

## Supplementary Information

*for*

### **Phase-engineering of Multiphasic 1T/2H MoS<sub>2</sub> Catalyst for Highly Efficient Hydrogen Evolution**

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## Experimental

### Synthesis of catalysts

The 1T/2H MoS<sub>2</sub> catalyst was prepared via a facile hydrothermal method. The ammonium molybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•H<sub>2</sub>O) and thioacetamide (CH<sub>3</sub>CSNH<sub>2</sub>) were used as molybdenum and sulphur sources, respectively. Typically, 0.88 g (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•H<sub>2</sub>O and 1.98 g ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>, marked as AB) were dissolved in 40 mL distilled water and then stirred to form a homogenous solution. Subsequently, 0.94 g CH<sub>3</sub>CSNH<sub>2</sub> were introduced into the homogenous solution with vigorous stirring for another 30 min. Then, the obtained solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 13 h in an electric oven. After being cooled down naturally to room temperature, the black product was acquired after centrifugation at 3000 rpm, washing with distilled water and ethanol for several times, and drying at 60 °C for 10 h. Besides, the 1T/2H MoS<sub>2</sub> was annealed at 400 °C for 2 h to obtain the annealed sample, labelled as A-1T/2H MoS<sub>2</sub>.

### Preparation of catalyst electrode

In a typical procedure, 3 mg of catalyst and 80 µL Nafion solution (5 wt %) were dispersed in 1 mL water-ethanol solution composed of 800 µL distilled water and 200 µL absolute ethanol by sonication for 30 min to form a homogeneous slurry. Then, 5 µL of the slurry was pipetted onto a polished glassy carbon electrode with a diameter of 3 mm. Finally, the modified GCE with a catalyst loading of 213 µg cm<sup>-2</sup> was dried at room temperature and retained for use.

### Characterizations

X-ray diffraction (XRD) patterns were collected using a D/max-2500 system with a Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) from 5° to 80°. DSC/TGA curves were recorded using a SDT Q600 (Ta Instruments, USA). Raman spectroscopy was performed using a LabRAMHR-800 of French company HRIBA with a 633 nm laser. The scanning electron microscopy (SEM) images were acquired using a FEI Sirion 200 scanning electron microscope. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained by a JEOL 2010 transmission electron microscope. The X-ray photoelectron spectroscopy (XPS) measurements were conducted using the ESCALAB 250Xi with a monochromatic Al K $\alpha$  source. The binding energy value of each element was corrected using C 1s=284.6 eV.

### Electrochemical measurements

All the electrochemical measurements were performed using a CHI 660E electrochemical workstation with a standard three-electrode system at room temperature. The glassy carbon electrode modified with catalysts was used as the work electrode, the saturated calomel electrode was used as the reference electrode, and the carbon rod was used as the counter electrode. Linear sweep voltammetry (LSV) for the hydrogen evolution reaction (HER) was conducted from 0.1 V to -0.4 V with a scan rate of 2 mV s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The electrochemical impedance spectroscopy (EIS) was performed in a frequency range from 10<sup>6</sup> Hz to 1 Hz at an overpotential of -220 mV. The long-term cycling test was conducted using cyclic voltammetry (CV) from 0.1 V to -0.4 V with a scan rate of 50 mV s<sup>-1</sup> for 1000 cycles. All the potentials reported in this manuscript are against RHE though the equation ( $E_{vs\ RHE} = E_{vs\ SCE} + E_{o\ SCE} + 0.059\ pH$ ).

### Electrochemically Active Surface Area

The electrochemically capacitance measurements was conducted by cyclic voltammograms from 0.10 to 0.50 V with various scan rates (20, 40, 60, 80, 100, 120, 140 mV s<sup>-1</sup>). The capacitive currents were measured in a potential range where no faradic processes are observed, i.e. at 0.40 V vs. RHE. According to the previous report, the specific capacitance, a flat standard with 1 cm<sup>2</sup> of real surface area, is approximately 60 μF cm<sup>-2</sup>.<sup>2,1,2</sup> Thus, the electrochemical active surface area can be calculated by the following formula:

$$A_{ECSA} = \frac{\text{electrochemical capacitance}}{60\ \mu\text{F cm}^{-2}\ \text{per cm}^2_{ECSA}}$$

### Turnover Frequency Calculations

The turnover frequency can be calculated by the following formula:

$$TOF = \frac{\text{no. of total hydrogen turnovers/cm}^2\ \text{of geometric area}}{\text{no. of active sites/cm}^2\ \text{of geometric area}}$$

The total number of hydrogen turnovers per current density can be calculated by the formula:

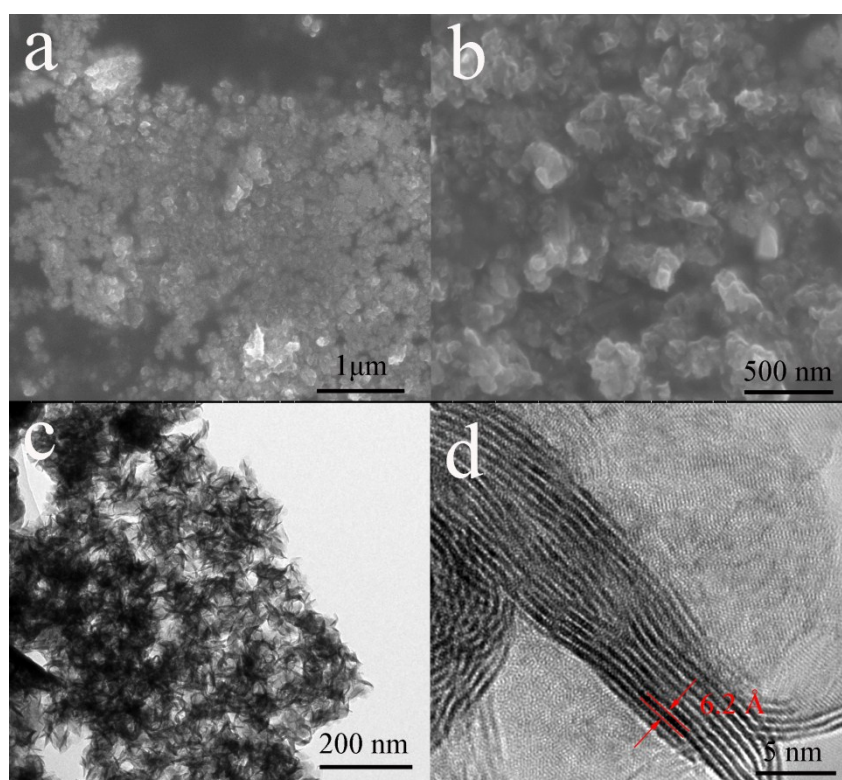
$$\begin{aligned} \text{No. of H}_2 &= \left(\text{per } \frac{\text{mA}}{\text{cm}^2}\right) \left(\frac{1\ \text{C s}^{-1}}{1000\ \text{mA}}\right) \left(\frac{1\ \text{mol of e}}{96485.3\ \text{C}}\right) \left(\frac{1\ \text{mol of H}_2}{2\ \text{mol of e}}\right) \left(\frac{6.022 \times 10^{23}\ \text{H}_2\ \text{molecules}}{1\ \text{mol of H}_2}\right) \\ &= 3.12 \times 10^{15} \frac{\text{H}_2\ \text{s}^{-1}}{\text{cm}^2} \text{ per } \frac{\text{mA}}{\text{cm}^2} \end{aligned}$$

The number of active sites per real surface area of MoS<sub>2</sub> was reported to be 1.164×10<sup>15</sup> atoms cm<sup>-2</sup> real.<sup>1</sup>,

3

Finally, the plot of current density can be converted into a TOF plot according to:<sup>4</sup>

$$\text{TOF} = \frac{(3.12 \times 10^{15} \frac{\text{H}_2 \text{ s}^{-1}}{\text{cm}^2} \text{ per } \frac{\text{mA}}{\text{cm}^2}) \times |j|}{(1.164 \times 10^{15} \text{ atoms cm}_{\text{real}}^{-2}) \times A_{\text{ECSA}}}$$



**Fig. S1** (a) and (b) SEM image, (c) TEM image, (d) HRTEM images of A-1T/2H MoS<sub>2</sub>

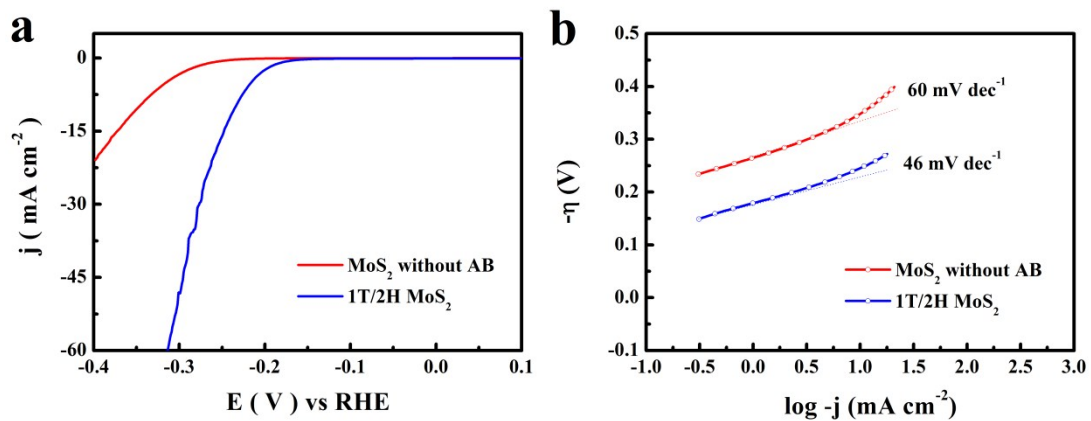


Fig. S2 (a) Polarization curves, (b) Tafel slopes of 1T/2H MoS<sub>2</sub> and MoS<sub>2</sub> obtained without the addition of ammonium bicarbonate (AB)

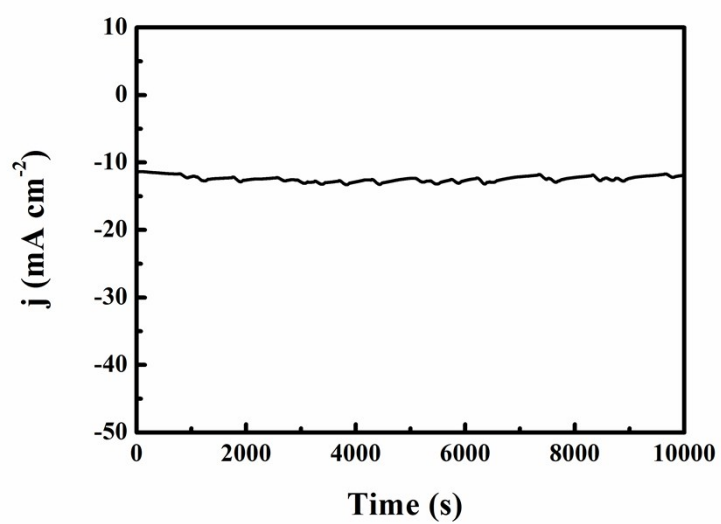


Fig. S3 I-t curve of 1T/2H MoS<sub>2</sub>

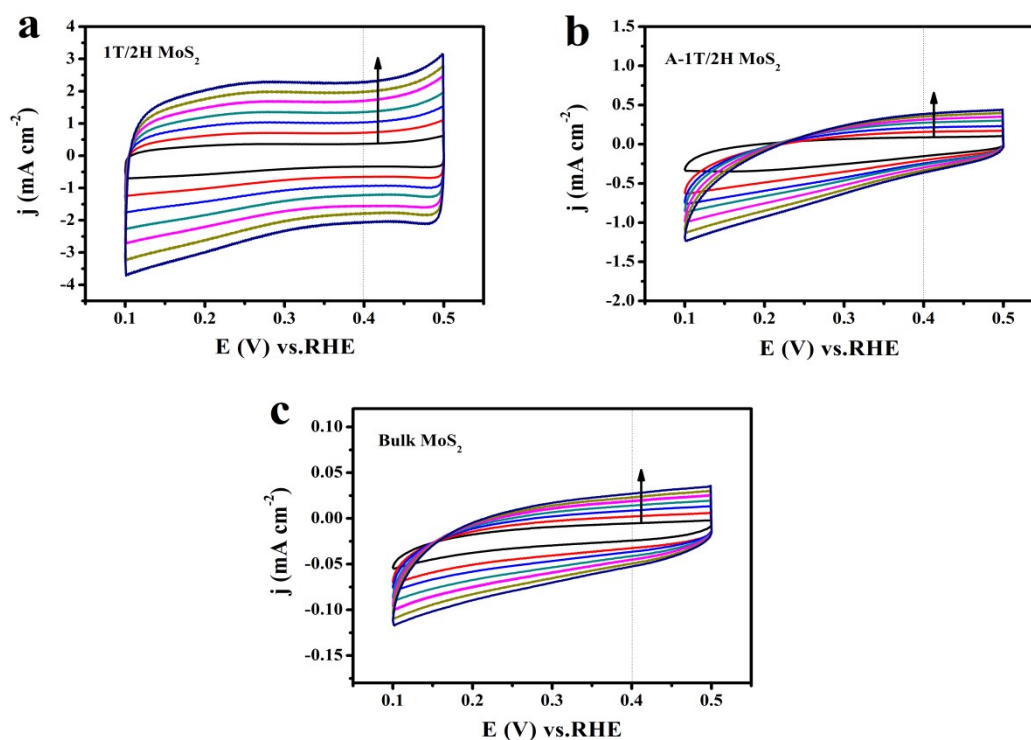


Fig. S4 Electrochemical capacitance measurements: (a) 1T/2H MoS<sub>2</sub>; (b) A-1T/2H MoS<sub>2</sub>; (c) Bulk MoS<sub>2</sub>

Table S1 Summary of MoS<sub>2</sub>-based catalysts for the HER

Catalysts	Loading (mg cm <sup>-2</sup> )	Tafel slope (mV dec <sup>-1</sup> )	Overpotential $\eta$ (mV)	Current density at the corresponding $\eta$ (mA cm <sup>-2</sup> )	Ref
MoS <sub>2</sub> nanoflowers	0.213	52	-300	-13.8	5
Defect-rich MoS <sub>2</sub>	0.285	50	-300	-70	6
MoS <sub>2</sub> nanosheets	0.285	68	-150	-4.56	7
Exfoliated MoS <sub>2</sub>	-	54	-195	-10	8
MoS <sub>2</sub> /RGO	0.285	41	-	-	9
Hollow MoS <sub>2</sub> spheres	0.205	74	-300	-58	2
MoS <sub>2</sub> /carbon	0.2	64	-216	-10	10
MoS <sub>2</sub> nanodots	0.28	61	-300	-18	11
Flower-like MoS <sub>2</sub>	-	49	-200	-10	12
MoS <sub>x</sub>	-	60	-200	-10	1
MoS <sub>2</sub> Nanoporous Films	-	50	-300	-18.6	13
MoS <sub>2</sub> Nanoplates	0.136	53	-	-	14
MoS <sub>2</sub> on Au foils	-	61	-300	-50	15
Double-gyroid MoS <sub>2</sub>	0.06	50	-300	-11.7	16
Edge-exposed MoS <sub>2</sub>	-	54	-300	-43	17
1T/2H MoS <sub>2</sub>	0.213	46	-300	-48	this work

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