Fe$_x$Mo$_{1-x}$S$_2$/CNT@CC nanosheets as an efficient bifunctional electrocatalyst for overall water splitting

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The Fe$_x$Mo$_{1-x}$S$_2$ nanosheets with different Fe doping content $x$ were grown on carbon nanotubes @ carbon cloth (CNT@CC) substrate using a hydrothermal method by varying the molar ratio of FeSO$_4$·7H$_2$O to Na$_2$MoO$_4$·2H$_2$O in the precursor solution. The effect on HER, OER and overall water splitting (OWS) performance of Fe doping content $x$ were studied. The Fe$_x$Mo$_{1-x}$S$_2$ nanosheets have the optimal HER and OWS performance for $x=0.050$ and the optimal OER performance for $x=0.075$. The overpotential at current density of 100 mA/cm$^2$ and Tafel slope are 198 mV and 44.7 mV/dec$^{-1}$ for HER; and they are 279 mV and 24.5 mV/dec for OER in 1 M KOH electrolyte. The electrolytic cell using Fe$_{0.05}$Mo$_{0.95}$S$_2$/CNT@CC as both cathode and anode achieves a voltage of 1.69 V at current density of 100 mACm$^{-2}$. The bifunctional catalytic activities of the Fe$_x$Mo$_{1-x}$S$_2$/CNT@CC catalyst come from the synergistic effect between Fe$_x$Mo$_{1-x}$S$_2$ nanosheets and CNT.

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1. Introduction

Hydrogen generation through water splitting is regarded as an attractive way to solve the energy crisis and environmental pollution [1, 2]. The water splitting consists of the cathode hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER). Due to the slow reaction kinetics and large energy barrier of HER and OER in water splitting process, it is important to design and fabricate of high-efficiency, low-cost and durable catalysts [3-5]. Although Pt, Ru, and Ir-based noble metal catalysts exhibit extremely outstanding HER and OER electrocatalytic activities, but their high cost and scarcity limits their large-scale industrial application [6, 7]. Therefore, it is highly desirable but remains challenging to develop the nonprecious metal bifunctional catalysts to simultaneously catalyze the HER and OER process.

Both theoretical and experimental researches have proved that the two-dimensional (2D) layered transitional-metal dichalcogenides such as MoS$_2$ is high-efficiency and low-cost catalysts for HER process [8-10]. However, MoS$_2$ has poor catalytic activity for OER process. Since the
transition metals Fe, Ni and Co-based sulfides, selenides, phosphides, hydroxides and oxyhydroxides are believed to be high-efficiency and low-cost OER catalysts because of their appropriate electronic structures [11-16]. Therefore, in this work, the Fe_xMo_{1-x}S_2/CNT@CC nanosheets with different Fe doping content x (x=0, 0.025, 0.050, 0.075 and 0.100) were designed and prepared as an efficient bifunctional electrocatalyst for overall water splitting. The effect on HER, OER and Overall water splitting (OWS) performance of Fe doping content x were studied.

2. Experimental section

2.1. Fe_xMo_{1-x}S_2 nanosheets growth on a CNT@CC substrate

The total thickness of CNT@CC substrate used in this work is 0.2 mm. The loading of carbon nanotube is 3-4 mg cm^{-2}. The diameter of carbon nanotube is 25-50 nm and the diameter of carbon fiber is 10-25 µm. The conductivity of CNT@CC is 138-150 S cm^{-1}. The Fe_xMo_{1-x}S_2 nanosheets were grown onto the CNT@CC substrate by hydrothermal method. The hydrothermal reaction continued for 8 hours at 200 °C. The samples were removed and washed several times with water and ethanol, and then were dried in the atmosphere at 60°C. To study the effect of Fe doping content x on the morphology, phase structure and electrocatalytic performance of the Fe_xMo_{1-x}S_2/CNT@CC, a series of samples with different Fe doping content x were prepared by varying the molar ratio of FeSO_4·7H_2O to Na_2MoO_4·2H_2O in the precursor solution. The preparation process parameters of various samples are listed in Table 1.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Fe content</th>
<th>FeSO_4 mmol</th>
<th>Na_2MoO_4 mmol</th>
<th>CS(NH_2)_2 mmol</th>
<th>C_2H_2O_4·2H_2O mmol</th>
<th>N_2H_2·H_2O µL</th>
<th>Water ml</th>
<th>T °C</th>
<th>Time h</th>
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<tr>
<td>A1</td>
<td>0</td>
<td>0</td>
<td>0.40</td>
<td>4</td>
<td>0.1</td>
<td>20</td>
<td>60</td>
<td>200</td>
<td>8</td>
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<tr>
<td>A2</td>
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<td>0.01</td>
<td>0.39</td>
<td>4</td>
<td>0.1</td>
<td>20</td>
<td>60</td>
<td>200</td>
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</tr>
<tr>
<td>A3</td>
<td>0.050</td>
<td>0.02</td>
<td>0.38</td>
<td>4</td>
<td>0.1</td>
<td>20</td>
<td>60</td>
<td>200</td>
<td>8</td>
</tr>
<tr>
<td>A4</td>
<td>0.075</td>
<td>0.03</td>
<td>0.37</td>
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<tr>
<td>A5</td>
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<td>0.36</td>
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<td>60</td>
<td>200</td>
<td>8</td>
</tr>
</tbody>
</table>

2.2. Characterization of the Fe_xMo_{1-x}S_2/CNT@CC

The morphology of the Fe_xMo_{1-x}S_2/CNT@CC was observed by using scanning electron microscopy (SEM, SU8010, Hitachi). The crystallographic structure and phase purity of the Fe_xMo_{1-x}S_2/CNT@CC were investigated using X-ray diffraction (XRD, D/MAX-Ultima, Rigaku) and Raman spectroscopy (LabRAM HR Evolution, HORIBA Jobin Yvon). The element distribution map, chemical state and atom ratio of Fe, Mo and S elements in the Fe_xMo_{1-x}S_2/CNT@CC were analyzed using energy dispersive spectroscopy (EDS, Escalab 250Xi, Thermo Fisher) and X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher).
2.3. Electrochemical measurement of the Fe$_x$Mo$_{1-x}$S$_2$/CNT@CC

The catalytic performance of the Fe$_x$Mo$_{1-x}$S$_2$/CNT@CC for HER and OER was tested in 1 M KOH electrolyte using a classical three-electrode system with the Fe$_x$Mo$_{1-x}$S$_2$/CNT@CC as the working electrode, Ag/AgCl as the reference electrode and graphite as the opposite electrode. All potentials are converted to reversible hydrogen electrodes (RHE) according to the following formula

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{pH} + 0.098 \text{V}$$

LSV polarization curves were tested in the potential range from -1.5 V to -0.5 V (vs. Ag/AgCl) for HER and from 0 V to 0.8 V (vs. Ag/AgCl) for OER with a scan rate of 5 mV/s. 95% IR correction was performed. CV measurement was carried out in the non-Faraday range from -0.9 to -0.8 V (vs. Ag/AgCl) for HER and from 0.1 V to 0.2 V (vs. Ag/AgCl) for OER at different scan rates of 5, 10, 15, 20 and 25 mV/s. Electrochemical impedance spectroscopy (EIS) was carried out in frequency range from 0.01 Hz to 100 kHz with amplitude of 5 mV. For the HER, the test potential was -1.2 V (vs. Ag/AgCl), while for the OER, the test potential was 0.6 V (vs. Ag/AgCl). The Overall water splitting experiment was carried out in an electrolytic cell system using Fe$_x$Mo$_{1-x}$S$_2$/CNT@CC as both anode and cathode in a 1 M KOH electrolyte.

3. Results and discussion

3.1. Characterization of the Fe$_x$Mo$_{1-x}$S$_2$/CNT@CC

Fig.1 shows the SEM images of blank CNT@CC substrate and Fe$_x$Mo$_{1-x}$S$_2$/CNT@CC with different Fe doping content x. The SEM image of a blank CNT@CC substrate shows that the dense CNT networks are covered on the surface of carbon cloth (Fig1a). The Fe$_x$Mo$_{1-x}$S$_2$ nanosheets were grown on surface of CNT@CC substrate. The Fe doping content x has some effect on the morphology of the Fe$_x$Mo$_{1-x}$S$_2$ nanosheets. When the Fe doping content x is equal to 0 or 0.025, the Fe$_x$Mo$_{1-x}$S$_2$ nanosheets are flower-like microspheres that are formed by many gathering together nanosheets perpendicular to the spherical surface. The intertwined CNT networks are no longer observed, as shown in Fig. 1b and Fig.1c. When the Fe doping content x increase from 0.050 to 0.100, many Fe$_x$Mo$_{1-x}$S$_2$ nanosheets wrap around CNT, and the intertwined CNT networks can be distinguished. However, the size and density of the Fe$_x$Mo$_{1-x}$S$_2$ nanosheets gradually decrease as the Fe doping content x increases from 0.050 to 0.100. Compared with pure MoS$_2$ and Fe$_{0.025}$Mo$_{0.975}$S$_2$ nanosheets, the Fe$_x$Mo$_{1-x}$S$_2$ nanaosheets prepared at Fe doping content x of 0.050-0.100 have a larger edge/basal ratio, resulting in more exposed edge sites, which is beneficial to improve the catalytic performance.

Fig.2 shows the standard diffraction peaks of 2H-MoS$_2$ (JCPDS No. 37-1492) and the X-ray diffraction patterns of the Fe$_x$Mo$_{1-x}$S$_2$/CNT@CC with various Fe doping content x. Firstly, The diffraction peaks (marked by *) at 2θ=25.6° and 43.5° correspond to the (0 0 2) and (1 0 0) crystal planes of CNT@CC substrate. The diffraction peaks located at 2θ=14.4°, 33.6° and 39.6°are assigned the (002), (101) and (103) planes of hexagonal phase of MoS$_2$ (JCPDS No.
37-1492), respectively. The diffraction peaks of the Fe₉Mo₁₋ₓS₂ nanosheets are very weaker compared with the stronger diffraction peaks of the CNT@CC substrate, and only the (0 0 2) peak at 14.4° is easy to observe. The Fe doping content x has no significant effect on the diffraction peaks of the FeₓMo₁₋ₓS₂ nanosheets. The peaks marked by # come from impurity phase MoOₓ. In order to confirm the effective incorporation of Fe into MoS₂, the Fe₀.₀₅Mo₀.₉₅S₂CNT@CC was analyzed using EDS. Fig.2b-Fig.2e are the SEM images and the corresponding elemental distribution mappings of the Fe₀.₀₅Mo₀.₉₅S₂/CNT@CC. It can be clearly seen that element S, Mo and Fe are uniformly distributed throughout the entire Fe₀.₀₅Mo₀.₉₅S₂ nanosheets, which confirm that Fe is uniformly doping into MoS₂.

![SEM images of bare CNTs/CC substrate and the FeₓMo₁₋ₓS₂/CNT@CC with various Fe doping content x.](image)

**Fig. 1.** SEM images of bare CNTs/CC substrate and the FeₓMo₁₋ₓS₂/CNT@CC with various Fe doping content x.
Fig. 2. (a) X-ray diffraction patterns of Fe$_x$Mo$_{1-x}$S$_2$/CNT with various Fe doping content $x$; (b) SEM image; (c, d, e) EDS elemental mapping images of the Fe$_{0.05}$Mo$_{0.95}$S$_2$ nanosheets.

X-ray photoelectron spectroscopy (XPS) was used to characterize the elemental composition and chemical valence states of the Fe$_x$Mo$_{1-x}$S$_2$/CNT@CC. Fig.3a is the full spectrum of XPS, showing that the Fe$_x$Mo$_{1-x}$S$_2$ contain the elements C, O, S, Mo and Fe. Fig.3b shows the high-resolution XPS spectra of Mo 3d for all samples. For pure MoS$_2$, Mo 3d orbitals split into Mo 3d$_{3/2}$ and Mo 3d$_{5/2}$ with binding energies of 232.5 eV and 229.0 eV, respectively, correspond to Mo$^{4+}$ in MoS$_2$. The asymmetry of the lines in Fig. 3b especially for the samples at $x = 0.050$ and 0.075 may be come from Mo$^{6+}$ because the surface of samples is oxidized [17]. The shoulder at high energy corresponds to the Mo$^{6+}$ binding energy. Mo may be oxidized to Mo$^0$, Mo$^{4+}$ and Mo$^{6+}$ species. The binding energy of Mo 3d$_{3/2}$ and Mo 3d$_{5/2}$ gradually shifts to the high energy with the valence increasing. This is consistent with result shown in the XRD pattern in Fig. 2a. In addition, compared with pure MoS$_2$ nanosheets, Mo 3d peaks of the Fe$_x$Mo$_{1-x}$S$_2$ nanosheets shift to a lower binding energy, indicating that Fe induces a p-type doping effect in MoS$_2$ [18,19]. The asymmetry of the lines for doping Fe sample in Fig.3b may come from Mo$^{6+}$ and Mo$^{5+}$ because the surface of MoS$_2$ nanosheets is oxidized. Fig.3c shows the high-resolution XPS spectra of Fe 2p. The peaks located at 721.1 eV and 708 eV are attributed to 2p$_{1/2}$ and 2p$_{3/2}$ of Fe-S binds with two satellite peaks at 723.1 eV and 710.2 eV which prove that Fe-S bind form and the Fe partly replace Mo in MoS$_2$ crystal structure [20]. Fig.3d displays the high-resolution XPS spectra of S2p. The double peaks at 163.1 eV and 161.9 eV are attributed to the S 2p$_{1/2}$ and S 2p$_{3/2}$ binding energy of S-Mo binds, respectively; while the peaks at 164.1 eV is attributed to Fe-S bind.
3.2. HER Electrocatalytic performance of the Fe<sub>x</sub>Mo<sub>1-x</sub>S<sub>2</sub>/CNT@CC

To study the HER performance of the Fe<sub>x</sub>Mo<sub>1-x</sub>S<sub>2</sub>/CNT@CC nanosheets, LSV, CV and EIS tests were performed in 1M KOH solution. Fig.4a shows the LSV curves of Fe<sub>x</sub>Mo<sub>1-x</sub>S<sub>2</sub>/CNT@CC catalyst. In Fig.4a, the potentials corresponding to current densities 10 and 100 mAm<sup>-2</sup> are called as the overpotentials η<sub>10</sub> and η<sub>100</sub>, respectively. The values of η<sub>10</sub> and η<sub>100</sub> for all samples are given in Fig.4a. The Fe<sub>0.05</sub>Mo<sub>0.95</sub>S<sub>2</sub>/CNT@CC prepared at Fe doping content x=0.050 has the smallest overpotentials of η<sub>10</sub>=116 mV and η<sub>100</sub>=198 mV. The Tafel slope is an important parameter to characterize HER and OER kinetic processes. Fig.4b shows the Tafel curves of the Fe<sub>x</sub>Mo<sub>1-x</sub>S<sub>2</sub>/CNT@CC catalyst. The Tafel slope b is obtained by fitting the linear part and the values of Tafel slope b for all samples are given in Fig.4b. The Tafel slope of the Fe<sub>0.05</sub>Mo<sub>0.95</sub>S<sub>2</sub>/CNT@CC is smaller than that of the other samples. The smaller Tafel slope represents more favorable HER kinetics and the faster charge-transfer ability. Tafel slope can determine the rate-determining step. The kinetics reactions for the HER in alkaline electrolyte are shown in the following equations [21, 22].

\[
\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}^+ + \text{OH}^- \quad \text{(Volmer)} \quad (2)
\]

\[
\text{H}^+ + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^- \quad \text{(Heyrovsky)} \quad (3)
\]
The HER process includes two principal steps of hydrogen adsorption and desorption. The first step is hydrogen adsorption, where the hydrogen atoms bind to the catalyst and generate H* on surface of catalys by the reaction of H₂O and an electron (Volmer step), as described in equation (2). The second step is hydrogen desorption, where H₂ is generated via H* reaction with H₂O and an electron (Heyrovsky step) or via two H* reaction on surface of catalys (Tafel step), as described in equation (3) and (4) [22, 23]. Theoretically, the Tafel slopes for the Volmer, Heyrovsky and Tafel steps are 120 mVdec⁻¹, 40 mVdec⁻¹, and 30 mVdec⁻¹, respectively[23, 24]. The Tafel slope values of the FeₓMo₁₋ₓS₂/CNT@CC nanosheets prepared at different Fe doping content are in the range from 44.7 mVdec⁻¹ to 66.9 mVdec⁻¹, suggesting the Volmer-Heyrovsky is the possible reaction mechanism in which Heyrovsky is the rate-determining step.

The electric double layer capacitance Cdl and the electrochemical surface area ECSA are also key parameters used to evaluate the HER and OER catalytic activity of the catalyst. The CV curves of the FeₓMo₁₋ₓS₂/CNT@CC catalysts were carried out in the non-Faraday potential range from -0.9 to -0.8 V (vs. Ag/AgCl) at scan rates of 5, 10, 15, 20 and 25 mVs⁻¹, respectively. The current density difference ΔJ(ΔJ=|Jmax-Jmin|/2) as a function of scan rate is plotted in Fig. 4c. The dependence of the current density difference ΔJ on the scan rate is approximately linear, and the slope of the linear portion is defined as the electric double layer capacitance Cdl. The Cdl values of various samples are given in Fig.4c. The electrochemical surface area (ECSA) of the catalysts is proportional to Cdl. ECSA can be calculated using the Randles–Sevcik equation

\[
\text{ESCA} = \frac{c_{dl}}{c_{s}} A.
\]

where A is the effective area of the working electrode (our working electrode of 1 cm²) and Cᵢ is usually taken as 0.04 mF cm⁻². The FeₓMo₁₋ₓS₂/CNT@CC prepared at Fe doping content of 0.050 has the largest ECSA of 5755 cm². The larger ECSA corresponds to a larger number of active sites on the catalyst surface. A larger ECSA value can in general be ascribed to the formation of vacancies and defects in the basal planes of the FeₓMo₁₋ₓS₂ nanosheets. Fig.4d shows the Nyquist plots of the FeₓMo₁₋ₓS₂/CNT@CC catalysts. The diameter of the semicircle in the Nyquist plot is related with its charge transfer impedance Rct. The charge transfer resistance Rct, the solution resistance Rs and the capacitance CPE can be obtained by fitting Nyquist plot using an equivalent circuit model shown in the inset of Fig.4d. The charge transfer resistance Rct for all samples is listed in Fig.4d. The FeₓMo₁₋ₓS₂/CNT@CC catalyst prepared at Fe doping content of 0.050 has the lowest charge transfer resistance and the fastest electron transfer rate.

The good HER catalytic activity of the FeₓMo₁₋ₓS₂/CNT@CC catalyst can be mainly attributed to the following two aspects. (1) The intrinsic HER activity of 2H MoS₂ arises from its edge sites and its basal planes are inactive [22, 25]. However, the introduction of Fe into the basal planes can create active sites and improve HER activity. (2) The good electrical conductivity of CNT facilitates fast charge transport. The synergistic effect between the FeₓMo₁₋ₓS₂ nanosheets and CNT reduces the charge transfer resistance Rct at the interface of FeₓMo₁₋ₓS₂/CNT@CC catalyst and the electrolyte and results in a faster HER kinetic process.
3.3. OER electrocatalytic performance of the Fe_{x}Mo_{1-x}S_{2}/CNT@CC

For comparison, the LSV curves of CC, CNT@CC, MoS_{2}/CNT@CC and Fe_{0.075}Mo_{0.925}S_{2}/CNT@CC are provided in Fig.5a. For OER, the potential (V vs. RHE-1.23 V) corresponding to current densities 100 mA/cm^{2} are called as the overpotential \( \eta_{100} \). The overpotential \( \eta_{100} \) of CNT@CC, MoS_{2}/CNT@CC and Fe_{0.075}Mo_{0.925}S_{2}/CNT@CC are 353, 301 and 273 mV, respectively. Compared with pure MoS_{2} nanosheets, Fe doped MoS_{2} can reduce the overpotential and improve OER catalytic performance. In addition, CNT@CC as a substrate is more favorable than CC as a substrate for improving the electrocatalytic performance of OER.

The OER electrocatalytic performance of the Fe_{x}Mo_{1-x}S_{2}/CNT@CC was tested in 1 M KOH solution, and the results are shown in Fig.5. As can be seen from the LSV curves in Fig.5b, Fe_{0.075}Mo_{0.925}S_{2}/CNT@CC has the lowest overpotential and the best OER catalytic activity. All the Fe doped Fe_{x}Mo_{1-x}S_{2} catalysts exhibit better OER catalytic performance than pure MoS_{2} nanosheets, suggesting that the Fe dopant could trigger more active sites in MoS_{2} and enhance the intrinsic activity of MoS_{2}. The Tafel curves of the Fe_{x}Mo_{1-x}S_{2}/CNT@CC are shown in Fig.5c. The Tafel slope value of pure MoS_{2} are 117.2 mV/dec; while the Tafel slope values of Fe_{x}Mo_{1-x}S_{2} are 34.9, 31.3, 24.5 and 34.8 mV/dec for \( x = 0.025, 0.050, 0.075 \) and 1.00, respectively, indicating
that the introduction Fe into MoS₂ can significantly reduce the Tafel slope and improve the OER reaction kinetics. The oxygen evolution reaction (OER) involves a four-electron transfer process. Generally, the kinetic reaction processes for the OER in alkaline electrolytes are described in the following equations [26].

\[
\begin{align*}
\text{OH}^- + * & \rightarrow \text{OH}^* + e^- \\
\text{OH}^* + \text{OH}^- & \rightarrow \text{O}^* + \text{H}_2\text{O} + e^- \\
\text{O}^* + \text{OH}^- & \rightarrow \text{OOH}^* + e^- \\
\text{OOH}^* + \text{OH}^- & \rightarrow \text{O}_2 + \text{H}_2\text{O} + * + e^- 
\end{align*}
\]

where * represents the active sites on the surface of catalyst. OH*, OOH*, O* represent the intermediate species adsorbed on the active sites. The Tafel slopes of reactions (6), (7), (8) are 120 mVdec⁻¹, 60 mVdec⁻¹ and 30 mVdec⁻¹, respectively [27]. The Tafel slope of the FeₓMo₁₋ₓS₂/CNT@CC catalyst prepared at various Fe doping content are in the range from 24.5 to 34.9 mVdec⁻¹, suggesting the absorption of *O and the generation of *OOH as the rate-determining step.

Further, Cdl and ECSA can be obtained by CV measurement and analysis. The relationship between current density difference and scan rate for all samples are shown in Fig.5d, and the Cdl values for various samples are also given in Fig.5d. The FeₓMo₁₋ₓS₂/CNT@CC prepared at Fe doping content of 0.075 has the largest ECSA of 840 cm². To further study the charge transfer resistance at the interface between the FeₓMo₁₋ₓS₂/CNT@CC catalyst and the electrolyte, electrochemical impedance spectra were tested, and the Nyquist plots of all samples are shown in Fig.5e. The FeₓMo₁₋ₓS₂/CNT@CC prepared at Fe doping content of 0.075 exhibits the smallest the charge transfer resistance of 1.00Ω, which reveals the fastest electron transfer rate in the OER process. Based on these experimental results, the excellent OER performance of FeₓMo₁₋ₓS₂/CNT@CC may come from two points. First, the FeₓMo₁₋ₓS₂ nanosheet can effectively adsorb OH*, OOH*, O* intermediate species and promote the decomposition of water. The superior performance of the FeₓMo₁₋ₓS₂/CNT@CC compared to that of MoS₂/CNT@CC and CNT@CC is attributed to the efficient catalytic properties of the FeₓMo₁₋ₓS₂ nanosheet. Second, CNT improves the conductivity of the FeₓMo₁₋ₓS₂ nanosheet, the smaller charge transfer resistance (Rct) at the FeₓMo₁₋ₓS₂/CNT@CC and electrolyte interface leads to a faster OER kinetic process.

### 3.4 Overall water splitting performance of the FeₓMo₁₋ₓS₂/CNT@CC

To further prove the OER and HER bifunctional catalytic activity of the FeₓMo₁₋ₓS₂/CNT@CC, overall water splitting (OWS) was performed using the FeₓMo₁₋ₓS₂/CNT@CC with the same Fe doping content as both anode and cathode in a 1 M KOH electrolyte. The LSV curves of the FeₓMo₁₋ₓS₂/CNT@CC || FeₓMo₁₋ₓS₂/CNT@CC system for OWS are provided in Fig.5f. The cell voltages of FeₓMo₁₋ₓS₂/CNT@CC at current densities 100 mAcm⁻² are 1.86, 1.74, 1.69, 1.76 and 1.78 V for samples with Fe doping content of 0, 0.025, 0.050, 0.075 and 0.010, respectively. This result indicates that FeₓMo₁₋ₓS₂/CNT@CC is an efficient bifunctional catalyst for overall water splitting.
Fig. 5. OER and OWS electrocatalytic performance of the Fe_xMo_1-xS_2/CNT@CC catalyst in 1M KOH electrolyte. (a) LSV polarization curves of CC, CNT@CC, MoS2/CNT@CC and Fe_0.075Mo_0.925S_2/CNT@CC; (b) LSV polarization curves of the Fe_xMo_1-xS_2/CNT@CC catalyst; (c) Tafel curves; (d) The relationship between current density difference and scan rate; (e) Nyquist plots; (f) Overall water splitting performance of the Fe_xMo_1-xS_2/CNT@CC//Fe_xMo_1-xS_2/CNT@CC.
4. Conclusions

The Fe$_x$Mo$_{1-x}$S$_2$ nanosheets with different Fe doping contents (x=0, 0.025, 0.050, 0.075, 0.100) were grown on CNT@CC substrates using a hydrothermal method by changing the molar ratio of FeSO$_4$·7H$_2$O to Na$_2$MoO$_4$·2H$_2$O in the reaction solution. The Fe$_x$Mo$_{1-x}$S$_2$/CNT/CC catalyst exhibits excellent bifunctional catalytic activities. For HER, Fe$_{0.05}$Mo$_{0.95}$S$_2$/CNT@CC has the optimal catalytic performance with the overpotential of 198 mV at a current density of 100 mAcm$^{-2}$, a Tafel slope of 44.7 mV/dec, and ECSA of 5755 cm$^2$. For OER, Fe$_{0.075}$Mo$_{0.925}$S$_2$/CNT@CC shows outstanding performance with the overpotential $\eta_{100}=279$ mV, a Tafel slope of 24.5 mV/dec, and ECSA of 840 cm$^2$. In particular, the electrolytic cell which used Fe$_{0.05}$Mo$_{0.95}$S$_2$/CNT@CC as both anode and cathode achieves a voltage of 1.69 V at current density of 100 mAcm$^{-2}$. The Fe$_x$Mo$_{1-x}$S$_2$/CNT@CC is an efficient bifunctional catalyst for overall water splitting. The bifunctional catalytic activities come from the synergistic effect between Fe$_x$Mo$_{1-x}$S$_2$ nanosheets and CNT.

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