Electronic Supplementary Information

# Urchin-like Mo<sub>2</sub>S<sub>3</sub> Prepared by Molten Salt Assisted Method for Efficient Hydrogen Evolution

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# **Experimental Section**

### Synthesis of urchin-like Mo<sub>2</sub>S<sub>3</sub>.

The urchin-like  $Mo_2S_3$  crystals were synthesized via a molten salt assisted solid-state reaction. Mo (99.95%, Strem Chemicals, Inc.) and S (99.95%, aladdin) were grounded together at the mole rate of 2 : 3. Then the powders were mixed with NaCl (99.8%, aladdin) at mass rate of 1 : x (x = 3, 5, 10, 20, 30, 50). Next, the raw materials were sealed in evacuated quartz tube, which were transferred into muffle furnace and annealed at 1173 K for 20 hours with the heating rate of 5 K min<sup>-1</sup>. After thermal treatment, the samples were cooled down to room temperature naturally. Finally, the products were washed with de-ionized water and dried in a vacuum oven at room temperature for 6 hours.

## Synthesis of urchin-like MoS<sub>2</sub>.

The urchin-like  $2H-MoS_2$  was synthesized by sealing equal amount of the urchin-like  $Mo_2S_3$  and S (99.95%, aladdin) in evacuated quartz tube, and annealing the quartz tube at 823 K for 5 hours, with the heating rate of 5 K min<sup>-1</sup>. Finally, the quartz tubes were cooled down to room temperature naturally.

# Synthesis of bulk 1T'-MoS<sub>2</sub>.

The 1T'-MoS<sub>2</sub> was obtained by the method described elsewhere<sup>1,2</sup>. Firstly, the ternary KMoS<sub>2</sub> precursor was prepared by sealing the mixture of K<sub>2</sub>S (99%, Sinopharm Chemical Reagent Co. Ltd.), MoS<sub>2</sub> (99%, Alfa Aesar), Mo (99.95%, Strem Chemicals, Inc.) in evacuated quartz tube and annealing at 1073 K for 10 h. Secondly, the obtained powder was stored in DI water for 24 h. After grinding and soaking in an I<sub>2</sub> acetonitrile solution (4 mmol, 15 ml) for 3 h, the treated powder was washed with DI water. High purity 1T'-MoS<sub>2</sub> was finally obtained and dried in a vacuum oven at room temperature for 6 hours.

#### Electrochemical measurements.

All electrochemical measurements were carried out using a CHI 760E electrochemical workstation. A threeelectrode system was adopted to evaluate the electrochemical performance with a graphite rod as the counter electrode and saturated calomel electrode (in saturated KCl solution) as the reference electrode. The catalyst was ultrasonically dispersed in a water-ethanol solution (v/v=1:1) containing 0.1 wt.% Nafion to form a homogeneous slurry. Then the mixed slurry was attached onto a glass carbon electrode with 5 mm diameter (loading 1.02 mg cm<sup>-2</sup>) as working electrode, followed by desiccation with dry N<sub>2</sub>. Linear-sweep voltammetry (LSV) measurements were conducted in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> at scan rate of 1 mV s<sup>-1</sup>. Before test, ventilation of N<sub>2</sub> into electrolyte for 20 min is necessary to eliminate the effect of O<sub>2</sub>. The working electrodes were cycled at least 20 cycles of cyclic voltammetry prior to any measurements.

### Characterization.

Scanning electron microscopy (SEM) images were carried out on a JEOL JSM-6510 SEM coupled with energy dispersive spectrometer (EDS). X-ray diffraction (XRD) measurements were performed on a Bruker D8 FOCUS (40 kV and 40 mA) using Cu K $\alpha$  radiation ( $\lambda$  = 0.15418 nm) with scan rate of 6 degree min<sup>-1</sup>. Transmission electron microscopy (TEM, JEOL-2100F, Japan) was applied to measure the structures and sizes of products. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo VG Scientific with Al K $\alpha$  radiation ( $\lambda$  = 1486.6 eV). Raman spectra were obtained using a thermal dispersive spectrometer with laser excitation at 532 nm. Resistivity measurements were performed on a Physical Property Measurement System (PPMS) using a four-probe method.



Figure S1. The XRD pattern of the as-prepared  $Mo_2S_3$  compared with the standard diffraction pattern (PDF #81-2031).



Figure S2. EDS result of the  $Mo_2S_3$  sample at x = 50. The result shows the mole ratio of Mo and S (2 : 3), which was close to the molar ratio of feeding.



Figure S3. (a) XPS full spectrum of the as-prepared  $Mo_2S_3$ . (b) High resolution S 2p spectrum of  $Mo_2S_3$ . (c) XPS spectra Mo 3d region and S 2s region of the obtained samples: (d) 2H-MoS<sub>2</sub>, (e) 1T'-MoS<sub>2</sub> and (f)  $Mo_2S_3$ .

Figure S7d-f exhibit the high resolution XPS spectra of Mo 3d region and S 2s region which can clearly distinguish constituent elements and the different valence states of Mo elements in different samples. Obviously, the binding energy of Mo  $3d_{3/2}$  and Mo  $3d_{5/2}$  gradually decreased in the order of 2H-MoS<sub>2</sub>, 1T<sup>2</sup>-MoS<sub>2</sub> and Mo<sub>2</sub>S<sub>3</sub> (Figure S7c), supporting that Mo<sub>2</sub>S<sub>3</sub> was more metallic than the other two phases.



Figure S4. (a-f) SEM images of the as-prepared samples (x = 3, 5, 10, 20, 30, 50) with different dosage of NaCl. (g) XRD patterns of the as-prepared samples (x = 3, 5, 10, 20, 30, 50). (h) The evolution of (-101) peak of the  $Mo_2S_3$  samples in detail, indicating that the size of  $Mo_2S_3$  decreases as the amount of NaCl increases.



Figure S5. SEM images of products quenched at 15 and 25 hours.



Figure S6. SEM images of (a) as-prepared urchin-like  $2H-MoS_2$  and (b) high purity  $1T'-MoS_2$ . (c) XRD patterns and (d) Raman spectra of as-prepared urchin-like  $2H-MoS_2$  and metallic  $1T'-MoS_2$ .

Through a short period of sulfuration reaction,  $Mo_2S_3$  (x=50) was transformed to 2H-MoS<sub>2</sub> completely as the XRD pattern illustrated (Figure S6c), and the morphology still remained (Figure S6a). The XRD pattern of as-prepared

 $1T'-MoS_2$  (Figure S6c) was very different from that of 2H-MoS\_2. The (002) peak of  $1T'-MoS_2$  shifted higher (15.06°) than that of 2H-MoS\_2 (14.45°), consistent with the result of previous work.<sup>2</sup> The Raman spectra of 2H-MoS<sub>2</sub>, and  $1T'-MoS_2$  were presented in Figure S6d, where the two strong peaks appeared at around 377 cm<sup>-1</sup> and 404 cm<sup>-1</sup> corresponded to the E<sub>2g</sub> and A<sub>1g</sub> vibration modes of 2H-MoS<sub>2</sub>.<sup>3</sup> The appearance of distinct J<sub>1</sub>, J<sub>2</sub>, J<sub>3</sub> and A<sub>1g</sub> peaks, and the disappearance of the typical peaks of  $1T-MoS_2$  (E<sub>g</sub> and A<sub>g</sub>) and 2H-MoS<sub>2</sub> (E<sub>2g</sub>), indicated the high purity of as-prepared  $1T'-MoS_2$ .<sup>4</sup> Based on XRD and Raman results, the successful preparation of pure  $1T'-MoS_2$  was realized.



Figure S7. The  $\rho\text{-}T$  curves of as-prepared Mo $_2\text{S}_3.$ 



Figure S8. Nyquist plots of the as-prepared  $Mo_2S_3$ , 1T'-MoS<sub>2</sub> and 2H-MoS<sub>2</sub> at an applied potential of -0.3V vs RHE. Inset: the equivalent circuit diagram and the zoom-out spectra.



Figure S9. Raman spectra of (a)  $Mo_2S_3$  and (b)  $1T'-MoS_2$  before and after one week of storage.  $E_{2g}$  and  $A_{1g}$  (blue dotted line frame) belong to  $2H-MoS_2$ .



Figure S10. Cyclic voltammograms (CVs) of as-prepared samples: (a)  $Mo_2S_3$ , (b)  $1T^2-MoS_2$ , (c)  $2H-MoS_2$ . (d) Plots of current density difference against scan rates,  $j_{0.12}$  is the difference between anodic and cathodic current densities at 0.12 V (vs RHE). In the plot, the capacitances were normalized by the geometric surface area of the electrodes.

As shown in Figure R4, although  $1T^{2}-MoS_{2}$  and  $Mo_{2}S_{3}$  exhibit different morphologies, their electrochemically active surface areas (ECSA) are close to each other (5294  $\mu$ F/cm<sup>2</sup> and 4494  $\mu$ F/cm<sup>2</sup>). The evolution of ECSA of the as-prepared samples was accessed by electrochemical double layer capacitance of the work electrodes with a geometric surface area of 0.19625 cm<sup>2</sup>. The capacitance was determined from current vs. sweep rate plots using the difference between anodic and cathodic currents at a constant potential of 0.12 V vs. RHE in order to eliminate

errors due to any occurring faradaic reaction. Considering the similar ECSA, the HER performance may be mainly determined by the conductivity of the samples.

mole ratio	S	Мо	Mo/S	Theoretical value (Mo/S)
Mo <sub>2</sub> S <sub>3</sub>	61.51	39.82	1.94/3	2/3
1T'-MoS <sub>2</sub>	58.36	30.78	1.05/2	1/2
2H-MoS <sub>2</sub>	66.71	31.80	0.95/2	1/2

Table S1. The mole ratio of Mo and S in the as-prepared samples.

We measure the element ratio of the as-prepared samples using the Electron-coupled plasma atomic emission spectrometry (ICP-AES), and the result is listed in Table R2. According to Table S1, the mole ratio of Mo and S (Mo/S) in  $Mo_2S_3$  and 2H-MoS<sub>2</sub> are slightly smaller than the theoretical value, however in  $1T^2-MoS_2$ , the mole ratio of Mo and S is larger than 1/2, which indicate that there is no S vacancies in  $Mo_2S_3$  and 2H-MoS<sub>2</sub>, but  $1T^2-MoS_2$  is S deficiency.

Table S2. HER performances of as-prepared  $Mo_2S_3$ , 1T'-MoS<sub>2</sub>, 2H-MoS<sub>2</sub> and other reported  $MoS_2$  catalysts in acidic electrolytes.

Catalysts	Overpotential (mV) at 10 mA/cm <sup>2</sup>	Tafel slope (mV/dec)	Reference
urchin-like Mo <sub>2</sub> S <sub>3</sub>	257	64	This work
Bulk 1T'-MoS <sub>2</sub>	332	84	This work
urchin-like MoS <sub>2</sub>	595	204	This work

1T'-MoS2 flakes	300	83	Adv. Mater. 2017, 29, 1701955
1T-MoS <sub>2</sub> nanosheet	230	45	ACS Energy Lett. 2018, 3, 7–13
Bulk 1T'-MoS <sub>2</sub>	-	100	Nature Chemistry, 2018, 10, 638 - 643
1T'-MoS <sub>2</sub> nanoflower	270	98	Catalysts 2018, 8, 235
1T-MoS <sub>2</sub> / SWNT	108	36	Chem. Mater. 2017, 29, 4738–4744
1T-MoS <sub>2</sub> nanosheet	130	49	J. Mater. Chem. A, 2017, 5, 11316 - 11330
MA-intercalated 1T <sup>2</sup> - MoS <sub>2</sub> nanosheet	170	38	J. Mater. Chem. A, 2018, 6, 5613 - 5617

# Notes and references

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