Supporting Information

High-performance hydrogen evolution electrocatalysis by layer-controlled MoS_2 nanosheets

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Experimental Section

Materials preparation.

All the chemicals were of analytical grade and used as received without further purification. Typically, for FL-MoS_2, hexaammonium heptamolybdte tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 900 mg) were first dissolved in deionized water (20 mL) to form a homogeneous solution. Then, the solution and carbon disulfide (CS_2, 10 mL) were transferred into a 40 mL stainless steel autoclave under N_2 and maintained at 400 ^oC for 4 h. The final product was treated with aqueous ammonia under stirring at room temperature for 3 h, followed by washing with water and absolute ethanol for several times and drying at 100 ^oC. For ML-MoS_2, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (3 g) and CS_2 (10 mL) were enclosed into the autoclave under N_2 and followed the same reaction and treatment process as FL-MoS_2. For SL-MoS_2-CNTs, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (150 mg) and CNTs (200 mg) were first dispersed in deionized water (20 mL) and CS_2 (10 mL) and then were enclosed into the autoclave under N_2, also followed the same reaction and treatment process as FL-MoS_2.

Materials characterization.

Scanning electron microscopy (SEM) was conducted on Hitachi S5500 operated at 30 kV. Transmission electron microscopy (TEM) was carried out on a FEI Tecnai F30 microscope and a G^2 microscope operated at an accelerating voltage of 300 and

120 kV, respectively. High angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray (EDX) mapping were carried out on a spherical aberration corrected transmission electron microscope (FEI Titan G2 80-200) which was operated at 200 kV. The scanning transmission electron microscopy (STEM) mode is capable to reach the space resolution to 0.08 nm. In order to guarantee an efficient X-ray collection rate to map the elements of the samples, an advanced ChemiSTEM technology (with four X-ray detectors) was adopted. X-ray diffraction (XRD) measurements were conducted on a Rigaku D/MAX 2500 diffractometer with Cu Kα radiation (λ=1.5418 Å) at 40 kV and 200 mA. Raman spectroscopy was performed on a Jobin Yvon LabRAM HR 800 instrument with a 532 nm excitation laser at a power of 0.7 mW.

Electrochemical analysis.

HER polarization curve tests were conducted on a 2273 potentiostat/galvanostat with a three-electrode electrochemical cell equipped with a gas flow controlling system. Graphite rod was used as the counter electrode and Ag/AgCl (saturated KCl-filled) as the reference electrode. A glassy carbon rotating disk electrode with a diameter of 5 mm covered by a thin catalyst film was used as the working electrode. Typically, 5 mg catalyst was suspended in 2 mL ethanol with 50 μL Nafion solution (5 wt.%, Du Pont) to form a homogeneous ink assisted by ultrasound. Then 125 μL of the ink was spread onto the surface of glassy carbon by a micropipette and dried under room temperature. The final loading for all catalysts and 40% commercial Pt/C electrocatalysts on work electrode is 1.6 mg/cm^2. HER tests were conducted in an N_2 saturated 0.1 M H_2SO_4 electrolyte at 25 ^oC. The potential range was from 0 to -1.0 V (vs. Ag/AgCl) and the scan rate was 2 mV s^{-1}. All the final potentials quoted have been calibrated with respect to a reversible hydrogen electrode (RHE).

All these materials synthesis and the HER performance mentioned above were well reproducible in our laboratory.

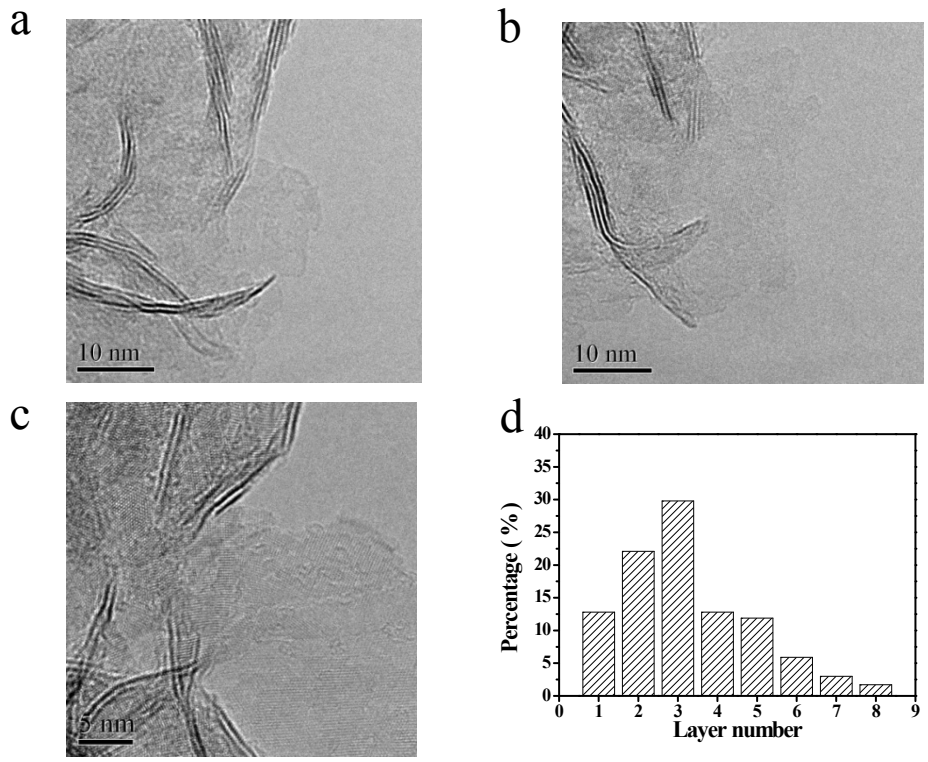

Figure S1. (a-c) HRTEM images of FL-MoS_2. (d) Layer number statistics of FL-MoS_2 by HRTEM.

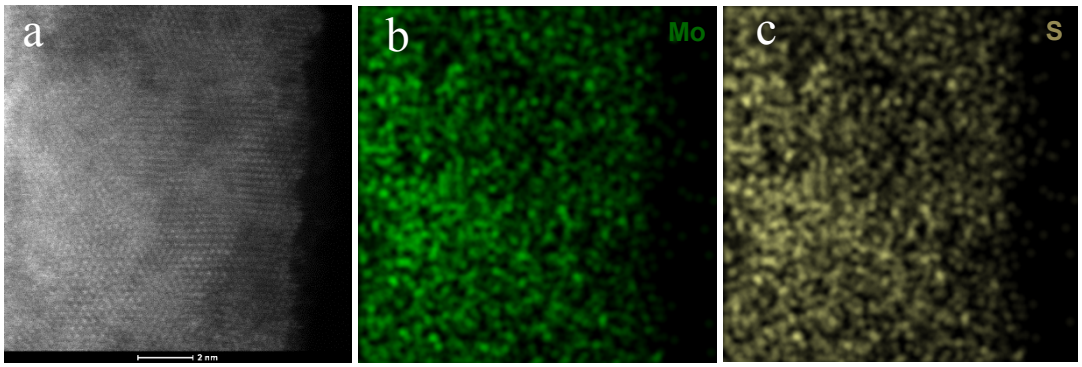

Figure S2. (a-c) HAADF-STEM image of FL-MoS_2 and corresponding EDX mapping images of Mo and S, respectively.

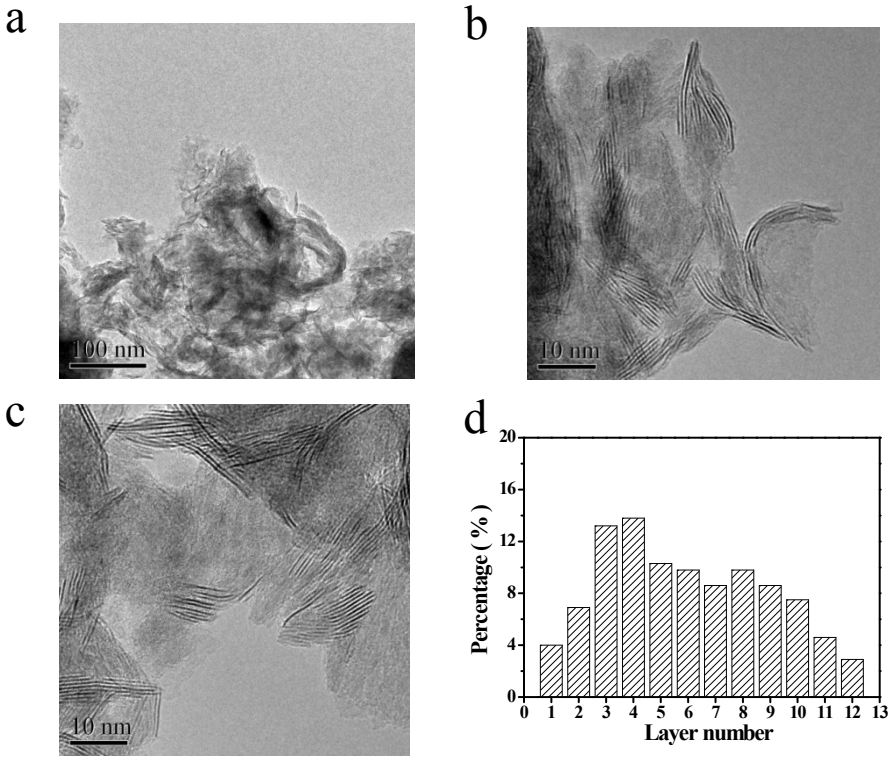

Figure S3. (a) TEM image of ML-MoS_2. (b), (c) HRTEM images of ML-MoS_2. (d) Layer number statistics of ML-MoS_2 by HRTEM.

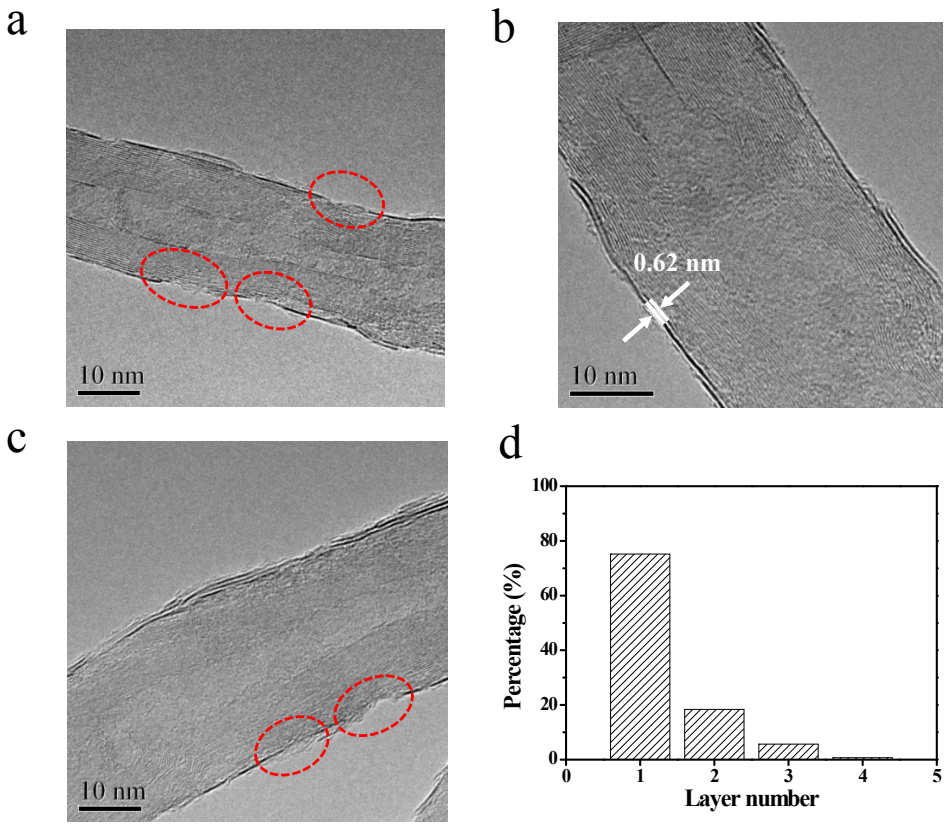

Figure S4. (a-c) HRTEM images of SL-MoS_2-CNTs. The inset in figure b shows a layer distance of 0.62 nm. The red dashed circles in figure a and c show the defects in MoS_2 nanosheets. (d) Layer number statistics of SL-MoS_2-CNTs by HRTEM.

Table S1. Summary of HER overpotential at different current density for SL-MoS_2-CNTs, FL-MoS_2, ML-MoS_2 and bulk MoS_2.

Catalyst	**Current density (mA cm^{-2})**	**Overpotential (vs. RHE)**
SL-MoS_2-CNTs	onset	~40 mV
	1	112 mV
	5	180 mV
	10	236 mV
FL-MoS_2	onset	~50 mV
	1	154 mV
	5	242 mV
	10	314 mV
ML-MoS_2	onset	~110 mV
	1	206 mV
	5	342 mV
	10	454 mV
bulk MoS_2	onset	~200 mV
	1	336 mV
	5	476 mV
	10	574 mV

Table S2. The comparison of exchange current densities for various MoS_2-based HER catalysts.

Catalyst	**Catalyst loading (mg/cm^2)**	**j_0 (A/cm^2)**	**j_0 (A/cm^2) normalized by mass**	**Reference**
MoO_3-MoS_2 nanowires	0.06	0.82×10^{-7}	0.14×10^{-5}	Nano Lett., 2011, 11, 4168
Amorphous MoS_3	0.031	8.9×10^{-7}	2.87×10^{-5}	Chem. Sci., 2012, 3, 2515
Engineered MoS_2	0.06	6.9×10^{-7}	1.15×10^{-5}	Nat. Mater., 2012, 11, 963
MoS_2/RGO	0.14	12×10^{-5}	8.57×10^{-4}	Chem. Commun., 2012, 48, 7687
Oxygen-incorporated MoS_2	0.285	1.26×10^{-5}	4.42×10^{-5}	J. Am. Chem. Soc., 2013, 135, 17881
MoS_2/Graphene	0.21	3×10^{-6}	1.43×10^{-5}	Adv. Funct. Mater., 2013, 23, 5326
Defect-rich MoS_2	0.285	8.91×10^{-6}	3.13×10^{-5}	Adv. Mater., 2013, 25, 5807
SL-MoS_2-CNTs	1.6	2×10^{-5}	1.25×10^{-5}	This work
FL-MoS_2	1.6	1.8×10^{-5}	1.13×10^{-5}	This work
ML-MoS_2	1.6	1.5×10^{-5}	0.94×10^{-5}	This work