Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information for

Engineering Active Sites of Two-Dimensional MoS_2 Nanosheets for Improving Hydrogen Evolution‡

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Experiment

Materials. All chemicals were purchased from Alfa Aesar Chemical Reagent Co. and used as received.

Preparation. The ultrathin MoS_2 nanosheets are prepared following a previous reported method.[1] In a typical synthesis, 1.236 g ammonium molybdate tetrahydrate ($(NH_4)6Mo_7O_{24}{\cdot}4H_2O$) and 2.284 g thiourea ($CH_4N_2S$) are dissolved into 35 ml deionized water under sonication and vigorous stirring to form a homogeneous solution. After being stirred for 30 min, the solution is transferred into a Teflon-lined stainless steel autoclave with the capacity of 45 ml and maintained at 180 ^{o}C for one day. After the hydrothermal reaction, the system is allowed to cool down to room temperature naturally. The final proudcts are collected via centrifugation, washed with deionized water and ethanol for several times, and dried under vacuum overnight.

For the annealing treatment, a certain amount of the obtained MoS_2 ultrathin nanosheets are put in the center of one quartz tube. Ar is introduced for 20 min and keeping it flowing during the whole heating process. The temperature is increased to different temperatures (i.e., 150, 350 and 550 ^{o}C) within 30 min and maintained at that temperature for 1 h. After that, the system is cooled to the room temperature with the rate set as 10 ^{o}C min^{-1}. Each annealing product is named as MoS_2--XXX, where XXX stands for the heating temperature.

Characterization. All of the samples are characterized by taking transmission electron microscopy (TEM) images using a JEOL JEM-1230 microscope with an accelerating voltage of 120 KV. High-resolution TEM (HRTEM) is taken using a FEI Tecnai G2 F20 microscope operated at 200 KV. The X-ray diffraction (XRD) patterns are measured on Rigaku's UItima IV with Cu K_α radiation (λ=1.54056 Å). Fourier transform infrared spectroscopy (FTIR) experiments are recorded using a Nicolet 6700 Spectrophotometer (Thermo-Scientific). Raman spectra are recorded based on Thermo Scientific DXR Raman Microscope with the laser source of 532 nm. X-ray photoelectron Spectroscopy (XPS) is conducted using PHI VersaProbe II Scanning XPS microprobe.

Electrochemical Measurements. All of the electrochemical measurements are carried out in a three-electrode system on an electrochemical workstation (CHI 760d, CH Instruments, Inc.). Typically, 5 mg of catalyst and 20 μl Nafion solution (Aldrich Co., 5 wt%) are dispersed in 5 ml water-isopropanol solution with volume ratio of 3:2 by sonicating for 20 min to form a homogeneous ink. Then 10 μl of the dispersion (containing 10 μg of catalyst) is loaded onto a polished glassy carbon electrode with 5 mm diameter. The electrochemical performance is studied in 0.5 M H_2SO_4 and 1 M KOH (purged with pure Ar) using Ag/AgCl (in 1 M KCl solution) electrode as the reference electrode, a

platinum wire as the counter electrode, and the glassy carbon electrode with various catalysts as the working electrode. All of the potentials are calibrated to a reversible hydrogen electrode (RHE) before the test. Cyclic voltammetry (CV) is studied between (-0.3 ad 0.0 V *vs*. RHE at 50 mV/s to investigate the cycling stability). Linear sweep voltammetry (LSV) is conducted with a scan rate of 5 mV/s to study the hydrogen evolution reaction activity. The Nyquist plots are performed in 1 M KOH with frequencies ranging from 100 kHz to 0.05 Hz at an overpotential of 250 mV.

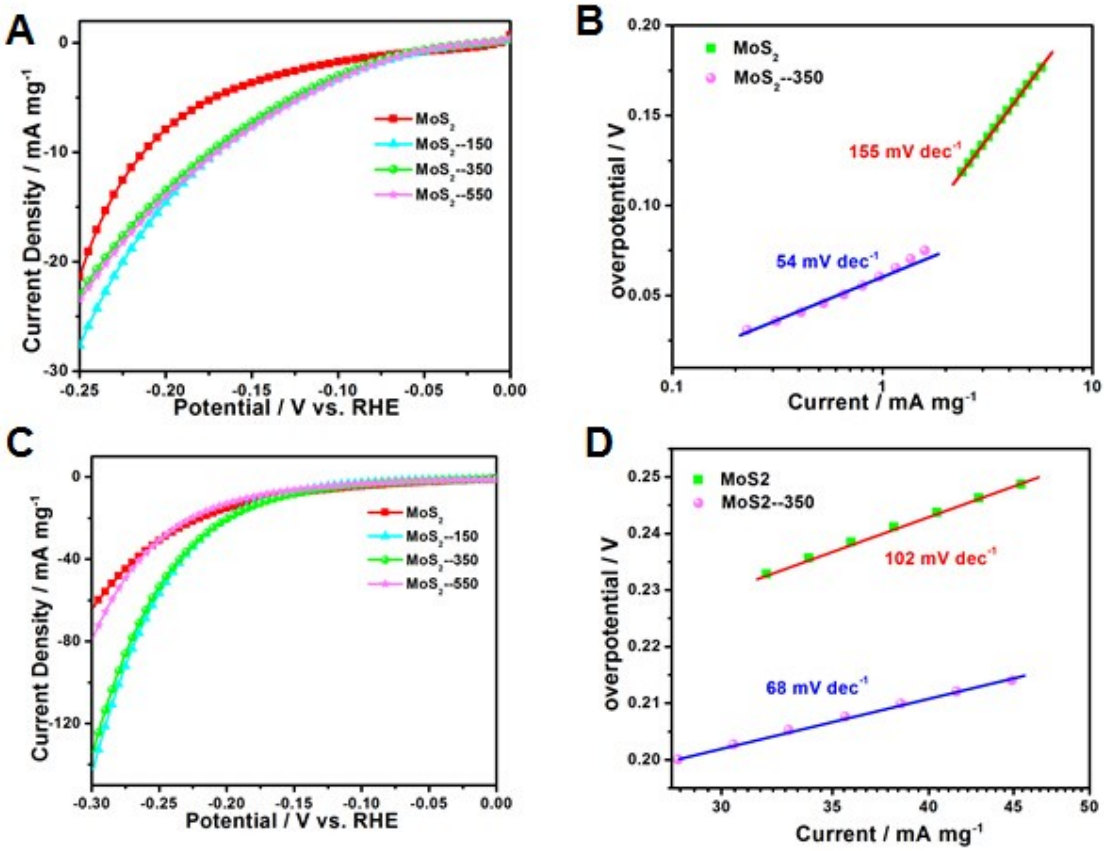

Fig. S1. (A) Mass-normalized LSV, (B) Tafel plots for pristine MoS_2 and the MoS_2—350 obtained in 0.5 M H_2SO_4, and (C) Mass-normalized LSV, (D) Tafel plots for pristine MoS_2 and the MoS_2—350 measured in 1 M KOH.

	0.5 M H_2SO_4		1 M KOH	
	η_{onset} / V	η @ 10 mA mg^{-1}/ V	η_{onset} / V	η @ 10 mA mg^{-1}/ V
MoS_2	0.078	0.215	0.175	0.188
MoS_2--350	0.053	0.171	0.150	0.162

Table S1. Comparison of onset overpotentials and overpotentials at 10 mA mg^{-1}.

Catalysts	TOF/ s^{-1}	Exchange current density / μA cm^{-2}	Electrolyte	Ref.
MoS_2--350	31.3 (η=200mV)	49.6	1M KOH	(this work)
MoS_2--350	20.6 (η=200mV)	18.8	0.5 M H_2SO_4	(this work)
MoS_2	23.5 (η=200mV)	43.7	1M KOH	(this work)
MoS_2	12.2 (η=200mV)	14.3	0.5 M H_2SO_4	(this work)
Amorphous MoS_2 films	0.8	13	1 M H_2SO_4	*Chem. Sci.*, 2011,2, 1262
MoS_x/NCNT forest	3.5 (η=200mV)	33.11	0.5 M H_2SO_4	*Nano Lett.* 2014, 14, 1228
N-MoS_2	0.32 (η=150mV)	980	1M KOH	*Energy Environ. Sci.* 2016, DOI: 10.1039/C6EE01786J.
Defect-free MoS_2 ultrathin nanosheets	0.496 (η=300mV)	3.16	0.5 M H_2SO_4	*Adv. Mater.* 2013, 25, 5807.

Table S2. Comparison of OER activity data with different MoS_2 based catalysts.

Reference:

1 J. Xie, J. Zhang, S. Li, F. Grote, X. Zhang, H. Zhang, R. Wang, Y. Lei, B. Pan, Y. Xie, *J. Am. Chem. Soc.*, 2013, **135**, 17881-17888.