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A highly active molybdenum multisulfide electrocatalyst for hydrogen evolution reaction

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Experimental Details

Preparation of the A-MoS_x materials: Firstly, the original MoS_2 powders (99.9%) were pressed into pellets and then were arc-melting treated in the closed arc furnace filled with Ar. During the treatment, the MoS_2 pellets were rapidly heated up to a very high temperature (>3000 °C) and melted, then cooled to room temperature within a few seconds on a copper substrate, which was kept thermostatic at 15 °C. The as-prepared black particles were ground to powders, followed by ball-milling for 4 h. Then, the A-MoS_x catalysts were obtained.

Electrochemical measurement: All of the electrochemical measurements were performed on CHI 660E electrochemical workstation in three-electrode systems. Typically, 4 mg of sample and 30 μL Nafion solution (5 wt %) were dispersed in 1 mL water-ethanol solution with volume ratio of 3:1 by sonicating for 30 min to form a homogeneous ink, then the mixed ink were attached onto a glass carbon (GC) electrode with 4 mm diameter (loading 2.1 mg cm^{-2}) as working electrode, polished with alumina slurry and cleaned with ethanol and DI water before experiment. A graphite rod and Ag/AgCl (in saturated KCl solution) electrode were used as counter and reference electrodes, respectively. All of the potentials were calibrated to a reversible hydrogen electrode (RHE). Linear-sweep voltammetry (LSV) measurements were conducted in 0.5 M H_2SO_4 and 1.0 M KOH at scan rates from 5 mV s^{-1} to 300 mV s^{-1}. All data have been corrected for a small ohmic drop based on impedance spectroscopy. The electrochemical impedance spectroscopy (EIS) measurements were carried out in the same configuration at overpotential of 0 mV from 10^5 to 0.1 Hz with an AC voltage of 5 mV.

Characterization: The morphology of the prepared samples was investigated by scanning electron microscopy (SEM, MERLIN VP Compact, Carl Zeiss, Germany) and transmission electron microscopy (TEM, JEM-2010). X-ray diffraction (XRD) patterns were obtained by using a D/max-2500 diffractometer with with a Cu Kα irradiation source (λ=1.54 Å). X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALAB 250Xi from Thermo Fisher Scientific electron spectrometer using an Al Kα radiation. The particle size of samples was measured by laser scattering particle analyzer (Hydro 2000NW, MAlver, Worcestershire, UK). Photoluminescence spectra and Raman spectra were measured on a microscopic confocal Raman spectrometer (Raman, LabRAM HR800, HORIBA Jobin Yvon, Villeneuve d'Ascq, France) using a 514 nm laser as the excitation source.

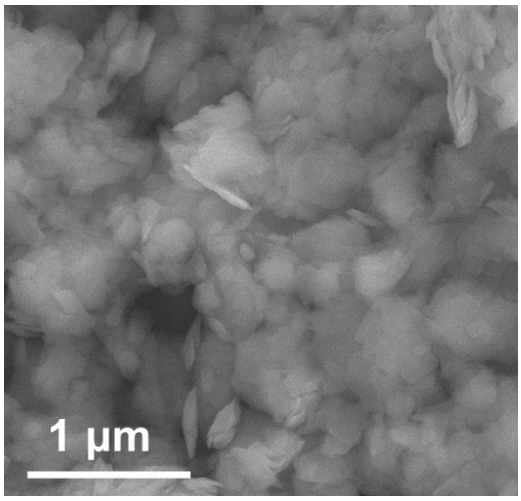

Fig. S1 SEM image of MoS_2.

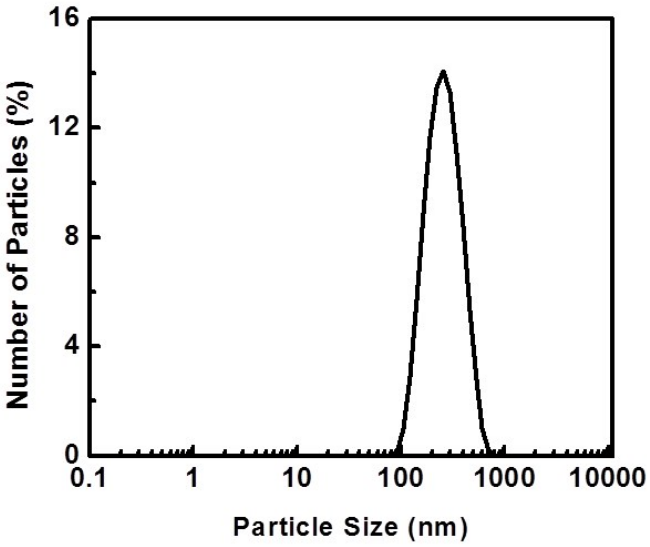

Fig. S2 Particulate size analysis of the MoS_2.

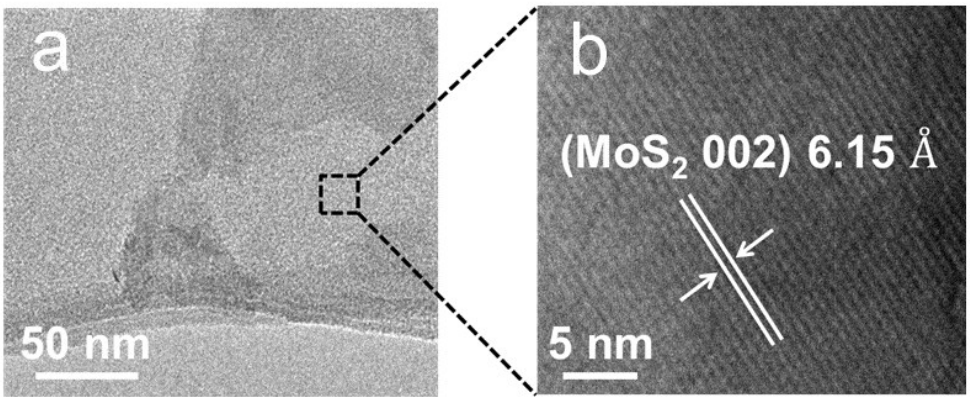

Fig. S3 (a) TEM image of MoS_2. (b) HRTEM image of MoS_2.

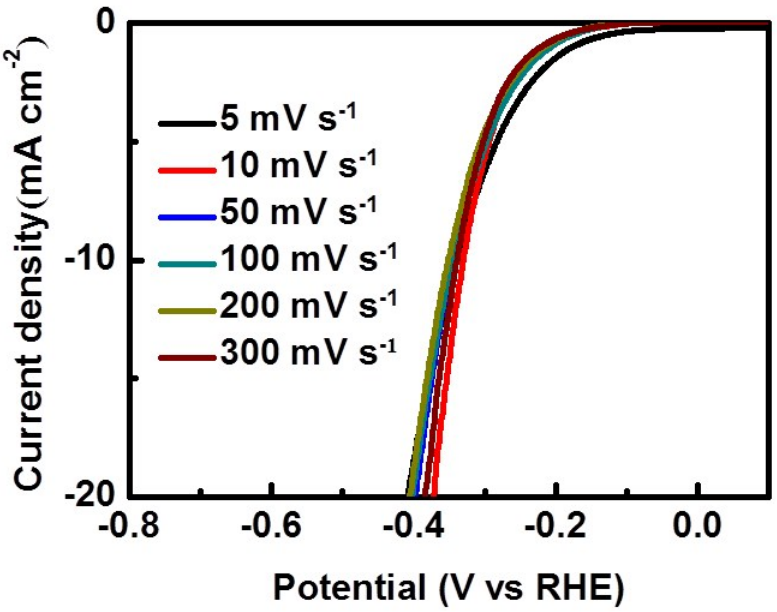

Fig. S4 The polarization curves of the MoS_2 with scan rates from 5 to 300 mV s^{-1} in 0.5 M H_2SO_4.

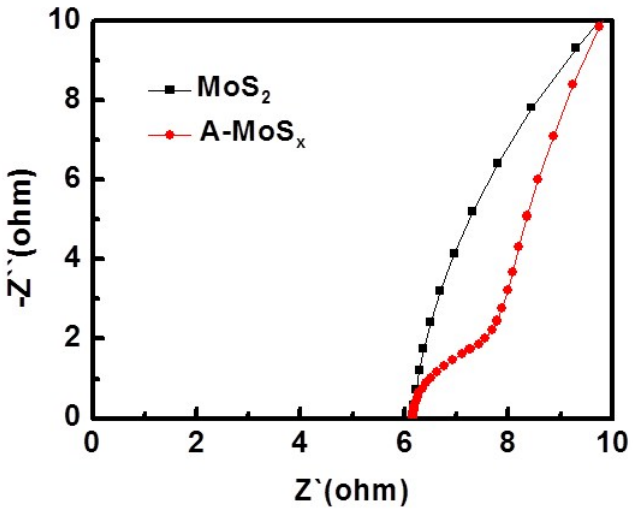

Fig. S5 Electrochemical impedance spectra of the A-MoS_x and MoS_2 in 1.0 M KOH.

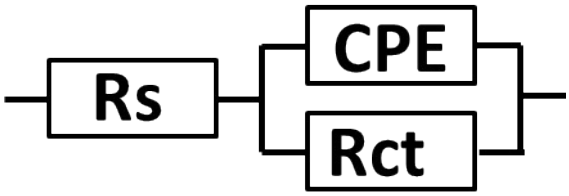

Fig. S6 The equivalent circuit used in EIS analysis.

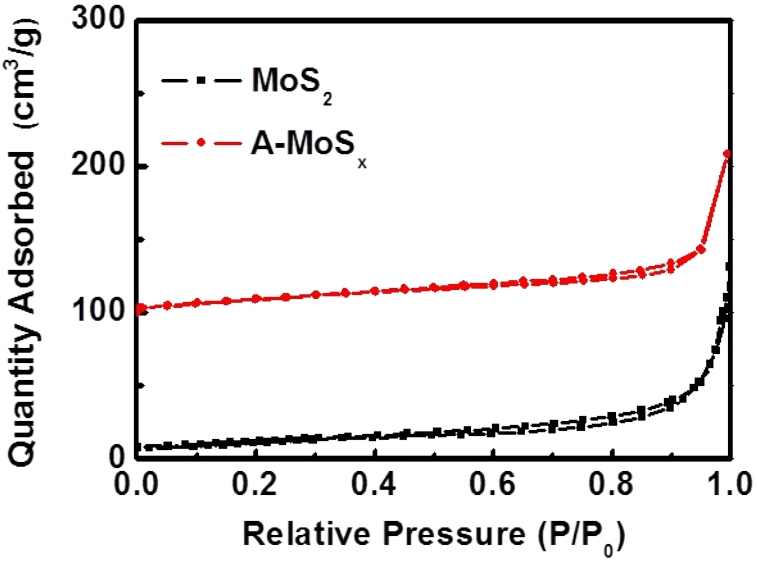

Fig. S7 N_2-sorption isotherms of the A-MoS_x and MoS_2.

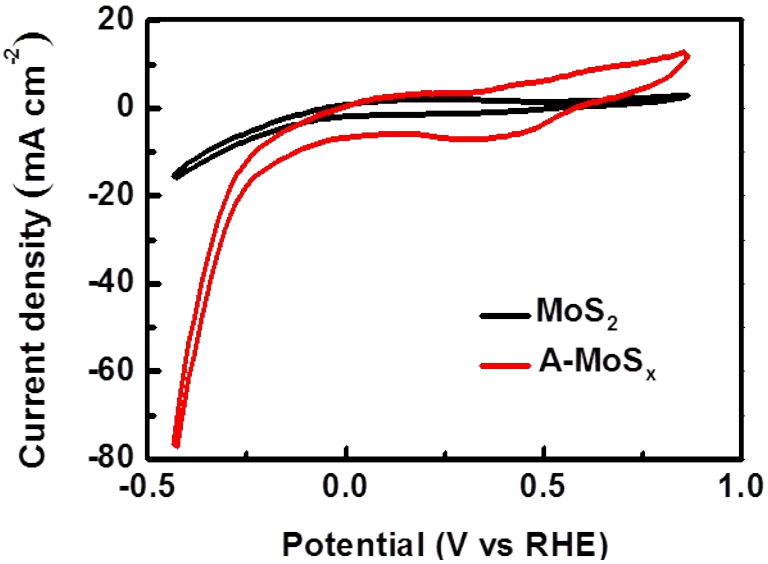

Fig. S8 The cyclic voltammetry (CV) curves of the A-MoS_x and MoS_2 with a scan rate of 50 mV s^{-1} in 0.5 M H_2SO_4.

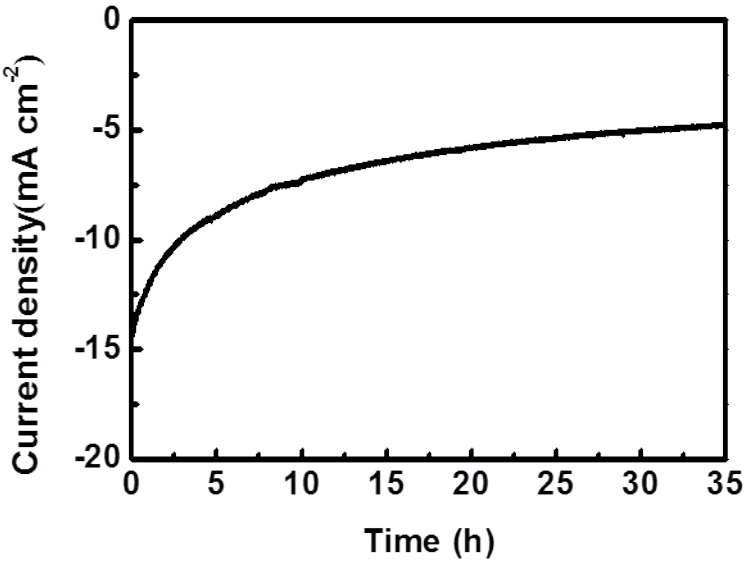

Fig. S9 Time-dependent HER performance of the A-MoS_x in 0.5 M H_2SO_4.

Table S1. HER parameters of the typical comparable samples.

Sample	Electrolyte	Current density	Tafel slope ($mV\ dec^{-1}$)	Ref.
A-MoS_x	0.5M H_2SO_4	10 mA cm^{-2} at η =156 mV	58	Our work
Double-gyroid MoS_2	0.5M H_2SO_4	10 mA cm^{-2} at η =260 mV	60	S1
Chemically exfoliated 1T- MoS_2	0.5M H_2SO_4	10 mA cm^{-2} at η=~187	43	S2
MoS_2/graphene hybrid	0.5M H_2SO_4	10 mA cm^{-2} at η=~140mV	41	S3
Defect-rich ultrathin MoS_2	0.5M H_2SO_4	13 mA cm^{-2} at η=200 mV	50	S4
Vertically aligned MoS_2 films	0.5M H_2SO_4	8 mA cm^{-2} at η=400 mV	86	S5
Strained vacancy MoS_2	H_2SO_4 (pH=2)	10 mA cm^{-2} at η=170 mV	60	S6
MoS_x from electro-polymerization	1M H_2SO_4	15 mA cm^{-2} at η=200 mV	40	S7
Wet-Chemical amorp MoS_x	1M H_2SO_4	10 mA cm^{-2} at η=~200	60	S8
MoS_x /N-CNT	0.5M H_2SO_4	10 mA cm^{-2} at η=110 mV	40	S9
$CoMoS_x$	H_2SO_4 (pH=1)	5 mA cm^{-2} at η=~210 mV 5 mA cm^{-2} at η=~210 mV	N/A	S10
MoO_3- MoS_2 Nanowires	0.5M H_2SO_4	10 mA cm^{-2} at η=~250 mV	50-60	S11
Defects Engineered Monolayer MoS_2	0.5M H_2SO_4	10 mA cm^{-2} at η=~590	161	S12

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