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# Mo-doping heterojunction: interfacial engineering in an efficient electrocatalyst for superior simulated seawater hydrogen evolution†

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Exploring economical, efficient, and stable electrocatalysts for the seawater hydrogen evolution reaction (HER) is highly desirable but is challenging. In this study, a Mo cation doped  $\text{Ni}_{0.85}\text{Se}/\text{MoSe}_2$  heterostructural electrocatalyst,  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$ , was successfully prepared by simultaneously doping Mo cations into the  $\text{Ni}_{0.85}\text{Se}$  lattice ( $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}$ ) and growing atomic  $\text{MoSe}_2$  nanosheets epitaxially at the edge of the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}$ . Such an  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  catalyst requires only 110 mV to drive current densities of  $10 \text{ mA cm}^{-2}$  in alkaline simulated seawater, and shows almost no obvious degradation after 80 h at  $20 \text{ mA cm}^{-2}$ . The experimental results, combined with the density functional theory calculations, reveal that the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  heterostructure will generate an interfacial electric field to facilitate the electron transfer, thus reducing the water dissociation barrier. Significantly, the heteroatomic Mo-doping in the  $\text{Ni}_{0.85}\text{Se}$  can regulate the local electronic configuration of the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  heterostructure catalyst by altering the coordination environment and orbital hybridization, thereby weakening the bonding interaction between the Cl and Se/Mo. This synergistic effect for the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  heterostructure will simultaneously enhance the catalytic activity and durability, without poisoning or corrosion of the chloride ions.

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## Introduction

Hydrogen fuel is considered as an ideal alternative to traditional fossil resources due to its superior energy density of  $142 \text{ kJ g}^{-1}$  and its environmentally friendly nature.<sup>1–3</sup> Water splitting is an economical strategy to generate hydrogen. However, current

mature water electrolysis technology typically relies on high-purity water.<sup>4,5</sup> If this water electrolysis were to be commercialized, it would place a significant strain on freshwater resources.<sup>6</sup> Seawater, which accounts for approximately 96.5% of the Earth's water,<sup>7</sup> shows promise as a natural electrolyte. Nevertheless, direct seawater electrolysis is still in its early stages and faces significant challenges, including the poisoning effect of non-innocent ions such as chlorine anions, and the low kinetics of the hydrogen evolution reaction (HER).<sup>8–10</sup> Furthermore, these will occur in the chlorine evolution reaction (CER) in an acid environment, and they compete with the oxygen evolution reaction (OER).<sup>11</sup> It is widely accepted that in alkaline conditions, the CER can be efficiently blocked, and the OER usually exhibits a reasonable performance.<sup>12,13</sup> Moreover, the possibility of seawater splitting in alkaline conditions has been widely demonstrated in recent years.<sup>13–15</sup> Platinum (Pt)-based materials are regarded as the state-of-art HER catalysts,<sup>16,17</sup> however, the scarcity and expensiveness of Pt limit its wide application.<sup>18–20</sup> In addition, the presence of chlorine anions in seawater will also poison Pt-based catalysts, which decreases the electrochemical performance for seawater splitting.<sup>21</sup> Therefore, it is crucial to explore earth-abundant, efficient, and non-poisonous electrocatalysts for HERs in seawater.

A great deal of effort has been made in developing efficient non-precious HER electrocatalysts over the past several

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decades.<sup>22–24</sup> Among these candidates, transition-metal chalcogenide heterostructural electrocatalysts have attracted significant attention due to their lower cost and outstanding electrochemical properties.<sup>25–27</sup> For example, Ni-based heterogeneous catalysts have attracted much attention as they have strong interfacial effects and unique electronic structures.<sup>28</sup> Although significant research has been made to improve the activity of HER, Ni-based selenides still suffer from the poisoning of the chlorine ions and poor stability.<sup>29</sup> However, the use of MoSe<sub>2</sub> as a HER catalyst has been extensively investigated because of its low Gibbs' free energy for hydrogen adsorption on the Mo-edge of MoSe<sub>2</sub>.<sup>30,31</sup> Thus, rational integration of NiSe<sub>x</sub> and MoSe<sub>2</sub> to construct a heterostructure can optimize the electrocatalytic activity for HER.<sup>32</sup> However, to the best of our knowledge, so far, the corresponding work on the NiSe<sub>x</sub>/MoSe<sub>2</sub> heterostructures as HER electrocatalysts in the seawater environment has seldom been studied in detail.

In this work, novel Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> heterostructures were successfully achieved using the edge epitaxy of atomic MoSe<sub>2</sub> nanosheets on Mo-doped Ni<sub>0.85</sub>Se using a one-pot selenization process of the precursor NiMoO<sub>4</sub> nanosheets. Such Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> heterostructures exhibited efficient electrocatalytic behavior in alkaline simulated seawater, with a low overpotential of 110 mV at 10 mA cm<sup>-2</sup>. Significantly, the Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> catalyst could be effective against the poisoning and corrosion of chloride ions, and displayed an impressive electrochemical stability over 80 h in alkaline simulated seawater. A deep insight into the outstanding electrochemical performance mechanism was obtained that showed that the built-in interfacial electric field of the Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> heterostructure would improve the charge transfer, and that the Mo cation could modify the local electronic environment of Ni<sub>0.85</sub>Se *via* the formation of sp<sup>3</sup>d<sup>2</sup> hybridization in the Ni–Se octahedral geometry, and sp<sup>3</sup>d hybridization in the Mo–Se square pyramidal geometry, thus weakening the bonding interaction between the Cl–Se and Cl–Mo.

## Results and discussion

### Synthesis and characterization of Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub>

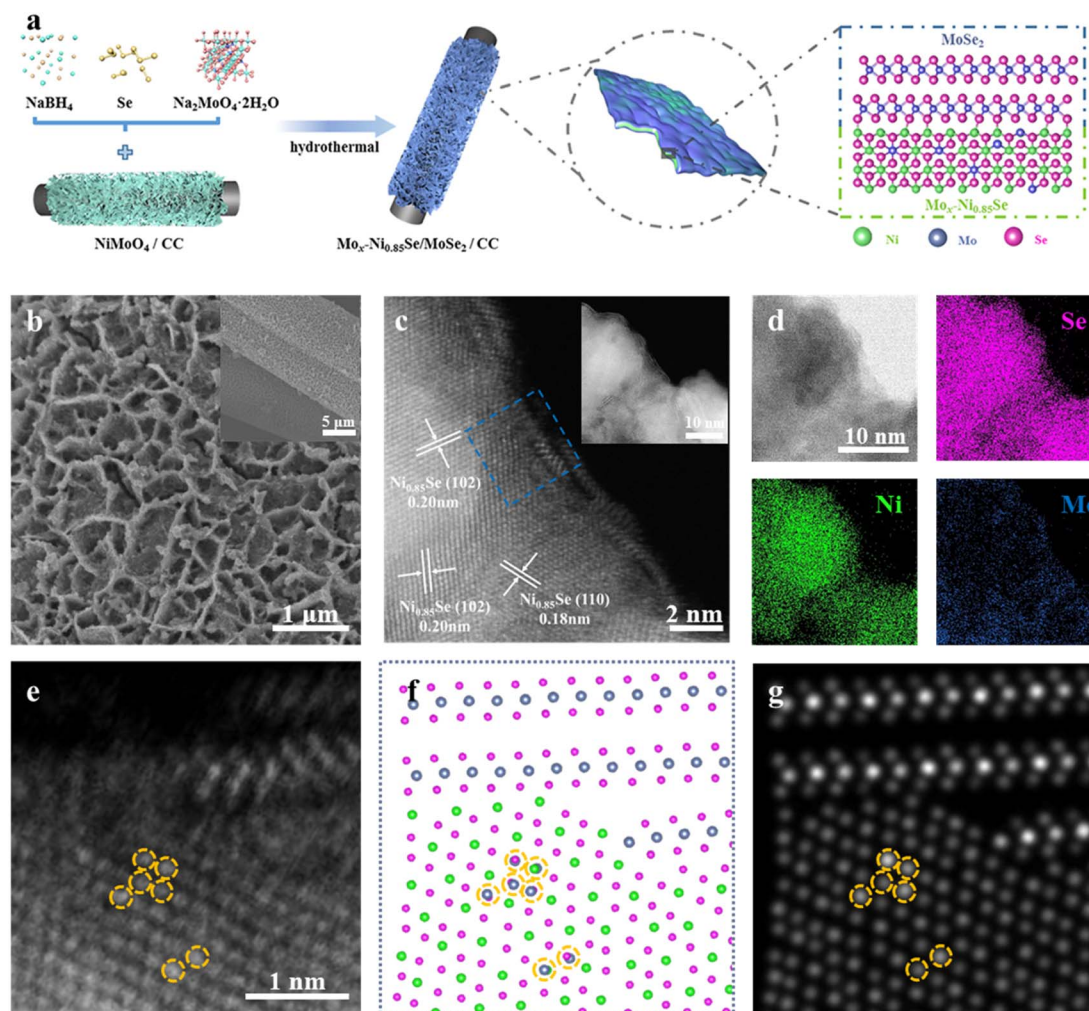
The Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> heterostructures anchored on carbon cloth (CC) were prepared by hydrothermal selenization of NiMoO<sub>4</sub> with adding Ni sources, a reducing agent (NaBH<sub>4</sub>), and additional Mo sources, as shown in Fig. 1a. Scanning electron microscopy (SEM) images (Fig. S1, ESI†) and X-ray diffraction spectra (XRD, Fig. S2, ESI†) of NiMoO<sub>4</sub> nanosheets indicated that they were vertically supported on a carbon fiber with a highly open structure made up of interwoven nanosheets. To optimize the morphology and performance, a series of different amounts of additional Mo sources were employed during the hydrothermal selenization process (Fig. S3, ESI†). It was clearly seen that when the weight of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O was below 60 mg, the obtained samples could maintain the nanosheet structure. When the additional weight of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O was 60 mg, the obtained sample (named as Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub>) shows a thin nanosheet structure (Fig. 1b, S3e and f, ESI†). When adding excess Mo sources, a large number of nanoparticles

accumulated. Their HER performance was studied and the results are shown in Fig. S4 (ESI),† and the Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> showed the best HER performance among these samples.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> (Fig. 1c) showed the epitaxially grown heterostructure of Ni<sub>0.85</sub>Se/MoSe<sub>2</sub>, *i.e.*, the epitaxially growing atomic MoSe<sub>2</sub> nanosheets at the edge of the Ni<sub>0.85</sub>Se nanoparticles. It was clearly seen that the epitaxial growth of a few atomic layers of MoSe<sub>2</sub> corresponded with elemental mapping results (Fig. 1d). The high-resolution STEM (HR-STEM) image clearly showed the lattice fringes of the inter-nanoparticle with a spacing of 0.20 and 0.18 nm, which corresponded to the (102) and (110) crystal planes of the Ni<sub>0.85</sub>Se, respectively. This result also demonstrated the heterostructure of the Ni<sub>0.85</sub>Se/MoSe<sub>2</sub>. Additionally, the HAADF-STEM image of Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> in Fig. 1e also shows bright dots in the Ni<sub>0.85</sub>Se nanoparticles. As the atomic number of Mo was the highest among these three elements, the bright dots could be attributed to Mo. Thus, it was concluded that the Ni<sub>0.85</sub>Se nanoparticles had been doped by the Mo cations. The model of the Mo cation doping Mo<sub>x</sub>-Ni<sub>0.85</sub>Se was also identified by simulating its atomic resolution HR-STEM image using QSTEM software (Fig. 1e–g and S5, ESI†).<sup>33</sup> The Mo cation doping is circled in yellow in Fig. 1e–g. These results also demonstrate the Mo cation doping of the Mo<sub>x</sub>-Ni<sub>0.85</sub>Se structure. We also prepared pure NiSe<sub>2</sub> and MoSe<sub>2</sub> as comparison and the results are shown in Fig. S6 and S7 (ESI).† Then, the XRD of these samples were employed to investigate their crystal structure and phase composition. As shown in Fig. S8 (ESI),† the two distinct peaks at about 26° and 43° were assigned to the carbon cloth. It was also noted that the MoSe<sub>2</sub> exhibited an amorphous structure, which also suggested its atomic layer structure. The peaks of NiSe<sub>2</sub> were in agreement with the standard card of NiSe<sub>2</sub> (PDF#65-1843). The Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> also presented the typical Ni<sub>0.85</sub>Se (PDF#18-0888), but the peak of (101) at 33.5° was positive shifted, indicating the successful Mo cation doping in the lattice of Ni<sub>0.85</sub>Se. To characterize the composition in the heterojunction, the Raman spectra were utilized and are shown in Fig. S9 (ESI).† The peak (A<sub>g</sub>) at 237 cm<sup>-1</sup> was attributed to the Se–Se stretching mode of NiSe<sub>2</sub>.<sup>34</sup> The Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> presented three peaks of 139, 235, and 284 cm<sup>-1</sup>, which were attributed to the phonon mode of MoSe<sub>2</sub>.<sup>35</sup> In addition, there was also a faint peak at ~510 cm<sup>-1</sup>, which was attributed to the unique stretch mode of the Ni–Se of Ni<sub>0.85</sub>Se with a hexagonal structure.<sup>34</sup>

Synchrotron X-ray absorption spectroscopy (XAS) (Fig. 2a–h) was performed to further investigate the charge states and the local structure of Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub>. Fig. 2a shows the Ni K-edge X-ray absorption near edge structure (XANES) spectra for Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub>, NiSe<sub>2</sub>, and Ni foil. It can be clearly seen that the white-line intensity of Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> was much lower than that of NiSe<sub>2</sub>, suggesting that its chemical state was lower than that of NiSe<sub>2</sub>. In addition, the Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> also shifted to a higher energy than the Ni foil, revealing that it had a higher chemical valence than Ni<sup>0</sup>. These results demonstrated that the Ni chemical state of Mo<sub>x</sub>-Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> was between 0 and +2. Fourier transform extended X-ray absorption





**Fig. 1** The synthetic scheme and characterization of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$ . (a) A schematic illustration for the synthesis of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$ . Low (inset) and high magnification (b) SEM, and (c) HAADF-STEM images of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$ . (d) Bright field STEM image and corresponding EDS elemental mapping of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$ . (e)–(g) From left to right are experimental HAADF-STEM image, structure model (Blue: Mo atom; Green: Ni atom; Red: Se atom), and simulated HAADF-STEM image of the selected area in (c), respectively.

fine structure (FT-EXAFS) spectra of the Ni K-edge for these samples are shown in Fig. 2d. The main peaks at 1.71 Å and 2.17 Å can be assigned to the Ni–Se coordination in  $\text{NiSe}_2$ , and the Ni–Ni coordination in Ni foil, respectively.<sup>36</sup> As for  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$ , the Ni–Se coordination exhibited was similar to that of  $\text{NiSe}_2$ , but the shift was in a positive direction, which was caused by the different bond lengths in  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$ .<sup>36–38</sup> The Mo K-edge XANES spectrum of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$  (Fig. 2b) showed a noticeable shift in the higher energy region compared to that of  $\text{MoSe}_2$ , which suggested there was a lower Mo chemical valency. The Mo EXAFS spectrum (Fig. 2e) of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$  showed the main peaks at 1.16 Å and 2.11 Å which were assigned to the Mo–Se coordination and Mo–Mo coordination, respectively.<sup>39</sup> The Mo–Mo peak of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$  was in agreement with that of  $\text{MoSe}_2$  (2.11 Å), but the Mo–Se peak of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$  is positive shift 0.06 Å than that of  $\text{MoSe}_2$  (1.22 Å), which could be attributed to the Mo cation doping in the  $\text{Ni}_{0.85}\text{Se}$ . The Se K-edge XANES for the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$  in Fig. 2c showed that it was more similar to that

of  $\text{MoSe}_2$ , which suggested that they shared similar coordination environments to the Se element. The Se EXAFS spectra (Fig. 2f) indicated that the chemical environment of Se in  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$  was similar to that in  $\text{MoSe}_2$ . To more clearly probe the coordination structures of the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$  epitaxially grown heterostructure, wavelet transforms (WT) with a high resolution in both the K and R spaces of the Ni K-edge and the Mo K-edge EXAFS oscillations were further performed and the results are shown in Fig. 2g, h and S10 (ESI).<sup>†</sup> Both the Ni and Mo in the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$  showed a certain degree of deviation, which indicated the change of the element coordination environment, resulting in the fast electron transfer in the heterostructure.<sup>40,41</sup> These results indicated that the heterogeneous structure of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$  may form an interfacial electric field, which facilitates the electron transfer.

The X-ray photoelectron spectroscopy (XPS) measurements (Fig. 2i–k, and S11, ESI<sup>†</sup>) were employed to further investigate the chemical and phase compositions. The Ni  $2p_{3/2}$  XPS spectra of the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se/MoSe}_2$  exhibited two peaks located at





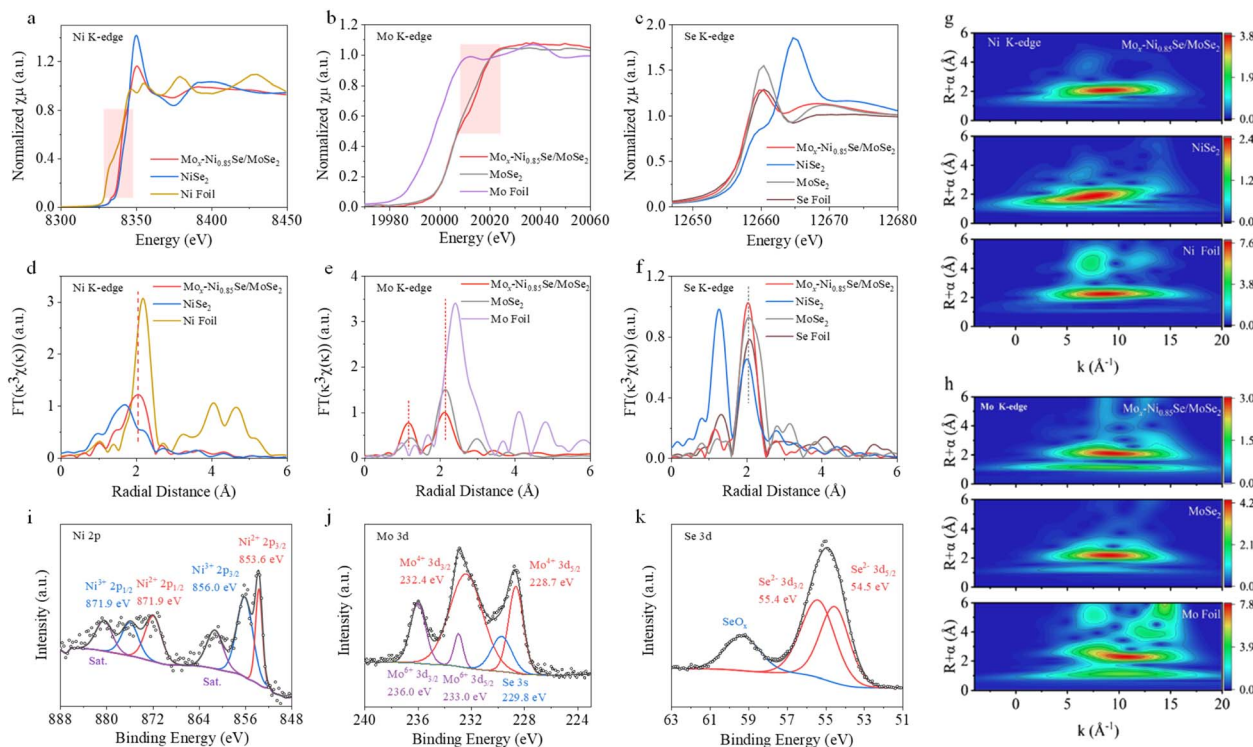


Fig. 2 Characterizations of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$ . (a)–(c) The XANES spectra of Ni, Mo, and the Se K-edge, and (d)–(f) the corresponding FT-EXAFS spectra for  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$ ,  $\text{NiSe}_2$ ,  $\text{MoSe}_2$ , Ni foil, Mo foil, and Se foil. The wavelet transform of (g) the Ni K-edge and (h) the Mo K-edge EXAFS for  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$ ,  $\text{NiSe}_2$ , Ni foil,  $\text{MoSe}_2$ , and Mo foil. The XPS spectra of (i) Ni 2p, (j) Mo 3d, and (k) Se 3d for  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$ .

853.6 eV ( $\text{Ni}^{2+} 2p_{3/2}$ ) and 856.1 eV ( $\text{Ni}^{3+} 2p_{3/2}$ ), which showed a slight decrease of  $\sim 0.2$  eV when compared with that of pure  $\text{Ni}_{0.85}\text{Se}$ .<sup>42</sup> The Mo 3d<sub>5/2</sub> XPS spectra (Fig. 2j) can be divided into  $\text{Mo}^{4+} 3d_{5/2}$  (228.7 eV) and  $\text{Mo}^{6+} 3d_{5/2}$  (233.0 eV), and the  $\text{Mo}^{4+} 3d_{5/2}$  showed an obvious increase of  $\sim 0.3$  eV in  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  compared to that of pure  $\text{MoSe}_2$ .<sup>43</sup> This shift strongly suggested the presence of an interfacial electric field that serves to expedite the transfer of electrons from the  $\text{MoSe}_2$  atomic layer to the  $\text{Ni}_{0.85}\text{Se}$  matrix. This observation significantly bolsters the evidence supporting the interaction between  $\text{MoSe}_2$  and  $\text{Ni}_{0.85}\text{Se}$  within the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  heterostructure. Moreover, the Se 3d spectrum showed two large peaks at 54.5 and 55.4 eV, which were attributed to  $\text{Se}^{2-} 3d_{5/2}$  and  $\text{Se}^{2-} 3d_{3/2}$ . In addition, the binding energy of 59.5 eV could be attributed to  $\text{SeO}_x$  resulting from the oxidation of the Se surface.<sup>1,32</sup>

### The electrocatalytic HER performance of $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$

The HER performance of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  was evaluated in 1 M KOH with high-purity water and alkaline simulated seawater (1 M KOH and 0.5 M NaCl) using a three-electrode device (Fig. 3, and S12–S21, ESI†). It can be clearly seen that the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  exhibited excellent HER performance in these two electrolytes, and only needed 110 mV to achieve  $10 \text{ mA cm}^{-2}$  in both 1 M KOH and alkaline simulated seawater. In contrast,  $\text{NiSe}_2$  and  $\text{MoSe}_2$  showed  $147 \text{ mV}@10 \text{ mA cm}^{-2}$  and  $211 \text{ mV}@10 \text{ mA cm}^{-2}$  in 1 M KOH, respectively. As for alkaline simulated seawater,  $\text{NiSe}_2$  and  $\text{MoSe}_2$  showed  $160 \text{ mV}@10 \text{ mA}$

$\text{cm}^{-2}$  and  $232 \text{ mV}@10 \text{ mA cm}^{-2}$ , respectively. It was noted that, to a certain extent, the  $\text{NiSe}_2$  could endure the  $\text{Cl}^-$  poisoning, whereas the activity of  $\text{MoSe}_2$  decreased significantly in the

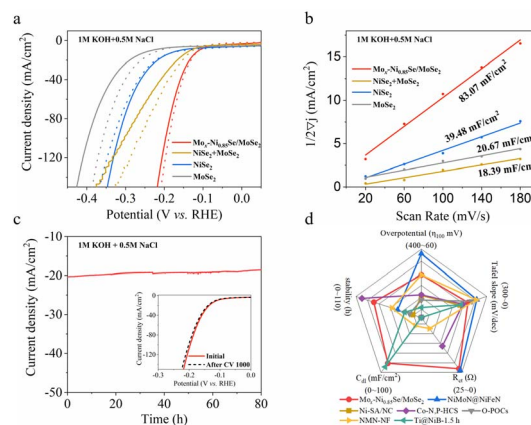


Fig. 3 The electrochemical properties of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  catalyst. (a) Polarization curves. (b) The capacitive currents at  $-0.5 \text{ V vs. RHE}$  as a function of the scan rate for the obtained catalysts. (c) Chronopotentiometry test results of the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  catalyst at  $20 \text{ mA cm}^{-2}$  for 80 h (inset: LSV curves before and after 1000 cycles) in alkaline simulated seawater (1 M KOH + 0.5 M NaCl). (d) The electrochemical performance comparison between  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  and previously reported values obtained in alkaline simulated seawater, found in the literature.

presence of  $\text{Cl}^-$ . The physical mixed  $\text{NiSe}_2$  and  $\text{MoSe}_2$  (named as  $\text{NiSe}_2 + \text{MoSe}_2$ ) showed  $126 \text{ mV}@10 \text{ mA cm}^{-2}$  (1 M KOH) and  $132 \text{ mV}@10 \text{ mA cm}^{-2}$  (alkaline simulated seawater), suggesting that the physical mixture cannot efficiently endure the  $\text{Cl}^-$  poisoning. These results demonstrated that the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  heterostructure showed an excellent performance in alkaline simulated seawater which should be attributed to the heterostructure structure. In addition, the Mo cation in  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  will also modify its local electronic structure, and thus enhanced the electron transfer between  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}$  and  $\text{MoSe}_2$  in the heterostructure.

The Tafel slope values of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  in 1 M KOH and alkaline simulated seawater (Fig. S14, ESI†) are the lowest among these catalysts and were  $70.12$  and  $86.19 \text{ mV dec}^{-1}$ , respectively. This indicated the favorable kinetics of the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  during the electrocatalytic hydrogen production process, even in the presence of  $\text{Cl}^-$ . Moreover, the value of the Tafel slope of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  is between the Volmer mechanism ( $120 \text{ mV dec}^{-1}$ ) and the Heyrovský mechanism ( $40 \text{ mV dec}^{-1}$ ), which indicated that it most likely obeys the Volmer–Heyrovský mechanism.<sup>1,44,45</sup> This was in agreement with previous reports where nickel chalcogenides were found to be efficient to produce  $\text{H}_2$  in the water dissociation process (Volmer step), resulting in  $\text{H}_{\text{ad}}$  migrating to the neighboring active site of  $\text{MoSe}_2$  to undergo the Heyrovský mechanism to produce  $\text{H}_2\text{O}$  molecules.<sup>44,46,47</sup> The electrochemical impedance spectroscopy (EIS) at an overpotential of  $250 \text{ mV}$  revealed that the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  has the lowest charge transfer resistance of  $1.749 \Omega$  in 1 M KOH (Fig. S15, ESI†) and  $1.508 \Omega$  in alkaline simulated seawater (Fig. S16, ESI†) when compared with the other three electrocatalysts. This implied its quick charge transfer capability, which could be attributed to the built-in interfacial electric field of  $\text{Ni}_{0.85}\text{Se}/\text{MoSe}_2$  heterostructure and the Mo cation doping, and this was in agreement with the XAS and XPS results.

To obtain insights into the electrochemical surface area (ECSA) of the materials, the electrochemical double-layer capacitance ( $C_{\text{dl}}$ ) values were estimated and are shown in Fig. 3b, S17 and S18 (ESI).† The  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  had the highest  $C_{\text{dl}}$  value of  $92.97 \text{ mF cm}^{-2}$  in 1 M KOH, and this indicated that it had a larger electrocatalytic active surface area. However, this decreased to  $83.07 \text{ mF cm}^{-2}$  in alkaline simulated seawater. This result suggested that the  $\text{Cl}^-$  will slightly influence the electrochemistry of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$ . The previously mentioned results demonstrated that the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  was an excellent electrocatalyst even in alkaline simulated seawater. However, in the practical application of electrocatalysts, stability is another important parameter, especially in the alkaline simulated seawater environment, due to the fact that the  $\text{Cl}^-$  can cause electrocatalyst poisoning and corrosion. The cyclic voltammetry (CV) was performed for 1000 cycles and the  $i$ - $t$  mode was performed at  $20 \text{ mA cm}^{-2}$  for a continuous 80 h  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  in alkaline simulated seawater (Fig. 3c). It can be clearly seen that after 80 h, the current density of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  only showed a slight decrease, as shown in the inset of Fig. 3c, after 1000 CV cycles, and the linear sweep voltammetry (LSV) curve of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  was almost

unchanged. Moreover, after 1000 CV cycles, the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  can maintain its structure (Fig. S21, ESI†). Both these results illustrated that the  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  has the ability for anti- $\text{Cl}^-$  ion corrosion, and a great performance even in alkaline simulated seawater. The radar chart (Fig. 3d) and the comparison with results reported in the literature (Table S1, ESI†) showed that the integrated HER performance of  $\text{Mo}_x\text{-Ni}_{0.85}\text{Se}/\text{MoSe}_2$  exhibited the best HER performance in alkaline simulated seawater.

Thus, the role of Mo cation doping has two distinct functions: firstly, it enhances the charge transfer capability of the built-in interfacial electric field within the  $\text{Ni}_{0.85}\text{Se}/\text{MoSe}_2$  heterostructure; secondly, the Mo cation doping can also modulate the local electronic state of Ni, effectively enabling the resistance against chloride ions in alkaline seawater solutions and safeguarding the electrode materials from chloride ion corrosion.

### Mechanism of cation tuning

The first-principles calculations were adopted to evaluate the effects of Mo absorption, and the  $\text{MoSe}_2/\text{NiSe}$  heterojunction. The absorption energies of  $\text{H}_2\text{O}$  on NiSe and Mo-NiSe (Fig. S22, ESI†) were  $-0.88$  and  $-0.70 \text{ eV}$ , respectively. The water dissociation barrier for NiSe was  $3.02 \text{ eV}$  (Fig. S23a, ESI†), however, the Mo cation doping of Mo-NiSe increased it to  $3.08 \text{ eV}$ . This indicated that the Mo substitution did not directly enhance the water dissociation. As for the  $\text{MoSe}_2/\text{NiSe}$  heterojunction, its water dissociation barrier was  $2.72 \text{ eV}$ , which was much lower than that of NiSe ( $3.02 \text{ eV}$ ) as shown in Fig. S23b (ESI),† indicating the great performance of  $\text{MoSe}_2/\text{NiSe}$  for hydrogen evolution. The lower water dissociation barrier of the  $\text{MoSe}_2/\text{NiSe}$  heterojunction could be attributed to its built-in interfacial electric field, which facilitated the charge-transfer.

The resistance to  $\text{Cl}^-$  corrosion for these samples was evaluated and the results are shown in Fig. 4. The absorption energy of  $\text{H}_2\text{O}$  around the Cl adatom on the surface of the NiSe + Cl increased from  $-0.88 \text{ eV}$  to  $-0.19 \text{ eV}$ , indicating that the Cl absorption hinders the  $\text{H}_2\text{O}$  absorption. Fig. 4a–c show that the Cl atom can only be absorbed on the top of the Se atom on the surface of NiSe (referred to as NiSe + Cl), whereas the Cl atoms can be absorbed on both the Se and Mo on the surface of Mo-NiSe (referred to as Mo-NiSe +  $\text{Cl}_1$  and Mo-NiSe +  $\text{Cl}_2$ , respectively). The absorption energies ( $G_{\text{abs}}$ ) were  $-0.54$ ,  $-0.06$ , and  $-0.26 \text{ eV}$  for NiSe + Cl, Mo-NiSe +  $\text{Cl}_1$ , and Mo-NiSe +  $\text{Cl}_2$ , respectively, as shown in Fig. 4g. The increased  $G_{\text{abs}}$  when compared to NiSe indicated that there was a resistance to Cl-ion corrosion after the Mo doping of NiSe. To explain this phenomenon, the charge density difference ( $\rho_{\text{diff}}$ ) and the projected density of states (PDOS) were calculated (Fig. 4 and S24, ESI†).

As shown in Fig. 4d–f, a polar covalent bond was formed between the Cl adatom and the Se atom in both NiSe + Cl and Mo-NiSe +  $\text{Cl}_1$ , whereas an ionic bond was formed between the Cl adatom and the Mo atom in Mo-NiSe +  $\text{Cl}_2$ . From Fig. S24 (ESI),† it can be seen that the bonding interaction arose from



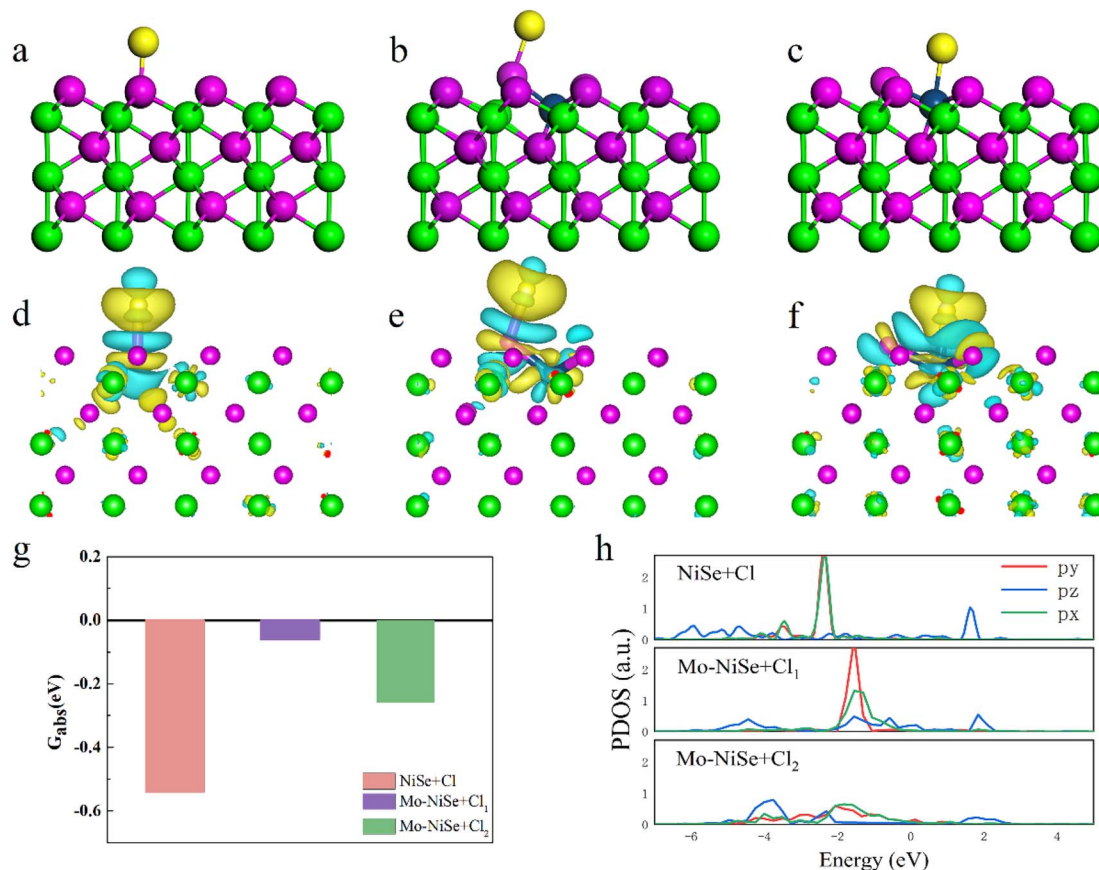


Fig. 4 Mechanistic studies using DFT. (a)–(c) Schematic diagrams of the atomic structure of NiSe + Cl, Mo-NiSe + Cl<sub>1</sub>, and Mo-NiSe + Cl<sub>2</sub>. (d)–(f) Distribution of  $\rho_{\text{diff}}$  in NiSe + Cl, Mo-NiSe + Cl<sub>1</sub>, and Mo-NiSe + Cl<sub>2</sub>. The isosurface level is set to  $10^{-3}$ . (g) and (h) The absorption energies and the PDOS of the Cl adatom in NiSe + Cl, Mo-NiSe + Cl<sub>1</sub>, and Mo-NiSe + Cl<sub>2</sub>, respectively.

the resonance between the Cl\_pz and Se\_pz states in both NiSe + Cl and Mo-NiSe + Cl<sub>1</sub>, whereas the bonding interaction corresponded to the coupling between the Cl\_pz and the Mo\_dz<sup>2</sup> in Mo-NiSe + Cl<sub>2</sub>. Compared to NiSe + Cl, a considerable shifting of the bonding state towards the Fermi level was found in Mo-NiSe + Cl<sub>1</sub> and Mo-NiSe + Cl<sub>2</sub> (Fig. 4h), and this indicated a weakening of the bonding interaction strength between the Cl adatom and the surface atom. The variation in the strength of the bonding interaction is related to the difference in the coordination environment between Mo and Ni, which modifies the crystal field splitting and orbital hybridization. As shown in Fig. 4a, the Ni atom bonds with six neighboring Se atoms, forming an octahedral geometry. In this octahedral geometry, the d orbitals form sp<sup>3</sup>d<sup>2</sup> hybridization, and the Ni exhibits a valency of +2. However, the Mo atom bonds with five neighboring Se atoms (Fig. 4b), forming a square pyramidal geometry. In this structure, the d orbitals form sp<sup>3</sup>d hybridization, and the Mo exhibits a valency of +3. The variation of the valency influences the charge transfer and weakens the bonding interaction between the Cl and Se in Mo-NiSe + Cl<sub>1</sub>. In the Mo-NiSe + Cl<sub>2</sub>, the Cl-Mo direction did not align with the Mo\_4d hybrid orbitals, indicating that the Cl-Mo direction was not suitable for electron pairing to form a chemical bond. Consequently, only a weak ionic bond was formed between the Cl and Mo atoms in Mo-NiSe + Cl<sub>2</sub>.

## Conclusions

In summary, a convenient strategy to synthesize Mo<sub>x</sub>Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> nanosheet network heterostructures supported on carbon cloth has been successfully developed by the selenization of the NiMoO<sub>4</sub> nanosheets precursor. The STEM and XAS results demonstrate that the atomic MoSe<sub>2</sub> nanosheets were grown epitaxially at the edge of the Mo<sub>x</sub>Ni<sub>0.85</sub>Se, and the Mo cation doping tuned the local electronic environment of the Mo<sub>x</sub>Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> heterostructures. This exhibits an excellent performance for HER in alkaline simulated seawater with a low overpotential of 110 mV at the current density of 10 mA cm<sup>-2</sup>, and shows almost no sign of waning even after 80 h at 20 mA cm<sup>-2</sup>. The excellent HER performance in alkaline simulated seawater could be attributed to the built-in interfacial electric field of the Mo<sub>x</sub>Ni<sub>0.85</sub>Se/MoSe<sub>2</sub> heterostructure and Mo cation doping, that improves the electron transfer between adsorbed species and Mo<sub>x</sub>Ni<sub>0.85</sub>Se/MoSe<sub>2</sub>. Moreover, the Mo cation doping also weakens the bonding interaction between Cl-Se and Cl-Mo, thereby protecting it against the poisoning and erosion of chloride ions.

## Data availability

The authors confirm that the data supporting the findings of this study are available within the article ESI.†





## Author contributions

ZH, CZ, and SG contributed equally to this manuscript. BZ and YL supervised this study. BZ, YL, and ZH conceived the idea. ZH and YJ planned and carried out the experiments, and collected and analyzed the experimental data. SG and NC performed SEM and TEM characterizations. SL performed the Raman characterizations. CZ conducted the theoretical calculations. BZ and ZH wrote the paper. All the authors have discussed the results and wrote the paper together.

## Conflicts of interest

The authors declare that they have no competing interests.

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