Electronic Supplementary Information (ESI)

Synthesis of 1T-$MoSe_2$ ultrathin nanosheets with an expanded interlayer spacing of 1.17 nm for efficient hydrogen evolution reaction

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Experimental

Synthesis

0.4 mmol of $MoCl_5$ and 0.8 mmol of SeO_2 powders were added into 25 mL of octylamine in a Teflon-lined autoclave (50 mL). After the solution was stirred for several minutes, the autoclave was sealed and kept in an oven at 180 °C for 6-12 h, and then cooled down to room temperature. The product was collected by centrifugation and washed with absolute ethanol and distilled water several times, and vacuum-dried. 2H-$MoSe_2$ was prepared by annealing the as-prepared sample at 300-400 °C in an Ar/H_2 (5% H_2) flow.

Characterization

Structures, morphologies and compositions of the samples were characterized with X-ray diffraction (XRD) (Rigaku D/MAX2500V, Cu Kα radiation), scanning electron microscopy (SEM) (Philips XL30 FEG), transmission electron microscopy (TEM) (Philips CM 20 FEG or JEOL JEM-2100F, 200 kV), Raman spectroscopy (Lab RAM HR, 532 nm excitation), X-ray photoelectron spectroscopy (XPS) (VG ESCALAB 220i-XL, Al Kα), and thermogravimetric (TG) analysis (Mettler Toledo TGA-DSC-1).

Electrochemical Measurements

Electrochemical measurement was performed in a standard three-electrode configuration on an electrochemical workstation (CHI 660E). The three-electrode configuration contains a glassy-carbon electrode with the $MoSe_2$

electrocatalysts as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt foil as the counter electrode. Typically, 10 mg of the $MoSe_2$ electrocatalysts was added in a mixture of 1600 μL of DI water, 400 μL of ethanol, 160 μL of Nafion solution (5 wt%). The mixture was vigorously sonicated for about 30 min to form a homogeneous ink solution. 5 μL of the ink was loaded onto a glassy-carbon electrode with a diameter of 3 mm, and dried at room temperature. The loading density of the catalysts is about 0.32 mg cm^{-2}. A 0.5 M H_2SO_4 solution was used as electrolyte and degassed by bubbling pure N_2 for 30 min. Linear sweep voltammetry was carried out at an scan rate of 5 mV s^{-1} for the polarization curves. All of the potentials were carefully calibrated to a reversible hydrogen electrode (RHE).

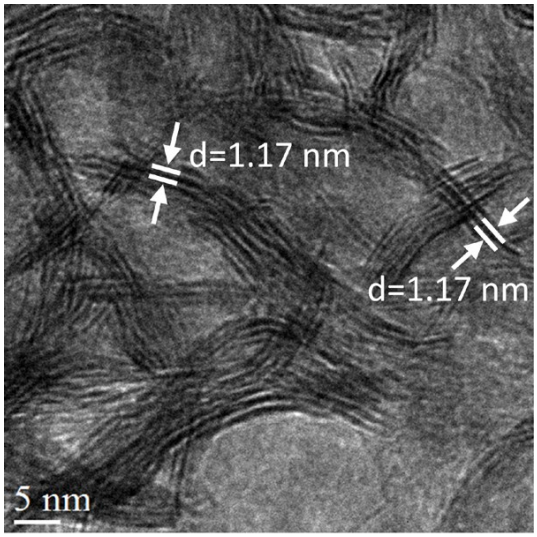

Fig. S1 HRTEM image of the as-prepared $MoSe_2$ flower-like assemblies in the internal area, showing that the nanosheets contain about 3-7 monolayers.

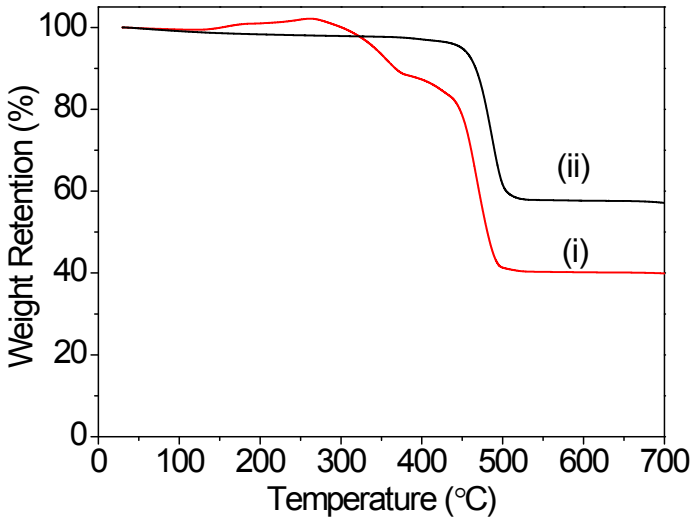

Fig. S2 TG analysis curves of (i) the as-prepared $MoSe_2$ sample and (ii) the $MoSe_2$ sample annealed at 300 °C. The larger weight loss in curve (i) is resulted from evaporation of octylamine molecules.

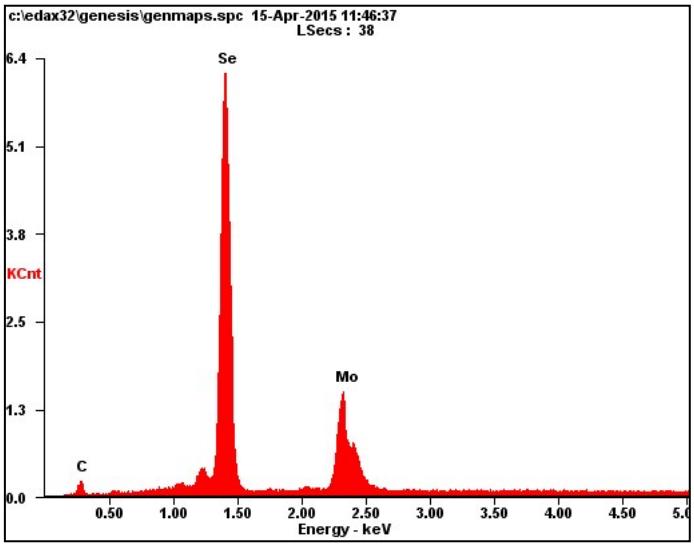

Fig. S3 EDX spectrum of the as-prepared $MoSe_2$ sample.

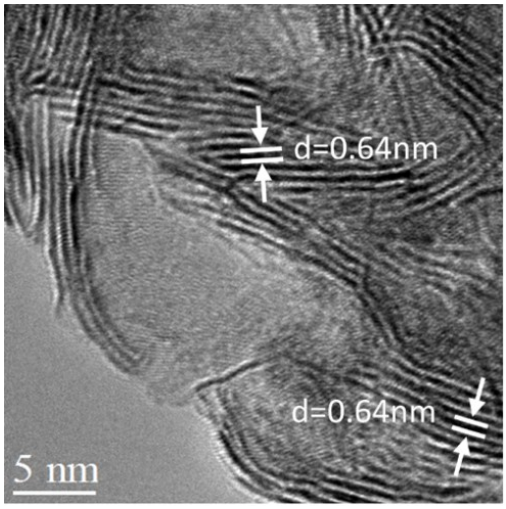

Fig. S4 HRTEM image of the $MoSe_2$ sample after annealing at 300 °C.

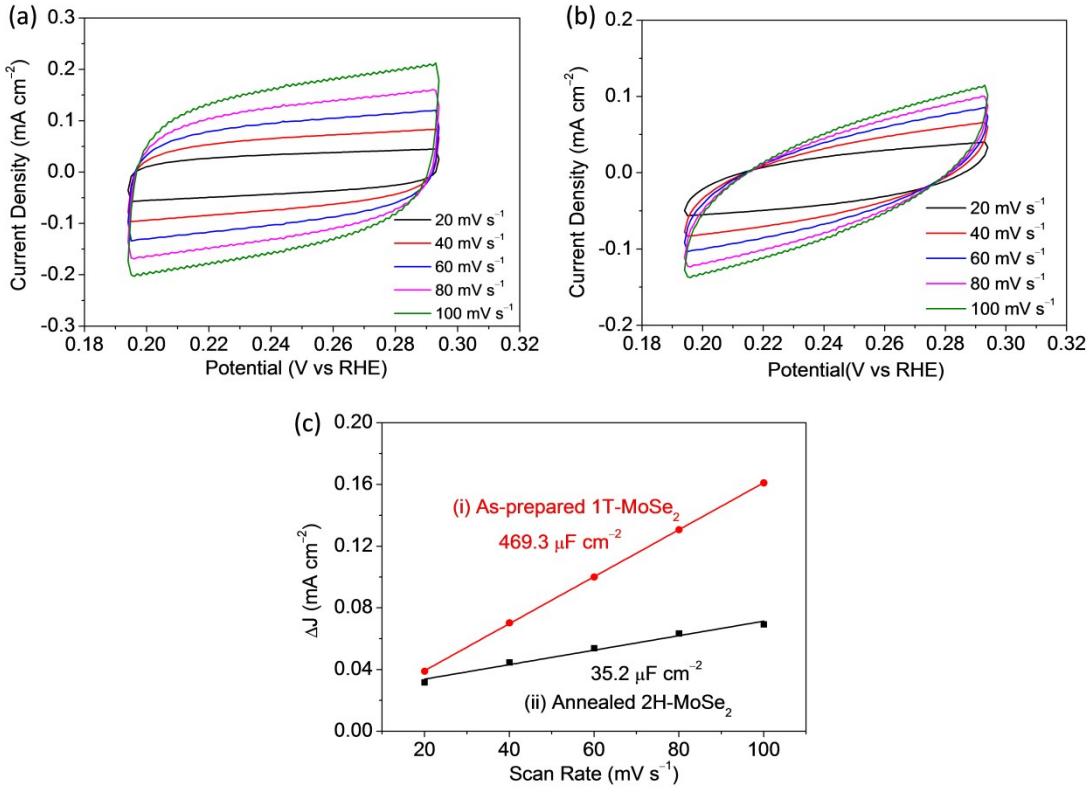

Fig. S5 (a) Cycling voltammetry (CV) curves of the as-prepared 1T-$MoSe_2$ electrocatalyst at scan rates from 20 to 100 mV s^{-1} in the region of 0.194-0.294 V vs. RHE, (b) CV curves of the annealed 2H-$MoSe_2$ electrocatalyst at scan rates from 20 to 100 mV s^{-1}, (c) The differences in current density variation ($\Delta J=\frac{1}{2}(J_a - J_c)$) at 0.244 V vs. RHE plotted against scan rate fitted to a linear regression for estimation of C_{dl}.

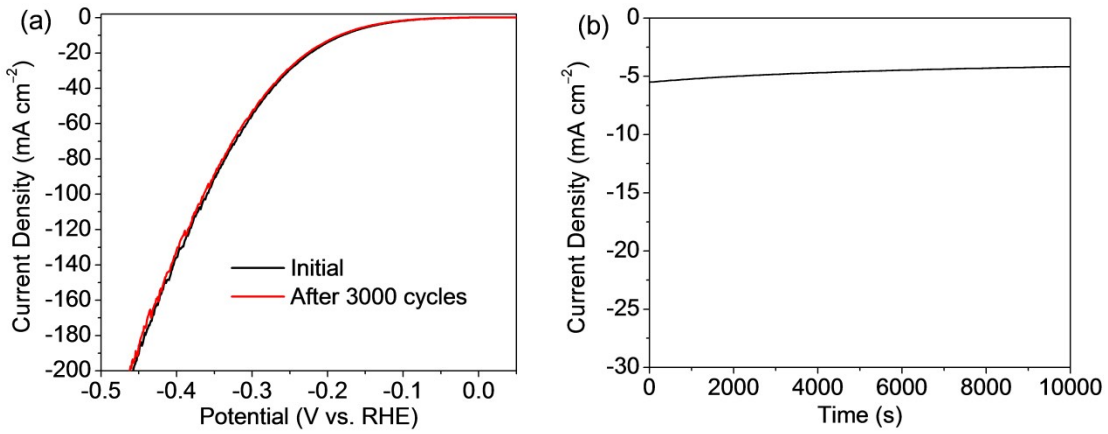

Fig. S6 (a) Polarization curves of the as-prepared 1T-$MoSe_2$ electrocatalyst, revealing that negligible degradation of HER activity after 3000 CV cycles. (b) Controlled potential electrolysis result of the as-prepared 1T-$MoSe_2$ sample at -0.20 V (vs RHE).

Table S1 Recent advance of HER perormance of $MoSe_2$-based catalysts.

No.	Samples	Onset potential (V vs. RHE)	Tafel slope (mV per decade)	Overpotential at 10 mA cm^{-2} (V vs. RHE)	References
1	Interlayer-expanded 1T-$MoSe_2$ nanosheets	0.060	78	0.179	This work
2	Exfoliated 1T-$MoSe_2$ nanosheets	~0.2	82	0.350	Chem. Commun., 2015, 51, 8450–8453
3	$MoSe_2$ film with vertically aligned layers	~0.2	105−120	NA	Nano Lett., 2013, 13, 1341−1347
4	Hierarchical ultrathin $MoSe_{2-x}$ nanosheets	0.17	98	~0.28	Nanoscale, 2014, 6, 11046–11051
5	$MoSe_2$ nanosheets	~0.12	45	0.181	ACS Catal., 2015, 5, 2213–2219
6	$MoSe_2$ porous microspheres	0.077	56	~0.125	Nano Res., 2015, 8, 1108–1115
7	Monolayered $MoSe_2$ nanosheets	~0.2	134	0.303	Nanoscale, 2015, 7, 10490–10497
8	S-doped $MoSe_2$ nanosheets	0.09	60	~0.10	J. Mater. Chem. A, 2014, 2, 5597–5601
	Pure $MoSe_2$ nanosheets	0.2	106	~0.22	
9	S-doped $MoSe_{2-x}$ nanosheets	~0.14	68	~0.21	Inorg. Chem. Front., 2015, 2, 931–937
	S-doped $MoSe_{2-x}$ nanotubes	~0.15	91	~0.23	
	$MoSe_2$ nanocaterpillars	~0.18	119	~0.28	
10	$MoSe_2$/rGO hybrid nanostructures	0.125	67	~0.19	J. Mater. Chem. A, 2015, 3, 19706–19710
	Pure $MoSe_2$ nanoflowers	0.223	103	~0.38	
11	$MoSe_2$/graphene hybrid nanosheets	0.05	69	~0.15	J. Mater. Chem. A, 2014, 2, 360–364
	Pure $MoSe_2$ nanosheets	0.15	101	~0.28	
12	Vertical aligned $MoSe_2$ nanosheets on carbon fiber paper	~0.16	77.4	0.25	Nano Lett., 2013, 13, 3426−3433
13	Epitaxial $MoSe_2$−NiSe nanohybrids	0.15	56	0.21	Chem. Mater. 2016, 28, 1838−1846
	Pure $MoSe_2$ nanosheets	0.17	95	~0.28	
14	Few-layer $MoSe_2$ grown on SnO_2 nanotubes	0.11	51	0.174	J. Mater. Chem. A, 2015, 3, 16263–16271