Electronic Supplementary Information

Beneficial Restacking of 2D Nanomaterials for Electrocatalysis: A Case of MoS₂ Membranes

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Experimental Section

*Preparation of layered MoS*₂ *membrane.*

The layered MoS₂ membrane was prepared via vacuum filtration of chemically exfoliated MoS₂ nanosheets. Chemically exfoliated MoS₂ was synthesized by lithium intercalation into MoS₂ powder. Briefly, 3 g of MoS₂ powder (Alfa Aesar) was dispersed in 20 mL of anhydrate n-hexane solution (Sigma-Aldrich) in Argon atmosphere. Afterwards, 10 mL of 1.6 M *n*-butyllithium n-hexane was added dropwise at 0 °C. This suspension was then heated and kept refluxing for 48 h under Ar. The mixture was filtrated and washed with anhydrate n-hexene to remove the excess organolithium regent and then dry in a vacuum oven at room temperature for 0.5 h to obtain lithiated Li_xMoS₂. Then, the lithiated Li_xMoS₂ product was exfoliated for 20 min and centrifuged at 8,000 rpm (RCF = 8,801) to remove unexfoliated nanosheets. A homogeneous MoS₂ dispersion (ca. 0.4 mg/mL) was yielded. The layered MoS₂ membrane was assembled by vacuum filtration on a porous PVDF substrate (Merck). The vacuum was disconnected immediately once the water on the MoS₂ membrane surface was drained, yielding a hydrated MoS₂ membrane.

*Modulation of the MoS*₂ *interlayer spacing.*

The hydrated MoS_2 membrane was used as a precursor to prepare interlayer-expanded- MoS_2 membrane. Typically, the hydrated MoS_2 membranes were first immersed into a 0.065M ionic liquid (IL) aqueous solution (i.e. EMIM BF₄ and BMIM BF₄, 99.0%, Sigma-Aldrich). Subsequently, the interlayer-expanded MoS_2 membranes were yielded after placing in a thermal mixer for 24 h with a frequency of 350 rpm in room temperature. Afterwards, the IL exchanged MoS_2 membrane was dried by vacuum evaporation at room temperature for 24 h to acquire the IL

modulated MoS_2 membrane. Finally, the IL modulated MoS_2 membranes were thoroughly exchanged with 0.5 M H₂SO₄ for at least 24 h to completely remove IL. These membranes are labelled as LS1-MoS₂ and LS2-MoS₂ for the membranes modulated using EMIM BF₄ and BMIM BF₄, respectively. The TS-MoS₂ was prepared by vacuum drying of the hydrated MoS₂ membrane without exchanging with IL solutions and also immerged into 0.5 M H₂SO₄ for at least 24 h. For comparison, the bulk-MoS₂ powder was treated using the same procedures.

Physical characterization

X-ray diffraction (XRD) spectrum were scanned on a Bruker D8 Advance diffractometer (40 kV, 40 mA, Cu K α radiation, $\lambda = 1.5418$ Å). The interlayer spacing of the MoS₂ membranes are calculated in accordance to the Bragg's formula: $2d^*\sin\theta = n^*\lambda$. Raman spectrum were recorded using a Renishaw inVia system with a 532 nm laser beam. The attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrum were measured on a Bruker Alpha II spectrometer, and a blank PVDF membrane is used for the background scanning. A blank PVDF membrane was scanned as a control. Scanning electrode microscopy (SEM) images were captured on a FEI Quanta 200 ESEM FEG microscope. Energy Dispersive X-Ray Spectroscopy (EDS) profiles were recorded by an EDAX TEAM[™] EDS System. Atomic force microscopy (AFM) scanning was conducted on an Asylum Research MFP3D using a silicon tip. X-ray photoelectron spectroscopy (XPS) data was acquired using a VG ESCALAB220i-XL spectrometer equipped with a hemispherical analyser. The incident radiation was monochromatic Al K α X-rays (1486.6 eV) at 220 W (22 mA and 10kV). Survey (wide) and high resolution (narrow) scans were taken at analyser pass energies of 100 eV and 20 eV, respectively. A low energy flood gun was used to compensate the surface charging effect.

Electrochemical measurements

All the electrochemical measurements were conducted using a three-electrode configuration setup on an electrochemical workstation (Bio-logical VSP-300). The electrochemical cell for measuring HER performance of stacked MoS₂ membranes is schematically presented in Scheme S1. The specific MoS₂ film was physically laid on a glassy carbon electrode with a diameter of 6 mm as the working electrode. Then this electrode was assembled into a T-shape cell (Scheme S1), in which the MoS₂ film was firmly sandwiched by a graphite rod electrode (counter electrode) and a glassy fibre separator. The electrolyte was injected into the chambers of this cell, and an Ag/AgCl/KCl (saturated) reference electrode was immersed into this electrolyte. The purpose of this design is to ensure that the MoS₂ membrane is tightly connected during the reaction.



Scheme S1. (a) A photo of as-prepared TS-MoS₂ membranes. (b) The setup of electrochemical cell (T-shape cell) for measuring the HER performance of stacked MoS₂ membranes.

HER tests were performed in N₂-saturated 0.5 M H₂SO₄ electrolyte with IR-correction. The linear sweep voltammetry (LSV) curves were obtained at the scan rate of 5 mV/s. Cyclic voltammetry (CV) was performed in the potential region of 0.076-0.176 V verse RHE at various scan rate to estimate the C_{dl} . The Ag/AgCl/KCl (saturated) reference electrode was calibrated with respect to reversible hydrogen electrode (RHE).^[1] The details of this calibration are shown in Figure S8.

SI1 Morphologies of MoS₂ nanosheets and membranes



Figure S1. Morphological characterization of MoS₂ membranes after the removal of ionic liquids. (a, b) AFM image and corresponding height profile (red line in (a)) of exfoliated MoS₂. (c-e) SEM images of cross sections of (c) TS-MoS₂, (d) LS1-MoS₂, (e) LS2-MoS₂. The porosities of those MoS₂ membranes are estimated in the range of 79% to 84% based on the bulk density of MoS₂ (5.06 g cm⁻³). The membranes with different interlayer spacing have similar thickness because most volume is occupied by voids (79%-84% porosity).



Figure S2. SEM image of bulk-MoS₂ powder.

SI2 Spectrum characterizations



Figure S3. XRD patterns of (a) XRD profiles of the TS-, LS1- and LS2-MoS₂ and bulk MoS₂ powder. The interlayer spacing of TS-, LS1- and LS2-MoS₂ are 0.62, 0.97 and 0.98 nm, respectively. The full width at half maximum (FWHM) values of the (002) peaks are 1.38, 1.36 and 1.10 degrees for TS-, LS1- and LS2-MoS₂, respectively. (b) bulk MoS₂ powder treated by the same procedure of preparing IL modulated MoS₂ membranes, and (c) ionic liquid modulated MoS₂ membranes before 0.5 M H₂SO₄ electrolyte exchange.

The different interlayer spacing of MoS₂ nanosheets is further supported by the shift of (002) peak in the X-ray diffraction (XRD) patterns. As shown in Figure S3a, the interlayer spacing of TS-MoS₂ is calculated to be 0.62 nm, consistent with the minimum interlayer spacing of MoS₂ bulk crystals^[2] While the membranes composed of loosely stacked MoS₂ nanosheets exhibit an enlarged interlayer spacing of 0.97 for LS1-MoS₂ and 0.98 nm for LS2-MoS₂.^[3] Notably, the full width at half maximum (FWHM) as well as the intensities of the (002) diffraction peak of the TS-, LS1and LS2-MoS₂ are close to each other (1.38, 1.36 and 1.10 degrees for TS-, LS1- and LS2-MoS₂, respectively), implying that the crystallinity of the MoS₂ nanosheets is nearly unchanged after the expansion of the interlayer spacing.^[4] To reveal the restacking inhabitation mechanism of MoS₂ nanosheets, we first compare the XRD patterns of the pristine bulk MoS₂ before and after the treatment of ionic liquid using the same procedure as preparing LS1- or LS2-MoS₂. There is no observable difference for the (002) peaks in their XRD patterns (Figure S3b), suggesting that ionic liquid cannot expand the interlayer spacing of the bulk MoS₂ under such an ambient condition. In the XRD patterns of the MoS₂ membranes with interlayer ionic liquid (before the exchange with electrolyte), the (002) peak is around 8.8 degrees, corresponding to the interlayer spacing of 0.98-0.99 nm (Figure S3c). This confirms that the restacking of MoS₂ nanosheets is effectively inhibited by ionic liquids. Moreover, the interlayer spacing was nearly unchanged after the following electrolyte replacement (step vi in Figure 1a of maintext), as concluded from the closely positioned (002) peak is achieved by replacing the interlayer water molecules with non-volatile ionic liquid ions.

To inspect the uniformity of the MoS_2 samples and exclude the interference of other factors that can affect HER activity except for the interlayer spacing, the intrinsic properties of these MoS_2 membranes were further characterized by spectroscopy studies (**Figures S4**-S6, and Tables S1-S2 in ESI).



Figure S4. Raman spectra of TS-, LS1-, LS2-MoS₂ and bulk MoS₂ powder.

The Raman spectrum is adopted to study the polymorph phase and defectiveness of the MoS₂ membranes. As shown in Figure S4, the Raman spectrum of the pristine bulk-MoS₂ powder has two sharp peaks at 381.9 and 404.8 cm⁻¹, corresponding to the in-plane E^{1}_{2g} and out-of-plane A_{1g} modes, respectively. In contrast, the Raman peaks of E^{1}_{2g} and A_{1g} models of the TS-, LS1- and LS2-MoS₂ are much weaker along with the emergence of J_1 , J_2 and J_3 peaks at 150.3, 216.5 and 326.1 cm⁻¹, respectively, indicating the formation of metallic 1T-phase MoS₂ after lithiation process.^[5] More importantly, the relative strength of A_{1g} and J_1 peaks in the TS-, LS1-, and LS2-MoS₂ are close to each other, suggesting the consistency of phases and crystallinity of these MoS₂ membranes. This agrees with the above observation from the XRD patterns, of which the FWHM



values and the intensities of (002) peaks are similar for TS-, LS1- and LS2-MoS₂ (Figure S3a).^{[5–}

Figure S5. XPS spectra of the MoS_2 samples. (a) the XPS survey spectrum in the whole measurement range, and the carbon peak at ca. 285 eV comes from the internal standard; (b) High-resolution Mo XPS spectra of the TS-, LS1-, LS2-MoS₂ and bulk MoS₂ powder. (c) High-resolution sulphur 2*p* XPS spectra; (d) High-resolution boron 1*s* XPS spectra.

Table S1. The assignment of XPS peaks in accordance to NIST X-ray Photoelectron Spectroscopy

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Binding energy (eV)	Element and line
538	Oxygen 1s
412	Molybdenum 3p _{1/2}
395	Molybdenum 3p _{3/2}
284	Carbon 1s (from internal standard)
229	Molybdenum 3d and Sulphur 2s
162	Sulphur 2p

Table S2. The analysis of the XPS results.

Sampla	Element content from whole survey (at.%) ^a			$1T-MoS_2$ content (%)		
Sample	Mo (229 eV)	S (162 eV)	O (532 eV)	Mo 3d _{3/2}	Mo 3d _{5/2}	
TS-MoS ₂	14.9	35.3	49.8	60.6	58.2	
LS1-MoS ₂	13.7	30.9	55.4	59.1	60.1	
LS2-MoS ₂	14.2	30.8	55.0	56.2	57.4	
Bulk-MoS ₂	23.2	43.9	32.9	0	0	

^a The carbon signal from internal standard is excluded. The S content of LS1- and LS2-MoS₂ dropped due to the H_2SO_4 inside the membrane.

The X-ray photoelectron spectroscopy (XPS) was employed to analyse the chemical and phase compositions of these MoS₂ membranes. As shown in Figure S5b, the high-resolution Mo 3d XPS spectrum of the 2H bulk MoS₂ powder displays two peaks at 233.0 eV (Mo $3d_{3/2}$) and 229.8 eV (Mo $3d_{5/2}$). Notably, the corresponding peaks of the TS-, LS1- and LS2-MoS₂ shift to the lower binding energy. These peaks can be fitted into two distinct species of MoS₂, i.e. 1T-phase (232.3 and 229.0 eV) and 2H-phase (233.0 and 229.8 eV).^[8,9] A quantitative analysis based on the peak area of Mo $3d_{5/2}$ shows that the TS-, LS1- and LS2-MoS₂ have very close 1T-MoS₂ content of 58 \pm 2% (Table S2).^[10,11] Similar results can also be obtained from the analysis of S 2p peaks (Figure S5c). Furthermore, the absence of both N 1s (Figures S5a) and B 1s (Figure S5d) signals in the XPS spectra confirms that both cations (EMIM⁺ or BMIM⁺) and anion (BF4⁻) are undetectable in the LS1- and LS2-MoS₂ after the electrolyte exchange.^[12]



Figure S6. ATR-FTIR spectrum of (a) the TS-, LS1- and LS2-MoS₂, (b) blank PVDF membrane and (c) unnormalized spectrum showing the absolute transmittance of a blank PVDF and the TS-MoS₂ membrane after deducing the blank PVDF membrane as the background. All MoS₂ membranes were not peeled off from the PVDF substrate and directly used for testing. It can be seen from (c) that the signal contributed by PVDF is ignorable in the TS-MoS₂ membrane. This is also similar as other MoS₂ samples. Thus, the ATR-FTIR spectra of the MoS₂ samples in (a) reflect the signal from MoS₂ nanosheets and the exchanged electrolytes inside the membrane.

The attenuated total reflection-Fourier-transform infrared spectroscopy (ATR-FTIR) was used to further probe whether the ionic liquid molecules have been completed removed in LS1- and LS2-MoS₂. As shown in Figure S6, all the ATR-FTIR spectra of TS-, LS1- and LS2-MoS₂ exhibit similar vibration peaks in the wavenumber ranging from 400 to 3,800 cm⁻¹, which are also consistent with the IR spectrum of MoS₂.^[13,14] No C-H stretching vibration peaks (2800-3200 cm⁻¹) can be detected in the ATR-FTIR spectra of LS1- and LS2-MoS₂, verifying that the ionic liquid cations, i.e. EMIM⁺ and BMIM⁺ have been completely removed.^[15,16] The examinations of XRD, Raman, XPS, and ATR-FTIR confirm that all the TS-, LS1- and LS2-MoS₂ show nearly identical chemical compositions, phase distributions and crystallinities. The above results in

together imply that the interlayer spacing is the most critical factor that causes the different HER performance of TS-, LS1- and LS2-MoS₂.



Figure S7. Energy Dispersive X-Ray Spectroscopy (EDS) profiles of the cross section (Figure S1c-1e) of dry-, E- and B-MoS₂ (a, b and c, respectively). The atomic percentages of elements are listed on the top right corner. In all the samples, the elements (the energy for B, C, N and F in EDS are 0.18, 0.28, 0.39 and 0.68 keV, respectively) from ionic liquids are below detection limitation, indicating the ignorable residual of ionic liquid after electrolyte exchange.

SI3 Additional electrochemical measurements



Figure S8. Potential calibration of the Ag/AgCl electrode in 0.5 M H₂SO₄ solution. In all measurements, the reference electrode was calibrated with respect to reverse hydrogen electrode (RHE). The calibration was conducted in a high purity hydrogen saturated electrolyte using a Pt net as the working electrode, with the protection of hydrogen atmosphere. Cyclic voltammetry was run at the scan rate of 1.0 mV/s, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reaction. In 0.5M H₂SO₄, $E_{RHE} = E_{Ag/AgCl} + 0.173$ V.



Figure S9. (a-c) The typical CV curves of TS-MoS₂ (a), LS1-MoS₂ (b) and LS2-MoS₂ (c) at the scan rates from 20 to 200 mV s⁻¹. (d) Linear fitting of current density verse CV scan rates to estimate the C_{dl} . Note: all the current values in these figures are normalized by geometric areas. The ECSA is calculated in accordance to a recent issued standard method,^[17] *i.e.*, a series of CV sweepings using exactly the same conditions were carried out on a bare glassy carbon electrode to estimate the electrochemical double layer capacitance on a flat surface (*i.e.* reference EDLC). Accordingly, the reference EDLC in our case is measured to be 0.024 ± 0.002 mF cm_{ECSA}⁻². The ECSAs are calculated by dividing the slopes from (d) by the reference EDLC.

Sample	Interlayer spacing [nm]	Onset overpotential [mV vs. RHE] ^{a)}	Tafel slope [mV dec ⁻¹]	$\frac{\text{ECSA}}{\text{cm}_{\text{geo}}^{-2}} [\text{cm}^2 \cdot $	Conductivity [S m ⁻¹]
TS-MoS ₂	0.62	78 ± 1	80.2 ± 1.0	342 ± 10	132.1 ± 1.8
LS1-Mo \overline{S}_2	0.97	114 ± 2	97.1 ± 0.5	571 ± 52	135.2 ± 5.8
$LS2-MoS_2$	0.98	126 ± 1	108 ± 6	579 ± 20	154.8 ± 3.6

Table S3. Summary of the electrochemical performance and properties of the TS-, LS1- and LS2-MoS₂ membranes.

^{a)} The "onset overpotential" in this work refers to the absolute value of potential where the absolute geometric current density is 0.1 mA cm⁻².



Figure S10. The HER stability of TS-MoS₂ in T-shaped cell measured at -240 mV vs. RHE by chronoamperometry. The HER polarization current gradually decreases due to the generation of hydrogen bubbles which partially blocks the nanochannels in TS-MoS₂ membrane.

Catalysts	Preparation	Polymorph	Interlayer spacing (nm)	Onset Overpotential (mV)	j = 10 mA cm ⁻² overpotential (mV)	Tafel slope (mV dec ⁻¹)	Ref
Nanoplates	Solvent- dependent	2Н	0.65	90	200*	53	[18]
Double-gyroid	Electrodeposition	2H	0.66	150-200	280*	50	[19]
3D nanospheres	Hydrothermal	2H	0.707	110	300*	72	[20]
Hierarchical microboxes	Hydrothermal	2Н	0.65	300	480*	134	[21]
Hollow spheres	Hydrothermal	2H	0.78	112	214	74	[22]
Nanoflowers	Hydrothermal	2Н	0.80	130	280*	52	[23]
Edge-terminated	Microwave	2Н	0.94	103	150*	49	[3]
Defect-rich	Hydrothermal	2Н	0.63	120	200*	50	[24]
Monolayer	Hydrothermal	2H	0.69	100*	250*	75	[25]
Multi-hierarchy monolayer	CVD	2H/1T	N/A	100	176	73	[26]
Chemical activated	CVD and Plasma	2Н	N/A	250*	540*	138	[27]
1T-nanoflowers	Hydrothermal	1T	N/A	171	252	45	[28]
Sulfur-rich nanoflowers	Hydrothermal	2Н	0.67	117	255	77.7	[29]
Cracked MoS ₂ powder	Exfoliating	1T	0.62	113	156	42.7	[30]
$\begin{array}{l} Stepped & edge \\ MoS_2 \end{array}$	Microwave	2Н	0.65	90*	104	59	[31]
Vertical MoS ₂	CVD	2H	0.63	200*	> 400	115	[32]
TS-MoS ₂ Membrane	Exfoliating- restacking	1T	0.62	78	240	80	This work
LS1-MoS ₂ Membrane	Exfoliating- restacking	1T	0.97	114	280	97	This work

Table S4. The comparison of HER performance of the electrocatalysts which are only composed of MoS_2 .

*These are approx. values derived from the LSV diagrams.

HER performance of TS-MoS₂ in comparison to state-of-art MoS₂ catalysts.

We acknowledge that the comparison of the specific electrocatalytic activity between $TS-MoS_2$ membrane and other catalysts would be made preferably on the basis of the current normalized by ECSA, which can exclude impacts from different surface area, catalyst loading, etc. However, the ECSA value was not reported in most of the previous studies. In this work, the HER performance of the TS-MoS₂ is compared to the state-of-the-art pure-MoS₂ electrochemical catalysts based on the geometric current densities that has been widely used in the previous literature. The key criteria for evaluating HER activity are listed in Table S3. The TS-MoS₂ exhibits an onset overpotential of 78 mV, which is lower than all the other pure-MoS₂ electrode materials. On the other hand, the Tafel slope (80 mV dec⁻¹) and j = 10 mA cm⁻¹ potential (240 mV) of the TS-MoS₂ are comparable to those of the state-of-art pure-MoS₂ electrochemical catalysts. The excellent performance is ascribed to the high activity sites at the edge of the firm and interlocked stacked nanosheets, which is supported by our DFT simulation as well as a recent experiment-simulation study on the HER performance of a hydrothermal synthesized MoS₂ with interlocked (a.k.a. stepped) edge sites.^[31] The TS-MoS₂ thus shows the potential in massive production of high-performance 2D materials based HER catalysts.

SI4 Simulation Section

Density functional theory calculations were performed using the plane-wave basis sets in Vienna ab initio simulation package (VASP).^[33] The ion–electron interaction was realized by the projected-augmented wave (PAW) method.^[34] Generalized gradient approximation Perdew–Burke–Ernzerhof (PBE-GGA) was adopted to express the exchange-correlation functional.^[35] The convergence threshold was 10⁻³ eV and 0.01 eV Å⁻¹ in energy and force, respectively. The energy cut-off for the plane-wave basis was set to 300 eV. DFT+D3 method was used to describe the van der Waals correction.^[36] The HER performance of MoS₂ was investigated by calculating the reaction Gibbs free energy for hydrogen adsorption (ΔG_H):^[37,38]

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T\Delta S$$

where ΔE_H is the adsorption energy of hydrogen atom, ΔE_{ZPE} is the zero-point energy difference between the adsorbed state and gas phases, and $T\Delta S$ is the gas-phase entropy contribution of a hydrogen molecule at 298 K.

The DFT simulation on the electronic structures of MoS_2 planar (Figure S11) indicates that the increase of the interlayer distance results in a dramatic decrease of isosurface (Table S5), suggesting that the interlayer electronic interactions between MoS_2 nanosheets be weakened as the expansion of interlayer spacing.



Figure S11. The cross-sectional view of MoS₂ structures at the nanosheet planar.

Interlayer spacing (nm)	Interlayer binding energy (eV)	Isosurface value (10 ⁻⁵ e bohr ⁻³)	d _{Mo-S} 1 (Å)	d _{Mo-S} 2 (Å)
0.62	-2.18	25	2.422	2.426
0.75	-0.01	3	2.430	2.427
0.85	-0.005	2	2.428	2.472
0.97	-0.002	2	2.427	2.426

Table S5. The dependence of MoS₂ properties on the interlayer spacing.

The cross-sectional view of the MoS_2 structures at nanosheet edges is shown in Figure S12, which is used for the DFT simulation of the hydrogen adsorption free energy in the main text. The bond length of Mo-S (edge) before and after hydrogen adsorption are summarized in Table S6. The trend of the change of bond length as the expansion of interlayer spacing is in agreement with the Mo-S (planar) bond lengths shown in Table S5. These results again indicate that the change of hydrogen adsorption free energy (Figure 3c of the maintext) is ascribed to the change of electronic interactions between MoS_2 nanosheets.





Figure S12. The cross-sectional view of MoS₂ crystal structures at the nanosheet edges.

Interlayer spacing (nm)	d _{Mo-S} (Å)	d _{Mo-S} after H adsorption(Å)
0.62	2.342	2.515
0.75	2.348	2.531
0.85	2.347	2.529
0.97	2.345	2.520

Table S6. The bond lengths of Mo-S in the edge site before and after H adsorption.

We noticed that a previous DFT simulation ^[7] suggests that the expansion of MoS_2 interlayer spacing weaken the adsorption of H* (increased ΔG_H), which appears to be opposite to our DFT simulation results shown in Figure 3c in the main text. The different trend from the DFT simulations can be ascribed to the difference in the MoS₂ polymorphs and stacking modes used in the simulations. In our DFT simulation, the MoS_2 nanosheets are 1T-phase and stacked in an interlocked mode to best match with the real structure of our experimental samples. In contrast, in the previous work,^[7] the MoS_2 nanosheets are 2H-phase and neatly packed with all the edges well aligned. The different results further suggest that the stacking model of MoS_2 nanosheets could have a significant effect on their electronic and electrocatalytic properties.

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