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3D dendritic WSe₂ catalyst grown on carbon nanofiber mats for efficient hydrogen evolution

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3D dendritic WSe₂ on conductive carbon nanofiber mats (d-WSe₂/CFM) was designed and synthesized by a diffusioncontrolled CVD method. The d-WSe₂/CFM was directly used as cathode for HER. The substantially improved HER performance are ascribed to the novel 3D structure with effectively exposed edge sites.

Electrocatalytic production of hydrogen from water splitting has been developed as an effective approach for reducing our reliance on hydrocarbon fuels.^{1,2} Various catalysts have been investigated for hydrogen evolution reactions (HER).³⁻⁵ Although platinum (Pt) or doped Pt catalyst are found to be highly active, the high cost heavily impedes its wide application in a large scale.⁶⁻⁸ Therefore, a number of alternative catalysts, such as transition metal dichalcogenides (TMDs) MX₂ (M=Mo, W and X=S, Se), are being extensively studied since their electrocatalytic activities were identified.9-12 Both experimental and computational studies has highlighted that the HER activity of TMDs correlates with the active edge sites,¹³ consequently, hierarchically constructing TMDs with high edge fraction is of high importantance to improve HER performance. For example, the density of edge sites of 2H MoS₂ is highly addressed since it dominates the HER activity while the basal plane is believed to be inert.¹⁴⁻¹⁶ As one of the most promising TMDs, WSe₂ has been investigated in the fields of batteries, fieldeffect transistors, diode, and so on.¹⁷⁻²⁰ Recently, the study on WSe₂ for HER are given on rational design of WSe2 catalyst with more exposure of active edge sites and the resluts shows that nanostructured WSe₂ is also a promising and appealing HER electrocatalyst.^{12,21} These results motivate us to design hierarchical

 WSe_2 with the aim at enhancing its HER performance. However, as far as we know, it is still of great challenge to control the growth of WSe_2 . In our previous study, the hierarchical structural TMDs were assembled on electrospun carbon nanofibers substrate, exhibiting excellent performance in electrochemical hydrogen evolution applications.²²⁻²⁴ This communication will provide a more efficient and facile approach to construct hierarchical WSe₂ electrode for HER with both high effective density of edge sites and high conductive carbon nanofiber mat substrate for HER.

According to classical crystal growth theory, dendritic growth, layer-by-layer (LBL) growth and screw-dislocation-driven (SDD) growth are the three basic growth types.²⁵ Generally, a high supersaturation condition is required for both dendritic growth and LBL growth.^{26,27} SDD growth is much more favorable at lower supersaturation than former ones.^{28,29} Under conditions where a rough interface is assumed, such as high supersaturation, the crystal is bounded by rounded noncrystallographic interfaces. If morphological instability occurs on such a rough interface, the crystal takes dendritic form.²⁵ The generated structure via dendritic growth can, thus, be fully dominated by changing the vapor concentration in chemical vapor deposition (CVD) process.

In this study, we proposed a method to synthesize 3D dendritic WSe₂ with carbon nanofiber mats (CFM) as the conductive substrate by using CVD method. In this method, the diffusion flux of Se vapor inversely depends on the lateral distance away from the left edge of the furnace.³⁰ At the upsteam of the furnace, the Se vapor concentration is supersaturated, then a rough reaction and growth interface is constructed, leading to morphological instability occurs on such a rough interface, resulting in the formation of WSe₂ nanostructure with dendritic crystal structure. However, at the downsteam, rose-like WSe₂ nanostructure formed due to the reduced driving force caused by the much lower Se vapor concentration. Therefore, the WSe₂ nanosheet growth is subject to strong influences of the diffusion of Se vapor through the boundary layer of Ar gas flows. Finally, the generated structures are tailored by the diffusion controlled concentration of Se vapor.

The obtained dendritic WSe_2 exhibits a rather low overpotential, higher current density at -300 mV vs RHE, and a small series resistance for HER even at a relatively low coverage of

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⁺ Electronic supplementary information (ESI) available: Experimental details. the EDS analysis and optical image of d-WSe₂/CFM. TEM and HAADF-STEM analysis of TS-WSe₂-CFM. XRD and Raman characterizations of d-WSe₂/CFM and r-WSe₂/CFM. Photo of the working electrode for d-WSe₂/CFM. The magnified SEM images of CFM and WO₃/CFM. CV plots of d-WSe₂/CFM electrode at 100 mV s⁻¹ for 1000 cycles in 0.5 M H₂SO₄.See DOI: 10.1039/X0xx00000x

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 WSe_2 and low atom fraction of W and Se (Figure S1). The excellent HER performance is correlated to the high dense edge sites and the high conductivity of substrates.

The facile CVD approach for WSe₂ with different hierarchical structures on CFM is exhibited as below, in which $(NH_4)_6H_2W_{12}O_{40}$ and PAN were selected as the precursors for W and CFM, respectively (see Supporting Information). Firstly, W-PAN FM was prepared by electrospinning their DMF solution. Then W-PAN FM on boat was transferred to the chamber of quartz furnace tube. Secondly, a heat treatment was employed to pre-oxide PAN FM and decompose $(NH_4)_6H_2W_{12}O_{40}$ into WO_3 . Se vapor was then introduced at saturated vapor pressure with Ar. Another heat treatment was applied leading to graphitization of PAN FM and generation of WSe₂ by selenization of WO₃ and the CFM with WSe₂ grown on was finally obtained (Figure S2 A). The boat's lateral distance from the upstream was adjusted in order to adjust the vapor concentration. The synthetic route is illustrated in Figure 1A. More detailed information about preparation can be found in SI. The obtained CFM with a thickness of 15 µm (Figure S2 B) exhibit good flexibility and excellent conductivity, and were used as electrodes directly. The WO₃ content within fiber decreases significantly after selenization as compared to that within WO₃/CFM (Figure S2, C and D).

Since the vapor concentration of Se can be diffusion-controlled by the lateral distance from upstream, its influence on the generated structure of WSe₂ on CFM is illustrated in Figure 1. A number of flower-like WSe_2 in the size of about 2~5 μm was obtained at three positions (Figure 1A, (a), (b) and (c)). It's interesting to find that three types of microstructures were obtained. Position (a) generated a novel dendritic WSe₂ on CFM (Figure 1B and 1E), which is defined as d-WSe₂/CFM. As shown in Figure 1D and 1G, position (c) can grow smooth leaves of WSe₂ on CFM with a vivid rose-like shape, which is defined as r-WSe₂/CFM. The leaves with bended triangular or hexangular contour can be distinguished for both d-WSe₂ (Figure 1 E, and Figure S3 A) and r-WSe₂ (Figure 1 G and Figure S3 C). The structure generated at position of (b) exhibited a transition morphology (Figure 1C, F and Figure S3B). The sample at position (b) is defined as TS-WSe₂/CFM. The structure evolution of WSe₂ is suggested to be Se vapor concentration sensitive and could be well diffusion-controlled at different lateral distance from upstream. When the location is close to the upstream, the vapor concentration is believed to be high supersaturation while a much lower concentration can be achieved at a faraway distance. The adjusted vapor concentrations at different locations thus lead to various structures, which is consistent with previous report.³¹



Figure 1. Schematic illustration of WSe₂ growth at different position in a quartz furnace tube. SEM images of d-WSe₂/CFM, TS-WSe₂/CFM and r-WSe₂/CFM at B, C and D low-, as well as E, F, and G high-magnification at positions (a), (b) and (c) in (A), respectively.

The d-WSe₂/CFM was fully characterized by TEM, selected area electron diffraction (SAED), high-angle annular dark field (HAADF) STEM, EELS spectra, element mapping and XPS spectra. As shown in Figure 2A, d-WSe₂ branches with 10-80 nm in diameter grew freely and artistically (Figure 2A). The effective density of edge sites on d-WSe₂/CFM is believed to be much higher in comparison to that of r-WSe₂/CFM. The light and shade contrast indicates the change in the thickness (layer number) of WSe₂ branches. The lattice distance observed on the terraces is 3.8 Å (left inset in Figure 2A), consistent with (100) planes of 2H-WSe2.³² The SAED (right inset in Figure 2A) clearly suggests that dendritic WSe₂ is configured in 2H phase,³² in good accordance with the observed triangular or hexangular morphology in Figure 1. As shown in EELS (Figure 2C) and highresolution element mapping (Figure 2D), both W and Se elements are homogenously distributed within branches. X-ray photoelectron spectroscopy (XPS) was conducted to investigate the chemical composition of d-WSe2. Two obvious peaks at 34.2 and 32.1 eV (Figure 2E) are ascribed to W 4f_{5/2} and W 4f_{7/2}, respectively.³³ In Figure 2F, Se 3d_{5/2} and Se 3d_{3/2} at 54.2 and 55.0 eV indicate divalent Se ion in good agreement with binding energy values for WSe₂ crystals.³³ Additonal two weak peaks at around 37.5 and 35.7 eV, correspondingly assigned to W $4f_{5/2}$ and W $4f_{7/2}\text{,}$ are due to a fraction of WO₃ (Figure S3D).³³ The TS-WSe₂/CFM was also characterized, as shown in Figure S3 E and F.

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Figure 2. A) TEM image of dendritic WSe₂ (left inset, HRTEM image; right inset, the corresponding SAED pattern). B) HAADF STEM images of d-WSe₂. C) The EELS spectra and D) high-resolution element mapping of the selected region in Figure B. E) and F) XPS analysis of W 4f and S 2p peaks of d-WSe₂/CFM, respectively.

The XRD was also employed to evaluate the crystal structure of d-WSe₂ and r-WSe₂. As shown in Figure S4, the diffraction peaks are in consistent with the standard pattern of hexagonal WSe₂ (JCPDS card No. 38-1388). The thickness obtained from the full width at half-maximum of (002) according to Scherrer equation is 1.2 nm, indicating 2 layers of Se-W-Se.³⁴ The XRD result indicates the same the crystal structure d-WSe₂ and r-WSe₂. Raman spectroscopy was also exploited to further obtain structural evidence of the catalysts (Figure S5). As both $E^{1}_{\ 2g}$ and A_{1g} modes are very closed to each other, at 250 and 253 cm⁻¹,²¹ accordingly, only one peak for WSe₂ is observed. The above Raman result for the two hierarchical structures further substantiates the same crystal structure. Two broad peaks at 1354.5 cm^{-1} and 1587.6 cm^{-1} correspond to the D and G band of the CFM. The intensity ratio of D and G bands (I_D/I_G) is 1.15. The presence of graphitic is expected to achieve a high conductive CFM substrate.³⁵

The d-WSe₂/CFM was directly used as hydrogen evolution cathode to highlight the merits of the novel architecture. The configuration of d-WSe₂/CFM electrode is shown in Figure S6. CFM, WO₃/CFM, WSe₂ NPs (Figure S7) and r-WSe₂/CFM electrodes were also tested as control. The electrochemical experiment was conducted in a standard three-electrode electrochemical cell setup in 0.5 M H₂SO₄ electrolyte. A resistance test was obtained (~8 Ω) via electrochemical impedance spectroscopy (EIS) and *iR* compensation was applied. Figure 3A shows the polarization curves at 5 mV s⁻¹ with current density normalized by geometric surface area. Initial cleaning of the electrocatalyst surface was performed by cycling

between 0–1.2 V vs. RHE at 100 mV s^{-1} for 100 cycles at 25 °C under Ar bubbling. Both d-WSe₂/CFM and r-WSe₂/CFM show onset HER activity near -150 mV vs. RHE, while CFM, WO₃/CFM and CVD synthesized WSe₂ NPs show negligible HER activity. A current density of 31.7 mA cm⁻² is achieved at -300 mV vs RHE for d-WSe₂/CFM, which is the highest value for WSe₂ catalyst to the best of our knowledge as shown in Table S1.^{12, 21, 36, 37} An enhancement in cathodic current density can also be observed for d-WSe₂/CFM as compared to that of r-WSe₂/CFM (Figure 3A), indicating that the dendritic structure is more active since its highly dense edge sites is beneficial for the hydrogen evolution. However, r-WSe2 is also a novel structure for WSe₂ and may be found application for other research fields. Tafel slope is associated with the elementary steps in HER. The first step of HER is a discharge step (Volmer reaction) in which protons are adsorbed to active sites on the surface of the catalysts and combined with electrons to form adsorbed hydrogen atoms.²¹ It is followed by a combination step (Tafel reaction) or a desorption step (Heyrovsky reaction). From the Tafel slope calculated (Figure 3B), we estimated the rate determining steps of our catalyst. As shown in Table S1, 80 mV dec⁻¹ and 163 mV dec⁻¹ were obtained for d-WSe₂/CFM and r-WSe₂/CFM , respectively. The high Tafel slope (163 mV dec⁻¹) of r-WSe₂/CFM, similar to the chemical exfoliated WSe₂ (120 mV dec⁻¹, ref. 36), indicates that the rate-determining step is the discharge step, with a very small surface coverage of adsorbed hydrogen. The significant decrease in Tafel slope can be observed for $d-WSe_2/CFM$ (80 mV dec⁻¹), which is attributed to the unique dendritic structure of WSe₂ that reduces free energy barrier of the discharge step.¹² The electrochemical double layer capacitance (EDLC) was employed to estimate the active surface areas of the 3D electrodes,³⁸ as shown in Figure S8. The EDLC of d-WSe₂/CFM is about 2.6 times larger than that of r-WSe₂/CFM, indicating a highly effective surface area of d-WSe₂. EIS was also conducted to study the electrode kinetics at -0.25 V vs RHE. The EIS results could well exhibit the advantage of the d-WSe₂/CFM quantitatively. As shown in Figure 3C, nyquist plots reveals a significant decrease in charge-transfer resistance (RCT) for d-WSe₂/CFM (~0.2 Ω) as compared to that of r-WSe₂/CFM (~1.2 Ω), WO₃/CFM (~610 Ω) and CFM (~260 Ω). The small resistances show the advantage of the facile approach for active electrocatalyst on conductive substrate, which enables simple and effective electrical integration that minimize Ohmic losses.³⁹ The HER catalytic activities of d-WSe₂/CFM, and r-WSe₂/CFM are believed associated with their diffierent morphologies and electronic properties, which play very important roles in the overall HER performance.³⁹ The assynthesized 3D dendritic WSe₂ electrode with a small Tafel slope, large available surface area as well as small resistances is a promising candidate for HER applications.



Figure 3. A) Polarization curves (after *iR* correction) obtained with several catalysts as indicated. B) Corresponding Tafel plots for r-WSe₂/CFM, d-WSe₂/CFM and Pt/C. C) EIS Nyquist plots collected at a bias voltage of -0.250 V vs RHE. D) Time dependence of current density under static overpotential of -0.215 V vs RHE. Inset is the enlargement of the area denoted by the dash circle.

Furthermore, two types of durability tests of d-WSe₂/CFM were also conducted. The CV test for 1000 cycles (Figure S9) indicated that excellent stability of the electrode. The SEM and TEM images of d-WSe₂/CFM after 1000 cycles were also obtained (Figure S10). In fact, the morphology and structure of d-WSe₂/CFM do not get obvious change after 1000 CV cycles, futher indicating the good stability of the catalyst. The other durability test, time dependence of current density at a constant potential for a period of time (Figure 3D) implied that the current density reach a constant after an acceptable slight decrease. Although a serrate shape of current was observed that is relative to the alternate processes of bubble accumulation and the bubble release.



Figure 4. Schematic illustration of electrochemical behavior of d-WSe₂/CFM and r-WSe₂/CFM for HER.

The electrochemical behaviors of d-WSe₂/CFM and r-WSe₂/CFM are illustrated in Figure 4. Electrons can transfer through the carbon nanofiber to WSe₂ catalyst that grown on the CFM.

Hydrogen ions at the active sites of WSe₂ catalyst are reduced by the transferred electrons, followed by release of hydrogen gas. For the d-WSe₂/CFM, the electrolyte containing hydrogen ions can access large amount of edge sites through the dendritic structure, leading to much more hydrogen bubbles released from the electrode. r-WSe₂/CFM exhibits a relatively poorer performance due to the less edge sites on the smooth leaves of WSe₂.

Conclusions

In summary, dendritic WSe₂ on conductive CFM was designed and synthesized by a diffusion-controlled CVD method. The d-WSe₂/CFM exhibits remarkable enhancement in HER performance due to the effectively exposed edge sites. Moreover, the much lower charge-transfer resistance of d-WSe₂/CFM, the high conductivity of carbon nanofiber and the formed 3D structure are experimentally verified and well correlated to the improvement of HER activity. Above all, a facile method for synthesizing 3D structural electrode was established. It will open up a new pathway for developing more efficient HER catalysts in the near future.

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Notes

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