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Electrospinning derivative fabrication of sandwichstructured CNF/Co₃S₄/MoS₂ as self-supported electrodes to accelerate electron transport in HER



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HIGHLIGHTS

- The sandwich-structured CNF/ Co₃S₄/MoS₂ were synthesized via electrospinning and carbonization.
- The Co_3S_4 nanoparticles accelerated the transfer of electrons from the substrate to the catalyst.
- The Co nanoparticles break through the blockade of the carbon layer via controlling carbonization temperature.
- CNF/Co₃S₄/MoS₂ only need 80 mV to drive 10 mA cm⁻², and the Tafel slope was 99.2 mV dec⁻¹.
- The structure of Co_3S_4 nanoparticles embedded on the carbon fiber stably improve the electron transmission efficiency.

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GRAPHICAL ABSTRACT



ABSTRACT

The substitution of noble metal catalysts with earth abundant TMs as electrocatalysts for hydrogen production is of great significance. One biggest bottleneck for high-efficiency water electrolysis in TM catalysts is the sluggish reaction kinetics or electron transport efficiency. The electrical coupling between the substrate and the catalytic material can accelerate the electron transport, enhancing the charge transfer kinetics, and thereby improve the catalytic performance of the catalyst. Herein, we report a sandwich-structured CNF/Co₃S₄/MoS₂, MoS₂ grown in-situ on N-doped nanofibers with Co₃S₄ nanoparticles via

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Keywords: Electrospinning Carbon nanofiber Accelerating electron transport Hydrogen evolution reaction electrospinning, carbonization and hydrothermal process, as self-supported electrodes for hydrogen evolution reaction. The sandwich structure is comprised of CNFs/Co₃S₄/MoS₂ as substrate/accelerator/catalyst. Thereinto, the three-dimensional CNF framework, intrinsically doped by nitrogen, can open accessible channels for reactants and served as substrates for the *in-situ* growth of Co₃S₄ and MoS₂ nanocrystals with high conductivity and massive active sites. Hence, the CNF/Co₃S₄/MoS₂ shows outstanding catalytical performance in water electrospinning, only 80 mV required to drive 10 mA cm⁻² current density with the Tafel slope of 99.2 mV dec⁻¹ in alkaline media. Besides, the performance can be maintained for at least 40 h with negligible decline. This experiment can provide a new idea for the design of efficient and stable self-supporting electrodes.

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Introduction

With the depletion of traditional petrochemical energy sources and the deterioration of environmental pollution, the lowcost, pollution-free, and renewable energy is of great urgency to be developed. Hydrogen has been regarded as the most promising futural energy source due to its high mass-toenergy ratio, non-polluting combustion, and rich element reserves [1]. Compared with the currently dominant hydrogen production from fossil energy, the electrocatalytic hydrolysis hydrogen production has become an alternative candidate in the laboratory, owing to its advantages of pollution-free and recyclability [2–4]. At present, noble metal-based (Pt, RuO₂, IrO₂, etc.) catalysts show the best catalytic performance, but their high cost and poor stability limit their large-scale applications [5,6].

Molybdenum disulfide (MoS₂), with unique layered structure and electronic configuration, has gradually attracted massive researcher's attention [7]. The Gibbs free energy for H adsorption (ΔG_{H^*}) on the edges of Mo and S atoms in MoS₂ is close to zero, making those sites active for Hydrogen Evolution Reaction (HER) catalysis [8]. However, the low carrier concentration and poor conductivity [9] of the most stable 2H phase of MoS₂ limit the catalytic performance. So far, most researches are therefore focusing on the phase transition of MoS₂, from 2H to 1T phase with improved conductivity and modified surfaces [10,11]. However, phase change engineering is usually complicated, besides 1T-MoS₂ is not stable and easily loses catalytic activity [12]. Someone reported the electrical coupling strategy to enhance the conductivity and then reduced the ΔG_{H^*} , significantly improving the HER electrocatalytic performance [8]. The coupling achieved by inserting a conductive layer between the substrate and the catalytic materials can accelerate the electron transport and enhance the charge transfer kinetics, therefore to enhance the conductivity [13]. For example, Manish Chhowalla and coworkers have demonstrated that reducing the contact resistance to promote charge injection from the substrate to the catalyst can achieve the intrinsic catalytic properties of the 2H substrate [14]. Here, the hydrogen evolution mechanism is obviously affected by the electron injection efficiency from the substrate to the catalyst and to the active center. Gong et al. designed a MoO₂/MoS₂/C hollow nanoreactor with great HER

performance, where the metallic MoO₂ substrate can enhance the conductivity [15]. Therefore, the design of the substrate is of great significance in the preparation of electrode materials.

Traditional non-self-supporting electrodes required polymer binders to bond the catalytic materials to the supporting electrodes (glass-carbon electrodes, nickel foam, etc.) [16]. The bonding process was complicated, and the binder may cover the catalyst, reducing the exposure of the active sites of the catalyst [17]. In addition, the polymer binder itself has poor conductivity, which will reduce the efficiency of electron transmission. Self-supported electrodes have great mechanical properties, higher specific capacity and energy density, which could be used directly as a substrate for in-situ growth catalyst with no need of additional binder, conductive agent and current collector [16,18,19]. The base of the self-supporting material should meet the following requirements: (1) high specific surface area, to carry more catalytic materials [20]; (2) good electrical conductivity [21,22]; (3) good mechanical strength [23,24]. Electrospinning is an excellent method for preparing nanomaterials with conductivity and adjustable pore structure [25-27]. Therefore, in recent years, nanomaterials prepared by electrospinning have been increasingly used in the fields of energy conversion and storage [28,29]. Usually, the diameter of nanofibers prepared by electrospinning was between tens to hundreds of nanometers, and has the characteristics of ultrahigh specific surface area, strong structural design, abundant defects or active centers, good conductivity and good flexibility [30]. By carbonizing the original fibers prepared by electrospinning at high temperature, carbon nanofibers can be prepared. While maintaining the ultra-high specific surface area of the nanofibers, they also have good electrical conductivity and are more suitable for electrode materials [31,32]. For example, Yong et al. self-assembled CoO_x@CoN_v core-shell structured nanorods on N-doped carbon nanofibers, exhibiting good catalytic activity and stability on both OER and ORR, among which N-doped carbon nanofibers Provides good conductivity as a substrate [33].

In order to speed up electron transport and enhance the catalytic activity of MoS₂-based materials, herein, we propose a new strategy to prepare a self-supporting composite catalyst (CNF/Co₃S₄/MoS₂) with the sandwich structure of "substrate/ accelerator/catalyst". Electrospinning and high-temperature carbonization were used to prepare three-dimensional network N-doped CNFs loaded with cobalt nanoparticles (CNF/

Co), and use it as a substrate to grow molybdenum disulfide nanosheets by solvothermal process. During the hydrothermal process, the cobalt nanoparticles on CNF were in situ transformed into Co₃S₄ particles with better catalytic activity and electron transport efficiency, and molybdenum disulfide nanosheets would grow on CNFs. Here, the three-dimensional network of N-doped CNFs served as a substrate to provide a larger specific surface area for the growth of molybdenum disulfide nanosheets. Molybdenum disulfide served as a catalyst to provide active sites for the HER reaction. The Co₃S₄ nanoparticles grown in situ on the CNFs accelerated the transfer of electrons from the substrate to the catalyst, and accelerated the decomposition of water molecules on the surface of the catalytic material to promote the HER reaction. Owning to the introduction of Co₃S₄ nanoparticles, the overpotential of CNF/Co₃S₄/ MoS₂ composite is only 80 mV at the current density of 10 mA cm⁻², and the Tafel slope is only 99.2 mV dec⁻¹. And because of the in-situ growth, the Co₃S₄ particles are embedded on the CNFs, which can stably accelerate the electron transport and accelerate the HER reaction during the process of catalyzing hydrogen evolution at long time HER. This work provides a new mothd for the preparation of high-performance water electrolysis catalysts.

Experimental

Reagents

Polyacrylonitrile (PAN, Mw = 150,000), thiourea, (CH₄N₂S, AR, 99%) and potassium hydroxide (KOH, 95%) were purchased from Shanghai Macklin Biochemical Co., Ltd. N,N-dimethylformamide (DMF, AR, 99.5%), cobalt acetate tetrahydrate (C₄H₆CoO₄·4H₂O, AR, 99.5%) and ammonium molybdate tetrahydrate (H₂₄Mo₇N₆O₂₄·4H₂O,AR) were supplied by Sigma-Aldrich.

Synthesis of CNF/Co/MoS₂

Synthesis of CNF

Typically, 3 g PAN was dissolved in 22 g DMF and stirred for 12 h. Then the solution was electrospinned at a voltage of 18 kV with a speed of 0.5 ml/h for 12 h. The nanofiber membrane was pre-oxidized at 230 °C for 3 h in air, then kept at 1000 °C in Ar atmosphere for 3 h to obtain carbon nanofibers (CNF).

Synthesis of CNF/Co

Similarly, 4 mmol of cobalt acetate and 3 g of PAN were dissolved in 22 g of DMF and stirred for 12 h. The subsequent steps were the same as CNF. CNF/Co with different Co content were all prepared under the same conditions, except that different molar amount of $C_4H_6CoO_4\cdot 4H_2O$ were used in the preparation of the spinning solution.

Other CNF/Co in different carbonization temperature were all prepared under the same condition except for different carbonization temperature.

Synthesis of CNF/Co₃S₄

2.0 mmol of thiourea were dissolve in 30 ml of deionized water, and stirred for 20min, pour it into a 50 ml tower reactor.

Then a piece of 4*1 cm CNF/Co was add into the solution and hydrothermally reacted at 190 $^{\circ}$ C for 18 h. After cooling to room temperature, clean it with deionized water and ethanol for three times, and then dried in an oven at 60 $^{\circ}$ C for 12 h. Then the precursor was heating at 300 $^{\circ}$ C for 2 h in Ar atmosphere.

Synthesis of CNF/Co₃S₄/MoS₂

 MoS_2 was grown to CNF/Co through traditional hydrothermal reaction. 1.0 mmol of ammonium molybdate and 2.0 mmol of thiourea were dissolve in 30 ml of deionized water, and stirred for 20min, pour it into a 50 ml tower reactor. Then a piece of 4*1 cm CNF/Co was add into the solution and hydrothermally reacted at 190 °C for 18 h. After cooling to room temperature, clean it with deionized water and ethanol for three times, and then dried in an oven at 60 °C for 12 h. Then the precursor was heating at 300 °C for 2 h in Ar atmosphere.

Other $CNF/Co_3S_4/MoS_2$ with Mo = x mmol were all prepared under the same condition, except that different contents of ammonium molybdate and thiourea were used (the amount of thiourea was always twice the amount of ammonium molybdate). And it was named as $CNF/Co_3S_4/MoS_2$ -X.

Other CNF/Co $_3S_4/MoS_2$ with CNF/Co in different carbonization temperature (800°C–1000 °C) were all prepared under the same condition.

Synthesis of CNF/MoS₂

The preparation of CNF/MoS₂ material was the same as CNF/ Co_3S_4/MoS_2 except using CNF instead of CNF/Co as the base material for hydrothermal reaction.

Synthesis of CC/MoS₂

The preparation of CC/MoS₂ material was the same as CNF/ Co_3S_4/MoS_2 except using carbon cloth (CC) instead of CNF/Co as the base material for hydrothermal reaction.

Apparatus

The morphology of the sample was obtained by Field Emission Scanning Electron Microscopy (FESEM, ULTRA55, ZESSI). The internal structure was obtained from the Transmission Electron Microscope (TEM, JEM-2100, JOEL), and the acceleration voltage is 200 kV. High-angle Dynamic Large-Scan Transmission Electron Microscope (STEM, Tecnai G2 F30S-Twin, Philips-FEI) and high resolution element images (STEM-EDX) analyze elemental component of the sample with the acceleration voltage of 300 kV. X-ray diffraction instrument (XRD, Bruker D8 DIECOVER) was used to analyze the internal structure of the sample, the scan range was 10° – 80° , and the scan rate was 5° min⁻¹. The surface element and the compound valence were obtained by X-ray photoelectron energy spectroscopy (XPS, Kratos Axis Ultra DLD).

Electrochemical characterizations

All electrochemical tests were carried out by a CHI Electrochemical Workstation (CHI Instruments 660E, China). In an electrolytic cell with 1 M KOH as electrolyte. The electrochemical test used a standard three-electrode system, with the as-synthesized electrocatalysts, Hg/HgO electrode and graphite rod were employed as the working electrode, reference electrode, and the counter electrode, respectively. All electrochemical test potentials in this experiment were converted to RHE reference by the equation: $E_{RHE} = E_{Hg/HgO} +$ 0.924 V. The polarization curve (LSV) was tested under a sweep of 1 mV/s. The Tafel slope was obtained by TAFEL curve by Tafel equation $[\eta = b*\log(j) + a]$. EIS (impedance) was tested at a voltage of -0.05 V (vs. RHE), the frequency ranges from 100 kHz to 0.1 Hz. The double-layer capacitance (C_{dl}) value was calculated by testing the cyclic voltammograms curve (CV) with different scan rate, then draw a curve of current density difference–scan rates, calculated the slope to get C_{dl} value. ECSA can be calculated from C_{dl} , by the following equation: $ECSA = S_{geo} * C_{dl}/C_s$, where the C_{dl} is the double-layer capacitance, S_{geo} represents the geometric area of the electrode, and the Cs specific electrochemical double-layer capacitance, and the value of is 0.040 mF $\rm cm^{-2}$ in the alkaline medium. RF was obtained from Equation $RF = ECSA/S_{geo}$. The hydrogenation stability of the material is a test at a constant voltage, a recording time-current curve.

Results and discussion

The carbon nanofibers derived from e electrospinning have high specific surface area and good conductivity [34]. After introducing transition metal ions into the electrospinning precursor, transition metal ions on the surface of electrospinning nanofiber will from different kinds of metal compounds (metal, alloy, carbide et al.) during high-temperature carbonization [35]. As shown in the Fig. 1(a), the carbon nanofiber loaded by Co nanoparticles (CNF/Co) was prepared via electrospinning and high temperature carbonization, which can be treated as substrate to grow molybdenum disulfide nanosheets.

Firstly, the crystal structure of the prepared material was determined by XRD pattern. Temperature is among most important influencing factors of CNF/Co structure. For the XRD pattern of CNF/Co, as shown in Fig. 1(b), the CNF/Co prepared at different carbonization temperatures (800°C-1000 °C) had the same characteristic peaks at 44.2°, 51.5°, 75.8°, which were corresponding to the (111), (200) and (220) crystal planes of Co respectively, indicating that the Co element added before electrospinning was transformed into metallic cobalt after carbonization. And the change of the carbonization temperature did not affect the crystal of CNF/Co structure. In addition, the characteristic peak at 26.3° was corresponding to graphite-2H, which was derived from the carbon nanofibers in CNF/Co. Besides, as shown in Fig. S1, as the carbonization temperature increased, the size of the nanoparticles gradually increased. And when the carbonization temperature was less than 900 °C, the nanoparticles were all wrapped by the carbon layers. When the temperature further rose to 1000 °C, the nanoparticles break through the blockade of the carbon layers and begin to be exposed on the surface. The exposed structure was more conducive to the transmission of electrons from the substrate to nanoparticles and then directly to the catalyst, without the hindrance of the carbon layers. When the carbonization temperature reached 1100 °C, the nanoparticles became super large, while the agglomeration or excessive size of the nanoparticles was negative to the electron transport inside the material.

For the XRD patterns of CNF/Co after hydrothermal reaction in solution containing molybdenum source and S source (as shown in Fig. 1(c)), the four distinct characteristic peaks at 14.3°, 32.6°, 39.5° and 60.1° in Fig. 1(c) corresponded to (002), (100), (103) and (110) crystal planes (JCPDS No. 37-1492) [36], and no obvious characteristic peaks of Co and graphite appeared. For CNF/Co (carbonization temperature over 1000 °C), since the nanoparticles were directly exposed on the surface of the carbon fibers without the hindrance of the carbon layer, in the hydrothermal reaction containing thiourea, Co (0) may react with the S source and be converted into Co-sulfides. Therefore, by directly reacting CNF/Co (carbonization temperature of 1000 °C) in an aqueous solution containing thiourea, the crystal phase of the reaction product was analyzed. As shown in Fig. S2, the obvious characteristic peaks at 16.1°, 26.6°, 31.3°, 38.0° and 55.0° corresponded to the (111), (220), (311), (400) and (511) planes of Co₃S₄ (JCPDS No. 42-1448) respectively, no obvious characteristic peaks of metallic Co appeared, indicating that the surface-exposed metallic Co particles of CNF/Co were transformed into Cosulfides (Co₃S₄) in the hydrothermal reaction containing the S source.

Fig. 1(a–b) showed the SEM morphology of CNF/Co, after carbonization, CNF/Co maintained a good fiber morphology and presented a three-dimensional network structure, which could provide a larger specific surface area for the growth of MoS₂ nanosheets. In addition, many nanoparticles were uniformly distributed on the fibers. In the TEM image of Fig. 1(c), the uniform nanoparticles can be observed more clearly. In the HRTEM image, by measuring the lattice spacing of the nanoparticles, the lattice spacing of 0.244 nm corresponded to the (111) crystal plane of Co, indicating that the nanoparticles were metal Co, which was also consistent with the previous XRD analysis results. Furthermore, as shown in Fig. S3 (the and TEM images of CNF/Co (Co = X mmol) obtained after carbonization), with the Co ions content increasing in the precursor, the number of nanoparticles on carbon fibers also gradually increased, and the size of the nanoparticles also increased. From the TEM image of CNF/Co₃S₄ after hydrothermal vulcanization (Fig. S4), it can be seen that the fiber morphology did not change greatly after vulcanization. By measuring the lattice spacing of the nanoparticles, the lattice spacing of 0.344 nm corresponded to the (220) crystal plane of Co_3S_4 , which was also consistent with the previous XRD analysis.

After the traditional hydrothermal reaction, as shown in Fig. 2(d–e), the carbon fiber was covered by uniform nanosheets, no obvious nanoparticles appeared. In the previous XRD results of CNF/Co₃S₄/MoS₂ (Fig. 1(c)), only characteristic peaks of MoS₂ appeared, which confirmed that the nanosheets on the surface were MoS₂, while no characteristic peaks of Co-existed. Since the electrolysis of water occurs on the surface of the electrode material, it can be inferred that due to the barrier of MoS₂ nanosheets, the water molecules cannot touch the surface of the nanoparticles during the water electrolysis process, so that the electrolysis reaction will only occur on the MoS₂ nanosheets. In Fig. 2(f), it was more clearly to observe the structure of nanosheets-wrapped



Fig. 1 – (a)The schematic illustration of the $CNF/Co_3S_4/MoS_2$ synthesis. The XRD pattern of CNF/Co in different carbonization temperature (b) and $CNF/Co_3S_4/MoS_2$ (c).



Fig. 2 – Different magnifications SEM images (a–b), TEM image and HRTEM image (c) of CNF/Co. Different magnifications SEM images (d–e), TEM image and HRTEM image (f) of CNF/Co/MoS₂, mapping images (g) of different elements of CNF/Co₃S₄/MoS₂.

carbon fiber, and the lattice spacing of the nanosheet was measured to be 0.65 nm, which was corresponding to (001) crystal planes of MoS₂. The distribution of each element was shown in Fig. 2(e), wherein the S and Mo elements were evenly distributed in the outer nanosheets, and the Co element was only distributed in the middle, which was also consistent with the results of the previous topography. The Co:Mo of CNF/ Co₃S₄/MoS₂ was tested to be 26.6:1, the content of Mo element was much higher than that of Co element. Furthermore, the content of MoS₂ nanosheets on the carbon fiber was adjusted by changing the content of Mo in the hydrothermal reaction. As shown in Fig. S5, with the Mo content increasing in the hydrothermal solution, the nanosheets on the carbon fiber was denser, and the diameter of the fiber was also getting larger (Fig. S5). More MoS₂ nanosheets could provide more catalytic sites for HER, however, the poor conductivity of MoS₂ could inhibited charge transfer kinetics [37], so that it's important to analyze the relationship between CNF/Co₃S₄/ MoS₂ structure and HER performance in subsequent HER testing.

Further, the valence states of surface elements of CNF/Co, CNF/Co₃S₄ and CNF/Co₃S₄/MoS₂ were analyzed by XPS. For CNF/Co, XPS spectrum shows Co, C, and N element signals in Fig. S7(a). The signal of C came from carbon nanofibers, and the spectrum of C 1s can be divided into three peaks at 284.8 eV, 285.75 eV and 289.85 eV (Fig. S8(a)), corresponding to C-C, C=C and C-N, respectively [38]. In the spectrum of Co 2p (Fig. S8(b)), the peaks at 778.5eV and 793.8eV were corresponded to Co (0), indicating the presence of metal Co [39]. The binding energies at 796.3 eV and 780.1 eV were corresponding to Co $2p_{1/2}$ and Co $2p_{3/2}$, while the peaks at 784.8 and 804.8eV were satellite peaks [40]. The N element came from the CNF, the peaks at 398.7 eV, 399.8 eV, 401.1 eV and 403.2 eV corresponded to pyridine-N, pyrrole-N, graphitic-N and oxided N through peak fitting in N 1s spectra (Fig. S8(c)) [41], which confirmed the existence of N-doped carbon nanofibers.

For the Co 2p spectrum of CNF/Co₃S₄ (Fig. 3(a)), the peaks at 778.8 eV and 793.8 eV were associated with Co²⁺, while 781.1 eV, 782.9 eV, 797.2 eV and 798.0 eV were associated with Co³⁺. The binding energy peaks at 786.85 eV and 803.05 eV were satellite peaks. No Co(0) peaks appeared, indicating that there was no metallic Co on the surface of CNF/Co₃S₄. The XPS survey pattern showed that the surface of the CNF/Co₃S₄/ MoS₂ was composed of Mo, S, O and C element (Fig. S7(b)), where C came from the internal environment of the test instrument, and the O element came from inevitable oxidation and surface absorption. In addition, no obvious signal peak of Co appeared, because the Co element was covered by MoS₂ nanosheets, which was also consistent with the previous analysis results, which was also consistent with the previous analysis results. For Mo 3d spectrum, it had four split peaks, the peaks at 229.5 eV and 232.6 eV were corresponding to Mo⁴⁺ of MoS_2 . And the peak at 235.8 eV was Mo^{6+} due to surface oxidation. In the S 2p spectrum, only two peaks (162.3 eV and 163.5 eV), both were related to S^{2+} in MoS_2 [42]. The phase analysis in Fig. 3 further confirmed the structure of hybrid material of the MoS₂ supported on CNF/Co. In addition, compare the Mo 3d and S2p spectrum of CNF/MoS₂ and CNF/ Co_3S_4/MoS_2 , the peaks were in the same position, and the introduction of Co₃S₄ does not change the valence states of the

most edge Mo and S elements because the length nanosheets was 100–200 nm.

In the previous characterization of the morphology and structure, it indicated that the Co nanoparticles were wrapped in the graphite carbon layer in the carbon nanofibers. During the subsequent hydrothermal reaction, Co on the CNF/Co surface converted to Co₃S₄, and the surface of the CNF/Co₃S₄ was covered by the molybdenum disulfide nanosheets. The HER performance of materials was evaluated in 1 M KOH through the traditional three-electrolysis system. Firstly, the influence of different amounts of Co element contained in the electrospinning solution on the properties of the CNF/Co₃S₄/ MoS₂ hybrid material HER was studied. The analysis in Fig. S3 showed that as the Co content x (x \leq 4) increased, the number of Co nanoparticles in CNF/Co also gradually increased. Meanwhile, the HER performance of the CNF/Co₃S₄-X/MoS₂ gradually improved (as shown in Fig. 4(a)), the overpotentials the CNF/Co₃S₄-X/MoS₂ (X = 0, 2, 3, 4 mmol) were 191, 120, 96, and 80 mV at a current density of 10 mA cm $^{-2}$ (η_{10}), respectively. And the Tafel slope calculated from the LSV curve also showed the same tendency, as shown in Fig. 4(b), the Tafel Slope of $CNF/Co_3S_4-X/MoS_2$ (X = 0, 2, 3, 4 mmol) were 122.3, 120.1, 107.3, 99.2 mV dec $^{-1}$. Since the Co $_3$ S $_4$ nanoparticles were inlays on the carbon nanofibers, and the surface of the carbon nanofibers was covered by the MoS₂ nanosheets, the Co₃S₄ nanoparticles cannot directly contact the electrolyte. The improvement of the electrocatalytic performance of the hybrid material should be caused by the metal Co₃S₄ nanoparticles, which may strengthen the electronic transmission. When the Co content X (X > 5) further increased, the HER performance of the CNF/Co₃S₄-X/MoS₂ began to decrease, the overpotential η_{10} were 85 and 97 mV (when x = 5,6), and the Tafel Slope were 111 and 116 mV dec⁻¹, respectively. The data of overpotential and Tafel were summarized in Fig. 4(c). The HER performance of CNF/Co₃S₄-X/MoS₂ indicated that a certain number of Co nanoparticles on the carbon fiber converted to Co₃S₄ nanoparticles after hydrothermal reaction could improve the electron transport of the material, but an excessive or larger size of nanoparticles will reduce the improved performance. The EIS impedance spectrogram in Fig. 4(d) further verified that. When $X \le 4$, as the Co content increased, the Nyquist plots of the CNF/Co₃S₄]-X/MoS₂ hybrid material showed lower and lower semicircles, which indicated that electron transmission efficiency was faster. When the Co content further increased (X \geq 5), the internal charge transfer efficiency began to decrease. The electric doublelayer capacitance (C_{dl}) was positively correlated with the electrochemically active area (ECSA) of the material. The C_{dl} value of the CNF/Co₃S₄-X/MoS₂ was calculated by testing the CV curves at different scan rate (Fig. S10, Fig. 4(e)). Compared with the lower C_{dl} value (349.2 mF cm⁻²) of CNF/Co₃S₄-0/MoS₂ (CNF/MoS₂), after the introduction of Co₃S₄ nanoparticles, the C_{dl} value of CNF/Co₃S₄-X/MoS₂ had a higher value (X = 2-6), and CNF Co_3S_4 -4/MoS₂ showed the largest C_{dl} value (624.8 mF cm⁻²), indicating that the introduction of Co₃S₄ nanoparticles accelerated electron transport and stimulated more activity sites. Besides, the calculated ECSA and RF (Roughness Factor) also showed the same tendency, confirming the previous point. And when Co = 4 mmol, CNF Co₃S₄-4/MoS₂ showed the highest ECSA and RF values.



Fig. 3 – XPS spectra of Co 2p (a) and S 2p (b) in CNF/Co₃S₄. XPS spectra of Mo 3d (c) and S 2p (d) in CNF/Co₃S₄/MoS₂.



Fig. 4 – (a) The lsv curves and (b) the corresponding Tafel slope of $CNF/Co_3S_4/MoS_2$ prepared with different content of Co measured at 1 M KOH with the scanning rate of 5 mV/s; (c) The Histogram of overpotential and Tafel value at 10 mA cm⁻²; (d) EIS, and (e)C_{dl} calculated by CV at different scan rate; (f) ECSA and RF histograms.



Fig. 5 – (a) The lsv curves and (b) the corresponding Tafel slope of CNF/Co₃S₄/MoS₂ prepared at different carbonization temperature measured at 1 M KOH with the scanning rate of 5 mV/s; (c) The Histogram of overpotential and Tafel value at 10 mA cm⁻²; (d) EIS, and (e)C_{dl} calculated by CV at different scan rate; (f) ECSA and RF histograms.

The carbonization temperature had a great influence on the structure of CNF/Co, so that affected the HER performance of CNF/Co₃S₄/MoS₂. As the carbonization temperature increased, Co nanoparticles gradually broke through the blockade of the carbon layers and were exposed on the surface. And the HER performance of CNF/Co₃S₄/MoS₂ also was better, CNF/Co₃S₄/MoS₂ prepared at 1000 °C (annealing temperature) showed the best HER performance (Fig. 5(a–c)), 80 mV (η_{10}) and Tafel slope of 99.2 mV dec⁻¹. It is better than 800 °C ($\eta_{10} = 120$ mV, 147.7 mV dec⁻¹) and 900 °C ($\eta_{10} = 120$ mV, 147.7 mV dec⁻¹). Since Co nanoparticles reacted with S source to form Co₃S₄ when exposed on the surface, CNF/Co₃S₄ may



Fig. 6 – (a) The lsv curves and (b) the corresponding Tafel slope of CNF/Co₃S₄/MoS₂ prepared with different content of Mo in the solvothermal process; (c) The Histogram of overpotential and Tafel value at 10 mA cm⁻²; (d) EIS, and (e)C_{dl} calculated by CV at different scan rate; (f) ECSA and RF histograms.

have better electron transport efficiency compared with CNF/ Co. To verify this point, compared CNF/Co with CNF/Co₃S₄ in 1 M KOH. CNF/Co₃S₄ had lower overpotential (η 10 = 186 mV), Tafel slope (126.9 mV dec⁻¹) and lower electron transfer resistance (as shown in Fig. S11). This indicated that CNF/ Co₃S₄ has a faster electron transport efficiency, which can effectively accelerate the rate of electrons from the substrate to the catalyst. When the carbonization temperature was increased to 1100 °C, the particles agglomerated sharply, the size became larger, the electron transfer resistance increased, and the HER performance began to decrease. And compared with other annealing temperatures, CNF/Co₃S₄/MoS₂(1000 °C) also had the largest C_{dl}, ECSA and RF values (Fig. 5(d–e), Fig. S12). This was also due to the faster electron transfer in Co₃S₄ nanoparticles, which stimulated more active sites.

The HER performance results of CNF/Co₃S₄/MoS₂ prepared with different Co content indicated that a certain content of Co₃S₄ nanoparticles could promote the electron transport inside the material, thereby improving its electrocatalytic activity. Though the outer MoS₂ provided catalytic active sites during the entire HER process, the relatively low charge carrier concentration and poor conductivity of MoS₂ also inhibited the charge transfer kinetics. Therefore, it is necessary to study the relationship between the load of MoS₂ and the catalytic activity of CNF/Co₃S₄/MoS₂. In the hydrothermal reaction, as the Mo content in the solution increased, the diameter of CNF/ Co₃S₄/MoS₂ also increased (as shown in Fig. S5), which indicated the amount of MoS₂ nanosheets supported on carbon fibers increased. Meanwhile, the HER catalytic activity of CNF/ Co₃S₄/MoS₂ showed a trend of first increasing and then decreasing (as shown in Fig. 6(a-c)). When the content of Mo in hydrothermal was increased from 0 mmol to 2 mmol, the overpotential (η 10) of CNF/Co₃S₄/MoS₂ was 186, 118, 80, 89 and 104 mV, respectively. The overpotential was the lowest when the Mo content was 1.0 mmol. In addition, the calculated Tafel Slopes were 126.9, 119.7, 99.2, 112 and 122.1 mV dec⁻¹, which was also the lowest when Mo = 1.0 mmol, indicated that it had the best hydrogen evolution reaction kinetics. EIS test results (Fig. 6(d)) showed that with the increase of Mo content, the charge transfer resistance of CNF/Co₃S₄/MoS₂ became larger



Fig. 7 – For CNF/Co₃S₄/MoS₂, CC/MoS₂ and Pt/C, the lsv (a), the corresponding Tafel slope curves (b) and the EIS (c) curves in 1 M KOH. (d) Time-current density curves of CNF/Co₃S₄/MoS₂ and CC/MoS₂ under a constant voltage. (e) Comparison of lsv curves before and after 2000 cycles of CV. (f) The Overpotential of different materials based on MoS₂ at 10 mA cm⁻².

and larger. Although more MoS_2 nanosheets could provide more catalytically active sites, it also brought bigger charge transfer resistance. It also had the largest C_{dl} (621.4 mF cm⁻²) (in Fig. S8), ECSA (0.89 m²) and RF (1.5*10⁴) values (Fig. 6(e-f)) when Mo = 1.0 mmol.

Finally, comparing CNF/Co substrates with commercial carbon cloth. After loading the MoS2 nanosheets, CC/MoS2 needed an overpotential of 170 mV to drive the current density of 10 mA cm⁻², which was much higher than CNF/Co₃S₄/MoS₂ (80 mV) and Pt/C (50 mV) (Fig. 7(a)). In addition, the Tafel slope of CC/MoS₂ was 138.2 mV dec⁻¹ (Fig. 7(b)). In contrast, CNF/ Co₃S₄/MoS₂ still exhibited a lower Tafel slope, and its rate determination step (RDS) were the Volmer step. Combined with the previous analysis, when the water adsorption capacity of CC/MoS2 and CNF/Co3S4/MoS2 remained same (because the surfaces were MoS₂ nanosheets prepared by the same method), the introduction of Co3S4 accelerated the electron transport, therefore accelerating the breaking of the H-O bond and promoted the Volmer step. These comparative results showed that the catalytic activity of the material can be greatly improved when only an excellent substrate was used to accelerate electron transport. In the EIS spectrum (Fig. 7(c)), the lower electron transfer resistance of $CNF/Co_3S_4/$ MoS₂ also confirmed this, compared to CC/MoS₂.

Stability is another important HER performance evaluation index. Under constant voltage, both CNF/Co₃S₄/MoS₂ and CC/ MoS₂ showed good stability (Fig. 7(d)), indicating that MoS₂ nanosheets had good stability in the process of water splitting. In addition, due to the special structure of the Co₃S₄ nanoparticles embedded on the carbon fiber, the Co₃S₄ nanoparticles could stably accelerate the electron transport ability and promoted the decomposition of water. In Fig. 7(e), after 2000 cycles of CV cycling, the lsv curve had little change, which also confirmed the excellent stability of CNF/Co₃S₄/ MoS₂. In addition, the HER performance of CNF/Co/MoS₂ prepared in this study was also better than that of other advanced MoS₂-based catalysts [1,43–57].

Conclusion

In summary, we proposed a strategy to prepare the CNF/ Co₃S₄/MoS₂ hybrid material to enhance the electron transport via the substrate in the HER reaction. Three-dimensional conductive N-doped carbon nanofibers supported by nanometal Co particles were prepared via electrospinning and high-temperature carbonization, which were used as a substrate for solvothermal reaction to grow MoS₂ nanosheets, and directly used as self-supporting electrodes for HER reaction. During the solvothermal process, the Co nanoparticles were transformed into Co₃S₄ nanoparticles with faster catalytic activity and electron transfer rate, the N-doped carbon nanofibers and introduction of Co3S4 nanoparticles greatly improved the electron transport capacity of the material to promote water splitting then speed up the HER process. In addition, by controlling the amount of Co in electrospinning, the number and particle size of nano-Co particles on the carbon fiber can be controlled. Co nanoparticles can break through the blockade of the carbon layer by controlling the carbonization temperature, and then be transformed into

Co₃S₄ particles the solvothermal process, which can transport electrons more efficiently. In this research, the CNF/Co3S4/ MoS₂ hybrid material prepared hydrothermally with CNF/Co containing a certain number of smaller-sized Co nanoparticles had the best HER performance, only need 80 mV to drive a current density of 10 mA cm⁻², and the Tafel slope was 99.2 mV dec⁻¹, which is better than most MoS₂-based catalyst. Due to the structure of Co₃S₄ nanoparticles embedded on the carbon fiber, it can stably improve the electron transmission efficiency during the continuous HER process, so that the CNF/ Co₃S₄/MoS₂ hybrid material also exhibited good stability and durability. Therefore, via designing a more advanced substrate for supporting high-efficiency water electrolysis catalysts, the water electrolysis efficiency and the catalyst utilization rate can be further improved. This work provides a new strategy for the development of high-activity and highdurability HER electrocatalysts via designing advanced substrate materials.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2022.03.013.

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