## **Electronic Supplementary Information**

## Synergy between active sites and electric conductivity of molybdenum sulfide for efficient electrochemical hydrogen production

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**Figure S1.** SEM images CNT (a), M300 (b), CNT modified M300 (c-g) and CNT modified M300 after 19 h electrochemical measurement under -179 mV vs RHE (h). Scale bars of a-c and h 500 nm. Scale bars of d, e, f and g, 2 μm, 2 μm, 500 μm and 1mm, respectively.



Figure S2. SEM images of M80 (a1 and a2), M300 (b1 and b2), M500 (c1 and c2) and M700 (d1 and d2).

Scale bars of a1, b1, c1 and d1, 5  $\mu m.$  Scale bars of a2, b2, c2 and d2, 1  $\mu m.$ 



**Figure S3.** TEM images of M80 (a1 and a2), M300 (b1 and b2), M500 (c1 and c2) and M700 (d1 and d2). HRTEM images of M80 (a3), M300 (b3), M500 (c3) and M700 (d3). Scale bars of a1, b1, c1 and d1, 100 nm. Scale bars of a2, b2, c2 and d2, 50 nm. Scale bars of a3, b3, c3 and d3, 20 nm.



**Figure S4.** SAED patterns of M80 (a), M300 (b), M500 (c) and M700 (d) correspond to c1, c2, c3 and c4 in Fig. 1, respectively. The vaguely bright circles in a and b indicate amorphous structure of M80 and M300. The bright dots in c and d indicate crystallized structure of M500 and M700.



Figure S5. Mo 3d XPS spectra of MoS<sub>x</sub>.

![](_page_5_Figure_2.jpeg)

![](_page_6_Figure_0.jpeg)

**Figure S6.** The first 10 polarization curves of M80 (a), M80-C (b), M300 (c), M300-C (d), M500 (e), M500-C (f), M700 (g) and M700-C (h). All the measurements were performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. The polarization curves were not IR- and background-corrected.

![](_page_7_Figure_0.jpeg)

**Figure S7.** Illustration of IR- and background-correction (using the data of M80-C). The IR-corrected potential is calculated by the formulation of  $V_{IR-corrected} = V_{RHE} - I \times R_s$ . Rs is obtained by the fitting results of EIS measurement. The background is fit to a line in the region prior to the onset potential. The IR- and background-corrected polarization curve is obtained by subtracting the background from the IR-corrected polarization curve.

![](_page_8_Figure_0.jpeg)

**Figure S8.** The optimization of catalyst loading. (a) Polarization curves of M300-C with varied catalyst loading. (b) The Tafel plot of M300-C with a catalyst loading of 0.43 mg cm<sup>-2</sup>. (c) Comparison of the first and the  $1000^{\text{st}}$  polarization curve of M300-C with a catalyst loading of 0.43 mg cm<sup>-2</sup>. (d) Stability test of M300-C (0.43 mg MoS<sub>x</sub> cm<sup>-2</sup>) under a potential of -179 mV vs RHE. (e) Stability test of M300-C (0.43 mg MoS<sub>x</sub> cm<sup>-2</sup>) under a potential of -179 mV vs RHE. (e) Stability test of M300-C (0.43 mg MoS<sub>x</sub> cm<sup>-2</sup>) under a current density of 10 mA/cm<sup>2</sup>. The measurements were performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. The polarization curves and the Tafel plot were IR- and background- corrected.

![](_page_9_Figure_0.jpeg)

**Figure S9.** The equivalent circuit for EIS fitting.  $R_s$  is solution resistance. CPE is constant phase element related to double layer capacitance.  $R_{ct}$  is charge transfer resistance.  $C_p$  and  $R_p$  are capacitance and resistance related to hydrogen adsorption.

![](_page_9_Figure_2.jpeg)

![](_page_10_Figure_0.jpeg)

**Figure S10.** Double layer capacitance measurement. CV scans at varied scan rate of M80 (a), M80-C (b), M300 (c), M300-C (d), M500 (e), M500-C (f), M700 (g) and M700-C (h). The current density difference between the positive and negative potential sweep at 220 mV versus RHE is fit to the scan rate to obtain the double layer capacitance.  $C_{dl}$ =0.5×slope. The measurements were performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. The curves were not IR- and background-corrected.

Catalyst	Atomic ratio of S/Mo by ICP-OES	Atomic ratio of S/Mo by XPS	Atomic ratio of low- BE <sup>a</sup> sulfur/ total sulfur	Atomic ratio of high- BE sulfur/ total sulfur
M80	3.7	3.8	0.25	0.69
M300	2.9	3.7	0.44	0.53
M500	1.9	2.3	0.68	0.18
M700	1.9	2.4	0.74	0.16

Table S1. Elemental analysis of MoS<sub>x</sub>.

<sup>a</sup>BE, binding energy.

Catalyst	Catalyst loading (mg cm <sup>-2</sup> )	Electrolyte	Overpotential at 10 mA cm <sup>-2</sup> (mV)	Tafel slope (mV dec <sup>-1</sup> )
MoS <sub>x</sub> -CNT <sup>a</sup>	0.24	0.5 M H <sub>2</sub> SO <sub>4</sub>	167	35
MoS <sub>x</sub> -CNT <sup>a</sup>	0.43	0.5 M H <sub>2</sub> SO <sub>4</sub>	154	31
mPF-Co-MoS <sub>2</sub> -16.7 <sup>1</sup>	0.5	0.5 M H <sub>2</sub> SO <sub>4</sub>	156	74
H-MoS <sub>2</sub> <sup>2</sup>	1	0.5 M H <sub>2</sub> SO <sub>4</sub>	167	70
MoS <sub>2</sub> /CNT-graphene <sup>3</sup>	0.65	0.5 M H <sub>2</sub> SO <sub>4</sub>	255	100
CoMoS <sub>3</sub> <sup>4</sup>	0.5	0.5 M H <sub>2</sub> SO <sub>4</sub>	171	56.9
SV-MoS <sub>2</sub> <sup>5</sup>	-	H <sub>2</sub> SO <sub>4</sub> (pH=0.2)	170	60
MoS₂@OMC <sup>6</sup>	0.3	0.5 M H <sub>2</sub> SO <sub>4</sub>	178-192	60-65
Exfoliated MoS <sub>2</sub> <sup>7</sup>	-	0.5 M H <sub>2</sub> SO <sub>4</sub>	187	43
M-MoS <sub>2</sub> <sup>8</sup>	0.043	0.5 M H <sub>2</sub> SO <sub>4</sub>	175	41
Interlayer-expanded MoS <sub>2</sub> 9	0.28	0.5 M H <sub>2</sub> SO <sub>4</sub>	149	49
Defect-rich MoS <sub>2</sub> <sup>10</sup>	0.285	0.5 M H <sub>2</sub> SO <sub>4</sub>	195	50
MoS <sub>x</sub> /N-doped CNT <sup>11</sup>	-	0.5 M H <sub>2</sub> SO <sub>4</sub>	110	40
MoS <sub>2</sub> -CNT <sup>12</sup>	~0.05	0.5 M H <sub>2</sub> SO <sub>4</sub>	~290	~90

Table S2. Summary of representative MoS<sub>2</sub>-based HER catalysts in acidic electrolyte.<sup>1</sup>

<sup>a</sup>Results of this work.

**Note S1.** Relationships between hydrogen evolution reaction mechanism and Tafel slope.

Mechanism of HER in acidic solution:

Volmer reaction:  $H^+ + e^- \rightarrow H_{ads}$ 

Heyrovsky reaction:  $H_{ads} + H^+ + e^- \rightarrow H_2$ 

Tafel reaction:  $2H_{ads} \rightarrow H_2$ 

Tafel slopes of 116 mV dec<sup>-1</sup>, 38 mV dec<sup>-1</sup> and 29 mV dec<sup>-1</sup> correspond to Volmer reaction, Heyrovsky reaction and Tafel reaction as the rate-determining step, respectively.<sup>13</sup>

Note S2. The calculation of turnover frequency.

The per-site turnover frequency is calculated with the method reported in reference 14. TOF is calculated with the following formula:

TOF per site =  $\frac{\text{#Total hydrogen turn overs / cm}^2 \text{ geometric area}}{\text{#Surface sites (catalyst) / cm}^2 \text{ geometric area}}$ 

The total number of hydrogen turn overs is calculated as follows:

$$(j\frac{mA}{cm^2}) (\frac{1 A}{1000 mA}) (\frac{1 C / s}{1 A}) (\frac{1 \text{ mol } e^-}{96485.3 C}) (\frac{1 \text{ mol } H_2}{2 \text{ mol } e^-}) (\frac{6.02214 \times 10^{23} \text{ molecules } H_2}{1 \text{ mol } H_2}) = 3.12 \times 10^{15} j\frac{H_2 / s}{cm^2}$$

The number of ecectrochemically assessible surface sites of MoS<sub>x</sub> is calculated as follows:

 $\frac{\text{\#Surface sites (catalyst)}}{\text{cm}^2 \text{ geometric area}} = \frac{\text{\#Surface sites (flat standard)}}{\text{cm}^2 \text{ geometric area}} \times \text{Roughness factor}$ 

The number of the surface sites of flat standard is estimated as  $1.164 \times 10^{15}$  MoS<sub>2</sub> cm<sup>-2</sup>. The roughness

factor is calculated as follows:

Roughness factor= $\frac{C_{dl} \text{ (catalyst)}}{C_{dl} \text{ (flat standard)}}$ 

 $C_{dl}$  (catalyst) is extracted from Fig. S9, Fig. 4c and Fig. 4d.  $C_{dl}$  (flat standard) is estemated as 60  $\mu$ F cm<sup>-2</sup>.

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