Supporting Information

A metallic MoS₂ nanosheet array on graphene-protected Ni foam as a high efficient electrocatalytic hydrogen evolution cathode

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Materials and Methods

Synthesis of metallic MoS₂ nanosheets on Graphene/Ni foam

A modified CVD method was used to synthesize graphene layer on NF. ^{1,2} In brief, the three-dimensional NF (110 ppi; 1.5 mm thick, Changde lyrun new material Co. Ltd, China) was cut into pieces of $30 \times 10 \text{ mm}^2$, and then placed in the center of a tube furnace with a one-inch tube. Firstly, to eliminate the surface oxide layers, the NF was annealed at 1000 °C for 10 min with a gas flow of Ar (200 sccm) and H₂ (50 sccm), under ambient pressure. Then 5 sccm CH₄ was introduced into the reaction chamber for 5 min. Finally, the quartz tube was rapidly cooled down to room temperature under the protection of Ar (200 sccm) and H₂ (50 sccm) at a cooling rate of 100 °C min⁻¹.

1T-MoS₂/G/NF is prepared by a facile one-step solvothermal reaction. Briefly, 24 mg MoO₃ and 48 mg thioacetamide (C₂H₅NS) were dissolved in 20 mL ethanol to form a homogeneous solution. The solution was transferred into a Teflon-lined stainless steel autoclave. Lately, a piece of the pretreated G/NF was firstly wrapped by Teflon tape with an exposure area of ~ 2 cm², and then immersed into the mixed solution. After sonication for 30 min to form a homogeneous suspension around the NF, the autoclave was sealed and transferred into an oven for the solvothermal reaction at 200 °C for 18 h. After the autoclave was cooled down to room temperature naturally, the as-synthesized samples were taken out of the Teflon-lined autoclave and then were repeatedly rinsed with distilled water and ethanol and finally dried in a vacuum oven at 60 °C for 12 h.

In a control experiment, one piece of the as-prepared 1T-MoS₂/G/NF was further

annealed at 500 °C for 3 h in a gas flow of Ar (200 sccm) and H₂ (20 sccm) at a heating rate of 10 °C min⁻¹. We denote this sample as 2H-MoS₂/G/NF.

Characterization

The surface morphology and corresponding energy dispersive spectroscopy (EDS) mapping were captured on a scanning electron microscopy (FEI, Quanta 250 FEG). Further details of the nano-morphology including high-resolution TEM (HRTEM) images and the selected area electron diffraction (SAED) patterns were obtained by transmission electron microscopy (JEOL, JEM-2100F) at an acceleration voltage of 200 kV. Raman spectroscopy analysis was achieved by LabRAM Aramis at an excitation wavelength of 532 nm with 2 mW incident power (to avoid sample damage or laser-induced heating). The silicon line at 520.7 cm⁻¹ was used as the calibration reference. The crystal structures of the as-synthesized samples were identified by X-ray diffraction (Rigaku Dmax/2550VBz) using Cu-K α radiation (λ =0.15406 nm). Chemical configurations were characterized by XPS (Thermo Fisher Scientific, K-Alpha 1063) equipped with an Al-K α X-ray source (1486.6 eV). The binding energy calibrations were done by the C 1s peak to eliminate shifts in energy during analysis.

Electrochemical measurements

All the electrochemical measurements were performed with a standard three-electrode configuration in N₂-saturated 0.5 M H₂SO₄. The as-prepared MoS₂ decorated NFs were directly used as the working electrode, an Ag/AgCl (KCl saturated) electrode was used as the reference electrode, and a graphite rod as the counter electrode. Linear sweep voltammetry was recorded with a scan rate of 5 mV/s. The cyclic stability test was carried out by taking

continuous cyclic voltammograms with a scan rate of 50 mV/s. Electrochemical impedance spectroscopic measurements were conducted at an overpotential of 200 mV from 100 kHz to 0.01 Hz. The experimental impedance data were then fitted to a simplified Randles circuit to extract the series and charge transfer resistances. LSV and CVs were recorded by the CHI660E electrochemical workstation. EIS was conducted by the Zennium, Zahner electrochemical analyzer. All potentials were calibrated to a reversible hydrogen electrode (RHE = Ag/AgCl + 0.21 V), and all polarization curves were recorded with iR correction.

The electro-catalytic performance of powdery MoS2 nanosheets loaded onto a glassy carbon electrode (GCE, 3 mm diameter) was measured according to previous literature reports.⁹ 4 mg of these MoS₂ nanosheets were dispersed in a solution (1 mL) composed of 3:1 (v/v) distilled water and ethanol containing Nafion (100 μ L, 5% wt) to form a homogeneous emulsion by sonication. Then, the catalyst was dropped on the surface of the glassy carbon electrode with a mass loading of 0.285 mg cm⁻².



Fig. S1 The diffraction patterns of the MoS₂ nanosheets scratched down from 1T-MoS₂/G/NF and 2H-MoS₂/G/NF.

After carefully decomposing the XRD pattern of $1T-MoS_2/G/NF$, a little amount of Ni_xS_y (Ni_3S_2 and NiS_2) with low crystallinity have been formed after the solvothermal synthesis. Moreover, a little amount of MoO_3 stems from the residual MoO_3 precursor can also be found in the composite.

 Ni_3S_2 and NiS_2 with low crystallinity have already been proved to be electroactive in HER process. ³⁻⁶ To further prove the hypothesis that NixSy with low crystallinity would contribute to the HER activity, a sample prepared in the same procedure to $1T-MoS_2/G/NF$ but with a pristine Ni foam (without the graphene layer) substrate. And we donated this sample as $1T-MoS_2/NixSy/NF$. Then we measured the HER activity of this sample. The polarization curves of $1T-MoS_2/NixSy/NF$ and $1T-MoS_2/G/NF$ with iR correction are shown below:



Fig. S2 Polarization curves of 1T-MoS₂/G/NF, 1T-MoS₂/NixSy/NF with iR correction.

Though 1T-MoS₂/NixSy/NF exhibits higher HER activity, the nickel foam substrate turns vulnerable to chemical corrosion and become unstable in acidic solutions. The long-term chronoamperometry measurement was performed to check the stability of 1T-MoS₂/NixSy/NF, as shown below.



Fig. S3 the time-dependent current density curve for 1T-MoS₂/NixSy/NF at an overpotential of 180 mV.

The volumetric current density is the current density that takes the thickness of the nickel foam into account. The thickness of the nickel foam is 1.5 mm. The large pores (ca. 0.5 ± 0.1 mm) dominate the three dimensional structure and the porous nickel foam is isotropous in the distribution of the strut interconnections. So the volumetric current density, if there is, is when the thickness if also normalized to unit length. And the new plotted polarization curves of 1T-MoS₂/G/NF, 2H-MoS₂/G/NF, G/NF, NF with iR correction when volumetric current density is shown below.



Fig. S4 Polarization curves of 1T-MoS₂/G/NF, 2H-MoS₂/G/NF with iR correction (the specific current density normalized to volumetric current density).



Fig. S5 The electrochemical double layer capacitance was probed by cyclic voltammetry at nonfaradaic potentials to estimate the effective electrode surface area for (a) 1T-MoS₂/G/NF and (b) 2H-MoS₂/G/NF.

The electrochemically active surface area (ECSA) was measured from electrochemical double layer capacitance by cyclic voltammetry at nonfaradaic potentials. The calculation of ECSA is based on the following equation: ⁷

$$ECSA = C_{dl}/C_s \tag{1}$$

Here we use a general specific capacitance of 0.035 mF cm⁻² in 0.5 M H₂SO₄ based on typical values reported for metal electrodes. ⁸ The extracted double-layer capacitances for $1T-MoS_2/G/NF$ and $2H-MoS_2/G/NF$ electrodes from **Fig.8b** are 14 mF and 4 mF, respectively. So the calculated ECSA of these samples are:

1T-MoS₂/G/NF: A_{ECSA} =400 cm² 2H-MoS₂/G/NF: A_{ECSA} =114 cm² And the specific current density normalized to electrochemical surface area plotted against the potential applied onto the $1T-MoS_2/G/NF$, $2H-MoS_2/G/NF$, G/NF, NF electrodes with iR correction is shown below.



Fig. S6 Polarization curves of 1T-MoS₂/G/NF, 2H-MoS₂/G/NF with iR correction (the specific current density normalized to electrochemical surface area).



Fig. S7 The diffraction patterns of the pure MoS₂ nanosheets prepared without the addition of G/NF substrates during the solvothermal synthesis.



Fig. S8 Polarization curves of the pure phase of 1T-MoS₂ and 2H-MoS₂ nanosheets with iR correction.



Fig. S9 Nyquist plots of the pure phase of $1T\text{-}MoS_2$ and $2H\text{-}MoS_2$ nanosheets

Table S1	Comparison	of HER	catalytic	performance	of	1T-MoS ₂ /G/NF	with	other
MoS ₂ based powdery catalysts								

	onset							
Catalyst	Morphology	Electrolyte	overpotential	η(mV)@ j =	Tafel slope	Ref.		
			(mV)	$10 \mathrm{mA~cm}^{-2}$	$(mV dec^{-1})$			
1T-MoS ₂ /Graph						our		
ene/Ni foam	nanosheets	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	89	-117	38	work		
defect-rich								
MoS_2	nanosheets	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	120	-180	50	9		
Oxygen-incorpo								
rated MoS ₂	nanosheets	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	120	-180	55	10		
MoS ₂								
(H ₂ teatment)	nanofilm	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	300	~-600	147	11		
Co-MoS ₂ /C	nanoparticles	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	90	~-130	50	12		
mesoporous								
MoS_2	nanosized	$0.5 \text{ M H}_2 \text{SO}_4$	~150	~-250	50	13		
metallic MoS ₂	nanosheets	0.5 M H ₂ SO ₄	~150	-187	43	14		
MoSx-								
Graphene	nanoparticles	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	120	~-180	43	15		
MoS ₂ /graphene								
oxide	nanosized	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	~180	-220	59	16		
Conducting								
MoS_2	nanosheets	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	100	-200	40	17		
Cracked								
$1T-MoS_2$	nanosheets	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	113	-156	43	18		
2H-MoS ₂ /SWN								
Т	nanofilm	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	109	-150	41	19		
FeS ₂ -MoS ₂	nanoflower	0.5 M H ₂ SO ₄	100	-136	82	20		
1T/2H-MoS ₂	nanostructure	0.5 M H ₂ SO ₄	120	-220	61	21		
2H/1T-MoS ₂	nanosheets	0.5 M H ₂ SO ₄	129	-203	60	22		
N doped MoS ₂	nanosheets	0.5 M H ₂ SO ₄	~100	-168	41	23		

Table S2Comparison of HER performance of 1T-MoS2/G/NF with other MoS2decorated self-supported catalysts

			onset			
Catalyst	Morphology	Electrolyte	overpotential	η(mV)@ j =	Tafel slope	Ref.
			(mV)	10mA cm ⁻²	$(mV dec^{-1})$	
1T-MoS ₂ /Graph						our
ene/Ni foam	nanosheets	$0.5 \mathrm{~M~H_2SO_4}$	89	-117	38	work
MoS ₂ /graphite						
paper	flakes	$0.5 \mathrm{~M~H_2SO_4}$	150	-350	54	24
MoS ₂ /carbon						
cloth	nanosheets	$0.5 \mathrm{~M~H_2SO_4}$	115	-150	50	25
MoS ₂ /Graphene/						
Ni foam	nanoparticles	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	~110	-160	43	26
MoS ₂ /						
rGO/Mo	nanosized	$1 \text{ M H}_2 \text{SO}_4$	~120	~-180	52	27
MoS ₂ /						
nanoporous gold	monolayer flakes	$0.5 \mathrm{~M~H_2SO_4}$	120	-226	46	28
Superaeropho-bi						
c MoS ₂ film	nanosized	$0.5 \mathrm{~M~H_2SO_4}$	150	~-200	51	29
LiMoS ₂ / carbon						
cloth	nanofilms	$0.5 \mathrm{~M~H_2SO_4}$	113	~-200	44	30
LiMoS ₂ / carbon						
fiber paper	nanoparticles	$0.5 \mathrm{~M~H_2SO_4}$	~90	-118	62	31
MoS ₂ /Graphene						
framework	nanoparticles	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	107	-210	86.3	32

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