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Symmetrical synergy of hybrid CoS₂-WS₂ electrocatalysts for hydrogen evolution reaction

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A highly active and stable hybrid electrocatalyst 3D hierarchical CoS₂ nanosheets incorporated with WS₂ (CoS₂@WS₂) has been developed via a one-step sulfurization method for the first time, where the contents of WS₂ can be adjusted easily. We first prove the addition of small amounts of WS₂ enhances the hydrogen evolution reaction (HER) performance of CoS₂, and vice versa. In other words, we validated the symmetric synergy for HER between the Co- and W-based sulfide hybrid catalysts. In addition, we confirmed that the formation of nanointerfaces of Co-S-W between CoS₂ and WS₂ was responsible for the excellent HER activity (an overpotential of -97.2 mV at -10 mA/cm², a small Tafel slope of 66.0 mV/dec, and prominent electrochemical stability) of hybrid electrocatalyst CoS₂@WS₂.

Introduction

Hydrogen, as a clean and sustainable carbon-free energy carrier for replacing the traditional fossil fuel, has attracted broad interest.¹⁻³ The electrochemical water splitting technology is one of the most effective and promising ways for obtaining high-quality hydrogen.⁴⁻⁶ However, the key of this technology is the development of efficient electrocatalysts for hydrogen evolution reaction (HER).^{7,8} Till now, among all the reported HER electrocatalysts, the most effective HER electrocatalysts for water electrolysis are noble metals (Pt, Ru, Rh, Ir, and Pd etc) and their alloys such as platinum and IrO₂, nevertheless, their low-abundance and high cost of noble metals impede their large-scale commercial application.⁹⁻¹¹ Therefore, it's necessary to search the cost-effective and earth-abundant alternative materials with high HER activity to replace the platinum group metals, which is crucial to pave the way for the hydrogen economy era.

Recently, research efforts have been devoted to synthesizing and modifying the traditional hydrosulfurization (HDS) catalysts due to the similar step of adsorption hydrogen atoms as the intermediate in the HDS and HER process,¹² such as CoS₂,¹³ MoS₂,^{14,15} WS₂,¹⁶ CoP,¹⁷ MoP,¹⁸ WP,¹⁹ FeP,²⁰ and Mo₂C²¹ etc. Among them, cobalt pyrite (CoS₂) with the intrinsic metal-like conductivity has

recently demonstrated as effective HER catalyst based on both computational and experimental studies.^{2,3,22,23} And the HER performance of CoS₂ can be further enhanced by the doping of nonmetal elements, such as N,²⁴ P,²⁵ etc. There have been many important reviews^{5,12,14,26} in molybdenum disulfide (MoS₂) because it is one of the very promising HER catalysts for replacing Pt. In addition, the HER performance WS₂ has been expected to be good due to its structural and electronic similarities to MoS₂.²⁷⁻³⁰ Recently, Gao's group has found that N-doped WS₂ nanosheets can greatly improve the HER performance, verified by first-principle calculations.³¹ They revealed that N-doping can introduce more charge carriers and improve the intrinsic conductivity of the material, resulting in the enhancement of HER performance.³¹ In addition, high quality WS₂ nanodots with a high concentration of octahedral phase were successfully prepared by liquid-phase exfoliation from bulk WS₂ crystals, showing outstanding HER performance (with an onset potential as low as 90 mV, a Tafel slope of 51 mV decade⁻¹).³² Although exfoliation is a commonly adopted process to prepare 2D flakes or particles,³³ there are only a few scattered studies focusing on the synthesis of WS₂-based electrocatalysts for HER. Although various approaches including high-temperature sulfurization, chemical vapor deposition, and thermal annealing have been investigated to obtain WS₂-based with different morphologies and structures, it is still a major challenge to prepare WS₂-based electrocatalysts with high HER performance.^{16,29,30,34}

Except the single metallic HER catalysts, bimetallic hybrid catalysts for HER including CoMoS,³⁵⁻³⁷ NiMoS,^{38,39} NiWS,⁴⁰ MoWP,⁴¹ CoMoN,⁴² and MoFeC⁴³ have also been extensively studied due to their excellent performance in the areas of hydrotreating, hydrogen evolution, and oxygen reduction reaction than the corresponding single component. For HER, it is found that the superior HER

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activities of those hybrid catalysts were ascribed to the synergistic effect of different components, which not only regulates the intrinsic electric properties of hybrid materials, but also tunes the surface structure of hybrids to increase the number of exposed active sites. Recently Chorkendorff et al.³⁰ put forward a model based on a density functional theory (DFT) analysis that the doping of cobalt into WS₂ can decrease the free energy of hydrogen adsorption of S-edge, resulting in the improvement of HER performance. Also, the result of DFT calculation was further confirmed by many reported experiment results.^{22,35,36,39} Very recently, we experimentally confirmed the existence of the symmetric synergy for the Co₉S₈-MoS_x hybrids system in HER reaction, i.e., the HER activity of Co₉S₈ or MoS_x can be promoted by doping a small percentage of the MoS₂ or Co₉S₈.⁴⁴ It is fundamentally interesting to see whether the similar symmetric synergy also exists in the Co-S-W system?

Herein, we have successfully synthesized WS₂-doped CoS₂ nanosheet arrays on carbon fiber cloth (denoted as CoS₂@WS₂/CC) through a one-step sulfuration strategy for the first time. Also, the effect of doping content of WS₂ to the HER performance was systematically investigated. Firstly, we fabricated Co(OH)₂ nanoplates on CC using Co(NO₃)₂ solutions by the electroplating method; then it was annealed in a tube furnace at 400 °C under a H₂S/Ar environment after dip-coating the ammonium tetrathiotungstate dimethylformamide (DMF) solution, as illustrated in Figure 1. And the WS₂ was well dispersed into the surface of CoS₂ with 3D hierarchical porous structure (Figure 1). The obtained CoS₂@WS₂/CC hybrid not only displayed the metallic properties of CoS₂, but also showed the enhanced stability compared to CoS₂. Spectroscopic measurements evidenced a strong interaction between the WS₂ and CoS₂ in the hybrid catalysts by intermediate sulfur atoms. Our results directly validate the synergistic effect of CoS₂ promoted by WS₂, supporting the symmetric synergy arguments. In other words, we validate that the existence of symmetric synergy for HER in the W- and Co-based sulfide hybrid catalysts for the first time, a long-standing question requiring clear experimental proofs. In addition, it shows impressive improved HER activity (an overpotential of -97.2 mV at -10 mA/cm², a small Tafel slope of 66.0 mV/dec) compared to pure WS₂/CC and CoS₂/CC nanostructures. The enhanced HER activity is attributed to the good dispersion of WS₂ nanoparticles, the improved electric conductivity, and the formation of nanointerfaces of Co-S-W with the doping of WS₂.

Figure 1. The schematic illustration for the synthesis of hybrid electrocatalyst CoS₂@WS₂/CC.

Experimental

Materials

All chemical reagents including cobalt (II) nitrate hexahydrate ($\geq 98\%$), ammonium tetrathiotungstate ((NH₄)₂WS₄, $\geq 99.9\%$ trace metals basis), dimethylformamide (DMF, 99.8%), sulfuric acid (H₂SO₄, 95%-98%), Nafion® perfluorinated resin solution (5 wt. % in lower aliphatic alcohols and water), and isopropanol (99.5%) were purchased from Sigma-Aldrich. The commercial Pt/C (20% for platinum) was purchased from Alfa Aesar. The water was purified through a Millipore system.

Electrochemical deposition of Co(OH)₂ nanosheets on carbon fiber cloth (CC)

The carbon cloth (CC) with the size 1 cm×2.5 cm was washed with deionized water and isopropanol. Part of the CC (1 cm ×1 cm) was then immersed in a 0.1 M Co(NO₃)₂ solution for the electrodeposition of Co(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 min in a PGSTAT 302 N Autolab workstation. After electrodeposition, the deposited green CC was taken out and dried under vacuum for further dip-coating of ammonium tetrathiotungstate solution. The obtained sample named as Co(OH)₂/CC.

Preparation of CoS₂/CC, WS₂/CC, and CoS₂@WS₂/CC electrocatalysts

The obtained Co(OH)₂/CC was drop-coated with an ammonium tetrathiotungstate solution (3 wt% of (NH₄)₂WS₄ in DMF). Then, the samples were dried under vacuum for four hours. And the subsequent sulfidation and annealing processes were conducted in a CVD tube furnace at 400 °C for three hours in an Ar/H₂S environment (Ar:H₂S=54:6) to form the CoS₂@WS₂/CC (about 2.9 mg/cm²) electrodes. For the hybrid catalysts, the WS₂ loading is controlled at 1.0 mg/cm². In addition, the sulfuration of bare Co(OH)₂/CC and (NH₄)₂WS₄ samples were also performed in a 54:6 Ar:H₂S atmosphere for three hours to prepare the CoS₂/CC (2 mg/cm²) and WS₂/CC (1 mg/cm²) catalysts, respectively. In this preparation process, we used the concentration of H₂S is 10% for security reasons. Note: the amount of CoS₂ and WS₂ in the hybrid CoS₂@WS₂/CC sample can be simply regulated by tuning the electrodeposition time and drop-coating volume of ammonium tetrathiotungstate solution (3 wt% of (NH₄)₂WS₄ in DMF), respectively.

Electrochemical measurements

The electrochemical measurements were performed in a PGSTAT 302N Autolab Potentiostat/Galvanostat (Metrohm) at room temperature. 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 H_2SO_4 (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 $\text{CoS}_2@/\text{WS}_2/\text{CC}$ 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 fix the catalyst on the CC surfaces. 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. 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. The electrochemical impedance spectroscopy (EIS) was performed using the FRA Impedance Potentiostat modules at the overpotential of -235 mV. The amplitude of AC signal was 10 mV. Impedance was measured in the range of 10^5 Hz to 0.1 Hz. To obtain the solution-resistance (R_s) and charge transfer resistance (R_{ct}), each EIS spectrum was fitted using a simplified electrochemical circle fitting method. The measurement of Faradaic efficiency was carried out under the condition of a constant current of -10 mA for 150 min by using a sealed electrochemical cell. The faradaic yield was calculated from the total amount of charge passed through the cell and the total amount of hydrogen produced, assuming that two electrons are needed to produce one H_2 molecule.

Characterizations

The crystalline structures of the samples were analyzed by X-ray diffraction (XRD, Bruker D8 Discover diffractometer, using $\text{Cu K}\alpha$ 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). The details of the TEM sample preparation are as follows. Firstly, the sample was cut into pieces using a scissor sonication in an alcohol solution. Then, the sample solution was drop-casted onto a TEM grid for analysis. XPS studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al $\text{K}\alpha$ 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 line at 284.8 eV.

Results and discussion

Figure 2. SEM images of CoS_2/CC (a), WS_2/CC (b), and $\text{CoS}_2@/\text{WS}_2/\text{CC}$ (c) samples. The insets are the corresponding higher-magnification SEM images.

The structural morphologies of the as-synthesized samples are revealed by scanning electron microscopy (SEM). Figure S1 shows the SEM images of electrodeposited sample $\text{Co}(\text{OH})_2/\text{CC}$, from which the 3-dimensional (3D) nanosheet structures (Figure S1) perpendicularly grown on the fiber surfaces are easily observed.^{17,44} As displayed in Figure 2(a), after the process of sulfurization in $\text{Ar}/\text{H}_2\text{S}$ atmosphere, some of the 3D hierarchical CoS_2 nanosheets obtained after sulfurization are peeled off and agglomerated from CC due to the high heat treatment temperature. Figure 2(b) shows that the WS_2 coating on CC is inhomogeneous many micrometer-scale clumps were formed on the surfaces of carbon fibers, likely due to the poor surface wetting to CC. Figure 2(c) displays the SEM image of $\text{CoS}_2@/\text{WS}_2/\text{CC}$ sample, the well-reserved 3D hierarchical sponge-like structures (the inset of Figure 2(c)) are seen, indicating that the proposed drop-cast coating of $(\text{NH}_4)_2\text{WS}_4$ helps to improve the adhesion of CoS_2 nanosheets on CC.

Figure 3. XRD patterns of CoS_2/CC , WS_2/CC , and $\text{CoS}_2@/\text{WS}_2/\text{CC}$ (a), TEM image (b), and HRTEM image (c) of the $\text{CoS}_2@/\text{WS}_2/\text{CC}$ sample. The weight ratio of WS_2 to CoS_2 is 1:1.9 in the $\text{CoS}_2@/\text{WS}_2/\text{CC}$ sample.

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The X-ray diffraction (XRD) patterns of $\text{Co}(\text{OH})_2/\text{CC}$, CoS_2/CC , WS_2/CC , and $\text{CoS}_2@\text{WS}_2/\text{CC}$ samples were shown in Figure S2 and Figure 3(a). Before the process of sulfuration, the XRD pattern of electroplated sample $\text{Co}(\text{OH})_2/\text{CC}$ (Figure S2) shows strong similarity to $\text{Co}(\text{OH})_2$ (JCPDS No. 74-1057) except the peaks of CC. After sulfuration, all the peaks ascribed to $\text{Co}(\text{OH})_2$ disappear while a series of new peaks identified as CoS_2 (JCPDS No. 41-1471) are observed (Figure 3(a)). For the sample WS_2/CC , several weak and broad XRD peaks can be assigned to WS_2 (JCPDS No. 084-1398) (Figure 3(a)). Note that the weak and broad peaks are possibly due to its poor crystallinity. Compared to CoS_2/CC and WS_2/CC , the hybrid $\text{CoS}_2@\text{WS}_2/\text{CC}$ clearly displays several signals ascribed to CoS_2 and almost no obvious peaks belonged to WS_2 were observed, suggesting that the WS_2 nanoparticles were well dispersed in the CC supported CoS_2 .

To clarify the microstructure of hybrid $\text{CoS}_2@\text{WS}_2/\text{CC}$, TEM and high-resolution TEM (HRTEM) measurements were performed. As displayed in Figure 3(b), the nanosheets with hierarchical porous structures were verified. In the corresponding HRTEM image (Figure 3(c)), clear layered WS_2 with an interlayer separation of 0.62 was confirmed, and the other lattice spacing is measured to be about 0.32 nm, which can be assigned to the (111) crystal planes of CoS_2 , further demonstrating the presence of WS_2 and CoS_2 in the hybrid material. In addition, Raman spectroscopy was also utilized to analyse three different electrocatalysts. As shown in Figure S3, characteristic peaks for WS_2/CC at about 354 cm^{-1} and 421 cm^{-1} corresponding to the E_{2g} and A_{1g} modes are observed.⁴⁵ Also, two characteristic peaks at about 289 cm^{-1} and 393 cm^{-1} for CoS_2/CC are also present.² The Raman spectrum (Figure S3) for the hybrid catalyst of $\text{CoS}_2@\text{WS}_2/\text{CC}$ displays relatively weak and wide characteristic peaks of WS_2 and CoS_2 , indicating that the strong interaction between two different phases may exist.

The X-ray photoelectron spectroscopy (XPS) was used to further investigate the surface electronic state and chemical composition of $\text{CoS}_2@\text{WS}_2/\text{CC}$. The XPS survey spectrum in Figure S4 shows that the $\text{CoS}_2@\text{WS}_2/\text{CC}$ comprises Co, W, S, C, and O elements. Figure 4(a) displays the high-resolution scan of Co 2p and two distinct peaks can be identified at 778.7 and 793.8 eV, ascribed to Co 2p_{3/2} and Co 2p_{1/2}, respectively.^{13,22} In addition, the major peak of 778.7 eV is very close to the reported for the Co 2p spectra in CoWS phases (778.6–778.8 eV).^{40,46,47} The doublet peaks for the binding energy of W 4f_{7/2-5/2} (Figure 4(b)) appear at 32.4 and 34.5 eV, respectively.^{48,49} Compared to the XPS spectra of pure WS_2 (32.8 and 34.9 eV, Figure 4(d)), the binding energies of W 4f shift to 32.4 and 34.5 eV, respectively. These correspond well to the Raman analyse results (Figure S3), corroborating the strong interaction between the WS_2 and CoS_2 . Moreover, the major peak at 32.4 eV is attributed to a W⁴⁺ species from a CoWS material (W4f_{7/2} 31.9–32.4 eV).^{40,46} In the high-resolution S 2p region (Figure 4(c)), the S 2p_{1/2} and 2p_{3/2} energies at 163.7 and 162.6 eV suggest the presence of S²⁻. In addition, a small peak doublet (36.0 and 38.0 eV) for W⁶⁺ of WO₃ (Figure 4(b)) and the S 2p in S–O bonds at 169.0 eV are also observed due to the air exposure during this preparation process.^{22,48}

Figure 4. (a) XPS spectra of the hybrid $\text{CoS}_2@\text{WS}_2/\text{CC}$ sample : (a) Co 2p, (b) W 4f, (c) S 2p, and those of (d) W 4f for the WS_2/CC and $\text{CoS}_2@\text{WS}_2/\text{CC}$ samples.

Linear-sweep voltammetry (LSV) measurements were performed to investigate the HER performance of hybrid $\text{CoS}_2@\text{WS}_2/\text{CC}$ electrocatalyst in 0.5 M H_2SO_4 with a typical three-electrode setup at a scan rate 0.5 mV/s. Additionally, for comparison, the HER activities of all the studied electrocatalysts, i.e., bare CC, WS_2/CC , CoS_2/CC , and commercial Pt/C/CC (20 wt%) catalysts were evaluated in Figure 5. As displayed in Figure 5(a), the pure CC exhibited negligible HER activity. The hybrid $\text{CoS}_2@\text{WS}_2/\text{CC}$ electrode showed a much better HER performance than WS_2/CC and CoS_2/CC . These values are already comparable to or lower than most the reported CoS_2 -based and WS_2 -based electrocatalysts for HER (Table S1). For instance, the overpotential of $\text{CoS}_2@\text{WS}_2/\text{CC}$ sample at -10 mA/cm^2 was -97.2 mV, prominently smaller than those of WS_2/CC (-151.7 mV) and CoS_2/CC (-140.3 mV), demonstrating the existence of the synergistic effects between CoS_2 and WS_2 . The HER kinetics of the above catalysts was probed by the corresponding Tafel plots. The Tafel slopes of these three HER catalysts are 66.0, 71.5, 79.6 mV/dec for $\text{CoS}_2@\text{WS}_2/\text{CC}$, CoS_2/CC , and WS_2/CC , respectively (Figure 5(b)), further confirming the outstanding intrinsic HER kinetics of the $\text{CoS}_2@\text{WS}_2/\text{CC}$. In addition, the Faraday efficiencies of three electrocatalysts i.e., $\text{CoS}_2@\text{WS}_2/\text{CC}$, CoS_2/CC , and WS_2/CC in an acid medium were monitored during a 150-min galvanostatic (-10 mA) electrolysis (Figure S5), showing that the amount of hydrogen production for each sample corresponded to the theoretical Faraday yield.

The charge transfer resistance (R_{ct}) of $\text{CoS}_2@\text{WS}_2/\text{CC}$, WS_2/CC , and CoS_2/CC in 0.5 M H_2SO_4 electrolyte can be obtained by a simplified electrochemical circle fitting method from Nyquist plots (Figure 5(c)). Under the condition of the same overpotential (-0.235 V), the hybrid $\text{CoS}_2@\text{WS}_2/\text{CC}$ catalyst shows the smallest R_{ct} (0.64 Ω) by comparing the samples of CoS_2/CC (0.97 Ω) and WS_2/CC (1.60 Ω), suggesting more facile electron-transfer kinetics for enhancing the catalytic activity. Because the HER current is also affected by surface area of catalyst, and the double-layer capacitance is proportional to the sample surface area.⁵⁰ The measured capacitance for WS_2/CC , CoS_2/CC , and $\text{CoS}_2@\text{WS}_2/\text{CC}$ samples were

summarized in Figure 5(d), from which we conclude that the catalyst with a large HER current exhibits to a higher double-layer capacitance, this demonstrating that the enhancement in the surface area after hybridization.

Figure 5. (a) Polarization curves of the bare CC, WS₂/CC, CoS₂/CC, CoS₂@WS₂/CC, and commercial Pt/C/CC (20 wt%) samples, where the current is normalized by the geometrical area of carbon cloth and the potential is after internal resistance correction; (b) Tafel slopes of samples WS₂/CC, CoS₂/CC, and CoS₂@WS₂/CC extracted from the polarization curves in (a); (c) electrochemical impedance spectroscopy (EIS) Nyquist plots and (d) double-layer capacitance for the corresponding electrocatalysts.

In addition to the HER performance, the stability of a catalyst is another critical evaluating factor. Figure 6(a) displays the time dependent measurement for CoS₂/CC, WS₂/CC, and CoS₂@WS₂/CC at a low working current density (*ca.* 50 mA/cm²). It is observed that the decay of the HER current for CoS₂/CC is about 92% in the first 3 h, but the decay is around 52% for WS₂/CC and 20% for hybrid CoS₂@WS₂/CC after evaluating for 7 h. This difference may be closely connected with the stripping phenomenon of all the three studied catalysts from CC, which was further confirmed by the following SEM and XRD analysis. The more severe agglomeration and stripping phenomenon (Figure 2(a)&2(c)) caused by higher sulfuration temperature may be the main reason for the declining stability compared with our previous study.⁴⁴ In addition, in comparison with the stability results from other reports,^{13,22} the high current density we adopted for measuring the stability is the other main reason for the declining stability. Figure 6b-d displays the SEM images of three samples after the stability test for 7 h, it is obviously seen that almost all of the CoS₂ (Figure 6(b)) and some of WS₂ (Figure 6(c)) were stripped from CC or dissolved during the process of stability evaluation, respectively, while the CoS₂@WS₂/CC (Figure 6(d)) with 3D hierarchical sponge-like structures can be well maintained on the CC. The largest internal stress of CoS₂ on CC may lead to this phenomenon, and the incorporation of WS₂ particles to CoS₂ can decrease the tensile internal stress values or even changed the stress character from tensile to compressive.⁵¹ The similar phenomenon was also observed for the hybrid CoS₂@MoS₂/CC system in our previous

study.⁴³ So, the CoS₂/CC presents the worst stability. Also, the XRD analysis (Figure S6) was performed for further confirming the crystallinity of CoS₂/CC, WS₂/CC, and CoS₂@WS₂/CC samples after the stability testing. For the XRD pattern of CoS₂/CC, almost no peaks ascribed to CoS₂ (Figure S6) were observed, corresponding well with the SEM analysis result. However, the relatively weak intensity of XRD peaks (Figure S6) belonged to WS₂ was seen from the sample of WS₂/CC, indicating some WS₂ crystallinity was remained on the surface of CC. For the CoS₂@WS₂/CC sample, the clear XRD signals belonged to CoS₂ was displayed in Figure S6, further demonstrating that the better stability of this catalyst.

Figure 6. Time-dependent HER performance of the CoS₂/CC, WS₂/CC, and CoS₂@WS₂/CC conducted in 0.5 M H₂SO₄ solution for 7 h (a), SEM images of samples CoS₂/CC (b), WS₂/CC (c), and CoS₂@WS₂/CC (d) after the stability evaluation. The insets are their corresponding higher-magnification SEM images.

As mentioned before, many previous studies including both DFT calculations and experiments have verified the fact that the doping of cobalt into WS₂ can improve the HER performance of WS₂.^{22,30,35,36,39} It is fundamentally important to prove whether small amount of WS₂ is able to promote the activity of CoS₂. In order to complete the symmetric synergy arguments, we have two sets of samples: (1) CoS₂@WS₂/CC with a fixed amount of WS₂ (4.0 mg/cm²) and various deposition times (from 2~20 min) of CoS₂ as displayed in Figure S7; (2) CoS₂@WS₂/CC catalysts with a fixed deposition time (10 min) of CoS₂ (2.0 mg/cm²) and different WS₂ loading weights from 0-1.2 mg/cm² (details in Figure S8). The overpotential η_{10} values for both sets of catalysts are plotted as a function of CoS₂ weight percentage in Figure 7. The results for both sets of catalysts strongly support that addition of small amount CoS₂ or WS₂ synergistically enhance the HER activity of WS₂ or CoS₂, respectively. Taking WS₂ doped CoS₂ for an example, Figure S8 shows the polarization curves, which show that the CoS₂@WS₂/CC with 1.0 mg/cm² of WS₂ exhibits the best performance (-97.2 mV at -10 mA/cm²; Tafel slope 66.0 mV/dec). If higher content of WS₂ (1.2 mg/cm²) was synthesized for hybrid CoS₂@WS₂/CC, some of the

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exposed active sites may be overlapped due to the bad disperse, resulting in the decrease of HER activity. It is well known that small differences in structures of catalysts lead to major changes in the physicochemical properties.^{36,52} When WS₂ was dip-coated to CoS₂, a new structure of CoS₂@WS₂ nanointerfaces was formed and may lead to the creation of open latent vacancy sites between W and Co atoms, which was similar with the system of Co₉S₈@MoS₂.^{11,44,53,54} And strong electron transfer may generate between W and Co via the intermediate sulfur atoms bonded to both metals can generate, resulting in the promising promoted electrocatalytic activity.⁴⁴ To verify the improvement of HER performance due to the formation Co-S-W nanointerfaces, another important comparison experiment that the mixed CoS₂/WS₂/CC catalyst (the loading amount is about 3.0 mg/cm²) was prepared by a two-step of themolysis process (first for preparing of CoS₂/CC (electrodeposition for 10 min), then dip-coating of ammonium tetrathiotungstate solution for preparing mixed CoS₂/WS₂/CC catalyst) was conducted. The HER activities (Figure S9) demonstrate that the catalyst CoS₂@WS₂/CC prepared by one step of annealing process displays the better, suggesting that the interactions between the CoS₂ and WS₂ are existed by one step of themolysis approach.

Figure 7. Synergistic effect: the overpotential η -10 values for both sets of catalysts plotted as a function of CoS₂ weight percentage.

The superior HER performance of the hybrid CoS₂@WS₂/CC catalyst with 3D hierarchical nanosheets structure could be summarized as follows: (1) the high conductivity of the carbon fiber cloth substrate and the metallic conductor nature of CoS₂ boosted electron transportation during the process hydrogen evolution; (2) the metal-like CoS₂ with 3D hierarchical nanosheets structure provided the better dispersion for the formation of nanoparticles of WS₂, which will exposes more edge-sites for HER catalysis, and the 3D hierarchically porous structure contributes to improve the electrolyte diffusion and the accessibility of CoS₂ and WS₂ active sites; (3) the W-doped CoS₂ hybrid produced a fair amount of valence electrons, which would form more lattice defects (defects in general are caused by the lattice mismatch and unsaturated or imperfect bonding in each phase (CoS₂ or WS₂) of the interfaces of the hybrid CoS₂@WS₂/CC), resulting in increasing the accessible internal surface area and exposure of more active edge sites, then greatly improve the electrocatalytic HER performance; (4) the

formation of nanointerfaces of Co-S-W between CoS₂ and WS₂ induced electron transfer through intermediate sulfur atoms bonded to both metals, resulting in better HER performance.

Conclusions

In summary, we have developed a facile one-step sulfuration method to synthesize a new hybrid 3D hierarchical structure of CoS₂ nanosheets coated with WS₂, where the contents of WS₂ and CoS₂ in the hybrid CoS₂@WS₂/CC catalyst can be well regulated by the drop-coating volume of ammonium tetrathiotungstate solution and the electrochemical deposition time. The obtained hybrid catalyst CoS₂@WS₂/CC exhibits an excellent activity (-97.2 mV at -10 mA/cm²; Tafel slope 66.0 mV/dec), which is comparable to or lower than all the reported CoS₂-based and WS₂-based catalysts. The improved HER activity is mainly due to the formation of nanointerfaces of Co-S-W after W-doping into CoS₂ nanosheets through the intermediate sulfur atoms, as well as the high electrochemically active surface area of the 3D hierarchically porous structure of CoS₂. More importantly, our experiments clearly show that WS₂ enhances the HER activity of CoS₂, validating the symmetric synergy arguments in Co-S-W systems.

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Notes and references

1. Y. Li, H. Zhang, T. Xu, Z. Lu, X. Wu, P. Wan, X. Sun and L. Jiang, *Adv. Funct. Mater.*, 2015, **25**, 1737-1744.
2. H. Zhang, Y. Li, T. Xu, J. Wang, Z. Huo, P. Wan and X. Sun, *J. Mater. Chem. A*, 2015, **3**, 15020-15023.
3. M. Cabán-Acevedo, M. L. Stone, J. Schmidt, J. G. Thomas, Q. Ding, H.-C. Chang, M.-L. Tsai, J.-H. He and S. Jin, *Nat. Mater.*, 2015, **14**, 1245-1251.
4. M.-R. Gao, J.-X. Liang, Y.-R. Zheng, Y.-F. Xu, J. Jiang, Q. Gao, J. Li and S.-H. Yu, *Nat. Commun.*, 2015, **6**, 5982.
5. Y. Yan, B. Xia, Z. Xu and X. Wang, *ACS Catal.*, 2014, **4**, 1693-1705.
6. J. Wang, W. Cui, Q. Liu, Z. Xing, A. M. Asiri and X. Sun, *Adv. Mater.*, 2016, **28**, 215-230.
7. C. G. Morales-Guio and X. Hu, *Acc. Chem. Res.*, 2014, **47**, 2671-2681.
8. Y. Jiao, Y. Zheng, M. Jaroniec and S. Z. Qiao, *Chem. Soc. Rev.*, 2015, **44**, 2060-2086.

- 9 A. Le Goff, V. Artero, B. Jousselme, P. D. Tran, N. Guillet, R. Métayé, A. Fihri, S. Palacin and M. Fontecave, *Science*, 2009, **326**, 1384-1387.
- 10 Y. H. Chang, C. T. Lin, T. Y. Chen, C. L. Hsu, Y. H. Lee, W. Zhang, K. H. Wei and L. J. Li, *Adv. Mater.*, 2013, **25**, 756-760.
- 11 H. Zhu, J. Zhang, R. Yanzhang, M. Du, Q. Wang, G. Gao, J. Wu, G. Wu, M. Zhang and B. Liu, *Adv. Mater.*, 2015, **27**, 4752-4759.
- 12 C. G. Morales-Guio, L.-A. Stern and X. Hu, *Chem. Soc. Rev.*, 2014, **43**, 6555-6569.
- 13 M. S. Faber, R. Dziedzic, M. A. Lukowski, N. S. Kaiser, Q. Ding and S. Jin, *J. Am. Chem. Soc.*, 2014, **136**, 10053-10061.
- 14 J. D. Benck, T. R. Hellstern, J. Kibsgaard, P. Chakthranont and T. F. Jaramillo, *ACS Catal.*, 2014, **4**, 3957-3971.
- 15 E. O. Ortiz-Quiles and C. R. Cabrera, *FlatChem*, 2017, **2**, 1-7.
- 16 D. Voiry, H. Yamaguchi, J. Li, R. Silva, D. C. Alves, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy and G. Eda, *Nat. Mater.*, 2013, **12**, 850-855.
- 17 X. Yang, A.-Y. Lu, Y. Zhu, M. N. Hedhili, S. Min, K.-W. Huang, Y. Han and L.-J. Li, *Nano Energy*, 2015, **15**, 634-641.
- 18 Z. Xing, Q. Liu, A. M. Asiri and X. Sun, *Adv. Mater.*, 2014, **26**, 5702-5707.
- 19 Z. Pu, Q. Liu, A. M. Asiri and X. Sun, *ACS Appl. Mater. Interfaces*, 2014, **6**, 21874-21879.
- 20 X. Yang, A.-Y. Lu, Y. Zhu, S. Min, M. N. Hedhili, Y. Han, K.-W. Huang and L.-J. Li, *Nanoscale*, 2015, **7**, 10974-10981.
- 21 F. X. Ma, H. B. Wu, B. Y. Xia, C. Y. Xu and X. W. D. Lou, *Angew. Chem. Int. Ed.*, 2015, **54**, 15395-15399.
- 22 J. Huang, D. Hou, Y. Zhou, W. Zhou, G. Li, Z. Tang, L. Li and S. Chen, *J. Mater. Chem. A*, 2015, **3**, 22886-22891.
- 23 W. Liu, E. Hu, H. Jiang, Y. Xiang, Z. Weng, M. Li, Q. Fan, X. Yu, E. I. Altman and H. Wang, *Nat. Commun.*, 2016, **7**, 10771.
- 24 J. Y. Zhang, W. Xiao, P. X. Xi, S. B. Xi, Y. H. Du, D. Q. Gao and J. Ding, *ACS Energy Lett.*, 2017, **2**, 1022-1028.
- 25 C. B. Ouyang, X. Wang and S. Y. Wang, *Chem. Commun.*, 2015, **51**, 14160-14163.
- 26 Y. Zheng, Y. Jiao, M. Jaroniec and S. Z. Qiao, *Angew. Chem. Int. Ed.*, 2015, **54**, 52-65.
- 27 M. A. Lukowski, A. S. Daniel, C. R. English, F. Meng, A. Forticaux, R. J. Hamers and S. Jin, *Energy Environ. Sci.*, 2014, **7**, 2608-2613.
- 28 D. Merki and X. Hu, *Energy Environ. Sci.*, 2011, **4**, 3878-3888.
- 29 Z. Wu, B. Fang, A. Bonakdarpour, A. Sun, D. P. Wilkinson and D. Wang, *Appl. Catal. B*, 2012, **125**, 59-66.
- 30 J. Bonde, P. G. Moses, T. F. Jaramillo, J. K. Nørskov and I. Chorkendorff, *Faraday Discuss.*, 2009, **140**, 219-231.
- 31 C. Q. Sun, J. Y. Zhang, J. Ma, P. T. Liu, D. Q. Gao, K. Tao and D. S. Xue, *J. Mater. Chem. A*, 2016, **4**, 11234-11238.
- 32 X. Zhao, X. Ma, J. Sun, D. H. Li and X. R. Yang, *ACS Nano*, 2016, **10**, 2159-2166.
- 33 S. H. Lin, Y. S. Chui, Y. Y. Li and S. P. Lau and C. R. Cabrera, *FlatChem*, 2017, **2**, 15-37.
- 34 L. Cheng, W. Huang, Q. Gong, C. Liu, Z. Liu, Y. Li and H. Dai, *Angew. Chem. Int. Ed.*, 2014, **53**, 7860-7863.
- 35 X. Dai, K. Du, Z. Li, M. Liu, Y. Ma, H. Sun, X. Zhang and Y. Yang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 27242-27253.
- 36 L. Yu, B. Y. Xia, X. Wang and X. W. Lou, *Adv. Mater.*, 2016, **28**, 92-97.
- 37 J. Staszak-Jirkovský, C. D. Malliakas, P. P. Lopes, N. Danilovic, S. S. Kota, K.-C. Chang, B. Genorio, D. Strmcnik, V. R. Stamenkovic and M. G. Kanatzidis, *Nat. Mater.*, 2016, **15**, 197-203.
- 38 J. Miao, F.-X. Xiao, H. B. Yang, S. Y. Khoo, J. Chen, Z. Fan, Y.-Y. Hsu, H. M. Chen, H. Zhang and B. Liu, *Sci. Adv.*, 2015, **1**, e1500259.
- 39 D. Merki, H. Vrubel, L. Rovelli, S. Fierro and X. Hu, *Chem. Sci.*, 2012, **3**, 2515-2525.
- 40 P. D. Tran, S. Y. Chiam, P. P. Boix, Y. Ren, S. S. Pramana, J. Fize, V. Artero and J. Barber, *Energy Environ. Sci.*, 2013, **6**, 2452-2459.
- 41 X.-D. Wang, Y.-F. Xu, H.-S. Rao, W.-J. Xu, H.-Y. Chen, W.-X. Zhang, D.-B. Kuang and C.-Y. Su, *Energy Environ. Sci.*, 2016, **9**, 1468-1475.
- 42 B. Cao, G. M. Veith, J. C. Neufeind, R. R. Adzic and P. G. Khalifah, *J. Am. Chem. Soc.*, 2013, **135**, 19186-19192.
- 43 C. Wan and B. M. Leonard, *Chem. Mater.*, 2015, **27**, 4281-4288.
- 44 X. Zhou, X. Yang, M. N. Hedhili, H. Li, S. Min, J. Ming, K.-W. Huang, W. Zhang and L.-J. Li, *Nano Energy*, 2017, **32**, 470-478.
- 45 J. Lin, Z. W. Peng, G. Wang, D. Zakhidov, E. Larios, M. J. Yacaman and J. M. Tour, *Adv. Energy Mater.*, 2014, **4**, 1301875.
- 46 L. Coulier, G. Kishan, J. A. R. van Veen and J. W. Niemantsverdriet, *J. Phys. Chem. B*, 2002, **106**, 5897-5906.
- 47 S. M. A. M. Bouwens, J. A. R. Van Veen, D. C. Koningsberger, V. H. J. De Beer and R. Prins, *J. Phys. Chem.*, 1991, **95**, 123-134.
- 48 T.-Y. Chen, Y.-H. Chang, C.-L. Hsu, K.-H. Wei, C.-Y. Chiang and L.-J. Li, *Int. J. Hydrogen Energy*, 2013, **38**, 12302-12309.
- 49 J. Yang, D. Voiry, S. J. Ahn, D. Kang, A. Y. Kim, M. Chhowalla and H. S. Shin, *Angew. Chem. Int. Ed.*, 2013, **52**, 13751-13754.
- 50 A. J. Smith, Y. H. Chang, K. Raidongia, T. Y. Chen, L. J. Li and J. Huang, *Adv. Energy Mater.*, 2014, **4**, 1400398.
- 51 E. Saraloğlu Güler, İ. Karakaya and E. Konca, *Surf. Eng.*, 2014, **30**, 109-114.
- 52 A. Kumar, F. Ciucci, A. N. Morozovska, S. V. Kalinin and S. Jesse, *Nat. Chem.*, 2011, **3**, 707-713.
- 53 G. Hagenbach, P. Courty and B. Delmon, *J. Catal.*, 1973, **31**, 264-273.
- 54 M. Ramos, G. Berhault, D. A. Ferrer, B. Torres and R. R. Chianelli, *Catal. Sci. Technol.*, 2012, **2**, 164-178.

Table of contents entry:

A new hybrid $\text{CoS}_2@\text{WS}_2/\text{CC}$ catalyst with high HER performance was synthesized by a facile one-step sulfurization method.