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Supporting Information

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

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Experimental

Preparation of electrospun polyacrylonitrile nanofiber mats (PAN FM) and ammonium metatungstate hydrate contained PAN FM (W-PAN FM).

PAN FM were synthesized by electrospinning method. Typically, 3.86 g PAN powder was dissolved in 30 mL dimethyl formamide (DMF, 99.5%) under magnetic stirring to get a homogeneous solution. Therefore, the mass fraction of PAN in the DMF solution was 12 wt%. The solutions were transferred into a syringe with a stainless copper needle at the tip and then electrospun under a fixed voltage of 12 kV and the needle to collector distance was 12 cm with the flow rate at 0.01 mL min⁻¹. During electrospinning process the temperature was 25 ± 2 °C and the humidity was 45% RH. The electrospun nanofiber mats were collected onto a piece of irrotational aluminum foil. W-PAN FM were prepared by adding additional 0.384 g Ammonium metatungstate hydrate $((NH_4)_6H_2W_{12}O_{40}, 99.99\%, from Aldrich)$ powder in above PAN/DMF solution by electrospinning under the same condition. Finally, the mass fraction of $(NH_4)_6H_2W_{12}O_{40}$ in PAN FMs was 10 wt%.

Preparation of carbon nanofiber mat (CFM) and WO₃ contained CFM (WO₃/CFM).

The PAN FM and W-PAN FM obtained from electrospinning for 6 h were collected and peeled off from the aluminum foil, cut into pieces, placed into a boat, and put into a CVD furnace for heat treatment. Typically, the nanofiber mats were heated to 280 °C from room temperature within 1 h, and maintained for 6 h for the sufficient pre-oxidation of the nanofiber mats as well as the thermal decomposition of $(NH_4)_6H_2W_{12}O_{40}$ to form WO₃ nanoparticles (NPs). The furnace was then heated to 1000 °C within 2.5 h

and maintained at this temperature for another 8 h for the graphitization of the nanofiber mats under Ar flow (150 sccm). Finally, the products were cooled to room temperature under Ar atmosphere.

Preparation of dendritic WSe₂ on CFM (d-WSe₂/CFM) and rose-like WSe₂ on CFM (r-WSe₂/CFM).

W-PAN FM were placed carefully to the adjusted locations in the tube furnace to prepare WSe₂ with different morphology on CFM. Firstly, the process of pre-oxidation was the same as mentioned above. Secondly, 200 mg Se powder was placed upstream side of the furnace and heated at high temperature, then Ar gas was acted as the precursor carrier, and the pressure and flow rate were kept at 1 Torr and 150 sccm, respectively. The furnace was heated to 1000 °C within 2.5 h and maintained at this temperature for another 8 h for both the graphitization process and the growth of WSe₂. The Se precursor was kept around 300 °C during the growth process.

Preparation of WSe₂ NPs.

50 mg WO₃ NPs (99.9%, from Aldrich) were placed at the middle of the france. 200 mg Se powder was placed upstream side of the furnace at the same position as mentioned above. Firstly, the france was deaired by Ar for 30 mins and heated to 1000 °C from room temperature at 5 °C min⁻¹. Then Se powder was sublimated under high temperature and carried by As flow. The temperature was mantained for 1.5 h before cooled down to temperature. Finally, the WSe₂ NPs were obtained.

Electrochemical characterization.

3

The HER activities of electrodes were tested in 0.5 M H₂SO₄ (aq) electrolyte (deaerated by N₂). The catalysts (except for WSe₂ NPs and commerial Pt/C) were cut into a certain rectangle and fixed in a Teflon electrode clamp (Figure S6) and used as the working electrode, and the mass density of the d-WSe₂/CFM and r-WSe₂/CFM is about 2.2 to 2.5 mg cm⁻². The WSe₂ NPs and commerial Pt/C were cast on a glassy carbon disk of 3 mm diameter with a catalyst loading of 0.21 mg cm⁻². Using a Pt mesh as the counter electrode, and a saturated calomel electrode (*E*(RHE) = *E*(SCE) + 0.265 V after calibration) as the reference electrode. The performance of the hydrogen evolution catalysts was measured using linear sweep voltammetry beginning at +0.3 V and ending at -0.50 V vs RHE with a scan rate of 5 mV s⁻¹. The polarization curves were obtained after *iR*-compensation. Electrochemical impedance spectroscopy (EIS) was performed when the working electrode was biased at a constant -0.250 V vs RHE while sweeping the frequency from 5 MHz to 20 mHz with a 10 mV AC dither. Chronoamperometric response was required under static overpotential of 0.215 V vs RHE.

Characterizations.

The morphology of the prepared samples was observed by a JSM-6700F FE-SEM (JEOL, Japan) at an acceleration voltage of 3 kV. Transmission Electron Microscope (TEM) images and SAED patterns of all the samples were obtained with a JSM-2100 transmission electron microscopy (JEOL, Japan) at an acceleration voltage of 200 kV. X-ray photoelectron spectra of the samples were recorded using an X-ray Photoelectron Spectrometer (Kratos Axis Ultra DLD) with an aluminum (mono) Kα source (1486.6 eV). Raman spectra were recorded by a Renishaw inVia Raman microscope using a 633 nm

4

laser excitation source. The high-angle annular dark field scanning TEM (HAADF-STEM) images, EDS mapping images, and EELS spectra were recorded by a STEM (Tecnai G2 F30 S-Twin, Philips-FEI) at an acceleration voltage of 300 kV. X-ray diffraction (XRD) patterns of the hybrid films were obtained on a diffractometer (Bruker AXS D8) using the Cu K α radiation (k = 0.15418) with a 2 θ scan from 5 to 80 degree at a step of 0.02. All electrochemical studies were performed with an Autolab potentiostat/galvanostat (PGSTAT302N/FRA2) in a three-electrode configuration.

| | В | | | | Peak table | |
|-------------------------------|---------|---------|---------|---|------------|---------|
| | Element | Weight% | Atomic% | | Name | Atomic% |
| 在国家以下が自然が見た。 | ск | 59.11 | 91.30 | | W 4f | 1.28 |
| | οк | 3.02 | 3.51 | | Se 3d | 4.77 |
| | Se K | 10.25 | 2.41 | | C 1s | 83.16 |
| the stand of the stand of the | WМ | 27.00 | 2.79 | | N 1s | 4.99 |
| | Totals | 100.00 | | | 0 1s | 5.8 |
| | | | | - | | |
| 400 µm | | | | | | |

Figure S1. A) the spectrum of d-WSe₂/CFM obtained from the EDS analysis. B) The corresponding element content from image A. C) The atomic content in d-WSe₂/CFM

taken from XPS analysis.



Figure S2. A) Optical image of d-WSe₂/CFM electrode. B) The SEM image of the cross section for d-WSe₂/CFM electrode. TEM images of WO₃/CFM: C) before and D) after

selenization treatment.



Figure S3. TEM images of the typical A) d-WSe₂, B) TS-WSe₂, and C) r-WSe₂. D) SAED pattern obtained from r-WSe₂. E) HAADF-STEM image of a representative ST. F) High resolution element mappings taken on the certain position of Figure E.

Figures S3 A, B and C show the typical TEM images of d-WSe₂, TS-WSe₂ and r-WSe₂, respectively. Figure S3 D is the SAED pattern of the r-WSe₂, which reveals the 2H phase of WSe₂. Figures S3 E and F are the HAADF-STEM image and elemental mapping images of TS-WSe₂. The W and Se elements distribute uniformly either across the leaf or the branch.



Figure S4. XRD pattern of d-WSe₂/CFM and r-WSe₂/CFM.



Figure S5. Raman spectrum of d-WSe₂/CFM and r-WSe₂/CFM.



Figure S6. Photo of the working electrode for d-WSe₂/CFM.



Figure S7. The magnified SEM images of A) CFM and B) WO₃/CFM. C) SEM and D) TEM

images of WSe₂ NPs synthesized by a CVD method.

| Structure of WSe ₂ | Supporting | Tafel slope mV dec ⁻¹ | η (r | nV) | Exchange current | Reference |
|-------------------------------|--------------------------|-------------------------------------|--------------------------|--------------------------|----------------------|-----------------|
| | material | | @ 10 mA cm ⁻² | @ 30 mA cm ⁻² | mA cm ⁻² | |
| 2D nanotube | 3D carbon fibers | 99 | 350 | 400 | 0.003 | 12 |
| Vertically aligned 2D sheets | 3D carbon fiber paper | 77.4 | 300 | / | - | 21 |
| Exfoliated 2D sheets | / | 120 | 800 | / | 3.6×10 ⁻⁵ | 36 |
| 2D sheets | W foils | / | 350 | / | - | 37 |
| 3D dendritic | 3D carbon nanofiber mats | 80 | 228 | 295 | 0.015 | Present work |

Table S1. Comparisons of different WSe₂ and hybrid materials reported in the literatures.



Figure S8. CV curves of A) d-WSe₂/CFM and B) r-WSe₂/CFM electrode at various scan rates (0.5-5 mV s⁻¹). C) Linear fitting of the capacitive currents of the catalysts vs scan rates



Figure S9. CV plots of d-WSe₂/CFM electrode at 100 mV s⁻¹ for 1000 cycles in 0.5 M H_2SO_4 .



Figure S10. A) SEM and B)TEM images of d-WSe₂/CFM after 1000 cycles