

# Dissolution reconstruction of electron-transfer enhanced hierarchical NiS<sub>x</sub>-MoO<sub>2</sub> nanosponges as a promising industrialized hydrogen evolution catalyst beyond Pt/C



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technology, electrocatalytic water splitting stands out among the in various hydrogen production technologies since it produces high-purity hydrogen with unlimited water resources. Moreover, it can easily be bundled with other renewable energy sources, such as solar wind energy [3]. There are two types of industrial electrolyzers depending on the water pH. However, the alkaline electrolyzer is widely used because of less corrosion and lower capital cost. On the other hand, the acidic electrolyzer generates higher current density [4]. Nevertheless, the price of H<sub>2</sub> generated from water electrolysis is still much higher than that of steam reforming. Therefore, producing scalable, low-cost, durable, and efficient electrode is an important step to reduce the capital cost of electrolyzer subsequently generate cheaper H<sub>2</sub>. The hydrogen evolution reaction (HER) that occurred in the cathode is hindered by low conductivity and a lack of active sites. Currently, Pt-based noble metal alloys are by far the most effective catalysts for HER [5]. However; their low reserves and high cost limit their widespread application. Therefore, developing efficient and earth-abundant HER catalysts are highly desirable. At present, the earth-abundant transition metal alloys [6] and their oxides [7,8], nitrides [9,10], sulfides [11], phosphides [12], and selenides [13] have been extensively studied as cathodes catalysts for HER. But, the weak intrinsic activities and poor electrical conductivities limit their HER performances [14]. Furthermore, to satisfy the strict industrial standard, the HER catalyst should be operated at a high current density [15] (>400 mA cm<sup>-2</sup>) with relatively low overpotential for an extended period. Based on the above considerations, a simple process of fabricating a rationally engineered HER catalyst with excellent conductivity, high active site density as well as the durability at high current density is a critical step to compete with the ongoing industrial process. It is almost impossible to find a single material that can satisfy all those requirements; therefore, designing a hybrid material is necessary.

In recent years, there is an extensive investigation on MoO<sub>2</sub> with a distorted rutile structure due to its metal-like conductivity (1.14 × 10<sup>4</sup> S at 300 K for bulk materials) and high chemical stability [16]. However, most studies have focused on improving HER performance by building specific nanostructures, which have not worked much on MoO<sub>2</sub>-based composites [17,18]. In spite of these advantages, the nanostructured MoO<sub>2</sub> materials are limited by a lack of active sites for HER [19]. On the other hand, Ni-based electrocatalysts have high corrosion resistance in alkaline solution and abundant active sites [20,21]. But, the nickel-based electrocatalysts are mostly in powder form and need to be coated on a conductive substrate for HER application [22,23]. The catalyst coating on the substrate causes a decrease in the catalytic performance of the powder catalyst because of the mechanical shedding. Moreover, the catalyst conductivity may decrease due to the use of polymer binders during the preparation. Furthermore, the catalytic performance of the materials is closely related to their morphology and composition. The sponge-like porous structure provides high surface area, sufficient active site and better mass transfer. Moreover, it also prevents catalyst aggregation [24,25]. To the best of our knowledge, there is no report on the HER application of NiS<sub>x</sub>-MoO<sub>2</sub> nanosponges.

Herein, we develop a highly-active NiS<sub>x</sub>-MoO<sub>2</sub> nanosponge decorated carbon cloth as HER catalyst (NiS<sub>x</sub>-MoO<sub>2</sub>/CC). It is the first report of a simple yet industrial compatible strategy based on NiS<sub>x</sub>-MoO<sub>2</sub>/CC. The synthesis process includes a two-step electrodeposition followed by vulcanization processing (Scheme 1). In this design, we not only combined the unique features of both components such as high conductivity of MoO<sub>2</sub> and high HER activity of NiS<sub>x</sub> but also eliminated the coating process by growing NiS<sub>x</sub> directly on the surface of MoO<sub>2</sub>. The optimized NiS<sub>x</sub>-MoO<sub>2</sub>/CC catalyst only requires overpotentials of 60 and 149 mV (vs. RHE) to reach 10 and 100 mA cm<sup>-2</sup> in 1.0 M KOH, respectively. Moreover,

it outperforms the Pt/C catalyst when the overpotential is higher than 114 mV. Most importantly, the optimized NiS<sub>x</sub>-MoO<sub>2</sub>/CC requires much smaller overpotentials to reach large current densities (500 mA cm<sup>-2</sup>@208 mV and 1000 mA cm<sup>-2</sup>@230 mV) than the industrial HER catalyst-Raney Ni (500 mA cm<sup>-2</sup>@300–500 mV) in 30% KOH solution [26–28], suggesting a strong industrial perspective.

## 2. Experimental

### 2.1. Materials

Nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, ≥98%), ammonium molybdate tetrahydrate (H<sub>24</sub>Mo<sub>7</sub>N<sub>6</sub>O<sub>24</sub>·4H<sub>2</sub>O), sulfur sublimed (S, 99%). All the reagents were analytical reagent and used without further purification. Commercial Pt/C (20 wt% for platinum) was purchased from Alfa Aesar.

### 2.2. Electrodeposition of Ni-, Mo- and Ni-Mo-species on carbon cloth

Initially, the carbon cloth (CC, 1 cm × 1.5 cm) was ultrasonically cleaned in sulfuric acid, deionized water, and ethanol for 5 min, respectively, and cycled 3 times to remove impurities. Electrodeposition was performed in a standard three-electrode system, in which the treated CC, graphite plate, and saturated calomel electrode (SCE) were used as working, counter, and reference electrodes, respectively. The Ni-species/CC samples were fabricated by continuous electrodeposition for 1.0 h at -10 mA cm<sup>-2</sup> in 0.1 M Ni(NO<sub>3</sub>)<sub>2</sub> solution. These obtained samples were rinsed with a large amount of water and naturally dried for use. Subsequently, the samples of Ni-species/CC were used as working electrodes at -10 mA cm<sup>-2</sup> for electrodeposition different times from 0.5 to 2.0 h in 0.1 M H<sub>24</sub>Mo<sub>7</sub>N<sub>6</sub>O<sub>24</sub> solution. The resulted samples are nominated as Ni-Mo-species/CC-0.5 h, Ni-Mo-species/CC-1 h and Ni-Mo-species/CC-2 h, respectively. As a control, electrodeposition of Mo-species on fresh CC surface (Mo-species/CC) was also prepared at -10 mA cm<sup>-2</sup> for 1.0 h in 0.1 M H<sub>24</sub>Mo<sub>7</sub>N<sub>6</sub>O<sub>24</sub> solution.

### 2.3. Synthesis of NiS<sub>2</sub>/CC, MoO<sub>2</sub>/CC and NiS<sub>x</sub>-MoO<sub>2</sub>/CC

The catalyst of NiS<sub>x</sub>-MoO<sub>2</sub>/CC was prepared by coating 0.5 g of sulfur powder on a series of Ni-Mo-species/CC surfaces, and slowly heating (3 °C min<sup>-1</sup>) to a specific temperature (400, 500 or 600 °C) for 4.0 h in Ar atmosphere (20 sccm), and then cooling down to room temperature. After sufficient water washing and drying, the prepared materials were nominated as NiS<sub>x</sub>-MoO<sub>2</sub>/CC (from XRD data). As a comparison, the NiS<sub>2</sub>/CC and MoO<sub>2</sub>/CC were also prepared by a similar method as mentioned above.

### 2.4. Characterization

Scanning electron microscopy (SEM, Quanta FEG 200, Holland) and transmission electron microscopy (TEM, JEOL, JEM-2100F) were used to investigate the morphologies and microstructures of the designed materials. X-ray powder diffraction (XRD) data was detected by a D/Max 2500 V PC with Cu Kα radiation from Rigaku. The chemical states of the samples were examined by X-ray photoelectron spectroscopy (XPS, model: JPS-9010 TR Photoelectron Spectrometer, Japan). Raman spectroscopy was acquired from an inVia confocal Raman microscope (Renishaw, England).

### 2.5. Electrochemical measurements

The electrochemical performance of the as-prepared catalysts were studied by an electrochemical workstation of Biologic

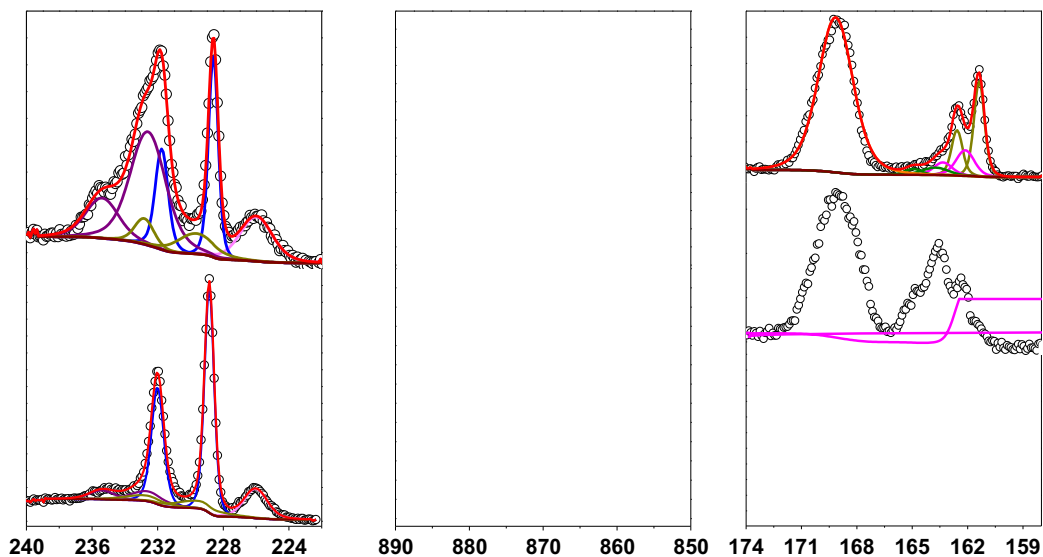
VMP3 with a typical three-electrode system in 1.0 M KOH electrolyte. The catalysts modified carbon cloth, graphite plate and SCE were used as working, counter and reference electrodes, respectively. Cyclic voltammetry (CV) tests were firstly carried out for about 5 cycles to stabilize the electrocatalytic performance of the catalyst at a scan rate of  $20 \text{ mV s}^{-1}$ . Then, liner sweep voltammetry (LSV) curves were performed at a low scan rate of  $0.5 \text{ mV s}^{-1}$ , and electrochemical impedance spectroscopy (EIS) was evaluated near the onset potential in the frequency range from 200 kHz to 10 mHz. All potentials (vs. SCE) in this work were cal-

Ni-species arrays grow vertically on CC surface and created large holes between the nanosheets (Fig. 2a). After electrodeposited Mo-species, a certain level of porosity is visible on the Ni-Mo composite (Fig. 2b). After vulcanization at 500 °C in Ar atmosphere, some particulate materials appear on the surface of NiS<sub>x</sub>-MoO<sub>2</sub>/CC (Fig. 2c). Interestingly, the cross-sectional SEM image shows a uniformly nanosponge-like NiS<sub>x</sub>-MoO<sub>2</sub> structure (inset of Figs. 2c and S3a). These porous structures not only facilitate mass transfer but also expose more active sites, thereof improve the electrochemical performance. The TEM image shows some flaky and granular structures, which is consistent with the SEM results (Figs. 2d and S3b). High-resolution TEM image shows clear lattice stripes with a lattice spacing of 0.242, 0.283 and 0.198 nm corresponding to the (1 1 1) crystal plane of MoO<sub>2</sub>, (2 0 0) plane of NiS<sub>2</sub> and (1 0 2) plane of NiS, respectively (Fig. 2e) [35–37]. Moreover, we have observed the layer stacking characteristics of two-dimensional materials, which belong to the typical MoS<sub>2</sub> species [38]. The high-angle annular dark field (HAADF) TEM elemental mappings reveal that Ni, Mo, S, and O are uniformly distributed in NiS<sub>x</sub>-MoO<sub>2</sub>/CC (Fig. 2f–g). As comparison, we also present the SEM images of NiS<sub>x</sub>-MoO<sub>2</sub>/CC catalysts with different deposition times of Mo species (Figs. S3c–f). In addition, the inductively coupled plasma mass spectrometry (ICP-MS) test results showed that the mass fractions of Ni and Mo in the NiS<sub>x</sub>-MoO<sub>2</sub>/CC composite were 28.1 and 15.1 wt%, respectively. The atomic ratio of Ni /Mo was 3.03/1 (Table S1).

The surface composition and chemical states of NiS<sub>x</sub>-MoO<sub>2</sub>/CC are further clarified through X-ray photoelectron spectroscopy (XPS). The typical XPS survey spectra in Fig. S4a confirms the existence of Mo, Ni, O, S, and C elements in NiS<sub>x</sub>-MoO<sub>2</sub>/CC, where the high-resolution C 1s spectrum is convoluted into four peaks at C=C (284.0 eV), C–C (284.8 eV), C–O (286.0 eV) and C=O (288.0 eV) as shown in Fig. S4b [39,40]. The high-resolution Mo 3d spectrum of NiS<sub>x</sub>-MoO<sub>2</sub>/CC and MoO<sub>2</sub>/CC is displayed in Fig. 3a. The XPS peak of NiS<sub>x</sub>-MoO<sub>2</sub>/CC at 228.6 eV is assigned to Mo 3d<sub>5/2</sub>. The corresponding Mo 3d<sub>5/2</sub> peak of NiS<sub>x</sub>-MoO<sub>2</sub>/CC

shows a negative shift by 0.25 eV as compare to that of MoO<sub>2</sub>/CC (228.85 eV) [41–43]. Besides, the high-resolution Ni 2p<sub>3/2</sub> region of NiS<sub>x</sub>-MoO<sub>2</sub>/CC presents two peaks at 853.4 eV and 857.2 eV, accompanied by a strong satellite at 861.8 eV, which represent the two different chemical states of Ni in NiS<sub>x</sub>-MoO<sub>2</sub>/CC [44,45]. In addition to the same Ni<sup>2+</sup> and satellite peak positions, the Ni<sup>4+</sup> species of NiS<sub>x</sub>/CC material has a binding energy of 856.3 eV, which results a positive shift of 0.91 eV as compared to that of NiS<sub>x</sub>-MoO<sub>2</sub>/CC (Fig. 3b). The peaks at 161.4 eV, 162.1 eV and 163.7 eV of S 2p<sub>3/2</sub> are corresponding to S2p of MoS<sub>2</sub>, NiS and NiS<sub>2</sub> species, respectively (Fig. 3c) [46]. Moreover, there is a strong peak at 169.1 eV, which can be assigned to S–O species arising from surface oxidation. It should be noted that the slight negative shift on Mo 3d<sub>5/2</sub> (Mo<sup>4+</sup>) and the significant positive shift on Ni 2p<sub>3/2</sub> (Ni<sup>4+</sup>) peaks in NiS<sub>x</sub>-MoO<sub>2</sub>/CC as compare to those of MoO<sub>2</sub>/CC and NiS<sub>x</sub>/CC. This result indicates that the MoO<sub>2</sub> species have a higher electron density than these of NiS<sub>x</sub> species in the composite [47], and the improved electron density can synergistically promote the HER catalytic activity [48].

The HER electrocatalytic activity of NiS<sub>x</sub>-MoO<sub>2</sub>/CC was firstly optimized by the effect of vulcanization temperatures and electroplating times of Mo-species on the catalytic performance. The results show that the catalyst obtained at vulcanization temperature of 500 °C has the best HER catalytic activity and minimum Tafel slope in 1.0 M KOH solution (Fig. S5). The electrocatalytic activities of the optimized NiS<sub>x</sub>-MoO<sub>2</sub>/CC catalyst together with MoO<sub>2</sub>/CC, NiS<sub>x</sub>/CC, NiMo-species/CC and commercial Pt/C (Johnson



NiS<sub>x</sub>-MoO<sub>2</sub>/CC is significantly better than that of commercial Pt/C catalyst indicating a great potential for industrial applications because it only requires overpotentials of 208 and 230 mV to reach 500 and 1000 mA cm<sup>-2</sup> in 30 wt% KOH solution (Fig. S6). The Tafel slope is usually employed to evaluate the reaction kinetics and the rate-determining step during HER process. According to the kinetic

modeling results, the Tafel slope values of Volmer, Heyrovsky and Tafel reactions correspond to 120, 40 and 30 mV dec<sup>-1</sup>, respectively [49]. It is well understood that the hydrogen evolution reaction under alkaline conditions involves two steps [50]. The step 1 is the water dissociation and the intermediates formation (Volmer reaction): H<sub>2</sub>O + M + e<sup>-</sup> → M-H<sub>ad</sub> + OH<sup>-</sup>, followed by either the

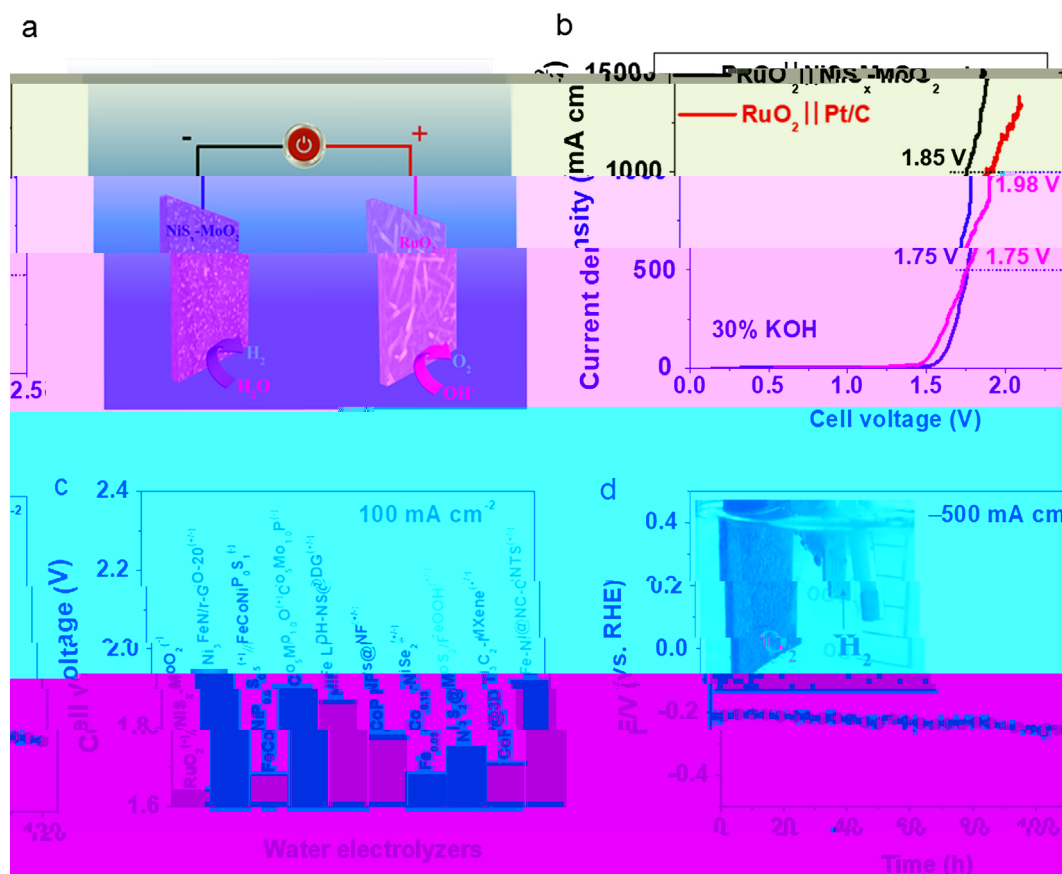
desorption step (Heyrovsky reaction):  $\text{H}_2\text{O} + \text{M-H}_{\text{ad}} + \text{e}^- \rightarrow \text{M} + \text{H}_2 + \text{OH}^-$ , or a recombination step (Tafel reaction):  $2\text{M-H}_{\text{ad}} \rightarrow 2\text{M} + \text{H}_2$  [51]. As show in Fig. 4b, the Tafel slope of  $\text{NiS}_x\text{-MoO}_2/\text{CC}$  is  $89 \text{ mV dec}^{-1}$ , which is obviously less than that of all control catalysts, indicating a fast Volmer-Heyrovsky mechanism [52]. Moreover, the exchange current density ( $j_0$ ), the key parameter reflecting the intrinsic activity of HER, was calculated by extrapolation the Tafel slope. As shown in Fig. 4c, the  $\text{NiS}_x\text{-MoO}_2/\text{CC}$  exhibited the highest value of  $2.056 \text{ mA cm}^{-2}$  compared to those of Ni-Mo-species/CC ( $0.042 \text{ mA cm}^{-2}$ ),  $\text{MoO}_2/\text{CC}$  ( $0.433 \text{ mA cm}^{-2}$ ),  $\text{NiS}_2/\text{CC}$  ( $0.297 \text{ mA cm}^{-2}$ ) and Pt/C ( $1.462 \text{ mA cm}^{-2}$ ). Meanwhile, the  $\text{NiS}_x\text{-MoO}_2/\text{CC}$  also shows the lowest charge transfer resistance (Fig. S7), suggesting the fastest HER kinetics [53].

In general, a better electrocatalytic activity is accompanied by a larger electrochemically active surface area (EASA), and the EASA is normally proportional to the electrochemical double-layer capacitance ( $C_{\text{dl}}$ ). The  $C_{\text{dl}}$  was calculated by measuring the CV curves in a non-faradaic potential window (Fig. S8). As shown in Fig. 4d, the  $C_{\text{dl}}$  value of  $\text{NiS}_x\text{-MoO}_2/\text{CC}$  is  $602 \text{ mF cm}^{-2}$ , which is much higher than those of  $\text{NiS}_2/\text{CC}$  ( $233 \text{ mF cm}^{-2}$ ),  $\text{MoO}_2/\text{CC}$  ( $216 \text{ mF cm}^{-2}$ ) and Ni-Mo-species/CC ( $2 \text{ mF cm}^{-2}$ ). The results reveals that the  $\text{NiS}_x\text{-MoO}_2$  nanospheres with dual active sites generate more accessible active sites in alkaline electrolyte than those of other catalysts, thereby promoting  $\text{H}_2$  evolution. At the same time, the turnover frequency (TOF) was adopted to measure the amount of  $\text{H}_2$  molecules released per second per active site, which was normally used to evaluate the intrinsic catalytic activity of the catalyst [54]. As show in Fig. S9a, the TOF value increases rapidly as the applied voltage increases in 30 wt% KOH solution. In particular, when the overpotentials are at 150 and 200 mV, the corresponding

TOF values are ca. 2.8 and  $13.7 \text{ s}^{-1}$  (Fig. S9b), which are much larger than most reported in the literature [6,55]. It was confirmed that  $\text{NiS}_x\text{-MoO}_2/\text{CC}$  has excellent intrinsic catalytic activity.

To satisfy industrial compliance, the optimized HER catalysts coupled with  $\text{RuO}_2$  as a counter electrode was tested at high current density in a two-electrode system (Fig. 5a). The steady-state potential polarization curve of the coupled  $\text{RuO}_2^{(+)}//\text{NiS}_x\text{-MoO}_2^{(-)}$  is show in Fig. 5b. Interestingly, the overall voltage required for total water splitting of the  $\text{RuO}_2^{(+)}//\text{NiS}_x\text{-MoO}_2^{(-)}$  is slightly higher than that of benchmark system of  $\text{RuO}_2^{(+)}//\text{Pt/C}^{(-)}$  at a low current density and reaches the same value at 1.74 V ( $\sim 500 \text{ mA cm}^{-2}$ ). However, it starts to over the catalytic performance of both  $\text{RuO}_2^{(+)}//\text{Pt/C}^{(-)}$  and the existing industrial system ( $200\text{--}400 \text{ mA cm}^{-2}$  at 1.8–2.4 V) at high current density ( $>500 \text{ mA cm}^{-2}$ ). Besides, it only needs 0.1 V extra voltage for reaching the current density from 500 to  $1000 \text{ mA cm}^{-2}$ . Furthermore, we gathered some of the high performance the HER catalysts reported in the literatures (Table S3) and compared their results with our optimized catalyst (Fig. 5c). The optimized  $\text{NiS}_x\text{-MoO}_2/\text{CC}$  shows the lowest cell voltage for achieving  $100 \text{ mA cm}^{-2}$  as compared to the rest. Finally, we performed a durability test. As shown in Fig. 5d, the  $\text{NiS}_x\text{-MoO}_2/\text{CC}$  catalyst was continuously operated for 120 h in the industrial condition (30 wt% KOH) at a constant current of  $500 \text{ mA cm}^{-2}$  and almost no degradation was observed indicating a great industrial perspective.

As discussed above, the excellent HER electrocatalytic activity is due to the unique structure of the composite catalyst and the synergistic effect between the two active species. The XPS spectra prove that there is a strong electron transfer effect between  $\text{MoO}_2$  and NiS<sub>x</sub> species, which makes  $\text{MoO}_2$  have a partial negative



**Fig. 5.** (a) Schematic diagram of overall-water-splitting electrolytic cell using  $\text{NiS}_x\text{-MoO}_2$  and  $\text{RuO}_2$  as cathode and anode, respectively. (b) Comparison of overall-water-splitting activity of  $\text{RuO}_2^{(+)}//\text{NiS}_x\text{-MoO}_2^{(-)}$  with noble metal  $\text{RuO}_2^{(+)}//\text{Pt/C}^{(-)}$  at high current in 30 wt% KOH. (c) Comparing the cell voltage of the currently available electrolytic cell at  $100 \text{ mA cm}^{-2}$  in 1.0 M KOH. (d) Durability tests of  $\text{NiS}_x\text{-MoO}_2$  at  $-500 \text{ mA cm}^{-2}$  in 30 wt% KOH.

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charge, and NiSx takes a somewhat positive charge. In an alkaline environment, the positively charged NiSx species can adsorb H<sub>2</sub>O molecules at the interface of the two active sites and synergistically promote the dissociation of H<sub>2</sub>O, thereby forming a reactive intermediate of adsorbed hydrogen (M-H<sub>ad</sub>) on the surface of the MoO<sub>2</sub> species. The formed M-H<sub>ad</sub> can further bind with one electron and one H<sub>2</sub>O molecule, synchronously releasing H<sub>2</sub> through the Heyrovsky step ( $M - H_{ad} + e^- + H_2O \rightarrow M + H_2 + OH^-$ ) (Scheme 2) [51].

#### 4. Conclusion

In summary, we have developed an excellent NiSx-MoO<sub>2</sub>/CC electrocatalyst using two-step electrodeposition and subsequent vulcanization. The resulted NiSx-MoO<sub>2</sub>/CC catalyst exhibits superior catalytic activity with a low overpotential of 60 mV at -10 mA cm<sup>-2</sup>, a small Tafel slope of 89 mV dec<sup>-1</sup>, a significant exchange current density of 2.065 mA cm<sup>-2</sup>, and long-term stability in 30 wt% KOH. The excellent results are attributed to the hierarchical porous structures as well as a synergistically catalytic effect for HER between NiSx and MoO<sub>2</sub> species. Therefore, the reported method of HER catalyst with unique architecture and enhanced electron transfer effect is also useful for future construction of other high-efficiency materials, such as fuel cells, photocatalysis, lithium-ion batteries, and so on.

#### CRedit authorship contribution statement

**Benzhi Wang:** Investigation, Methodology. **Hexiu Huang:** Data curation. **Tingting Sun:** Formal analysis. **Puxuan Yan:** Data curation. **Tayirjan Taylor Isimjan:** Writing - original draft. **Jianniao Tian:** Supervision. **Xiulin Yang:** Writing - review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Notes

The authors declare no competing financial interest.

#### Appendix A. Supplementary data

Figs. S1–S9 and Tables S1–S3 give more details on characterization of our synthesized materials and their electrocatalytic performance data; additional XPS and electrocatalytic performance data (PDF). Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2020.02.027>.

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