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Beyond Colloidal Synthesis: Nanofiber Reactor to Design Self-Supported Core-Shell Pd₁₆S₇/MoS₂/CNFs Electrode for Efficient and

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Supporting Information

ABSTRACT: Developing an efficient and stable hydrogen evolution catalyst is the core issue to promoting the wide application of hydrogen energy. Herein, we report a novel strategy to design a self-supported core-shell Pd₁₆S₇/MoS₂/CNFs electrode by the electrospinning technology and sulfur vapor-assisted chemical vapor deposition. The unique Pd₁₆S₇/MoS₂ core-shell structures with high content of unsaturated sulfur atoms were synthesized in situ in the carbon nanofiber (CNF) reactors. The formation of Pd-S-Mo nanointerfaces in Pd₁₆S₇/MoS₂ core/shell heterostructures can effectively regulate the electron orbital of MoS₂ and expose more sulfur vacancies, which were active sites for the hydrogen evolution reaction (HER). Beyond the colloidal synthesis, the self-supported Pd₁₆S₇/MoS₂/CNFs could be directly used as electrode materials, and the electrode with excellent

Durable Hydrogen Evolution Catalysis



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hydrophobic properties can accelerate the bubble desorption during the reaction and improve hydrogen evolution stability. The $Pd_{16}S_7/MoS_2/CNFs$ electrode affords a small overpotential of 83 mV at a geometric current density of 10 mA cm⁻² and Tafel slope of 113 mV dec⁻¹, suggesting a higher intrinsic activity (88 mV at 1 mA cm⁻²_{ECSA}) and remarkable durability.

KEYWORDS: electrospinning, carbon nanofiber reactor, core-shell, sulfur vacancies, electrocatalytic water splitting

1. INTRODUCTION

With the launch of the clean and sustainable banner in the energy sector, hydrogen has become a strong contender for renewable energy.¹ Hydrogen generation through electrocatalytic water splitting provides a promising approach to solve the energy crisis and environmental problems in modern society.² Highly efficient and stable electrocatalysts are required to break the chemical bond between hydrogen and oxygen in H₂O molecules and accelerate the hydrogen evolution kinetics during the water splitting process.³ Even though the Pt group metals are considered as state-of-the-art electrocatalysts, the scarcity and high cost of Pt group metals limit their practical applications in water splitting.⁴ Therefore, it is desirable to develop highly efficient and cost-effective alternative catalysts for electrocatalytic water splitting.

Recently, metal sulfides including Rh₂S₃,⁵ CoS₂,⁶ and NiS₂⁷ have drawn attention due to their superior activity in the hydrogen evolution reaction (HER). It is reported that the excellent HER performance is originated from the S edge active site, which could significantly reduce the adsorption energy for hydrogen protons.⁸ However, their pristine semiconductor properties and lack of less active sites limit their wide application.9-13 Polysulfides usually exhibit good

chemical stability and catalytic properties due to the higher content of unsaturated sulfur atoms on crystal surfaces which are active sites for the hydrodesulfurization catalysis.¹⁴ Solid state synthesis, the solvothermal method, template-assisted synthesis, thermal decomposition of complexes, and the hydrothermal method have been reported to prepare polysulfides nanocrystals.^{15–18} These methods usually involved complex conditions and surfactants, and it was difficult to achieve the desirable structure and morphology, especially the synthesis of polymetallic sulfide. Therefore, the facile synthesis of a specific structure with abundant active sites on the catalyst surfaces still remained huge challenge.

In order to design the polymetallic sulfide with abundant active sites and highly efficient activity, we proposed a concept of experiments to synthesize the binary Pd₁₆S₇/MoS₂ coreshell nanocrystals by combining electrospinning technology and chemical vapor deposition. The Pd₁₆S₇/MoS₂ core-shell nanocrystals were synthesized in situ in the carbon nanofiber (CNF) reactors, and the $Pd_{16}S_7/MoS_2$ and CNF host became

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Figure 1. (a) FE-SEM and (b) TEM images of the $Pd_{16}S_7/MoS_2/CNFs$ hybrid. (c) HAADF-STEM image of the $Pd_{16}S_7/MoS_2/CNFs$ hybrid. (d) HRTEM image of $Pd_{16}S_7/MoS_2$ nanocrystals. (e) HR-TEM image of $Pd_{16}S_7/MoS_2$ nanocrystals, and the inset shows the HRTEM images of $Pd_{16}S_7/MoS_2$ nanocrystals. (f) The line-scan EDX spectra of the $Pd_{16}S_7/MoS_2/CNFs$ hybrid, and the inset shows the line-scan nanocrystals. (g–k) The STEM-EDS mapping images of the $Pd_{16}S_7/MoS_2/CNFs$ hybrid.

an integrate. The Pd₁₆S₇ served as cores and the MoS₂ served as shells. The Pd₁₆S₇/MoS₂ core-shell nanocrystals possess a high content of unsaturated sulfur atoms, and the Pd-S-Mo nanointerfaces between the core and shell possess bridging S_2^{2-} and apical S^{2-} species, which were active sites for HER.¹ Different from the nanocrystals prepared by colloidal synthesis, the self-supported Pd₁₆S₇/MoS₂/CNFs could be directly used as electrode materials and the CNF hosts can protect the Pd₁₆S₇/MoS₂ nanocrystal from the corrosion of acidic electrolyte. The core-shell structure endows more hydrophobic character for the key progress of accelerating hydrogen desorption and improving HER performance. The Pd₁₆S₇/ MoS₂/CNFs self-supported electrode exhibited superior HER performance with a small overpotential of 83 mV at a geometric current density of 10 mA cm⁻² and a Tafel slope of 113 mV dec⁻¹, as well as remarkable durability. Meanwhile, the Pd₁₆S₇/MoS₂/CNFs electrode also shows a higher intrinsic activity (88 mV at 1 mA $\text{cm}^{-2}_{\text{ECSA}}$) for HER. This study provides a broad road for the future application of polysulfide catalysts in efficient and stable HER performance.

2. EXPERIMENTAL SECTION

2.1. Materials. Palladium chloride was acquired from Shanghai Civi Chemical Technology Co., Ltd. N_1N' -dimethylformamide (DMF) was purchased from Hangzhou GaoJing Fine Chemical Co., Ltd. Ammonium tetrasulfide molybdate ((NH₄)₂MoS₄) was purchased from Beijing Bai Ling Wei Technology Co., Ltd. Polyacrylonitrile (PAN, $M_w = 1.49 \times 10^5$, copolymerized with 10 wt % acrylate) was acquired from Sinopec Shanghai Petrochemical Co., Ltd.

2.2. Synthesis of the $Pd_{16}S_7/MoS_2/CNFs$. In a typical procedure, first, 0.4 g of palladium chloride and 0.4 g of ammonium tetrathiomolybdate were added into PAN/DMF solution with a mass fraction of 12 wt %. The homogeneous solution was formed after stirring at room temperature for 12 h. Then, the solution was transferred to a syringe of stainless steel needle with an inner diameter

of 0.7 mm. The needle was connected to a high-voltage power source connected with 14 kV. A receiving plate for collecting the spinning film was placed 15 cm from the needle, and the advance speed of the syringe was 0.5 mL/h. Finally, after spinning for 15 h, the collected spin film was placed in a vapor deposition furnace carrying an alumina boat for calcination. Another alumina boat with 0.5 g of sulfur powder was placed at the front end of the Ar flow. The PdMo/PAN film was first heated to 230 °C in air and kept for 3 h. Then, the furnace was heated to 400 °C while another heating section ceramics boat was heated to 250 °C and maintained for 2 h. At last, the furnace was heated to 900 °C under argon protection for 3 h. All heating rates were at 5 °C min⁻¹.

2.3. Materials Characterizations. The structure of the prepared materials was investigated by field emission scanning electron microscopy (FE-SEM) with a Hitachi S-4800 instrument at an acceleration voltage of 3 kV and by transmission electron microscopy (TEM) with a JEM-2100 instrument plus transmission electron microscope (JEOL, Japan) at an acceleration voltage of 200 kV. The Pd₁₆S₇/MoS₂/CNFs hybrid materials were characterized by STEM (Tecnai G2 F30S-Twin, Philips-FEI) at an acceleration voltage of 300 kV to obtain the bright field images and high-angle annular dark field images, STEM mapping, and line-scan energy dispersive X-ray spectroscopy (EDX). In order to determine the phase composition and elemental composition of the prepared material, X-ray diffraction (XRD) of the Bruker AXS D8 and X-ray photoelectron spectroscopy (Kratos Axis Ultra DLD), which was operated at 15 kV and 10 mA with an Al (mono) K_{α} source (1486.6 eV), were used. The X-ray diffraction pattern was recorded at the scanning rate of 0.02 $2\theta \text{ s}^{-1}$ in the 2θ range of 10-90°. The contact angle was tested by a video optical contact angle measuring instrument (OCA15EC, Dataphysics). Electron spin resonance (ESR) measurement was performed on a Bruker E580 spectrometer at room temperature. The microwave frequency was maintained in the range from 9.8591 to 9.8599 GHz (Xband), and the microwave power was fixed at ~ 20 mW.

2.4. Electrochemical Characterization. The electrochemical measurements were performed in a round glass electrolyzer with the CHI660E electrochemical workstation at room temperature. A saturated calomel electrode was used as the reference electrode and a carbon rod was used as counter electrodes. The membrane after



Figure 2. (a) XRD pattern of the Pd₁₆S₇/MoS₂/CNFs hybrid. (b) The Raman spectra of the Pd₁₆S₇/MoS₂/CNFs and MoS₂/CNFs hybrids.

calcination in the tube vacuum furnace was cut into thin square pieces, which were fixed on a Teflon motor clip as the working electrode. Three electrodes were put into the 0.5 M $\rm H_2SO_4$ (aq.) electrolyte with saturated argon. In order to achieve a relatively stable state of the catalyst, the cyclic voltammetry for 200 scans was taken. Linear sweep voltammetry was carried out with the scan rate of 5 mV s⁻¹, and the 50 h stability test was acquired by time-dependent current density, while saturated argon gas was introduced to remove the bubbles. Electrochemical impedance spectroscopy (EIS) was obtained under the same conditions from 10⁻² to 10⁶ Hz at 0.3 V of the EIS voltage.

3. RESULTS AND DISUSSION

In a typical synthesis procedure, the Pd and Mo precursor were homogeneously dissolved in PAN/DMF solutions and then electrospun into PdMo/PAN precursor nanofibers. Through the S vapor-assisted graphitization, the Pd₁₆S₇/MoS₂ core/shell nanocrystals were synthesized in situ in the nanofiber hosts along with the conversion from PAN nanofibers to carbon nanofibers. As shown in Figure 1a, the field emission scanning electron microscope (FE-SEM) image indicates that the Pd₁₆S₇/MoS₂ core/shell nanocrystals were uniformly grown on CNFs. To gain a clearer understanding of the morphology, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Figure 1b, c) images illustrate that large numbers of teardrop-shaped Pd₁₆S₇/MoS₂ nanocrystals with the average diameter of 30-60 nm were attached on the surface of CNFs. In comparison, the individual MoS₂ and Pd₁₆S₇ were also prepared using the same condition, which were shown in Figure S1. The MoS₂ nanocystals exhibit a twodimensional nanoplate morphorlogy, and the high-resolution TEM (HRTEM) image displays the distinct lattice fringe with a lattice spacing of 6.5 Å, corresponding to the (002) crystal planes. Focusing on the Pd₁₆S₇/CNFs, the nanocrystal exhibits a teardrop-shaped morphorlogy, and HRTEM image indicates the (321) crystal plane with a visible lattice spacing of 2.4 Å.²⁰

As shown in Figure 1d and 1e, when the MoS_2 meets $Pd_{16}S_7$ together in the CNFs, it becomes unique core/shell structures with the $Pd_{16}S_7$ as cores and MoS_2 as the shell. The $Pd_{16}S_7/$ MoS_2 core/shell structure offered a Pd–S–Mo nanointerfaces, which can enhance the charge redistribution and electron transfer between the Pd and Mo atoms. In addition, the core/ shell nanocrystals were surrounded by a carbon layer, and the carbon layer not only improved the conductivity of nanocomposites and shortened the electron transport but also played a great protective role for core–shell structures. The $Pd_{16}S_7$ cores exhibit a lattice fringe of (321) plane with interplanar spacing of 2.4 Å while the MoS_2 shell display the lattice fringe of (002) plane with interplanar spacing of 6.5 Å. The STEM energy-dispersive X-ray spectroscopy (STEM-EDX) mapping for images was carried out to reveal the presence of the contained elements, which were shown in Figure 1f–k. The C and S elements belong to the S doped CNFs. The Pd, Mo, and S elements were evenly distributed throughout the nanocrystal morphology, suggesting the successful synthesis of the binary metal sulfide core/shell structures. The line-scan EDX spectra of the Pd₁₆S₇/MoS₂ nanocrystal also demonstrated that the nanocrystals consist of Mo, Pd, and S elements, further confirming the formation of core–shell structures.

X-ray diffraction patterns (XRD) were obtained to further investigate the crystal structure of core/shell nanocrystals. As shown in Figure 2a, it is clearly shown that the peaks located at about 14.4°, 29.0°, 32.7°, 33.5°, 35.8°, and 39.5° correspond to the (002), (004), (100), (101), (102), and (103) peaks of MoS₂, confirming the existence of the 2H MoS₂ phase.²¹ Furthermore, it can be seen that the strongest peak located at 37.7° corresponds to the (321) plane, which was accorded well with the HRTEM results. The lattice parameter (a = 8.924 Å) of Pd₁₆S₇ has been calculated, which was consistent with the previously reported lattice parameter (a = 8.930 Å), suggesting the cubic phase of $Pd_{16}S_7^{22}$ In addition, the other peaks located at 19.9°, 24.4°, 31.7°, 34.8°, 40.4°, 42.9°, 45.4°, and 47.7° correspond to the characteristic peaks of the (200), (211), (310), (222), (400), (330), (420), and (332) planes of cubic $Pd_{16}S_{7}$.²³ In addition, the peak located at about 30.0° was attributed to the (102) plane of the PdS_2 phase (PDF#22-0774), indicating that the majority of palladium sulfide molecules were Pd₁₆S₇ and that there was only a small content of PdS₂ on CNFs. The XRD patterns of the MoS₂/CNFs and $Pd_{16}S_7/CNFs$ both exhibit the similar characteristic diffraction peaks (Figure S2), and therefore, the core/shell strutures are both composed of MoS₂ and cubic Pd₁₆S₇.

The Raman spectra of $Pd_{16}S_7/MoS_2/CNFs$ and $MoS_2/CNFs$ hybrids were obtained as shown in Figure 2b. It is clear that two characteristic peaks located at 377.4 and 402.2 cm⁻¹ correspond to the E_{2g} and A_{1g} modes of MoS_2 . The difference between the peak position values of the two vibration modes is very close to 25 cm⁻¹, which is smaller than the bulk molybdenum disulfide, indicating the presence of MoS_2 .²⁴ This result is also expected, which is consistent of the HRTEM results of the $Pd_{16}S_7/MoS_2/CNFs$ hybrid and $MoS_2/CNFs$ hybrid. The HRTEM images of the $Pd_{16}S_7/MoS_2/CNFs$



Figure 3. XPS spectra of (a) the survey of $Pd_{16}S_7/MoS_2/CNFs$ hybrid for (b) Pd 3d, (c) Mo 3d, and (d) S 2p of the $Pd_{16}S_7/MoS_2/CNFs$, $Pd_{16}S_7/CNFs$, and $MoS_2/CNFs$ hybrids.

indicate that the $Pd_{16}S_7/MoS_2$ was coated by layers of carbon, which could increase the disorder of carbon. Therefore, the ratio of I_D/I_G for $Pd_{16}S_7/MoS_2/CNFs$ is much higher than that of $MoS_2/CNFs$. Moreover, the degree of graphitization of materials is also quite high, so that the catalyst has excellent electrical conductivity.

X-ray photoelectron spectroscopy (XPS) was used to investigate the surface states of Pd₁₆S₇/MoS₂/CNFs and to explore the surface electronic interaction at the Pd-S-Mo nanointerfaces. All the binding energies were calibrated by the C 1s peak at 284.6 eV as a reference. The XPS survey spectra of Pd₁₆S₇/MoS₂/CNFs indicate the presence of C, N, O, Pd, Mo, and S, as shown in the Figure 3a. Figure 3b shows the Pd 3d XPS spectra of Pd₁₆S₇/MoS₂/CNFs and Pd₁₆S₇/CNFs. For the $Pd_{16}S_7/CNFs$, the two pairs of characteristic peaks located at 335.2 and 340.6 eV and at 337.4 and 342.7 eV correspond to the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ signals of the Pd₁₆S₇/CNFs, respectively. For the Pd₁₆S₇/MoS₂/CNFs, the characteristic peaks for Pd 3d_{5/2} and Pd 3d_{3/2} shifted to 335.7 and 341.1 eV, respectively. After the formation of Pd₁₆S₇/MoS₂, the binding energies of Pd 3d that moved to the relatively higher states can be attributed to the spin orbit coupling, and the higher electronegativity value of S is higher, resulting in significant changes in the binding energy positions of the core level of Pd.^{25,26} While the other pair of peaks at higher binding energy (336.6 and 342.0 eV) is assigned to PdO_x due to the surface oxidation.

Meanwhile, the electronic states of Mo 3d and S 2p were obtained as shown in Figure 2c and 2d. As shown in Figure 3c, for the individual $MoS_2/CNFs$, the two characteristic peaks for MoS_2 were located at 229.4 and 232.4 eV, corresponding to the Mo $3d_{3/2}$ and Mo $3d_{5/2}$ of Mo (IV) ions, respectively. The

binding energy at 226.9 eV is assigned to the S 2s characteristic peak. The broad peak located at 235.4 eV corresponds to the Mo^{6+} ions.²⁷ Focusing on the Pd₁₆S₇/MoS₂/CNFs, the binding energies of Mo 3d shifted to the relative lower states at 229.4 and 232.4 eV. Combining with the shifts of Pd 3d in the binding energies, it is demonstrated that there were strong electron interactions between the Pd and Mo atoms through the Pd–S–Mo nanointerfaces. As shown in Figure 3d, the S 2p spectra of MoS₂/CNFs display three characteristic peaks. The binding energies located at 162.5 and 163.7 eV were attributed to the spin orbit coupling of the S $2p_{3/2}$ and S $2p_{1/2}$ levels.²⁸ Meanwhile, the binding energies in the S 2p XPS spectra of Pd₁₆S₇/MoS₂/CNFs suggested the significant shifts. The characteristic peaks located at 162.1 and 163.3 eV correspond to S $2p_{3/2}$ and S $2p_{1/2}$, respectively. The peak located at 163.3 eV in the S 2p spectra was attributed to the formation of polysulfide, resulting from the formation of a metal-deficient surface layer.²⁹ It can be seen that the S 2p peak shifts to a low energy, suggesting the strong electronic interactions of S, Mo, and Pd, when compared with MoS₂/CNFs.

The hydrogen evolution performance of the catalyst was evaluated in a typical three electrode configuration of 0.5 M H_2SO_4 electrolyte. Figure 4a shows the HER performance of $MoS_2/CNFs$ hybrid, $Pd_{16}S_7/CNFs$ hybrid, and $Pd_{16}S_7/MoS_2/CNFs$ hybrid. The commercial Pt/C catalyst was used as a control. The $Pd_{16}S_7/MoS_2/CNFs$ hybrid shows the significant enhancement toward the HER performance with a low overpotential of 83 mV to achieve a geometric current of 10 mA cm⁻². In comparison, the $MoS_2/CNFs$ hybrid exhibits poor performance with an overpotential of 183 mV, and the $Pd_{16}S_7/CNFs$ hybrid shows inferior electrocatalytic activity with an overpotential over 245 mV (10 mA cm⁻²). Some of



Figure 4. (a) Polarization curves obtained for the $MoS_2/CNFs$ hybrid, $Pd_{16}S_7/CNFs$ hybrid, $Pd_{16}S_7/MoS_2/CNFs$ hybrid, and Pt/C catalysts based on geometric electrode surface area. (b) The corresponding Tafel plots and (c) polarization curves of $MoS_2/CNFs$ hybrid, $Pd_{16}S_7/MoS_2/CNFs$ hybrid, $Pd_{16}S_7/MoS_2/CNFs$ hybrid, $Pd_{16}S_7/MoS_2/CNFs$ hybrid, $Pd_{16}S_7/MoS_2/CNFs$ hybrid, $Pd_{16}S_7/MoS_2/CNFs$ hybrid, $Pd_{16}S_7/MoS_2/CNFs$ hybrid, and Pt/C catalyst geometric activity and intrinsic activity. (e) Capacitive currents (Δj) as a function of scan rates of $MoS_2/CNFs$, $Pd_{16}S_7/CNFs$, and $Pd_{16}S_7/MoS_2/CNFs$ hybrids. (f) The time dependence of the current density under the static overpotential of -0.2 V vs RHE. The inset in Figure 4f is the contact angle test.

the catalysts show a negative current for zero potential in Figure 4a and c. This is because the substrate CNFs were a carbon support and it has a background current density. In addition, the electric double layer capacitance of the material would lead to a negative current for zero potential. These phenomena were also reported previously in the literature.^{30,31}

Due to the higher surface area, the unique core-shell structure exhibits an excellent contact angle and the higher contact of electrolyte and additional active sites would facilitate the HER kinetics. The Tafel slope was also investigated for the MoS₂/CNFs hybrid, Pd₁₆S₇/CNFs hybrid, Pd₁₆S₇/MoS₂/CNFs hybrid, and commercial Pt/C, as shown in Figure 4b. The Tafel slope of Pd₁₆S₇/MoS₂/CNFs is 113 mV dec⁻¹ which was markedly smaller than that of the MoS₂/CNFs hybrid (194 mV dec⁻¹) and the Pd₁₆S₇/CNFs hybrid (225 mV dec⁻¹), indicating the enhanced HER kinetics in the core-shell structure. The exchange current density (j_0) is an important indicator to characterize the activity of materials. It can be derived by extrapolation according to the Tafel equation, as shown in Table S1.

It is interesting to note that the $Pd_{16}S_7/MoS_2/CNFs$ electrode has a larger j_0 of $1.42 \times 10^{-3}A$ cm⁻² compared to that of the MoS₂/CNFs (0.94 × 10⁻³A cm⁻²) and Pd₁₆S₇/CNFs (0.83× 10⁻³A cm⁻²), suggesting the excellent catalytic

activity of Pd₁₆S₇/MoS₂/CNFs. The electrochemical active area (ECSA) is an important parameter to characterize the intrinsic activity of the catalyst. ECSA can be estimated based on the C_{dl} divided by C_{s} , where C_{dl} is the value of catalyst capacitance and C_s is the specific capacitance (0.023 mF cm⁻²), according to the report of benchmarking protocol by Jaramillo et al.^{30,31} It is noteworthy that the $Pd_{16}S_7/MoS_2/$ CNFs electrode has the largest ECSA (2.67 cm^2) as compared to the $MoS_2/CNFs$ (0.92 cm²) and $Pd_{16}S_7/CNFs$ (1.44 cm²), as shown in the Table S1; this indicates that the $Pd_{16}S_7/MoS_2/$ CNFs possess a higher intrinsic activity. Polarization curves of MoS₂/CNFs hybrid, Pd₁₆S₇ /CNFs hybrid, and Pd₁₆S₇/MoS₂/ CNFs hybrid were obtained based on ECSA, as shown in Figure 4c. Obviously, the $Pd_{16}S_7/MoS_2/CNFs$ hybrid exhibits the smallest overpotential (88 mV) at 1 mA cm⁻² of ECSA as compared to the MoS₂/CNFs hybrid (114 mV) and Pd₁₆S₇/ CNFs hybrid (258 mV). Figure 4d shows the comparison of the HER geometric activity and intrinsic activity of the sample. It can be seen that the Pd₁₆S₇/MoS₂/CNFs have a higher geometric activity (83 mV at 10 mA cm^{$^{-2}$}_{geo}) and intrinsic activity (88 mV at 1 mA cm^{$^{-2}$}_{ECSA}). The double-layer capacitance (C_{dl}) values were determined by cyclic voltammetry tests at various scan rates from 10 to 100 mV s⁻¹, as shown in Figure S3. The C_{dl} value of Pd₁₆S₇/MoS₂/CNFs (75.1 mF

cm⁻²) is the highest compared to those at 35.4 and 19.4 mF cm⁻² for $MoS_2/CNFs$ and $Pd_{16}S_7/CNFs$ hybrids, respectively, as shown in Figure 4e, revealing the higher catalytic activity of $Pd_{16}S_7/MoS_2/CNFs$.

To understand the electrocatalytic kinetics in HER, electrochemical impedance spectroscopy (EIS) was also performed, as shown in Figure S4. It is well-known that a semicircle obtained from a lower frequency region shows that a smaller charge transfer resistance corresponds to a faster reaction process. The charge transfer resistance of Pd₁₆S₇/ $MoS_2/CNFs$ hybrid (3 Ω) was smaller than those at 7 and 59 Ω for MoS₂/CNFs and Pd₁₆S₇/CNFs hybrids, respectively, suggesting that the Pd₁₆S₇/MoS₂/CNFs hybrid possesses a superior conductivity and faster electron transfer efficiency at the catalyst and electrolyte interface. The stability of $Pd_{16}S_7/$ MoS₂/CNFs hybrid is very crucial for its practical application. The time-dependent current density was tested at -0.2 V vs RHE in 0.5 M H₂SO₄ for 50 h, as shown in Figure 4f. It is obvious that only small degradation in the current density after i-t test for 50 h, indicating the extraordinary durability of Pd₁₆S₇/MoS₂/CNFs hybrid. In heterogeneous catalysis, the hydrophobic structure of the material is more prone to gas release, which is beneficial for the catalytic reaction.³² To probe the interface property of Pd₁₆S₇/MoS₂/CNFs hybrid, the contact angle testing using $0.5 \text{ M H}_2\text{SO}_4$ as the wetting liquid was conducted, as shown in the inset in Figure 4f. The contact angle is 138° belonging to hydrophobic materials, which indicates that the hybrid material is beneficial for gas desorption. Reducing the surface tension between the electrode material and the electrolyte interface would reduce the destructive force on the catalyst when the hydrogen molecules left the catalyst surface.³³

To further investigate its stability, the SEM images of $Pd_{16}S_7/MoS_2/CNFs$ hybrid after stability test were obtained, as shown in the Figure 5a and b. It can be found that a three-



Figure 5. (a, b) SEM image of $Pd_{16}S_7/MoS_2/CNFs$ hybrid after the electrochemical stability test. (c) TEM image of $Pd_{16}S_7/MoS_2/CNFs$ hybrid after the electrochemical stability test. (d) HRTEM image of $Pd_{16}S_7/MoS_2/CNFs$ hybrid after the electrochemical stability test.

dimensional network woven from carbon nanofibers still exists, and a large number of nanocrystals were still attached on the carbon nanofibers, indicating the strong coupling between carbon nanofibers and nanocrystals. It can be seen that the nanocrystal size has not changed and was basically maintained at 30–60 nm, as shown in the Figure 5c. The nanocrystals after the stability test still exhibit core-shell structures, as shown in the Figure 5d, cofirming the excellent catalytic durability.

In addition, the XRD spectra of $Pd_{16}S_7/MoS_2/CNFs$ after the stability test are shown in Figure 6a. As seen in the XRD spectra, the peak for carbon was clearly visible, suggesting that the CNFs subtract were well retained. Meanwhile, comparing the XRD spectra before and after the stability test, the phase composition and spatial configuration of the catalyst did not change. The high-resolution XPS spectra of Pd 3d, Mo 3d, and S 2p of Pd_{16}S_7/MoS_2/CNFs before and after the durability test were also obtained to further confirm the stability.

As shown in the Figure 6b, the peaks observed at 335.7 and 336.6 eV belong to Pd $3d_{5/2}$, while the peaks at 340.6 and 341.1 eV can be assigned to Pd $3d_{3/2}$. The binding energies of the characteristic peaks did not show any shifts, indicating that the Pd electronic state of the catalyst surface did not change. Meanwhile, the Mo and S electronic states of the catalyst surface before and after *i*-*t* measurement are shown in Figure 6c and 6d. The peak position of the Mo 3d and S 2p doublets confirmed the MoS₂ phase, which was in accord with the result of the XRD. Moreover, the binding energies exhibit no significant changes, further confirming the stability of the catalyst structure for HER performance.

Moreover, in order to investigate the effect of the size of the Pd₁₆S₇/MoS₂ on the HER performance, the Pd₁₆S₇/MoS₂ core-shell nanocrystals with different sizes were prepared by adjusting the precursor solution of metal salt. As shown in Figure 7a, the TEM image indicates that the size of the $Pd_{16}S_7/$ MoS₂ core-shell nanocrystals is about 150 nm. As shown in Figure 7b, the nanopariticles exhibit a distinct core-shell structure. Figure 7c and 7d indicates the TEM and HRTEM images of the $Pd_{16}S_7/MoS_2$ with a size of about 60 nm. They all exhibited the core/shell structures. Polarization curves of $Pd_{16}S_7/MoS_2/CNFs\text{-}150$ and $Pd_{16}S_7/MoS_2/CNFs\text{-}60$ hybrids were also obtained, as shown in the Figure 7e. The HER performance of Pd₁₆S₇/MoS₂/CNFs-150 is relatively poor, requiring an overpotential of 189 mV to deliver a geometric current of 10 mA cm⁻². In contrast, Pd₁₆S₇/MoS₂/CNFs-60 only needs 83 mV of overpotential toward HER. The Tafel slope of Pd₁₆S₇/MoS₂/CNFs-60 is 113 mV dec⁻¹, markedly smaller than that of the $Pd_{16}S_7/MoS_2/CNFs-150$ hybrid (156) mV dec⁻¹), suggesting that the Pd₁₆S₇/MoS₂/CNFs with small sizes possess a faster proton transfer process. Therefore, the size of the core-shell nanocrystals would lead to the positive influence on the hydrogen evolution performance.

Above all, the excellent and stable self-support electrode for HER under acidic conditions of the prepared Pd₁₆S₇/MoS₂/ CNFs hybrid was attributed to following factors. First, the CNFs that served as the nanoreactor can precisely regulate the formation of core-shell nanocrystals, promoting the structural stability of the catalyst in an acidic electrolyte. Second the core-shell nanointerface composed of metal and semiconductor increases the catalytic active sites and superior synergy between the core and the shell. As shown in Figure S5, the electron spin resonance (ESR) spectra for $Pd_{16}S_7/MoS_2/$ CNFs confirmed that the Pd₁₆S₇/MoS₂ possess the S vacancy structures. The S signal is ascribed to the contribution from Mo-S dangling bonding. The MoS₂ shells have even more edges and S vacancies, which could be the active sites for the HER. After the epitaxial growth of the MoS₂ shell on the compressible Pd₁₆S₇ core, tensile stress between the core and shell can change the adsorption energy of intermediate hydrogen.^{34,35} Our previous results reported that the epitaxial



Figure 6. (a) XRD pattern of $Pd_{16}S_7/MoS_2/CNFs$ hybrid after the electrochemical stability test. The XPS spectra of the $Pd_{16}S_7/MoS_2/CNFs$ hybrid after the electrochemical stability test for (b) Pd 3d, (c) Mo 3d, and (d) S 2p.



Figure 7. (a) TEM and (b) HRTEM image of $Pd_{16}S_7/MoS_2/CNFs$ hybrid with particles of about 150 nm. (c) TEM and (d) HRTEM image $Pd_{16}S_7/MoS_2/CNFs$ hybrid with particle sizes of about 60 nm. (e) Polarization curves and (f) corresponding Tafel slopes of $Pd_{16}S_7/MoS_2/CNFs$ with different sizes.

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growth of MoS_2 on Co_9S_8 could induce the lattice strain,³⁴ which could change the adsorption energy of intermediate hydrogen. In this work, as shown in Figure S6, the density functional theory (DFT) models of the MoS_2 , $Pd_{16}S_7$, and $Pd_{16}S_7/MoS_2$ indicate that the bond length of the Pd–S is 3.174 Å and the bond length of Mo–S is 3.179 Å. After the epitaxial growth, the Pd–S bond length in $Pd_{16}S_7/MoS_2$ remains the same. However, the bond length of partial Mo–S changed to 3.220 Å, indicating the lattice strain between the $Pd_{16}S_7$ and MoS_2 . The generated lattice strain in core/shell structures could change the adsorption energy of intermediate hydrogen.^{34,35}

4. CONCLUSION

In summary, the $Pd_{16}S_7/MoS_2$ core-shell structures have been successfully prepared through electrospinning technology and S vapor-assisted graphitization. The Pd₁₆S₇ acted as cores and the MoS₂ served as shells. The Pd₁₆S₇/MoS₂/CNFs selfsupported electrode exhibits superior activity toward HER with low overpotential, high intrinsic activity, small Tafel slope, and good durability. The superior performance might be attributed to the Pd₁₆S₇/MoS₂ core-shell nanocrystals that possess a high content of sulfur vacancies and faster proton transfer at the Pd-S-Mo interfaces. The size of the core-shell nanocrystals would lead to the positive influence on the hydrogen evolution performance. In addition, due to epitaxial growth on the MoS₂ shell on the compressible Pd₁₆S₇ core, tensile stress between the core and shell can change the adsorption energy of intermediate hydrogen, leading to the accelerated kinetic process.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.8b02105.

TEM images, HRTEM images, and XRD patterns of $MoS_2/CNFs$ and $Pd_{16}S_7/CNFs$ hybrids; table of comparison of HER activity data among various catalysts; electrochemical cyclic voltammogram test and electrochemical impedance spectra of various catalysts; ESR results of the $Pd_{16}S_7/MoS_2/CNFs$ hybrid; and DFT models of MoS_2 , $Pd_{16}S_7$, and $Pd_{16}S_7/MoS_2$ (PDF)

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