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Symmetrical synergy of hybrid Co₉S₈-MoS_x electrocatalysts for hydrogen evolution reaction

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Abstract:

There exists a strong demand to replace expensive noble metal catalysts with efficient and earth-abundant catalysts for hydrogen evolution reaction (HER). Recently the Co- and Mo-based sulfides such as CoS₂, Co₉S₈, and MoS_x have been considered as several promising HER candidates. Here, a highly active and stable hybrid electrocatalyst 3D flower-like hierarchical Co₉S₈ nanosheets incorporated with MoS_x has been developed via a one-step sulfurization method. Since the amounts of Co₉S₈ and MoS_x are easily adjustable, we verify that small amounts of MoS_x promotes the HER activity of Co₉S₈, and vice versa. In other words, we validate that symmetric synergy for HER in the Co- and Mo-based sulfide hybrid catalysts, a long-standing question requiring clear experimental proofs. Meanwhile, the best electrocatalyst Co₉S₈-30@MoS_x/CC in this study exhibits excellent HER performance with an overpotential of -98 mV at -10 mA/cm², a small Tafel slope of 64.8 mV/dec, and prominent electrochemical stability.

¹ These authors contribute equally

Graphical Abstract

Keywords: hydrogen evolution reaction; hybrid; $\text{Co}_9\text{S}_8@\text{MoS}_x$; electrocatalyst; symmetric synergy.

1. Introduction

There is a strong demand using clean and renewable energy source to lessen the global warming effects resulted from burning fossil fuels. Hydrogen displays great promise as an energy carrier owing to its carbon-free and high energy density features [1,2]. Water electrolysis is one of the most efficient methods to generate hydrogen [3]. The key of this technology is to develop novel electrocatalysts with high performance and low cost. At present, the most effective catalysts for hydrogen evolution reaction (HER) under acidic conditions are noble metals such as Pt, which has zero overpotential [4,5]; however, the scarcity and expensive cost limit their large-scale applications [6]. Therefore, the synthesis of earth-abundant and cost-effective HER electrocatalysts is of great significance [7]. In this respect, considerable research efforts [8] have been devoted to developing various HER electrocatalysts such as CoS_2 [9], CoP [10], MoS_x (including MoS_2) [11-15], MoC_x [16], WS_2 [17], MoP [18], Ni_8P_3 [19], NiMoZn [20], CoMoS [21], CoPS [22], NiMoS [23], MoWP [24], NiMoN [25], and NiCoS [26,27]. Among these catalysts, Co- and Mo-based sulfides are the popular catalysts since they

have been proved to display high activity and several excellent reviews relevant to these electrocatalysts are also available [7,8].

In fact, Co- and Mo-based catalysts have been widely used in classical hydrodesulfurization (HDS) reactions. In 1959, Beuther *et al.* have already observed the phenomenon of HDS activity enhancement when the Co was incorporated into molybdenum sulphide [28]. The combination of Co and MoS₂ to form so-called Co-Mo-S catalysts has been confirmed to promote the HDS catalytic activity [29,30]. Recently, the HDS activity enhancement was found in the MoS₂ system doped with Co₉S₈ [29], and the synergetic effect was originated from the interfacial areas between MoS₂ and Co₉S₈ phases [29,31,32]. Meanwhile, the HDS activity of Co₉S₈ can also be promoted by adding MoS₂ [31]. This is called “symmetric synergy”; meaning that the activity of the MoS₂ or Co₉S₈ can be enhanced by adding a small percentage of the Co₉S₈ or MoS₂. Since the hydrogen adsorption is a key intermediate step for both HDS and HER in these catalysts, and they possess similar requirements for binding energy of hydrogen on surfaces. In addition, similar volcano plots of activity as a function of ΔG_{H^*} have been found for these two types of reactions [8,33,34]. Hence, good HDS catalysts should be regarded as logical candidates during the initial screening process of HER catalysts. Thus, much attention has been recently drawn to explore the ideal HER catalysts from good HDS catalysts, such as Co-and Mo-based systems. Chorkendorff *et al.* [35] have confirmed that the doping of Co atoms into the S-edge of MoS₂ could greatly decrease the free energy of hydrogen adsorption by Density Functional Theory (DFT) calculation, resulting in the improvement of HER performance. Also, many experimental results about the HER activity of amorphous MoS₃ or MoS₂ can be enhanced by the incorporation of Co-ions have been reported [36-39]. However, it is still not clear whether small amount of MoS₂ or amorphous MoS_x is able to promote the activities of Co-based sulfides, such as Co₉S₈. To our best

knowledge, the symmetric synergy arguments for the Co_9S_8 - MoS_x system are yet to be proved for HER reaction.

Here, we develop a simple and scalable process to synthesize a series of hybrid electrocatalysts comprising cubic Co_9S_8 and nanocrystalline MoS_x on carbon cloth (CC). The $\text{Co}(\text{OH})_2$ nanoplates were electroplated on CC, and then an ammonium thiomolybdate solution (3 wt% of $(\text{NH}_4)_2\text{MoS}_4$ in DMF) was drop-coated on them, followed by one-step sulfurization for completing the flower-like Co_9S_8 crystals surrounded by polycrystalline MoS_x ($\text{Co}_9\text{S}_8@\text{MoS}_x/\text{CC}$) as illustrated in Figure 1. The controlled amount of MoS_x was well dispersed onto the surface of Co_9S_8 with 3D hierarchical porous structure. The obtained $\text{Co}_9\text{S}_8@\text{MoS}_x/\text{CC}$ not only displayed the metallic properties of Co_9S_8 , but also showed the enhanced stability compared to pristine Co_9S_8 . Spectroscopic measurements evidence the electron transfer from Co_9S_8 to MoS_x in the hybrid catalysts by intermediate sulfur atoms. Our results directly validate the synergistic effect of Co_9S_8 promoted by MoS_x , supporting the symmetric synergy arguments. Meanwhile, the unique $\text{Co}_9\text{S}_8@\text{MoS}_x/\text{CC}$ co-catalysts system obtained from our proposed process exhibit the highest HER activity (a small Tafel slope of 64.8 mV/dec, and -98 mV overpotential at -10 mA/cm² current density) in acids media among all the reported Co_9S_8 -based electrocatalysts [39,40].

2. Experimental Section

2.1 Materials

All chemical reagents including cobalt (II) nitrate hexahydrate, ammonium tetrathiomolybdate ($(\text{NH}_4)_2\text{MoS}_4$), dimethylformamide (DMF), sulfuric acid (H_2SO_4), and isopropanol were purchased from Sigma-Aldrich. The commercial Pt/C was purchased from Alfa Aesar. Water was purified through a Millipore system.

2.2 Electrochemical deposition of $\text{Co}(\text{OH})_2$ nanosheets on carbon cloth

The carbon cloth (CC) with the size 1 cm $\times$ 2.5 cm was washed with deionized water and isopropanol. Part of the CC (1 cm $\times$ 1 cm) was then immersed in a 0.1 M $\text{Co}(\text{NO}_3)_2$ solution for the electrodeposition of $\text{Co}(\text{OH})_2$ nanosheets. A Pt foil and an Ag/AgCl (in a saturated KCl solution) electrode were used as the counter and reference electrodes, respectively. Electrodeposition was performed at a constant current mode (-10 mA/cm²) for 10-50 min in a PGSTAT 302N Autolab workstation. After electrodeposition, the CC was dried under vacuum. And the obtained sample was named as $\text{Co}(\text{OH})_2$ -t/CC (t=10~50 min).

2.3 Preparation of Co_9S_8 -t/CC, MoS_x /CC, and Co_9S_8 -t@ MoS_x /CC electrocatalysts

To convert the $\text{Co}(\text{OH})_2$ -t/CC (t=10~50 min) to Co_9S_8 , the sample was sulfurized in a CVD tube furnace at 200 °C for 3 hours with an environment containing H_2 and H_2S (H_2 : H_2S = 54:6 in volume). The sulfurized sample was named as Co_9S_8 -t/CC, where the Co_9S_8 -t/CC (t=10~50 min) loadings range from 1.7 to 8.4 mg/cm² (see Table S1 for details). To prepare the nanocrystalline MoS_x -decorated Co_9S_8 , the $\text{Co}(\text{OH})_2$ -t/CC was drop-coated with an ammonium thiomolybdate solution (3 wt% of $(\text{NH}_4)_2\text{MoS}_4$ in DMF), following by drying under vacuum for 4 hours. It was then subsequently sulfurized at 200 °C for 3 hours in the same H_2 / H_2S environment as mentioned above to obtain Co_9S_8 -t@ MoS_x /CC (t=10~50 min). In this hybrid catalyst, the MoS_x loading is about 1.2 mg/cm², the Co_9S_8 -t@ MoS_x /CC (t=10~50 min) loadings range from 2.7 to 9.4 mg/cm² (see Table S1 for details). In addition, we have also prepared the sample MoS_x /CC for comparison by casting an ammonium thiomolybdate solution (3 wt% of $(\text{NH}_4)_2\text{MoS}_4$ in DMF) solution on CC, followed by the same sulfurization process. In this study, we calculated the loading masses of Co_9S_8 -t/CC, MoS_x /CC, and hybrid samples Co_9S_8 -t@ MoS_x /CC by weighting using an analytical balance (precision 0.0001 g). Note that we used the analytical balance only for samples with loading amount large than 1 mg. For the MoS_x /CC loading amounts in hybrid samples less than 1 mg, we measured the drop-coating volume of ammonium thiomolybdate solution (3 wt% of

(NH_4)₂MoS₄ in DMF) by using eppendorf and correlated it to its weight. Using the total loading of Co₉S₈-t@MoS_x/CC hybrid minus the MoS_x loading amount, we can obtain the Co₉S₈-t loadings in hybrid samples.

2.4 Electrochemical measurements

The electrochemical measurements were carried on in a PGSTAT 302N Autolab Potentiostat/Galvanostat (Metrohm). Graphite rod and Ag/AgCl (in a saturated KCl solution) electrodes were used as the counter and reference electrodes, respectively. The HER activities of studied catalysts were evaluated by measuring polarization curves with linear sweep voltammetry (LSV) at a scan rate of 0.5 mV/s in 0.5 M H₂SO₄ (pH=0.34) solutions. Potentials were referenced to a reversible hydrogen electrode (RHE) by adding a value of 0.217 V ($0.197+0.0591\times\text{pH}$). The commercial Pt/C (20 wt% Pt on Vulcan carbon black) of the same loading as Co₉S₈-30@MoS_x/CC (5.8 mg/cm²) supported by CC was prepared by mixing the Pt/C and isopropanol, followed by sonicating for 30 min, and then drop-casting on the CC. In addition, 15 μL Nafion (0.5 wt%) solution in isopropanol was added to the surface of Pt/C to fix the catalyst onto the CC surface. The stability test for the studied catalyst was performed with the time dependent current density measurement, where a constant overpotential (vs. RHE; after internal resistance compensation) was provided. All data have been corrected for a small ohmic drop based on impedance spectroscopy. The electrochemical impedance spectroscopy (EIS) was carried out with an amplitude of 10 mV and frequency range from 100 kHz to 0.1 Hz. To obtain the solution-resistance and electron-transfer resistance (R_{ct}), the main arc in each EIS spectrum was fitted using a simplified electrochemical circle fit method. It is noted that we use a graphite rod as the anode for evaluating the HER performance since conventionally used Pt anode may dissolve in electrolytes and contaminate the cathode, leading to overestimation of HER currents.

2.5 Structural Characterization

The crystalline structures of the samples were analyzed by X-ray diffraction (XRD, Bruker D8 Discover diffractometer, using Cu K α radiation, $\lambda=1.540598$ Å). The morphologies of the catalysts were determined by field-emission scanning electron microscopy (FESEM, FEI Quanta 600) and transmission electron microscopy (FEI Titan ST, operated at 300 kV). XPS studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α X-ray source ($h\nu=1486.6$ eV) under a vacuum of 1×10^{-9} mbar. The spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV. The binding energies in XPS analysis were corrected by referencing C 1s peak at 284.8 eV.

3. Results and discussion

We first grow Co(OH) $_2$ nanosheets on carbon cloth (CC), where the CC is immersed in a 0.1 M Co(NO $_3$) $_2$ solution for the electrodeposition of Co(OH) $_2$ nanosheets. The electrodeposition time t (between 10 and 50 min) is a parameter which can tune the loadings of the Co-species and the sample is named as Co(OH) $_2$ - t /CC. The X-ray diffraction (XRD) pattern of the sample Co(OH) $_2$ -40/CC in Figure S1 confirms their crystal structure as Co(OH) $_2$ (JCPDS No. 74-1057). After sulfurization in a H $_2$ /H $_2$ S environment at 200 °C, the structure is transformed into Co $_9$ S $_8$ (JCPDS No. 86-2273) as shown in Figure 2(a). In previous research, it has been found that the thermal degradation of ammonium thiomolybdate less than 300 °C was able to produce MoS $_x$ structures [41-43]. Figure 2(a) shows that the MoS $_x$ produced by sulfurization at 200 °C exhibits no obvious crystalline peaks, indicating that the MoS $_x$ formed is either amorphous or nanocrystalline. To prepare the hybrid Co $_9$ S $_8$ @MoS $_x$ electrocatalysts, the Co(OH) $_2$ - t /CC was drop-coated with controlled amounts of ammonium thiomolybdate solution (3 wt% of (NH $_4$) $_2$ MoS $_4$ in DMF), following by the sulfurization in a H $_2$ /H $_2$ S environment. The XRD pattern for the MoS $_x$ -decorated Co $_9$ S $_8$ (such as Co $_9$ S $_8$ -30@MoS $_x$ /CC) displays peaks ascribed to Co $_9$ S $_8$, suggesting that the Co $_9$ S $_8$ crystals

together with MoS_x can be formed with a single sulfurization step. Note that in the hybrid catalyst, the MoS_x loading is a minor part (1.2 mg/cm^2), the Co_9S_8 loading ranges from 1.7 to 8.4 mg/cm^2 (with the t from 10 to 50 min). The presence of MoS_x shall be proved the following transmission electron microscopy (TEM) and XPS characterizations.

The TEM Energy Dispersive Spectrometer (EDS) spectrum (Figure 2(b)) demonstrates the presence of Co, Mo, and S in the sample of $\text{Co}_9\text{S}_8@\text{MoS}_x/\text{CC}-30$. Figure 2(c) shows the low-magnification TEM image for the $\text{Co}_9\text{S}_8-30@\text{MoS}_x/\text{CC}$. The high-resolution TEM (HRTEM) image in Figure 2(d) clearly reveals two interplanar distances 0.18 and 0.30 nm , corresponding to the (440) and (311) crystal planes of Co_9S_8 , respectively [44]. Furthermore, some nanocrystalline MoS_2 phases, with an interplanar distance $\sim 0.62 \text{ nm}$ ((002) plane of MoS_2), are clearly identified. The image proves that a thin shell of MoS_x was formed on the surface of the Co_9S_8 crystals.

The scanning electron microscopy (SEM) images in Figure S2(a) show that the surface of the CC fibers is smooth and the diameter is about $9 \mu\text{m}$. The SEM element mapping confirms that only C element is uniformly distributed in pristine CC (Figure S2(b)). The electrodeposited sample $\text{Co}(\text{OH})_2-40/\text{CC}$ exhibits sheet-like structures (Figure S3) perpendicularly grown on the fiber surfaces, consistent well with our previous report [10]. After sulfurization, the 3-dimensional (3D) hierarchical structures are revealed in $\text{Co}_9\text{S}_8-40/\text{CC}$ as shown in Figure 3(a), where the corresponding Energy Dispersive Spectrometer (EDS) mappings in Figure 3(a1) and Figure S4(a) shows uniformly distributed Co and S signals over the whole area. For the morphology of MoS_x grown on CC (Figure 3(b)), the coating is rather non-uniform, where the MoS_x is formed preferentially in the gaps between fibers and main shows large bulk particles structure, which can be confirmed by the corresponding SEM element mapping (Figure

3(b1) & Figure S4(b)). The SEM image of Co₉S₈-30@MoS_x/CC in Figure 3(c) reveals that the 3D hierarchical sponge-like structures are well retained. The SEM element mapping in Figure 3(c1) and Figure S4(c) shows that the Mo, Co, and S signals were uniformly distributed over the whole image area, indicating that the MoS_x is well dispersed on the surfaces of Co₉S₈ nanosheets.

The X-ray photoelectron spectroscopy (XPS) was adopted to further investigate the surface electronic state and chemical composition of Co₉S₈-30@MoS_x/CC. The XPS survey spectrum in Figure S5 shows that the Co₉S₈-30@MoS_x/CC comprises Co, Mo, S, C, and O elements. Figure 4(a) shows the high-resolution XPS spectra of Co 2p for the Co₉S₈-30@MoS_x/CC sample, and it is deconvoluted into two spin-orbit doublets and two shakeup satellites (defined as “Sat.”). The peaks at 779.0 and 794.1 eV are assigned to the 2p_{3/2} and 2p_{1/2} core levels of Co³⁺, whereas the peaks at 781.5 and 797.8 eV are attributed to the 2p_{3/2} and 2p_{1/2} core levels of Co²⁺ respectively, corresponding well with reported studies [39,44]. Compared with the XPS spectra of pure Co₉S₈/CC (778.4 and 793.5 eV, Figure 4(c)), the binding energies of Co 2p are up-shifted to 779.0 and 794.1, indicating a strong interaction between the Co₉S₈ and MoS_x. Also, the Co 2p_{3/2} binding energy (779.0 eV) of Co₉S₈-30@MoS_x/CC is very close to that in a Co-S-Mo phase [45,46]. For the Mo 3d, two main characteristic peaks at 232.3 and 228.9 eV, attributed to the Mo 3d_{3/2} and 3d_{5/2} binding energies for Mo⁴⁺ state of MoS_x (Figure 4(b)) [42,47,48], which are down-shifted ~0.5 eV from the normal value of pure MoS_x (229.4 eV and 232.6 eV, Figure 4(d)). The up-shift of the Co 2p binding energies and the down-shift of the Mo 3d binding energies together evidence that the electron transfer phenomenon from Co₉S₈ to MoS_x by intermediate sulfur atoms may occur when they form the hybrid crystals.

In the high-resolution S 2p region (Figure S6), as characterized by the S 2p_{1/2} and 2p_{3/2} doublet with an energy separation of 1.2 eV and intensity ratio of ~2:1 [49], the S

$2p_{1/2}$ and $2p_{3/2}$ energies at 164.0 and 162.8 eV suggest the existence of bridging S_2^{2-} or apical S^{2-} [42,50], in accordance with the formation of MoS_x . The other two S 2p peaks at 162.0 and 163.2 eV are attributed to S $2p_{3/2}$ and S $2p_{1/2}$ of Co-S bondings, respectively, which are consistent well with the previous report on Co_9S_8 crystals [39]. In addition, the characteristic peaks of Mo 3d in Mo-O at 235.6 eV (Figure 4(b)) and the S 2p in S-O bonds at 169.4 eV (Figure S6) are likely due to some surface oxidation [51].

The loading amount of Co_9S_8 in Co_9S_8 -t/CC and Co_9S_8 -t@ MoS_x /CC can be simply controlled by the Co species electrodeposition time t . Figure 5(a) displays the polarization curves (normalized by the sample geometrical area) for the Co_9S_8 -t/CC prepared with $t = 10$ min, 20 min, 30 min, 40 min and 50 min. To exclude the effect of solution resistance, the potential (V) is after internal resistance correction. It is observed that the HER current in 0.5 M H_2SO_4 increases with the t . The overpotential (vs. RHE) to reach -10 mA/cm^2 and -100 mA/cm^2 is -162 mV and -203 mV for Co_9S_8 -40/CC (Table S1) and the corresponding Tafel slope is 37.6 mV/dec (Figure 5(b)). These values are already lower than all reported Co_9S_8 -based catalysts for HER (Table S2). For the hybrid Co_9S_8 -t@ MoS_x /CC catalysts (Figure 5(c)), the HER performance increases and then decreases with t , where the optimized t is at 30 min. The overpotential of the Co_9S_8 -30@ MoS_x /CC sample to reach -10 mA/cm^2 (η_{10}) and -100 mA/cm^2 (η_{100}) is only -98 mV and -165 mV , smaller than most of the reported catalysts based on Co- or Mo-sulfides (Table S2). The Tafel slope is 64.8 mV/dec (Figure 5(d)), which is also comparable to the reported Mo/Co hybrid catalysts (Table S2). We noted that the overall loading amounts of the catalysts (determined by the electrodeposition time t) affects the morphology and HER performance of each catalyst, where the obvious delamination and crackings are observed in Co_9S_8 -t/CC when $t = 50$ min and in Co_9S_8 -t@ MoS_x /CC when $t = 40$ min (Figure S7). Hence, Co_9S_8 -40/CC and Co_9S_8 -30@ MoS_x /CC display best HER activity respectively due to the compromise of loading amounts and delamination.

To understand the behaviors of different catalysts, Figure 6 compares the HER performance of bare CC, MoS_x/CC, Co₉S₈-30/CC, Co₉S₈-40/CC, Co₉S₈-30@MoS_x/CC, and commercial Pt/C/CC (20 wt%). The bare CC electrode guarantees a minimal background activity for H₂ evolution. Also, the commercial Pt/C/CC catalyst exhibits the best HER catalytic performance with a near zero overpotential. The reference sample, pure MoS_x (loading: 1.2 mg/cm²)/CC, exhibits poor HER activity (-299 mV at -10 mA/cm² (η_{10}); Tafel slope 125.6 mV/dec). The overpotential η_{10} for the Co₉S₈-30@MoS_x/CC is -98 mV, obviously smaller than its constituent Co₉S₈-30/CC (η_{10} = -177 mV), MoS_x/CC (η_{10} = -299 mV), and Co₉S₈-40/CC (η_{10} = -162 mV) with the optimal electrodeposition time. Note that the HER activity for MoS_x/CC is still not comparable to Co₉S₈-30@MoS_x/CC even when the MoS_x loading amount is increased to 6.0 mg/cm² (Figure S8), meaning that the HER activity in our hybrid catalysts are mainly caused by Co₉S₈ rather than MoS_x. Commercial Pt/C/CC (20 wt%) catalyst showed the smallest Tafel slope of 30.7 mV/dec, which agreed well with the reported values [52-54]. The Tafel slopes of MoS_x/CC and Co₉S₈-30/CC (Figure 6(b)) are 125.6 mV/dec and 40.4 mV/dec respectively, suggesting that the HER kinetic rate-determining step is Volmer reaction for MoS_x and Heyrovsky reaction for Co₉S₈-30 [55,56]. However, the hybrid Co₉S₈-30@MoS_x/CC shows an intervenient Tafel slope value (64.8 mV/dec), demonstrating that the incorporation of MoS_x into Co₉S₈ brings about a remarkable change in the HER mechanism. The reason for larger Tafel slopes of hybrid Co₉S₈-t@MoS_x/CC samples than Co₉S₈-t/CC is that the doping not only leads to the improvement in intrinsic activity which results in the decrease of Tafel slope, but also induces disorder of the lattice that increases Tafel slope [54,57-59]. In addition, the exchange current density (j_o) under reversible conditions (at zero overpotential) and electron-transfer resistance (R_{ct}) under different overpotential are two important parameters in electrocatalysis related to HER performance. Compared with

exchange current density over different catalysts (Table S1), the hybrid Co_9S_8 -30@ MoS_x /CC sample with the best HER performance exhibits the largest exchange current density (0.34 mA/cm^2), indicating the fast rate of electron transfer. Meanwhile, as displayed in Figure S9, under the condition of the same overpotential, the hybrid Co_9S_8 -30@ MoS_x /CC catalyst shows the smallest electron-transfer resistance by comparing the samples of MoS_x /CC and Co_9S_8 -40/CC, demonstrating the very fast electron-transfer kinetics. It is consistent well with the evaluation results of HER performance over MoS_x /CC, Co_9S_8 -40/CC, and Co_9S_8 -30@ MoS_x /CC catalysts.

As mentioned before [36-39], the improved HER performance of MoS_2 was observed by the doping of Co. It is fundamentally important to prove whether small amount of MoS_x is able to promote the activity of Co_9S_8 . In order to complete the symmetric synergy arguments, we have two sets of samples; (1) Co_9S_8 -t@ MoS_x /CC with a fixed amount of MoS_x (1.2 or 6.0 mg/cm^2) and various weights of Co_9S_8 as discussed in Figure 5(c) and displayed in Figure S10. (2) Co_9S_8 -30@ MoS_x /CC catalysts with a fixed amount of Co_9S_8 -30 (4.8 mg/cm^2) and different MoS_x loading weights from 0 - 1.4 mg/cm^2 (details in Figure S11). The overpotential η_{100} values for both sets of catalysts are plotted as a function of Co_9S_8 weight percentage in Figure 6c. The results for both sets of catalysts strongly support that addition of small amount Co_9S_8 or MoS_x synergistically enhance the HER activity of MoS_x or Co_9S_8 , respectively. Taking MoS_x doped Co_9S_8 for an example, the enhancement effect is explained as follows. When MoS_x was added to Co_9S_8 , a new structure of Co_9S_8 - MoS_x nanointerfaces is formed, which creates open latent vacancy sites between Mo and Co atoms [29,39,60]. And the strong electron transfer from Co to Mo by intermediate sulfur atoms bonded to both metals may occur when they form the hybrid crystals, as proved from our XPS results, results in more negatively charged S sites in Co_9S_8 which are become more active for the interaction of the H^+ in HER.

The model of synergistic effect strongly relies on the interface structures. To confirm the improvement of HER performance is due to the formation Co-S-Mo nanointerfaces, we have prepared the hybrid sample Co₉S₈-30/MoS_x/CC catalyst with two step sulfurization, where Co₉S₈-30 was first formed and followed by MoS_x formation on it. The HER performance (Figure S12) is worse than the catalyst Co₉S₈-30@MoS_x/CC prepared by one step sulfurization due to the interfacial area with the 2-step process (the existence of cracking or delamination for the Co₉S₈ sheets as indicated by Figure S7(a)) is smaller than those prepared by one-step sulfurization. The result provides a strong argument that interface contact area dominates the synergistic effect.

In addition to the HER efficiency, the stability is another critical factor for evaluating a catalyst. Figure 6(d) displays the time dependent measurement for Co₉S₈-40/CC, MoS_x/CC, and Co₉S₈-30@MoS_x/CC at a low working current density (*ca.* 50 mA/cm²). It is observed that the decay of the HER current for Co₉S₈/CC is about 56% in the first 5 h, but the decay is around 12% for MoS_x/CC and 20% for hybrid Co₉S₈@MoS_x/CC after HER for 40 h. Figure S13 exhibits the SEM images of three samples after the stability test for 40 h, it is obviously seen that most of the Co₉S₈ was stripped from CC or dissolved, while the MoS_x and Co₉S₈-30@MoS_x were well kept on the CC. The obtained XRD results in Figure S14 for these catalysts after stability test also further confirm the same conclusion.

4. Conclusions

In summary, we have developed a facile one-step sulfurization method to synthesize a new hybrid 3D hierarchical structure of Co₉S₈ nanosheets coated with MoS_x, where the amounts of Co₉S₈ and MoS_x in the hybrid Co₉S₈-t@MoS_x/CC (t is from 10 to 50 min) catalyst can be well controlled by the electrochemical deposition time *t* of Co(NO₃)₃

solution and the drop-coating volumes of ammonium thiomolybdate solution. The hybrid catalyst $\text{Co}_9\text{S}_8\text{-30@MoS}_x/\text{CC}$ exhibits an excellent activity (-98 mV at -10 mA/cm^2 ; Tafel slope 64.8 mV/dec), which is among the best records over the Co_9S_8 -based catalysts. The enhanced HER activity is mainly due to the synergistic effects of Mo-doping into Co_9S_8 nanosheets through the intermediate sulfur atoms, as well as the high electrochemically active surface area of the 3D hierarchically porous structure of Co_9S_8 . Our experiments clearly show that MoS_x enhances the HER activity of Co_9S_8 , validating the symmetric synergy arguments in Co-S-Mo systems. The approach presented herein offers a new path for the design and engineering of effective HER catalysts with high electric conductivity and large area of exposed HER active sites. To our best knowledge, this is the first HER study for amorphous MoS_x doped to other metal sulfides, which can be expanded to other transition metal sulfide systems, such as FeS_2 , NiS_2 , and WS_2 .

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Figure 1. The schematic illustration for the synthesis of hybrid electrocatalyst $\text{Co}_9\text{S}_8@\text{MoS}_x/\text{CC}$.

Figure 2. XRD patterns of Co_9S_8 -40/CC, MoS_x /CC, and Co_9S_8 -30@ MoS_x /CC (a), TEM EDS spectrum (b), TEM image (c), and HRTEM image (d) of the hybrid catalyst Co_9S_8 -30@ MoS_x /CC.

Figure 3. SEM images of Co_9S_8 -40/CC (a), MoS_x /CC (b), Co_9S_8 -30@ MoS_x /CC (c), and their corresponding SEM element overlaid mappings. The insets in the left and right are the corresponding higher-magnification SEM images and mapping area image of each sample, respectively.

Figure 4. (a) Co 2p and, (b) Mo 3d XPS spectra for the $\text{Co}_9\text{S}_8\text{-30@MoS}_x/\text{CC}$ sample. Obvious binding energy shifts are observed in the XPS spectra of (c) Co 2p for the $\text{Co}_9\text{S}_8\text{-40/CC}$ and $\text{Co}_9\text{S}_8\text{-30@MoS}_x/\text{CC}$ samples, and those of (d) Mo 3d for the MoS_x/CC and $\text{Co}_9\text{S}_8\text{-30@MoS}_x/\text{CC}$ samples.

Figure 5. (a) Polarization curves, and (b) Tafel slopes of the Co₉S₈-t/CC with various Co₉S₈ loading amounts; (c) Polarization curves, and (d) Tafel slopes of the Co₉S₈-t@MoS_x/CC with various Co₉S₈ loading amounts. The loading weight is 1.2 mg/cm² for MoS_x and 1.7, 3.3, 4.8, 6.5 and 8.4 mg/cm² for the Co₉S₈ with the t= 10, 20, 30, 40, and 50 min respectively.

Figure 6. (a) Polarization curves of the bare CC, MoS_x/CC, Co₉S₈-30/CC, Co₉S₈-40/CC, Co₉S₈-30@MoS_x/CC, and commercial Pt/C/CC (20 wt%) samples; (b) Tafel slopes extracted

from the polarization curves in (a); (c) Synergistic effect: the overpotential η_{100} values for both sets of catalysts plotted as a function of Co_9S_8 weight percentage; (d) Time-dependent HER performance of the MoS_x/CC , $\text{Co}_9\text{S}_8\text{-40}/\text{CC}$, and $\text{Co}_9\text{S}_8\text{-30@MoS}_x/\text{CC}$ conducted in 0.5 M H_2SO_4 solution for 40 h.

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Highlights

- It is the first report to prepare Co_9S_8 by electrochemical deposition strategy.
- Strong electron transfer from Co to Mo via the S atoms was verified by XPS results.
- We firstly validated symmetric synergy for HER between Co- and Mo-based catalysts.
- The best HER records for Co_9S_8 -based catalysts were obtained in this study.