# **RSC** Advances



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Cite this: RSC Adv., 2021, 11, 26928

## Constructing NiSe<sub>2</sub>@MoS<sub>2</sub> nano-heterostructures on a carbon fiber paper for electrocatalytic oxygen evolution

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Although MoS<sub>2</sub> has shown its potential as an electro-catalyst for the oxygen evolution reaction (OER), its research is still insufficient. In this study, as a novel MoS<sub>2</sub>-based heterostructure electro-catalyst for OER, namely NiSe<sub>2</sub>@MoS<sub>2</sub> nano-heterostructure, was constructed on a carbon fiber paper (CFP) substrate by a simple approach, which includes electrochemical deposition of NiSe<sub>2</sub> film and hydrothermal processing of MoS<sub>2</sub> film. In addition to a series of observations on the material structure, electrocatalytic OER performance of NiSe<sub>2</sub>@MoS<sub>2</sub> was fully evaluated and further compared with other MoS<sub>2</sub>-based OER electro-catalysts. It exhibits an outstanding catalytic performance with an overpotential  $\eta_{10}$  of 267 mV and a Tafel slope of 85 mV dec<sup>-1</sup>. Only 6% loss of current density before and after 10 h indicates its excellent durability. The results indicate that the obtained NiSe<sub>2</sub>@MoS<sub>2</sub> is an excellent OER electro-catalyst and worth exploring as a substitute for noble metal-based materials.

Received 18th July 2021 Accepted 24th July 2021

DOI: 10.1039/d1ra05509g

rsc.li/rsc-advances

#### 1. Introduction

In order to solve the contradiction between environmental protection and energy demand, exploring clean energy such as hydrogen and oxygen has attracted wide attention.<sup>1</sup> Among different methods, splitting water into hydrogen and oxygen by the electrochemical method possesses advantages of high efficiency and abundant water resources, and is considered to be one of the most promising methods.<sup>2-7</sup> However, the application of this method is limited because the high overpotential in the oxygen evolution reaction (OER) process will lead to a significant loss of energy.<sup>8</sup> Although noble metal oxides such as IrO<sub>2</sub> and RuO<sub>2</sub> are considered to be efficient catalysts for the reduction of the OER overpotential, they cannot be used on a large scale owing to their scarcity and high-cost.<sup>9,10</sup> Therefore, it is of great importance to find other OER catalysts with low cost and abundant reserves, and a lot of efforts have been made in this regard.<sup>11-18</sup>

Recently, as a layered material, MoS<sub>2</sub> has been regarded as an efficient electro-catalyst for the hydrogen evolution reaction (HER) and exhibited an excellent performance.<sup>19,20</sup> However, research on its OER catalytic performance is still not sufficient. The theoretical calculation shows that the OER active sites of MoS<sub>2</sub> are at the edge with sulfur vacancies, which are similar to HER.<sup>21</sup> According to the reports, there are two main methods to improve the OER catalytic activity of MoS<sub>2</sub>. The first method is to increase the exposure of the active sites by reducing the grain size and increasing the substrate gap.<sup>22</sup> However, the improvement is limited owing to the intrinsic structure of MoS<sub>2</sub>.<sup>23</sup> The

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second method is to improve the electronic structure of  $MoS_2$ , for example, hybridizing  $MoS_2$  with other materials to facilitate the chemical adsorption of oxygen-containing intermediates, so as to reduce the kinetics of OER.<sup>24</sup> Recently, Co/Ni-sulfide@MoS\_2 heterostructures such as  $Co_9S_8@MoS_2,^{25}CoS_2-C@MoS_2,^{26}$  and  $MoS_2/$ Ni<sub>3</sub>S<sub>2</sub> (ref. 27) have demonstrated excellent OER activities. Compared with sulfide, the electronegativity of selenide is lower, which might weaken the chemical bond between the Se atom and the bonding electrons, and thus exhibits greater activity.<sup>28-31</sup> For example, in the OER process, the Tafel slope of NiSe<sub>2</sub> is 97 mV dec<sup>-1</sup>, which is lower than that of Ni<sub>3</sub>S<sub>2</sub> (118 mV dec<sup>-1</sup>).<sup>27,32</sup> Therefore, it is worthwhile to construct the nanoscale Niselenide@MoS<sub>2</sub> heterostructure on a substrate with abundant gaps and high conductivity as a catalyst for OER.

In this study, a novel  $MoS_2$ -based nano-heterostructure electrocatalyst,  $NiSe_2@MoS_2$ , was constructed on a carbon fiber paper (CFP) substrate for OER by a simple method, which includes the electrochemical deposition and hydrothermal processes. Various techniques were then employed to observe the material structure. Moreover, the electrocatalytic OER performances were fully evaluated by electrochemical measurements and further compared with other  $MoS_2$ -based OER electro-catalysts.

#### 2. Experimental

## 2.1. Construction of the NiSe<sub>2</sub>@MoS<sub>2</sub> nano-heterostructure on CFP

As shown in Fig. 1, the construction process of the  $NiSe_2@MoS_2$  nano-heterostructure includes two steps: electrochemical deposition of the  $NiSe_2$  film and hydrothermal synthesis of the  $MoS_2$  film.



Fig. 1 Construction process of NiSe<sub>2</sub>@MoS<sub>2</sub> nano-heterostructures on CFP.

First, the NiSe<sub>2</sub> film was electrodeposited on a carbon fiber paper (CFP,  $1 \times 1 \text{ cm}^2$ , TGP-H-60, Toray) by a three-electrode electrochemical cell (CHI660E, CH Instruments). The CFP substrate, a saturated calomel electrode (SCE), and a graphite rod were employed as the working, reference, and counter electrodes, respectively. The electrolyte composed of 100 mL deionized water, 4.45 g NiCl<sub>2</sub>·6H<sub>2</sub>O, 1.44 g SeO<sub>2</sub>, and 1.02 g LiCl. The potential was kept at -0.35 V ( $\nu$ s. SCE) for 40 min. Then, the deposited NiSe<sub>2</sub> film (CFP@NiSe<sub>2</sub>) was washed using deionized water and dried in a vacuum drying oven at 60 °C.

Second, the  $MoS_2$  film was coated on CFP@NiSe<sub>2</sub> by the hydrothermal synthesis. In this process, the amount of precursor and technological conditions are very strict. The precursor solution, including 0.06 g  $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ , 0.15 g SC $(NH_2)_2$ , and 30 mL deionized water, was magnetically stirred for 5 min and allowed to stand at 60 °C for 1 h. Then, it was transferred into a 50 mL airtight reactor and was allowed to stand at 180 °C for 12 h to afford CFP@NiSe\_2@MoS\_2. It was washed with deionized water and dried in a vacuum drying oven at 60 °C. Detailed procedures refer to ref. 33.

#### 2.2. Characterization

First, the material structure of the obtained samples was observed by various means. The morphology observation was carried out *via* scanning electron microscopy (SEM, S-4800, Hitachi), high-resolution transmission electron microscopy (HRTEM, TECNAI G2F20, FEI), and X-ray diffraction (XRD, X'Pert3, Panalytical). Before TEM characterization, the samples were ground into powder and transferred to a copper grid. XRD was carried out with Cu K $\alpha$  radiation ( $\lambda = 1.54$  Å) at 40 mA and 45 kV. The chemical elements of samples were observed *via* energy dispersive spectroscopy (EDS, S-4800, Hitachi) and X-ray photoelectron spectroscopy (XPS, EscaLab-250Xi, Thermofisher). XPS source is Al K $\alpha$  (*hv* = 1486.6 eV) with a power of 22.8 W.

Second, the electrocatalytic OER performances of the obtained samples were observed through a three-electrode electrochemical cell that employs Hg/HgO and graphite rod as reference and counter electrodes, respectively, in a 1 M KOH electrolyte solution. Before the measurement, high-purity oxygen was injected into the electrolyte for 20 min to eliminate the interference of oxygen. Then, the oxygen bubbles formed on the electrode surface were dislodged by magnetic stirring during the process of measurement. The potential  $E_{\rm RHE}$  was obtained by the equation of  $E_{\rm RHE} = E_{\rm Hg/HgO} + 0.059 \text{pH} + 0.098$ . OER polarization curves were obtained by linear sweep voltammetry (LSV) at a scan rate of 10 mV s<sup>-1</sup> from 0.5 to 2 V (*vs.* RHE). The result was corrected by the equation of  $\eta_{\rm corr} = \eta_{\rm exp} - iR$  to eliminate the effect of series resistance. Electrochemical impedance spectra (EIS) were obtained at 1.51 V (*vs.* RHE) in

a frequency range of  $10^5$ –0.1 Hz with an amplitude of 5 mV. The double-layer capacitance ( $C_{\rm dl}$ ), obtained by cyclic voltammetry (CV) tests at different scan rates from 20 to 200 mV s<sup>-1</sup> in a range of 0.68–0.78 V ( $\nu s$ . RHE), was used to evaluate the electrochemically active surface area (ECSA).

#### 3. Results and discussion

 $NiSe_2$  and  $MoS_2$  films were coated on a CFP substrate, respectively. According to Fig. 2(a–c), rich voids between carbon fibers in the CFP substrate can enlarge the contact of the catalyst to the electrolyte, which are beneficial to improving the OER activity. According to the enlarged view in the inset, due to the poor crystallinity induced by the low temperature in the constructing process, both NiSe<sub>2</sub> and MoS<sub>2</sub> nanosheets are disorderly distributed in the film. Owing to the disorderly distribution, abundant edges of NiSe<sub>2</sub> and MoS<sub>2</sub> nanosheets can further improve the contact area and activity. Moreover, the close contact between NiSe<sub>2</sub> and CFP obtained by the electrochemical deposition can reduce the charge transfer impedance in the OER process. As shown in Fig. 2(d), the thickness of the NiSe<sub>2</sub>@MoS<sub>2</sub> film is ~550 nm. According to further HRTEM observation (Fig. 2(e)), the NiSe<sub>2</sub>@MoS<sub>2</sub> heterostructure is composed of 0.27 nm MoS<sub>2</sub> (002) face and 0.66 nm NiSe<sub>2</sub> (210)



Fig. 2 SEM images of (a) CFP. (b) CFP@NiSe<sub>2</sub>, (c) CFP@NiSe<sub>2</sub>@MoS<sub>2</sub>. (d) TEM result of CFP@NiSe<sub>2</sub>@MoS<sub>2</sub>. (e) HRTEM result of NiSe<sub>2</sub>@MoS<sub>2</sub>. The NiSe<sub>2</sub>@MoS<sub>2</sub> nano-heterostructure composed of MoS<sub>2</sub> (002) and NiSe<sub>2</sub> (210) faces can be clearly observed. (f) EDS results of CFP@NiSe<sub>2</sub>@MoS<sub>2</sub>. Ratio of Se/Ni is close to 2, while that of S/Mo is close to 1, indicating that it is sulfur deficient.



Fig. 3 Raman results of the samples. Peaks A<sub>g</sub> and T<sub>g</sub> belong to NiSe<sub>2</sub>, while  $E_{2g}^1$  and A<sub>1g</sub> belong to MoS<sub>2</sub>. The presence of the peak S–Se confirms that the NiSe<sub>2</sub>@MoS<sub>2</sub> heterostructure was formed.

face. EDS spectra were further recorded to observe the element composition of the heterostructure (Fig. 2(f)). The ratio of Se/Ni is close to 2 while that of S/Mo is close to 1, indicating that the obtained  $NiSe_2@MoS_2$  is sulfur deficient.

As shown in Fig. 3, the samples were further observed by Raman spectroscopy. In the spectrum of CFP@NiSe<sub>2</sub>@MoS<sub>2</sub>, peaks  $A_g$  and  $T_g$  of NiSe<sub>2</sub> are shown at ~208 and ~235 cm<sup>-1</sup>, respectively, while  $E_{2g}^1$  and  $A_{1g}$  of MoS<sub>2</sub> are shown at ~379 and  $\sim$ 405 cm<sup>-1</sup>, respectively, indicating that NiSe<sub>2</sub>@MoS<sub>2</sub> is indeed deposited on CFP.<sup>34,35</sup> The interfering peak at ~290 cm<sup>-1</sup>, originating from internal strain of MoS<sub>2</sub>, is caused by the disorder of the grains and defects.36 The S-Se peak at  $\sim$ 360 cm<sup>-1</sup>, originating from S-Se pairs, further confirms that the NiSe<sub>2</sub>(a)MoS<sub>2</sub> heterostructure is formed.<sup>37</sup> Compared with CFP@MoS<sub>2</sub>, peaks E<sup>1</sup><sub>2g</sub> and A<sub>1g</sub> of MoS<sub>2</sub> in CFP@NiSe<sub>2</sub>@MoS<sub>2</sub> exhibit an obvious blue shift, because the crystal symmetry is destroyed by the defects. The defects are from the NiSe<sub>2</sub> substrate and NiSe2@MoS2 heterostructures, which can improve the exposure of active sites and OER activity of  $\text{MoS}_2.^{\scriptscriptstyle 38\text{--}40}$  Moreover, peaks  $A_{\rm g}$  and  $T_{\rm g}$  cannot be observed independently in CFP@NiSe2, indicating that the crystallinity of NiSe<sub>2</sub> prepared by the electrochemical deposition is relatively low. Then, the crystallinity is improved by the subsequent hydrothermal process of MoS<sub>2</sub>, which helps to reduce the charge transfer impedance in the process of OER.

As shown in Fig. 4, structures of the samples were also observed by XRD. The standard diffraction peaks of NiSe<sub>2</sub> and MoS<sub>2</sub> are shown in PDF no. 41-1945 and no. 37-1942, respectively. Peaks at 26.3 and 54.2° originate from the CFP substrate. In the spectra of CFP@NiSe<sub>2</sub>, peaks corresponding to (200), (210), (211), (220), (311), and (321) planes of NiSe<sub>2</sub> are clearly shown at around 29.4, 33.5, 36.6, 43.5, 50.7, and 57.5°, respectively.<sup>32</sup> According to the spectra of CFP@MoS<sub>2</sub>, the (002) peak of MoS<sub>2</sub> can be observed at 13.1°. The simultaneous appearance of peaks of NiSe<sub>2</sub> and MoS<sub>2</sub> are successfully deposited on the



Fig. 4 XRD spectra of the samples. The standard diffraction peaks of NiSe<sub>2</sub> and MoS<sub>2</sub> are shown in PDF no. 41-1945 and no. 37-1942 respectively. Peaks (002) of MoS<sub>2</sub>, (200), (210), (211), (220), (311), and (321) of NiSe<sub>2</sub> are clearly exhibited.

CFP substrate. Moreover, compared with CFP  $@MoS_2$ , the (002) peak has a blue shift from 13.1 to 13.5 in CFP@NiSe<sub>2</sub>@MoS<sub>2</sub> owing to the defects from the NiSe<sub>2</sub> substrate and NiSe<sub>2</sub>@MoS<sub>2</sub> heterostructures. This structure is in favor of the improvement of the OER activity, which is consistent with the Raman results.

The composition of the samples was further analyzed by XPS. According to the spectra of Ni 2p and Se 3d shown in Fig. 5(a and b), peaks of Ni  $2p_{1/2}$  and Ni  $2p_{3/2}$  belonging to Ni<sup>4+</sup> of NiSe<sub>2</sub> are shown at 870.2 and 853.1 eV with their satellite peaks at 875.7 and 859.2 eV, respectively.<sup>41</sup> Peaks of Se 3d<sub>3/2</sub> and Se 3d<sub>5/2</sub> at 53.5 and 52.7 eV, respectively, belong to  $\text{Se}_2^{2-}$  of NiSe<sub>2</sub>, while an oxidized Se peak is shown at 57 eV.42 Moreover, as shown in Fig. 5(c and d), peaks of Mo 3d<sub>3/2</sub> and Mo 3d<sub>5/2</sub> at 231.2 and 228 eV are attributed to Mo<sup>4+</sup> of MoS<sub>2</sub>, and the peak at 225.5 eV is due to the Mo-S bond. Peaks of S 2p1/2 and S 2p3/2 at 161.8 and 160.8 eV are due to  $S_2^{2-}$  of  $MoS_2$ .<sup>43</sup> Therefore,  $NiSe_2$  and  $MoS_2$  have been deposited on CFP successfully. In addition, compared with CFP@NiSe2 and CFP@MoS2, peaks of Ni 2p and Se 3d show a negative shift, while those of Mo 3d and S 2p have a positive shift in CFP@NiSe<sub>2</sub>@MoS<sub>2</sub>, further confirming that the NiSe<sub>2</sub>@MoS<sub>2</sub> heterostructure has been formed.44 The Mo-to-S ratio also needs to be observed because OER active sites of MoS<sub>2</sub> have been shown at its edge with S-vacancies.21 According to the peaks of Mo 3d and S 2p shown in Fig. 5(c and d), compared with CFP@MoS<sub>2</sub>, the Mo/S ratio increases from 0.81 to 0.93 in CFP@NiSe2@MoS2, indicating that S-vacancies increase by about 15% in the latter. Thus, the obtained NiSe2@MoS2 can expose more active sites and improve the OER activity.



Fig. 5 XPS spectra of (a) Ni 2p, (b) Se 3d, (c) Mo 3d, and (d) S 2p.

The electrocatalytic OER performances of the samples were evaluated by various electrochemical measurements. The OER polarization curves obtained by LSV in 1 M KOH solution are shown in Fig. 6(a). Unsurprisingly, the bare CFP with an almost zero current density shows no electrocatalytic OER activity in the potential window from 1.2 to 1.7 V (vs. RHE). For CFP@MoS<sub>2</sub>, the potential driving the current density of 10 mA  $cm^{-2}$  needs 1.62 V (vs. RHE), which indicates an overpotential  $\eta_{10}$  of 390 mV. Although it has some reduction than CFP, it is still relatively high and worthless as an OER catalyst. In the curve of CFP@NiSe<sub>2</sub>, the peak at  $\sim$ 1.36 V (vs. RHE) is attributed to the oxidation of Ni.<sup>32,45</sup> It was first oxidized to Ni(OH)<sub>2</sub>, which proceeded as Ni + 2OH<sup>-</sup>  $\rightarrow$  Ni(OH)<sub>2</sub> + 2e<sup>-</sup>. As the potential increased, Ni(OH)2 was further oxidized to NiOOH, which proceeded as Ni(OH)<sub>2</sub> + OH<sup>-</sup>  $\rightarrow$  NiOOH + H<sub>2</sub>O + e<sup>-</sup>. The overpotential  $\eta_{10}$  of 290 mV is lower than that of CFP@MoS<sub>2</sub>. When the current density increases to 20 mA cm<sup>-2</sup>, the overpotential  $\eta_{20}$  of 356 mV is also lower than that of CFP@MoS<sub>2</sub> (440 mV), indicating a better activity. However, it is not the best. Obviously, CFP@NiSe<sub>2</sub>@MoS<sub>2</sub> with  $\eta_{10}$  of 267 mV and  $\eta_{20}$  of 320 mV exhibits the highest catalytic performance.

Tafel slopes of the samples were further observed by fitting the polarization curves with the Tafel equation ( $\eta = a + b \log j$ , where *b* is the Tafel slope). According to Fig. 6(b) and Table 1, Tafel slopes of the samples are 159, 112, and 85 mV  $dec^{-1}$ , respectively. The much smaller Tafel slope of CFP@NiSe2@-MoS<sub>2</sub> further confirms its excellent OER catalytic performance. It is also compared with that of other MoS<sub>2</sub>-based and noble metal oxide electro-catalysts reported recently (Table 2). CFP@MoS<sub>2</sub> with  $\eta_{10}$  of 390 mV and *b* of 159 mV dec<sup>-1</sup> shows an obvious activity improvement than the exfoliated MoS<sub>2</sub>, which can be attributed to the more exposure of active sites induced by the small grain.<sup>23</sup> Compared with CFP@MoS<sub>2</sub>, the performance of CFP@NiSe2@MoS2 has a further improvement. Moreover, the performance of CFP@NiSe2@MoS2 and MoS2/Ni3S2 is similar. However, compared to the dependence of MoS<sub>2</sub>/Ni<sub>3</sub>S<sub>2</sub> on nickel foam, NiSe<sub>2</sub>@MoS<sub>2</sub> can be deposited on the surface of any conductor as shown in this study, which greatly expands its application.<sup>27</sup> Compared with that of Co<sub>3</sub>S<sub>4</sub>@MoS<sub>2</sub>, CoS<sub>2</sub>-C@MoS<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>@MoS<sub>2</sub>/CC, and RuO<sub>2</sub>, although the Tafel slope of CFP@NiSe<sub>2</sub>@MoS<sub>2</sub> is bigger, it has a smaller overpotential  $\eta_{10}$ , indicating that CFP@NiSe<sub>2</sub>@MoS<sub>2</sub> is an excellent OER electro-catalyst and worth exploring as a substitute for noble metal-based materials.

As shown in Fig. 6(c), electrochemical impedance spectra (EIS) of the samples were measured and fitted by the equivalent circuit (Fig. 6(d)), where  $R_s$  is the series resistance,  $R_{ct}$  is the charge-transfer resistance, and CPE is the constant phase



Fig. 6 (a) OER polarization curves, (b) Tafel plots, and (c) impedance analysis of the samples. (d) The equivalent circuit:  $R_s$  is the series resistance,  $R_{ct}$  is the charge-transfer resistance, and CPE is the constant phase elements.

elements. According to Fig. 6(c) and Table 3,  $R_s$  and  $R_{ct}$  of the samples are 1.81 and 567.6, 1.71 and 6.74, 1.68 and 3.03  $\Omega$ , respectively. It can be obtained that  $R_s$  values of the samples are

Table 1 Overpotential and Tatel slope of the obtained samples				
Catalyst	Overpotential $\eta_{10}$ (mV)	Overpotential $\eta_{20}$ (mV)	Tafel slope $b$ (mV dec <sup>-1</sup> )	
CFP@NiSe <sub>2</sub> @MoS <sub>2</sub> CFP@NiSe <sub>2</sub>	267 290	320 356	85 112	
CFP@MoS <sub>2</sub>	390	440	159	

 $\label{eq:table_constraint} \begin{array}{l} \mbox{Table 2} & \mbox{The electrocatalytic OER performances of CFP@NiSe_2@MoS_2} \\ \mbox{and other } MoS_2\mbox{-based electro-catalysts} \end{array}$ 

Catalyst	Tafel slope $b$ (mV dec <sup>-1</sup> )	Overpotential $\eta_{10}$ (mV)	Ref.
CFP@NiSe2@MoS2	85	267	This work
CFP@MoS <sub>2</sub>	159	390	This work
Exfoliated MoS <sub>2</sub>	322	420	46
Co <sub>9</sub> S <sub>8</sub> @MoS <sub>2</sub>	94	342	25
Co <sub>3</sub> S <sub>4</sub> @MoS <sub>2</sub>	43	280	47
CoS <sub>2</sub> -C@MoS <sub>2</sub>	46	391	26
MoS <sub>2</sub> /Ni <sub>3</sub> S <sub>2</sub>	88	218	27
Co <sub>3</sub> O <sub>4</sub> @MoS <sub>2</sub> /CC	58	360	48
RuO <sub>2</sub>	65	380	49

slightly different. However, the  $R_{\rm ct}$  value has a significant decrease from 567.6 to 3.03  $\Omega$ , which indicates that CFP@NiSe<sub>2</sub>@MoS<sub>2</sub> can substantially improve the OER activity.

 $C_{\rm dl}$  was used to evaluate ECSA of the samples. As shown in Fig. 7(a–c), CV tests of the samples were performed with different scan rates from 20 to 200 mV s<sup>-1</sup> in the regions of non-faradaic potentials (0.68–0.78 V (*vs.* RHE)). Current density differences between anodic and cathodic *versus* the scanning rate at 0.73 V a (*vs.* RHE) are shown in Fig. 7(d). Fitting these data linearly can obtain the  $C_{\rm dl}$  value. According to Fig. 7(d) and Table 3,  $C_{\rm dl}$  values of the samples are 0.78, 4.64, and 6.25 mF cm<sup>-2</sup>, respectively. The much larger  $C_{\rm dl}$  of CFP@NiSe<sub>2</sub>@MoS<sub>2</sub> among the samples indicates that the ECSA was significantly increased. Hence, the outstanding OER performance of CFP@NiSe<sub>2</sub>@MoS<sub>2</sub> is not only due to the faster electron transfer rate but also due to the increasing ECSA.

Table	3	Series	resistance	R <sub>s</sub> ,	charge-transfer	resistance	$R_{\rm ct}$ ,	and
double-layer capacitance $C_{dl}$ of the obtained samples								

Catalyst	Resistance $R_{\rm s}(\Omega)$	Resistance $R_{ m ct}(\Omega)$	$C_{ m dl}({ m mF~cm^{-2}})$
CFP@NiSe2@MoS2 CFP@NiSe2	1.68 1.71	3.03 6.74	0.78 4.64
CFP <sub>(a)</sub> MoS <sub>2</sub>	1.81	567.6	6.25



Fig. 7 CV tests of (a) CFP@MoS<sub>2</sub>, (b) CFP@NiSe<sub>2</sub>, and (c) CFP@NiSe<sub>2</sub>@MoS<sub>2</sub> with different scan rates from 20 to 200 mV s<sup>-1</sup> in a range of 0.68–0.78 V (vs. RHE). (d) Current density difference between anodic and cathodic versus the scanning rate at 0.73 V a (vs. RHE).  $C_{dl}$  obtained by linear fitting the data was used to evaluate ECSA of the samples because  $C_{dl}$  was proportional to ECSA.

The durability of CFP@NiSe<sub>2</sub>@MoS<sub>2</sub> was further measured by repeating the CV test for 1000 cycles. According to Fig. 8(a), the difference in current density is negligible before and after 1000 cycles. The current density *versus* time under a constant overpotential of 340 mV is shown in Fig. 8(b). Only 6% loss after 10 h indicates its outstanding durability.

The mechanism that  $NiSe_2@MoS_2$  has a better catalytic performance than pure  $MoS_2$  or  $NiSe_2$  can be summarized as follows:

(1) The disordered NiSe<sub>2</sub> increases the contact area between  $MoS_2$  and the electrolyte solution. NiSe<sub>2</sub>@MoS<sub>2</sub> samples are obtained by depositing  $MoS_2$  on NiSe<sub>2</sub>, while pure  $MoS_2$  and NiSe<sub>2</sub> are deposited directly on the bare CFP substrate. Compared with the smooth bare CFP substrate, the disordered distribution of NiSe<sub>2</sub> nanosheets (as shown in Fig. 2) can further increase the superficial area of  $MoS_2$ , so as to increase the contact area between  $MoS_2$  and the electrolyte solution. This is an effective way to improve the OER efficiency of  $MoS_2$ .



Fig. 8 (a) Durability measurement of CFP@NiSe2@MoS2. Difference in current density is negligible before and after 1000 cycles. (b) The current density versus time under a constant overpotential of 340 mV.

According to the  $C_{dl}$  results (as shown in Fig. 7), the ECSA of NiSe<sub>2</sub>@MoS<sub>2</sub> significantly increased than that of pure NiSe<sub>2</sub> and MoS<sub>2</sub>.

(2) The hybridization of NiSe<sub>2</sub> increases the defects of  $MoS_2$ , which can improve the exposure of active sites and OER activity of  $MoS_2$ . It has been demonstrated that defects such as doping, atomic vacancy and lattice distortion can increase the exposure of active sites of  $MoS_2$ .<sup>38-40</sup> According to the results of the material characterization, the defects of  $MoS_2$  do increase in NiSe<sub>2</sub>@MoS<sub>2</sub>. As shown in the Raman results (Fig. 3), some phenomena in NiSe<sub>2</sub>@MoS<sub>2</sub> such as the appearance of the interfering peak at ~290 cm<sup>-1</sup>, the blue shift and expansion of the characteristic peak of  $MoS_2$ , indicate that the crystal symmetry of  $MoS_2$  was damaged by the defects.

According to the XPS results (Fig. 5), the  $\sim$ 15% increase of S-vacancies in NiSe<sub>2</sub>@MoS<sub>2</sub> confirms that the hybridization of NiSe<sub>2</sub> increases the exposure of active sites of MoS<sub>2</sub>.

(3) Doping Ni atoms into MoS<sub>2</sub> at the interface of the NiSe<sub>2</sub>@MoS<sub>2</sub> heterostructure can effectively reduce the kinetic energy barrier of the initial water-dissociation step and facilitate the desorption of -OH,<sup>27</sup> so as to improve the OER performance. According to Raman and XPS results (Fig. 3 and 5), it can be confirmed that the chemical bonds between NiSe<sub>2</sub> and MoS<sub>2</sub> are generated at the interface of the NiSe<sub>2</sub>@MoS<sub>2</sub> heterostructure.

#### 4. Conclusion

In summary, the novel NiSe<sub>2</sub>@MoS<sub>2</sub> nano-heterostructure for electrocatalytic OER has been constructed on a CFP substrate by a simple method. The electrocatalytic OER performances were fully evaluated by electrochemical measurements and further compared with that of other MoS<sub>2</sub>-based and noble metal oxide electro-catalysts. It exhibits an outstanding catalytic performance with an overpotential  $\eta_{20}$  of 323 mV and a Tafel slope of 85 mV dec<sup>-1</sup>. Just 6% loss of current density before and after 10 h also indicates its excellent durability. Therefore, it is an excellent OER electro-catalyst and worth exploring as a substitute for noble metal-based materials.

#### Author contributions

Yazhou Huang: resources, conceptualization, methodology, investigation, writing – original draft, writing – review & editing. Jiacai Huang: writing – review & editing, methodology, formal analysis. Kunshan Xu: methodology, data curation. Ranran Geng: validation, formal analysis.

### Conflicts of interest

There are no conflicts to declare.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (51905259), the Natural Science Foundation of Jiangsu Province (BK20191017), the Natural Science Research Program for Higher Education of Jiangsu Province (19KJB460003, 20KJA510007), the Scientific Research Fund of Nanjing Institute of Technology (YKJ201859).

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