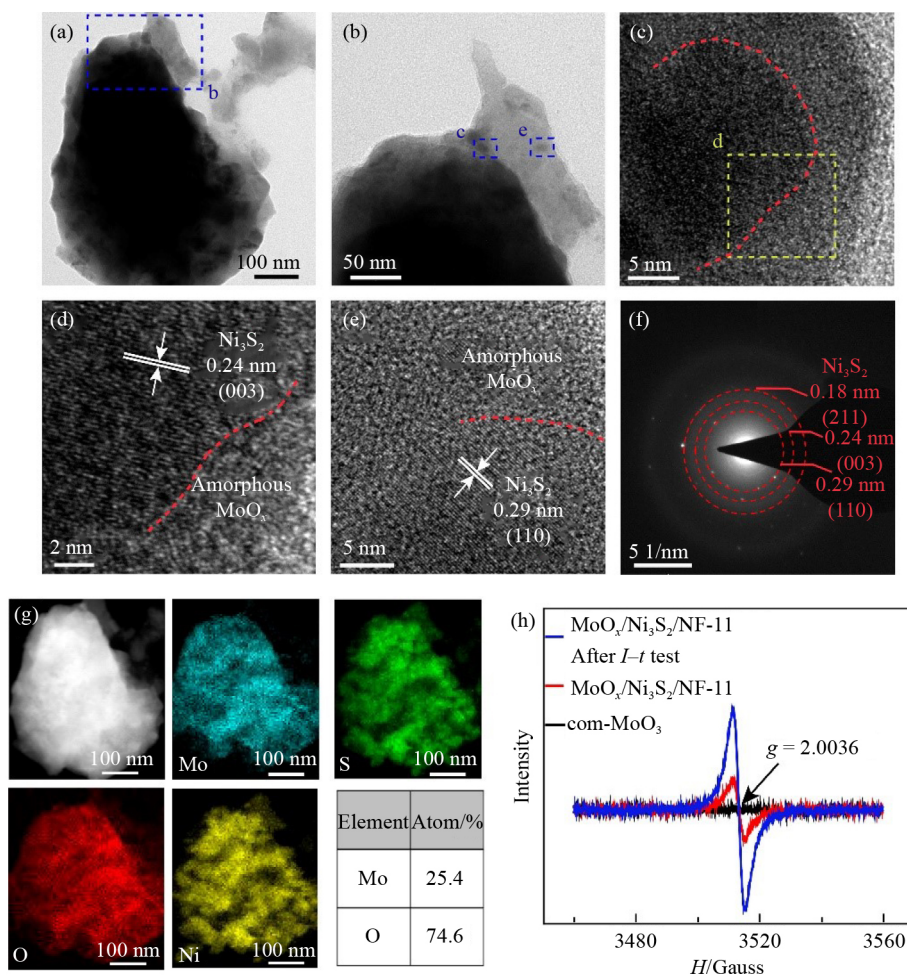
**Fig. 2** SEM images of (a, a') MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-01, (b, b') MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 and (c, c') MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-21.



crack on the surface of the sample, which means that the acid-resistant NF matrix is completely coated by  $\text{MoO}_x/\text{Ni}_3\text{S}_2$ , so that NF cannot be corroded by acid, paving the way for the excellent stability of the catalyst under acidic conditions. As the ethanol:water ratio is increased to 2:1 (with more ethanol), as found in  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF}-21$ , the formed  $\text{MoO}_x/\text{Ni}_3\text{S}_2$  spheres on the NF surface become larger (Figs. 2(c) and 2(c')).

For the  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF}-11$  with the most regular and perfect appearance, detailed morphology and structure were further explored by TEM (Figs. 3 and S3, cf. ESM) via scratching the samples from the NF substrate. TEM images (Figs. 3(a) and 3(b)) show that the  $\text{MoO}_x/\text{Ni}_3\text{S}_2$  spheres are comprised of nanoparticles. Figure 3(c) reveals the interface region of the  $\text{Ni}_3\text{S}_2$  nanoparticles, indicating that there are two clearly distinguishable phases between the inside and outside of the particle, and the  $\text{Ni}_3\text{S}_2$  nanoparticle is closely connected to the amorphous  $\text{MoO}_x$ . For clarity, the original image (without scaling) of Fig 3(c) is shown in Fig. S2 (cf. ESM). The

TEM investigations of  $\text{MoO}_x/\text{Ni}_3\text{S}_2-11$  (see Figs. 3(d) and 3(e)) further exhibit the tight connection between the  $\text{Ni}_3\text{S}_2$  particles and  $\text{MoO}_x$ . The lattices of 0.24 nm (Fig. 3(d)) and 0.29 nm (Fig. 3(e)) are ascribed to (003) and (110) crystal planes of  $\text{Ni}_3\text{S}_2$  [27], further proving its presence. The above results can be supported by the SAED pattern (Fig. 3(f)), which displays characteristic crystal planes of  $\text{Ni}_3\text{S}_2$  and diffuse rings of the amorphous  $\text{MoO}_x$ . The amorphous characteristic of  $\text{MoO}_x$  leads to the absence of XRD diffractions (see Fig. 1). The  $\text{MoO}_x$  surrounding for  $\text{Ni}_3\text{S}_2$  further ensures the acid resistance of the electrocatalyst. The compositional distributions of the  $\text{MoO}_x/\text{Ni}_3\text{S}_2-11$  sphere are confirmed by elemental mapping analyses (Fig. 3(g)), high angle annular dark field scanning transmission electron microscope (HAADF-STEM) image (Fig. S3(a)) and line scans (Fig. S3(b)). In Fig. 3(g), uneven distribution of Mo/O and Ni/S is clearly observed throughout the whole sphere. The elements of Mo and O appear in the same region, while Ni and S elements locate in other regions, indicating that the two

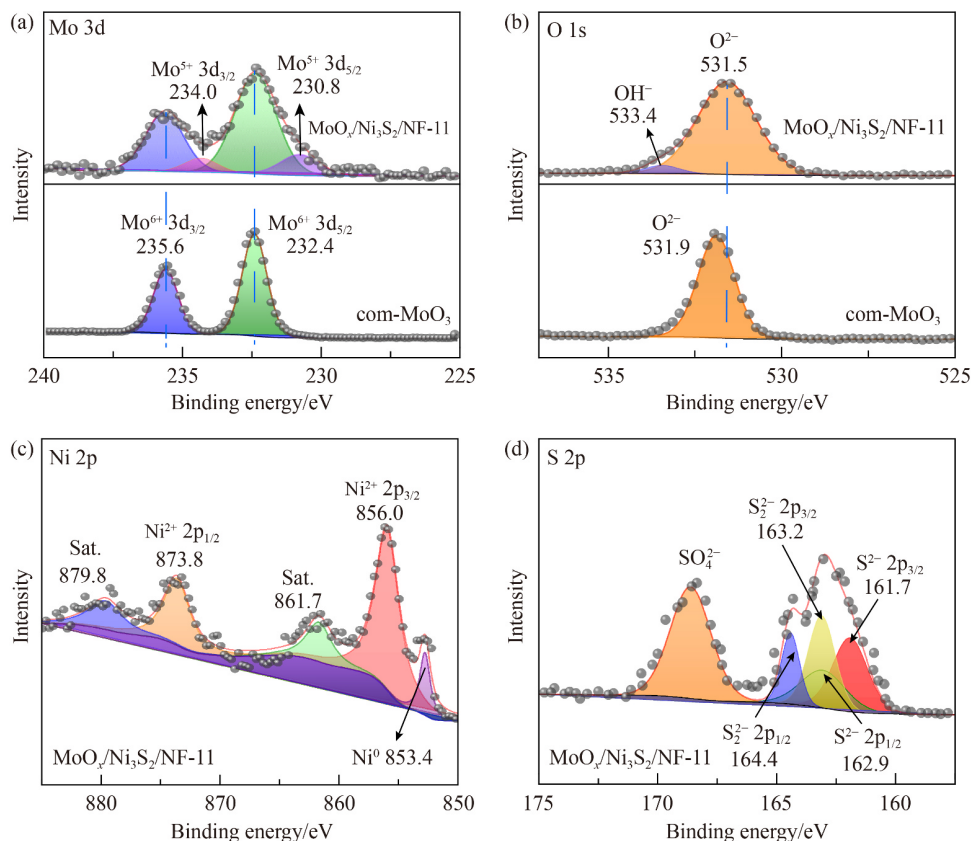


**Fig. 3** (a, b) TEM images of  $\text{MoO}_x/\text{Ni}_3\text{S}_2-11$ , (c, d, e) HR-TEM images of  $\text{MoO}_x/\text{Ni}_3\text{S}_2-11$ , and the visible lattice fringes images obtained from the blue and yellow square regions; (f) SAED pattern of  $\text{MoO}_x/\text{Ni}_3\text{S}_2-11$ ; (g) HAADF-STEM and energy dispersive spectroscopy elemental mappings of Mo, O and Ni of  $\text{MoO}_x/\text{Ni}_3\text{S}_2-11$ ; (h) electron paramagnetic resonance (EPR) spectrum of  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF}-11$  before and after 60 h  $I-t$  test, and the control sample of com- $\text{MoO}_3$ .

phases of MoO<sub>x</sub> and Ni<sub>3</sub>S<sub>2</sub> have distinct interfaces. From Fig. 3(g), the atom ratio of Mo:O is 1:2.94, which is close to MoO<sub>3</sub>, with the oxygen content slightly reduced. All these results prove the existence of Ni<sub>3</sub>S<sub>2</sub> crystalline phase along with amorphous MoO<sub>x</sub>.

To clarify the detailed structure of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11, EPR spectroscopy and X-ray photoelectron spectroscopy (XPS) were carried out and the results were shown in Fig. 4, with com-MoO<sub>3</sub> as a control sample. In Fig. 3(h), the EPR spectra of com-MoO<sub>3</sub> (black line) shows no signal, while MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 (red line) displays a signal at about 3512 Guass ( $g = 2.0036$ ), indicating the existence of oxygen vacancy. For XPS spectra of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 (Fig. 4(a)), the binding energies of 235.6 and 232.4 eV are related to Mo 3d<sub>3/2</sub> and 3d<sub>5/2</sub> of Mo<sup>6+</sup>, the same as found in com-MoO<sub>3</sub> [28]. In contrast to com-MoO<sub>3</sub>, MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 shows a pair of peaks of Mo<sup>5+</sup> (234.0 eV for Mo 3d<sub>3/2</sub> and 230.8 eV for Mo 3d<sub>5/2</sub>) [29]. Comparison of O 1s spectra of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 and com-MoO<sub>3</sub> is presented in Fig. 4(b). As shown, for com-MoO<sub>3</sub>, the binding energy of 531.9 eV is assigned to lattice oxygen (O<sup>2-</sup>) [30], while in MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11, the energy of O<sup>2-</sup> is reduced to a lower level (531.5 eV). Also, the half-peak width of O 1s core-level spectra of the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 is widened in comparison with that of the com-MoO<sub>3</sub>. The difference of half-peak width of O 1s

core-level spectra in the materials with and without oxygen vacancies has also been observed in other literature [31]. For MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11, the appearance of Mo<sup>5+</sup> and the shift of O 1s simultaneously prove the presence of oxygen vacancy, which is consistent with EPR results. All these indicate a changed coordination configuration between Mo and O, as discussed in literatures [13,16]. It was reported that the shift of O 1s to a lower energy level means the electron transfer to the neighboring oxygen vacancies [32]. Meanwhile, one weak peak detected at 533.4 eV can be assigned to O 1s of surface adsorbed species (here is OH<sup>-</sup>) [33]. In Fig. 4(c), for Ni 2p spectra of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11, the peaks at 873.8 and 856.0 eV are related to Ni 2p<sub>1/2</sub> and Ni 2p<sub>3/2</sub> of Ni<sup>2+</sup>, accompanied by two satellite peaks at 879.8 and 861.7 eV [34]. The peak at 853.4 eV is assigned to Ni<sup>0</sup>, which belongs to Ni<sub>3</sub>S<sub>2</sub> or NF [35]. In the spectra of S 2p (Fig. 4(d)), the two signals at 162.9 and 161.7 eV belong to 2p<sub>1/2</sub> and 2p<sub>3/2</sub> of S<sup>2-</sup>, and the other two signals at 164.4 and 163.2 eV are attributed to 2p<sub>1/2</sub> and 2p<sub>3/2</sub> of S<sub>2</sub><sup>2-</sup> [36], suggesting the presence of terminal unsaturated S of Ni-S bonds [37]. The peak at 168.2 eV is assigned to oxidized sulfur species (here is SO<sub>4</sub><sup>2-</sup>) owing to surface oxidation [38]. In Raman spectra of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 (Fig. S4, cf. ESM), the band at 324 cm<sup>-1</sup> is associated with A<sub>1</sub> vibration mode of the Ni<sub>3</sub>S<sub>2</sub> phase [39], and the

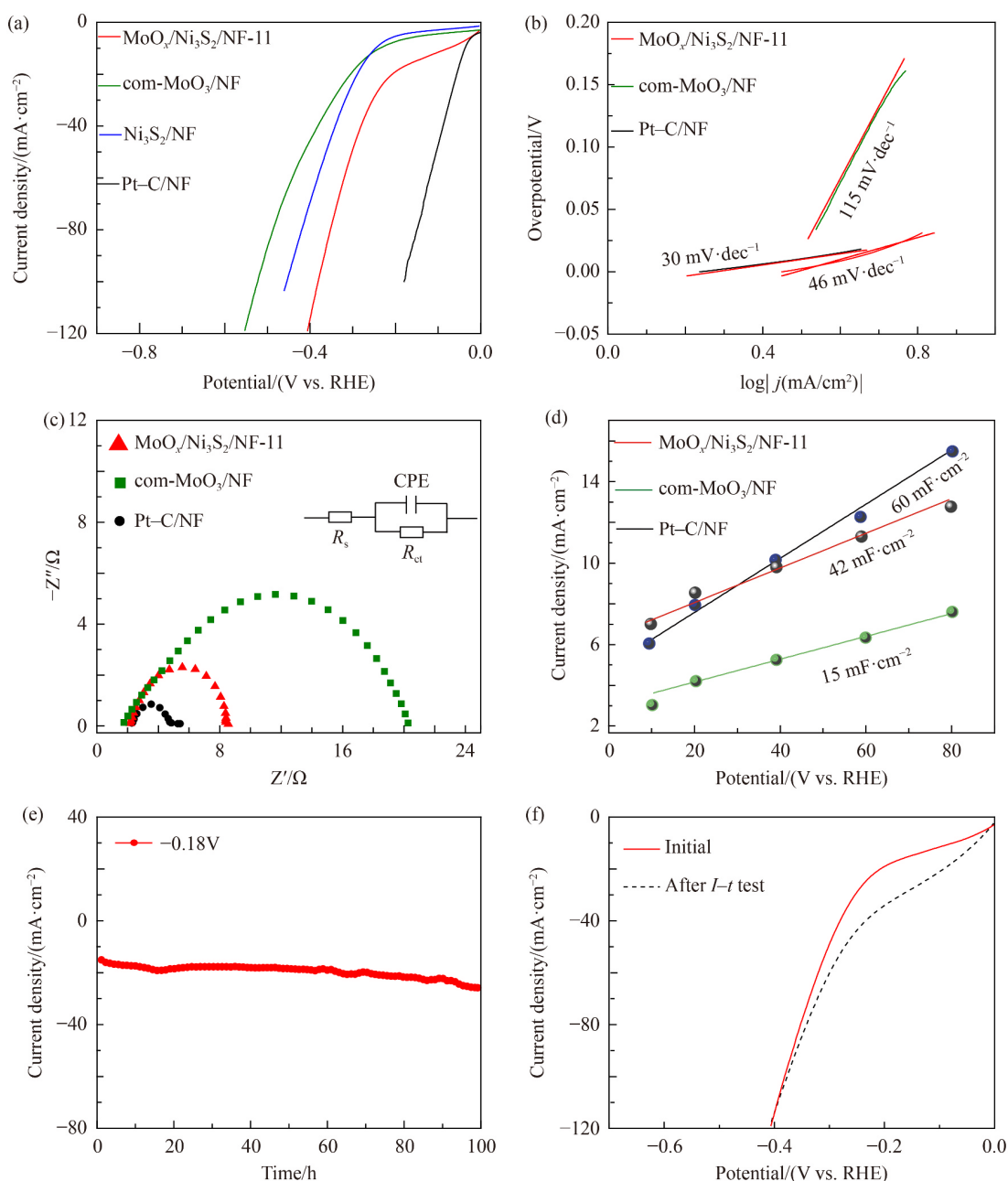


**Fig. 4** X-ray photoelectron spectra with deconvolution of (a) Mo 3d, (b) O 1s for MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 and com-MoO<sub>3</sub>, (c) Ni 2p, and (d) S 2p for MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11.

peaks ranging from 800 to 1000  $\text{cm}^{-1}$  are related to Mo=O modes [16]. We also measured the infrared spectrum of  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF-11}$  (Fig. S5, cf. ESM). The bands at 975 and 914  $\text{cm}^{-1}$  correspond to the stretching vibration of Mo=O, and the bands at 615 and 514  $\text{cm}^{-1}$  are assigned to stretching and bending vibrations of Mo–O, respectively [40]. No Mo–S related spectral peaks can be observed, which proves that the sample does not contain Mo–S bond.

### 3.2 Electrocatalytic performance for HER

HER performance of  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF-}mn$  synthesized at different ethanol: $\text{H}_2\text{O}$  ratios and control samples of com- $\text{MoO}_3/\text{NF}$ ,  $\text{Ni}_3\text{S}_2/\text{NF}$  and Pt–C/NF was measured (Fig. 5 and Fig. S6, cf. ESM). As observed (Fig. S6), among the three samples, the  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF-11}$  at an ethanol: $\text{H}_2\text{O}$  ratio of 1:1 exhibits an extremely low  $\eta_{10}$  value of 76 mV, demonstrating HER performance much better than



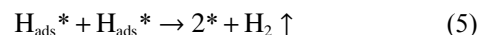
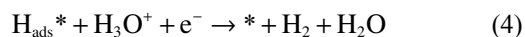
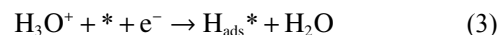
**Fig. 5** (a) Polarization curves of  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF-11}$ , com- $\text{MoO}_3/\text{NF}$ ,  $\text{Ni}_3\text{S}_2/\text{NF}$  and Pt–C/NF; (b) Tafel slopes of  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF-11}$ , com- $\text{MoO}_3/\text{NF}$  and Pt–C/NF derived from polarization curves; (c) Nyquist plots of  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF-11}$ , com- $\text{MoO}_3/\text{NF}$  and Pt–C/NF at  $-200$  mV versus RHE measured from electrochemical impedance spectroscopy (EIS) in the frequency range from  $10^5$  to 0.01 Hz; (d) plots of current density as a function of scan rates for  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF-11}$ , com- $\text{MoO}_3/\text{NF}$  and Pt–C/NF; (e) chronoamperometric curve of  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF-11}$  at a constant applied potential of  $-180$  mV versus RHE; (f) polarization curves of before and after 100 h  $I-t$  test of  $\text{MoO}_x/\text{Ni}_3\text{S}_2/\text{NF-11}$ . All the measurements were performed in a  $0.5 \text{ mol}\cdot\text{L}^{-1}$   $\text{H}_2\text{SO}_4$  electrolyte.



MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-01 ( $\eta_{10} = 127$  mV) without ethanol added during synthesis and MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-21 ( $\eta_{10} = 114$  mV) prepared at an ethanol:H<sub>2</sub>O ratio of 2:1. From the SEM images mentioned above, the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 has a relatively small particle size and no crack on the surface, which is conducive to increasing the contact area between the catalyst and the electrolyte and accelerating the electron transmission. Therefore, the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 exhibits the optimal HER performance. Furthermore, the  $\eta_{10}$  of 76 mV of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 is extremely lower than that (235 mV) of com-MoO<sub>3</sub>/NF, and is close to that (37 mV) of Pt-C/NF, showing performance exceeding com-MoO<sub>3</sub> and comparable to Pt-C. As listed in Table 1 [16,17,41–46], the  $\eta_{10}$  of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 is obviously lower compared with the reported Mo-related electrocatalysts. The excellent catalytic performance of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 may be mainly attributed to the oxygen vacancy. For the P-MoO<sub>3</sub> [16], though it also contains oxygen vacancies coming from P doping, it has a larger  $\eta_{10}$  of 166 mV, meaning an inferior HER activity than MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11. The outstanding HER activity of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 suggests that there may be heterojunctions formed in the two integrated phases of MoO<sub>3</sub> and Ni<sub>3</sub>S<sub>2</sub>. The heterojunction and oxygen vacancy would offer rapid electron transfer favorable to the HER activity.

To explore the catalytic mechanism of the electrocatalysts, Tafel plots were calculated (Fig. 5(b)). The Tafel slope of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 is 46 mV·dec<sup>-1</sup>, which is close to the value (30 mV·dec<sup>-1</sup>) of Pt-C/NF and much

lower than that (115 mV·dec<sup>-1</sup>) of com-MoO<sub>3</sub>/NF. Table 1 listed the Tafel slopes of reported Mo-based HER catalysts. The low Tafel slope of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 demonstrates its effectively enhanced kinetics during the H<sub>2</sub>O dissociation [17]. On the basis of kinetic models, the Tafel slopes of 120, 40 and 30 mV·dec<sup>-1</sup> are assigned to Volmer (Eq. (3)), Heyrovsky (Eq. (4)) and Tafel (Eq. (5)) reactions, respectively:



The first step is Volmer reaction (Eq. (3)), for which one proton (H<sub>3</sub>O<sup>+</sup>) first adsorbs on the surface of the catalyst and accepts one electron to generate one hydrogen atom (H<sub>ads</sub><sup>\*</sup>). The second step involves two kinds of reactions: one is Heyrovsky reaction and the other is Tafel reaction. For the Heyrovsky reaction (Eq. (4)), which is an electrochemical desorption, another proton (H<sub>3</sub>O<sup>+</sup>) accepts one electron and desorbs from catalyst surface and react with the former H atom to generate one H<sub>2</sub>. For the Tafel step (Eq. (5)), two H<sub>ads</sub><sup>\*</sup> desorb from catalyst surface and combine directly and then release one H<sub>2</sub>. The slope of 46 mV·dec<sup>-1</sup> for MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 indicates it follows the Volmer–Heyrovsky mechanism, while Pt-C/NF with the much lower slope of 30 mV·dec<sup>-1</sup> follows the Volmer–Tafel mechanism. Nyquist plots were obtained by measuring EIS and the charge-transfer resistance ( $R_{\text{ct}}$ ) values were fitted by the equivalent circuit model (Fig. 5(c)). It can be seen that the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 shows an extremely small  $R_{\text{ct}}$  of 6.51  $\Omega$ , which is much lower than the com-MoO<sub>3</sub>/NF (21.51  $\Omega$ ), indicating that the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 has faster charge transfer dynamics in HER process (see Table S2, cf. ESM). The fast charge transfer is probably attributed to synergetic effect of the amorphous MoO<sub>x</sub> and the Ni<sub>3</sub>S<sub>2</sub> nanoparticles. The abundant interfaces of the two phases make the hydrogen adsorption and desorption more effective [17].

In general, good electrocatalytic activity is accompanied by a large electrochemically active surface area, which is normally proportional to the electrochemical double-layer capacitance ( $C_{\text{dl}}$ ). From the cyclic voltammetry curves carried out at varied scan rates (Fig. S7, cf. ESM), the  $C_{\text{dl}}$  of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 is calculated as 42 mF·cm<sup>-2</sup> (Fig. 5(d)). This  $C_{\text{dl}}$  value is much larger than those many reported catalysts, such as MoO<sub>3</sub> (13.58 mF·cm<sup>-2</sup>) [14], UDSSL-MoS<sub>2</sub>-rGO (24 mF·cm<sup>-2</sup>) [42], MoP/NG (9.1 mF·cm<sup>-2</sup>) [45] and MoO<sub>2</sub>/MoSe<sub>2</sub> (18.68  $\mu\text{F}\cdot\text{cm}^{-2}$ ) [47]. This large  $C_{\text{dl}}$  unveils the large amount of electrochemical active sites in the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11. These results reveal that the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 with oxygen vacancies generates more accessible active sites, thereby promoting the H<sub>2</sub> evolution process.

**Table 1** HER performance of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 and some reported electrocatalysts in 0.5 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>

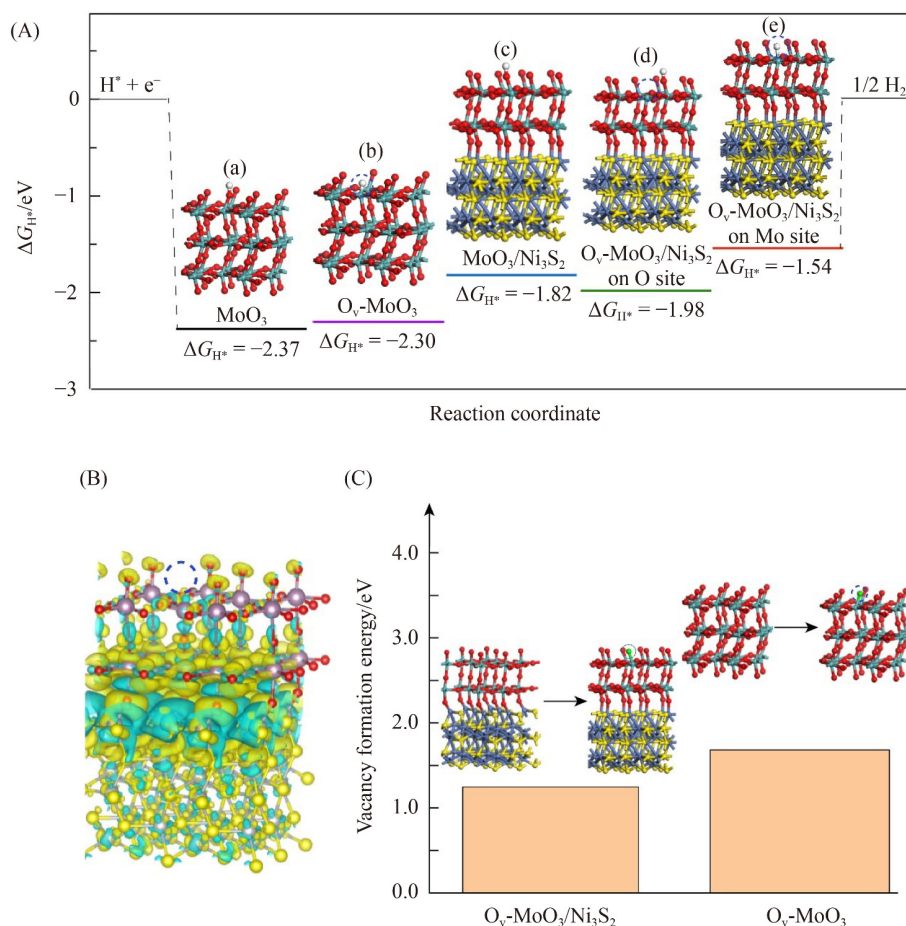
Catalysts	$\eta_{10}$ /mV	Tafel slope/(mV·dec <sup>-1</sup> )	Ref.
MoO <sub>x</sub> /Ni <sub>3</sub> S <sub>2</sub> /NF-11	76	46	This work
P-MoO <sub>3-x</sub> <sup>a)</sup>	166	42	[11]
MoO <sub>3</sub> @RuO <sub>2</sub> <sup>b)</sup>	110	62	[17]
Pd NDs/DR MoS <sub>2</sub> <sup>c)</sup>	103	41	[41]
UDSSL-MoS <sub>2</sub> -rGO <sup>d)</sup>	ca. 210	35	[42]
Mo/Mo <sub>2</sub> C <sup>e)</sup>	89	62	[43]
(1T/2H) MoS <sub>2</sub> /α-MoO <sub>3</sub> <sup>f)</sup>	232	81	[44]
MoP/NG <sup>g)</sup>	94	50	[45]
MoC <sub>x</sub> <sup>h)</sup>	142	53	[46]

a) P doped MoO<sub>3-x</sub>, prepared via two-step intercalation method by using dodecylamine (DDA) and 4-bromine benzyl phosphoric acid; b) RuO<sub>2</sub> nanoparticles supported on MoO<sub>3</sub> nanosheets, prepared by a sonochemical method followed by calcination in air; c) Pd nanodisks (NDs) assembled on the basal plane of defect-rich MoS<sub>2</sub> nanosheets (DR-MoS<sub>2</sub>); d) ultradispersed and single-layered MoS<sub>2</sub> nanoflakes coupled with reduced graphene oxide sheets (UDSSL-MoS<sub>2</sub>-rGO), synthesized by a hydrothermal method using (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, L-cysteine and GO under pH = 1; e) Mo/Mo<sub>2</sub>C heteronanosheets, obtained by a NaCl template method followed by the reduction and carbonization under H<sub>2</sub> and CH<sub>4</sub>, respectively; f) (1T/2H) MoS<sub>2</sub>/α-MoO<sub>3</sub> prepared by hydrothermal method using thiourea, MoO<sub>3</sub> and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O; g) MoP nanoflakes intercalated nitrogen-doped graphene nanobelts (MoP/NG), synthesized by inserting DDA into MoO<sub>3</sub> nanobelts followed by phosphorization; h) MoC<sub>x</sub> obtained by MOFs-assisted strategy followed by annealing under N<sub>2</sub> flow.

### 3.3 DFT calculations

DFT calculations (Fig. 6) were employed to well understand the influence of oxygen vacancy and  $\text{Ni}_3\text{S}_2$  component on the catalytic activity. According to TEM characterization,  $\text{MoO}_x$  was found to be wrapped outside the  $\text{Ni}_3\text{S}_2$ . Therefore, when building the optimized models, the possibility of  $\text{H}^*$  adsorption on  $\text{MoO}_3$  is given priority, and  $\text{Ni}_3\text{S}_2$  is regarded as the “substrate” of  $\text{MoO}_3$ . As shown in Figs. 6(A), we calculate the  $\Delta G_{\text{H}^*}$  of  $\text{MoO}_3$  (on O site), oxygen-deficient  $\text{MoO}_3$  (noted as  $\text{O}_v\text{-MoO}_3$ , on Mo site),  $\text{MoO}_3/\text{Ni}_3\text{S}_2$  (on O site), and  $\text{O}_v\text{-MoO}_3/\text{Ni}_3\text{S}_2$  (on O and Mo sites). The  $\text{MoO}_3$  (Fig. 6(A-a)) shows a  $\Delta G_{\text{H}^*}$  of  $-2.37$  eV, for which the negative value indicates easy H adsorption (Volmer reaction, Eq. (3) discussed above) but difficult H desorption (Heyrovsky reaction, Eq. (4) discussed above). Because the surface of  $\text{MoO}_3$  is all O atoms and the  $\text{O-H}^*$  bond is strong, the  $\text{H}^*$  is difficult to be desorbed. At this time, desorption step becomes the rate-determining step. When oxygen vacancy is present, as in  $\text{O}_v\text{-MoO}_3$  (Fig. 6(A-b)),

Mo sites are exposed to exhibit a smaller  $|\Delta G_{\text{H}^*}|$  of 2.30 eV. When  $\text{MoO}_3$  and  $\text{Ni}_3\text{S}_2$  form the heterojunction (Fig. 6(A-c)), the  $\text{MoO}_3/\text{Ni}_3\text{S}_2$  has a much smaller  $|\Delta G_{\text{H}^*}|$  of 1.82 eV, which means weakened binding between O and H, thus facilitating the H desorption. While for the heterojunction of  $\text{O}_v\text{-MoO}_3/\text{Ni}_3\text{S}_2$  containing oxygen vacancy,  $|\Delta G_{\text{H}^*}|$  on the O site adjacent to oxygen vacancy is slightly increased to 1.98 eV (Fig. 6(A-d)), indicating strengthened O–H bonding (difficult H desorption). More importantly and interestingly, the Mo site of  $\text{O}_v\text{-MoO}_3/\text{Ni}_3\text{S}_2$  has a much lower  $|\Delta G_{\text{H}^*}|$  of 1.54 eV (Fig. 6(A-e)), which is the most close to the value of 0. As known an electrocatalyst with  $|\Delta G_{\text{H}^*}|$  approaching to zero would have high HER activity. So the exposed Mo due to oxygen defect serves as active sites. By comparing (a) and (c), or (b) and (d) in Fig. 6(A), it can be seen that the heterojunction greatly improves the catalytic activity of both O and Mo sites, while comparison of (c), (d) and (e) in Fig. 6(A) shows that although oxygen deficiency slightly reduces the activity of O sites, the exposed Mo sites result in much better catalytic activity.



**Fig. 6** (A) Optimized structures of (a)  $\text{MoO}_3$ , (b)  $\text{O}_v\text{-MoO}_3$ , (c)  $\text{MoO}_3/\text{Ni}_3\text{S}_2$ , (d)  $\text{O}_v\text{-MoO}_3/\text{Ni}_3\text{S}_2$  with  $\text{H}^*$  on O site and (e)  $\text{O}_v\text{-MoO}_3/\text{Ni}_3\text{S}_2$  with  $\text{H}^*$  on Mo site and the corresponding H adsorption free energy ( $\Delta G_{\text{H}^*}$ ) at a potential  $U = 0$  V relative to standard hydrogen electrode at pH = 0; (B) differential charge density distribution of  $\text{O}_v\text{-MoO}_3/\text{Ni}_3\text{S}_2$ ; (C) vacancy formation energy of  $\text{O}_v\text{-MoO}_3/\text{Ni}_3\text{S}_2$  and  $\text{O}_v\text{-MoO}_3$  and corresponding models. Symbols for atoms: Mo is cyan in A and C while purple in B, S is yellow, Ni is blue in A and C while grey in B, O is red and  $\text{H}^*$  is white. The dotted box shows the position of oxygen vacancy.



Differential charge density distribution of the O<sub>v</sub>-MoO<sub>3</sub>/Ni<sub>3</sub>S<sub>2</sub> has been calculated, with results shown in Fig. 6(B). It is found that there is a strong charge transfer between Ni<sub>3</sub>S<sub>2</sub> and MoO<sub>3</sub>. Compared with MoO<sub>3</sub>/Ni<sub>3</sub>S<sub>2</sub> (without oxygen vacancy, Fig. S8, cf. ESM), the O atoms in O<sub>v</sub>-MoO<sub>3</sub>/Ni<sub>3</sub>S<sub>2</sub> (Fig. 6(B)) gain more electrons. The increase of surface charge of oxygen will strengthen the binding of O–H and make the desorption more difficult. This is the reason why the  $|\Delta G_{H^*}|$  on O site of O<sub>v</sub>-MoO<sub>3</sub>/Ni<sub>3</sub>S<sub>2</sub> is larger than that of MoO<sub>3</sub>/Ni<sub>3</sub>S<sub>2</sub>. In addition, Fig. 6(B) depicts electron deficiency of exposed Mo site in O<sub>v</sub>-MoO<sub>3</sub>/Ni<sub>3</sub>S<sub>2</sub>. During the Heyrovsky reaction, Mo–H\* bond needs to be dissociated prior to H<sub>2</sub> release. In this process, electrophilic Mo will pull the electrons between Mo and H, which will weaken the Mo–H\* bond thus promoting hydrogen evolution via the cleavage of Mo–H\* [48].

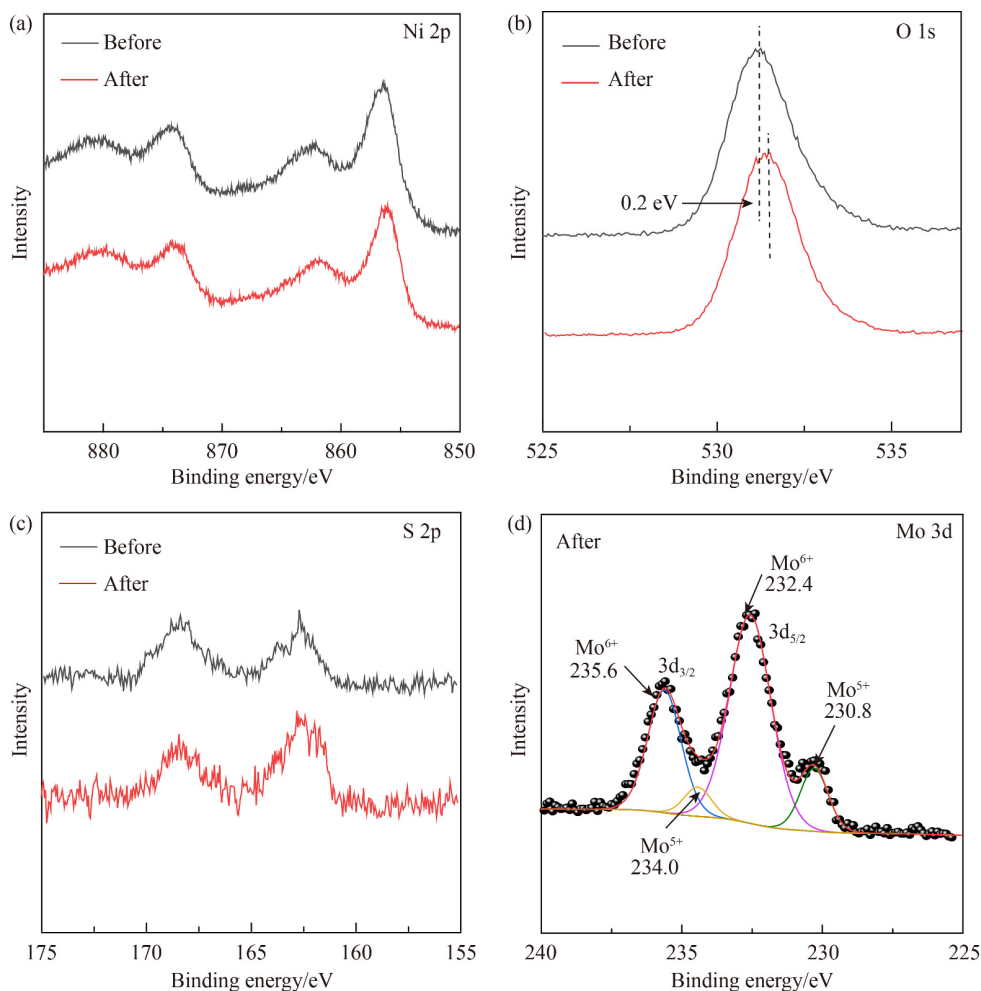
Long-term durability is another crucial requirement for the catalysts in real applications. To measure the durability of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11, the time-dependent current density was measured at a constant potential of –0.18 V for 100 h. The excellent stability is due to that the acid-resistant amorphous MoO<sub>x</sub> encases the Ni<sub>3</sub>S<sub>2</sub> and NF substrate which are unstable under acidic conditions. As seen in Fig. 5(e), the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 was continuously operated for 100 h with no significant degradation observed, confirming the ultra-durable stability. Figure 5(f) shows the linear sweep voltammetry before and after 100 h *I*-*t* HER test. As observed, the catalytic activity of the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 was even increased after the stability test. This may be thankful to the surface reconfiguration of the catalyst [49]. In order to deeply learn about the reaction mechanism in the HER process, we have carried out SEM and XPS for MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 after stability test. From the SEM images shown in Fig. S9 (cf. ESM), we see after the HER test, the microstructure of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 has not changed significantly, and many irregular small spheres are still attached to the surface of NF. From XPS (Fig. 7), after long-term stability test (100 h), the valence states of Ni and S do not change [50]. For Mo, the mixed valence state of Mo<sup>5+</sup> and Mo<sup>6+</sup> is still reflected after the stability test. The peaks at 235.6 and 232.4 eV correspond to Mo<sup>6+</sup> [28], and the binding energies of 234.0 and 230.8 eV are related to Mo<sup>5+</sup> [29]. At the same time, it can be seen from the integral area of the curve that the content of Mo<sup>5+</sup> increases compared with that before. In addition, the O 1s peaks shift towards lower binding energy by 0.2 eV after stability test. The increase of Mo<sup>5+</sup> content and the shift of O 1s with lower binding energy also prove that the oxygen vacancy content increased after long-term stability. The *in situ* surface reconfiguration may result in more oxygen vacancies on catalyst surface, which exposes more Mo active sites. EPR spectroscopy (Fig. 3(h)) shows that the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 after 60 h *I*-*t* test displays a much stronger signal, proving increased content of oxygen vacancy in the catalyst after HER

testing, which is consistent with the XPS characterization. To further confirm the *in situ* surface reconfiguration of the catalyst, we calculated the formation energy of oxygen vacancy in MoO<sub>3</sub> and MoO<sub>3</sub>/Ni<sub>3</sub>S<sub>2</sub>. As shown in Fig. 6(C), when MoO<sub>3</sub> and Ni<sub>3</sub>S<sub>2</sub> form heterojunction, the formation energy of oxygen vacancy is significantly reduced, and thus decreases the energy barrier for structural reconfiguration. This will enable MoO<sub>3</sub> to have more oxygen vacancies, thus exposing more active sites of Mo. The low  $|\Delta G_{H^*}|$  of exposed Mo sites is beneficial to the improvement of the HER activity. With the continuation of the electrolysis reactions, the performance of the catalyst will gradually improve. From the long-term durability test (Fig. 5(e)), the initial current density is 18.2 mA·cm<sup>-2</sup>, while until 100 h, the current density increases to 23.5 mA·cm<sup>-2</sup>. This phenomenon confirms the rationality of the above conjecture. The higher durability of the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 than that of the existing catalysts endows it a broad application.

Overall, from the above results we see clearly that the electrocatalytic performance of the MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 material exceeds most known transition metal sulfides and oxides catalysts. Benefiting from the oxygen vacancy and heterostructure, the exposed Mo sites exhibit much reduced  $|\Delta G_{H^*}|$ , which endows the function as active sites, leading to the excellent HER performance. The outstanding catalytic activity and wonderful durability of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 demonstrate it is a promising electrocatalyst for HER.

## 4 Conclusions

In summary, by a facile and cost-effective solvothermal method, amorphous and oxygen-deficient MoO<sub>x</sub> integrated with Ni<sub>3</sub>S<sub>2</sub> nanoparticles are embedded in the Ni foam to fabricate the new electrocatalysts of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-*mn*. The optimum oxygen-deficient MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 exhibits remarkable HER activity, requiring a much low  $\eta_{10}$  value of 76 mV and an extremely small Tafel slope of 46 mV·dec<sup>-1</sup> in acidic media. The oxygen vacancy leaves the Mo sites exposed, and the reduced  $|\Delta G_{H^*}|$  of Mo sites ensures the enhancement of HER activity. Moreover, the formed MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub> heterostructure further reduces the  $|\Delta G_{H^*}|$  of Mo and O sites, which is another key factor in improving the catalytic activity. The high activity of MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 can be maintained for more than 100 h at constant potential of 180 mV. The outside acid-resistant MoO<sub>x</sub> layer encases the inside Ni<sub>3</sub>S<sub>2</sub> and NF which are unstable under acidic conditions, thus increasing the acid resistance of the overall catalyst. In addition, the heterostructure can effectively reduce the formation energy of oxygen vacancy, which leads to the *in situ* reconstruction of the catalysts during the electrocatalytic process, thus



**Fig. 7** XPS spectra of (a) Ni 2p, (b) O 1s, and (c) S 2p for MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 before and after HER testing, and (d) Mo 3d for MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 after HER testing.

promoting HER performance. As a high-performance and ultra-durable electrocatalyst, MoO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>/NF-11 might be regarded as a cost-effective candidate to take the place of noble metals catalysts used in HER. This work could provide new ideas for the design of other oxygen-deficient materials, therefore starting new opportunities to develop high-performance materials for HER or other applications.

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