

Supporting Information

Amorphous Co-Mo-S ultrathin films with low-temperature sulfurization as high-performance electrocatalysts for hydrogen evolution reaction

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EXPERIMENT SECTION

Materials: Ti foil, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and urea ($\text{CO}(\text{NH}_2)_2$) were purchased from Yitai Metal Materials Co., Ltd, Sinopharm Chemical Reagent Co., Ltd and Tianjing Guangfu Technology Development Co., Ltd, respectively. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, thiourea ($\text{CS}(\text{NH}_2)_2$) and sulfur sublimed powder were obtained from Xi Long Hua Gong Co., Ltd. $\text{CH}_3\text{CH}_2\text{OH}$ (~99 wt%), H_2SO_4 (~98 wt%) and HCl (~37 wt%) were purchased from Beijing Chemical Reagent Co., Ltd. All the reagents were of A. R. grade and used as received without further purification.

Synthesis: Co-Mo-S hierarchical nanosheets/Ti foil was synthesized by a facile hydrothermal method followed by low-temperature sulfuration treatment. In a facile hydrothermal procedure, 0.119 g (0.5 mmol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.1766 g (1/7 mmol) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 0.15 g (2.5 mmol) $\text{CO}(\text{NH}_2)_2$ were dissolved in 36.0 mL distilled water and stirred to form a pink and clear solution. Ti foil (4 cm × 1 cm) was carefully cleaned with concentrated HCl solution (~37 wt%) in an ultrasound bath for 5 min, and then deionized water and absolute ethanol were used for 5 min each to ensure that the surface of the Ti foil was fully cleaned. The aqueous solution and Ti foil were transferred to a 40-mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 120

°C for 8 hours, and then allowed to cool to room temperature. The Co-Mo-O precursor was taken out from the autoclave and subsequently rinsed with distilled water, and dried at 60 °C for 30 minutes. In the sulfuration treatment, the typical process was carried out in a conventional tube furnace at about 300 °C, with a nitrogen flow-rate of about 50 sccm (standard cubic centimeter per minute). The Co-Mo-O precursor was loaded into a quartz boat and placed in the middle of the quartz tube. Excessive sulfur (about 0.5 g) was loaded into another quartz boat and placed in the upstream end of the tube. The furnace temperature increased from room temperature to 300 °C with the rate of 10 °C/min. After the sample had been annealed at 300 °C for 2 h, it was cooled in the furnace to room temperature in a nitrogen atmosphere.

With the above method, Co-Mo-S thin nanosheets/Ti foil was synthesized by adjusting the initial mass of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ reactant (0.0883 g, 1/14 mmol) in the hydrothermal synthesis.

With the above method, by adjusting the sulfurizing temperature to 400, 500 and 600 °C in the annealing step, we fabricated different hierarchical nanosheets on Ti foil.

MoS_2 nanosheet array was prepared by the hydrothermal method. 0.1766 g (1/7 mmol) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and 0.456 g (6 mmol) $\text{CS}(\text{NH}_2)_2$ were dissolved in 36.0 mL distilled water and stirred to form a clear solution. The aqueous solution and clean Ti foil were transferred to a 40-mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 180 °C for 12 hours.

Measurements: Scanning electron microscopy (SEM) images were taken on a Zeiss SUPRA55 scanning electron microscope with two accelerating voltages of 200 kV and 50 kV. X-ray powder diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku D/max 2500) at a scan rate of 10 (°)/min in the range from 5 to 90°. N_2 adsorption-desorption measurement and Raman spectrum were carried out by using the models of Quantachrome Autosorb-2 and LabRAM Aramis. High-resolution transmission electron microscope (HRTEM) images, line-scan energy-dispersive X-ray spectroscopy (EDS) and EDS elemental mapping were obtained on a JEOL 2100 High-resolution TEM system with operating at 200 kV. The interaction force between the gas bubbles and electrode interfaces can be assessed by a high-sensitivity micro-electromechanical balance system (Dataphysics DCAT21, Germany).

The as-prepared catalyst electrode as a binder-free cathode was measured for HER. All electrochemical measurements were performed on standard three-electrode setup under constant H_2 flow at room temperature at room temperature. Electrochemical measurements (using a CHI 660E

from Shanghai Chenghua Instrument *Co., Ltd*, China) were conducted in an electrochemical cell using saturated calomel electrode (SCE, 0.262 V vs. reversible hydrogen electrode (RHE) in 0.5 M H₂SO₄ solution) as the reference electrode, a 1 cm² Pt plate as the counter electrode and the sample with 1 cm² electrode area as the working electrode. Prior to the test measurements, H₂ was bubbled through the electrolyte solution to eliminate the dissolved oxygen and to maintain a fixed Nernst potential for the H⁺/H₂ redox couple. Linear sweep voltammetry with scan rate of 5 mV s⁻¹ was conducted in 0.5 M H₂SO₄ solution. AC impedance measurements were carried out in the same configuration at -0.15 V vs. RHE in the frequency range of 10⁻¹ to 10⁵ Hz with an AC voltage of 5 mV. The electrochemical double-layer capacitance (EDLC) measurements were carried out by using cyclic voltammetry curves for two cycles between 0.15 and 0.2 V vs. RHE with scanning rates of 1, 2, 4, 8 and 16 mV s⁻¹. The current densities at 0.175 V vs. RHE and the corresponding scanning rates were used to calculate the EDLC value (the slope of current density-scan rate plots), which served as an estimate of the effective electrochemically active surface area (ECSA) of the solid-liquid interface. The stability test was carried out by working at a constant potential for 10 hours.

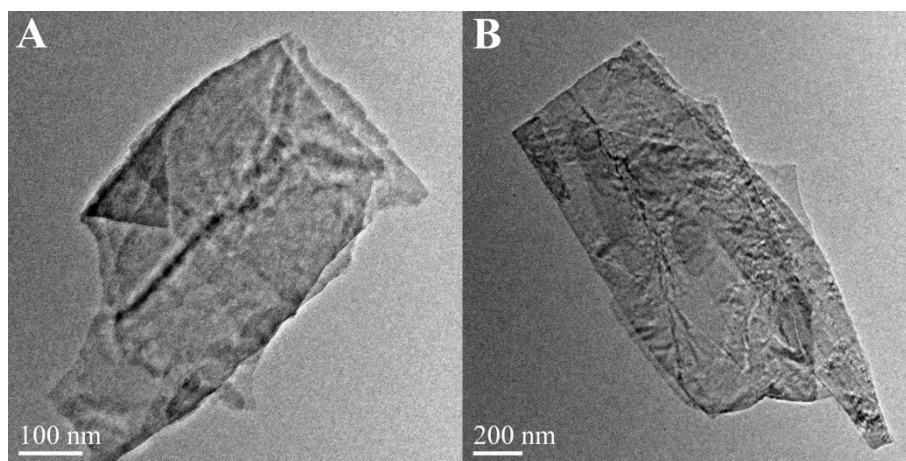


Figure S1. TEM images of (A) the Co-Mo-O hierarchical nanosheets and (B) thin nanosheets precursor.

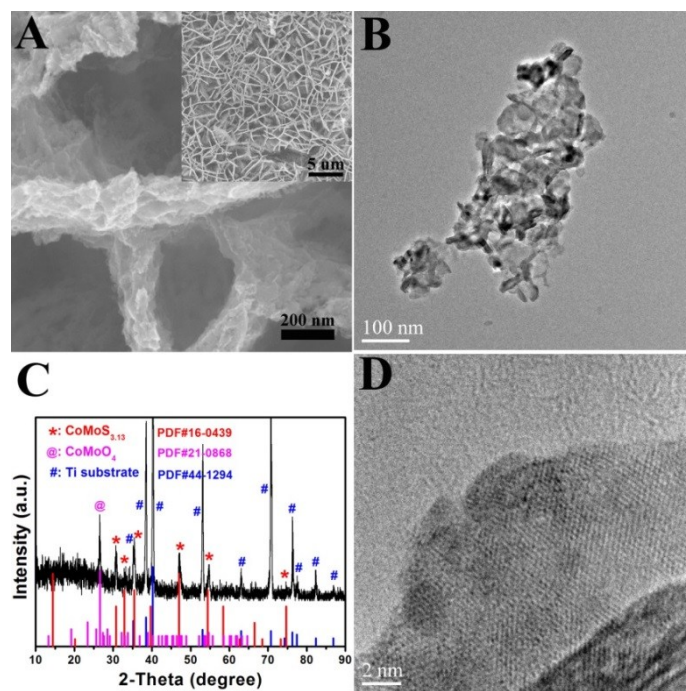


Figure S2. (A) High-resolution SEM image (inset: low-resolution image), (B) TEM image, (C) XRD patterns and (D) HRTEM image of $\text{CoMoS}_{3.13}$ nanosheets obtained at 400 °C.

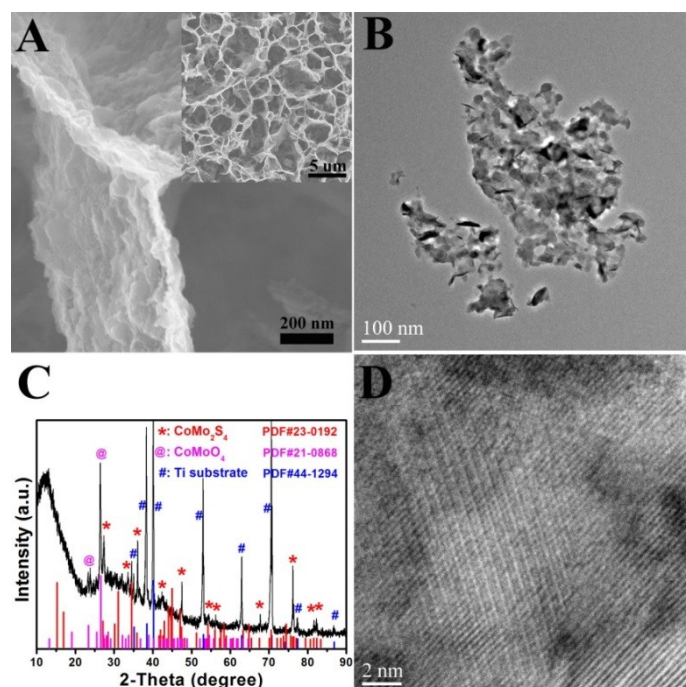


Figure S3. (A) High-resolution SEM image (inset: low-resolution image), (B) TEM image, (C) XRD patterns and (D) HRTEM image of CoMo_2S_4 nanosheets obtained at 500 °C.

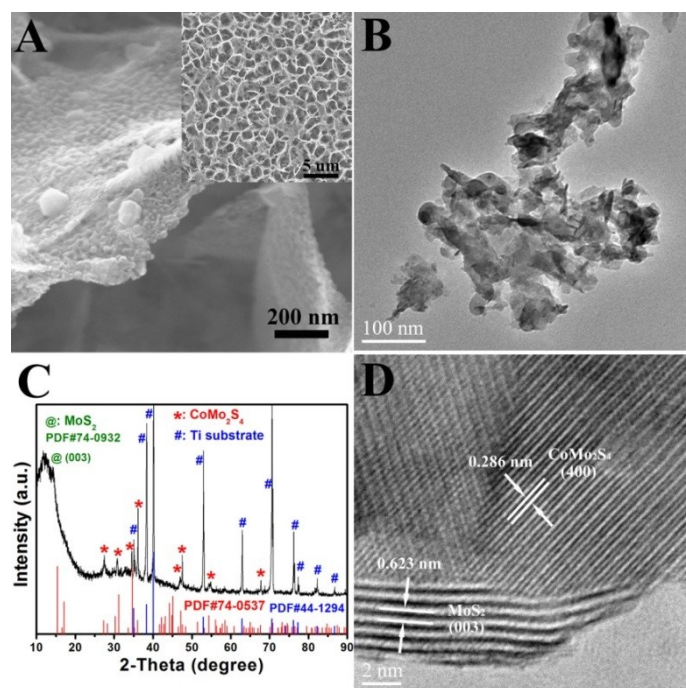


Figure S4. (A) High-resolution SEM image (inset: low-resolution image), (B) TEM image, (C) XRD patterns and (D) HRTEM image of CoMo_2S_4 nanosheets obtained at 600 °C.

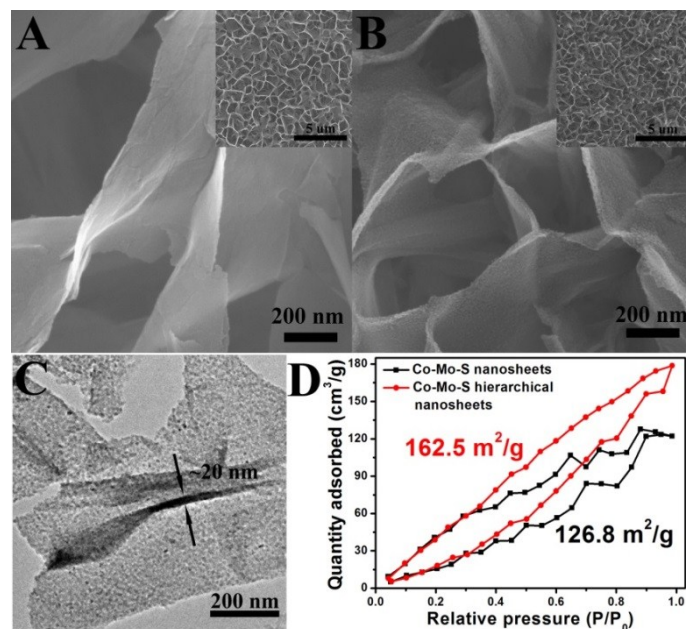


Figure S5. (A and B) high-resolution SEM images of Co-Mo-O precursor and Co-Mo-S nanosheets, inset: low-resolution SEM images; (C) TEM image of Co-Mo-S nanosheets; (D) N_2 adsorption–desorption isotherm of Co-Mo-S hierarchical nanosheets and Co-Mo-S nanosheets.

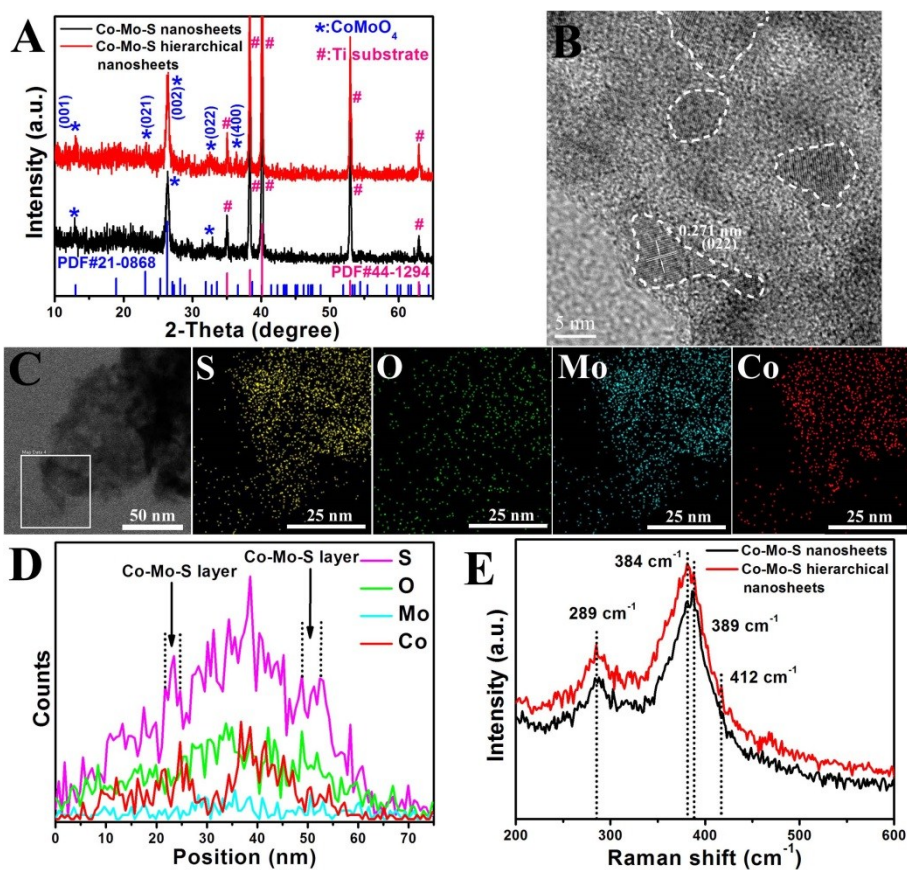


Figure S6. (A) XRD pattern, (B) high-resolution TEM image, (C) elemental mapping, (D) line-scan EDX spectra and (E) Raman spectrum of Co-Mo-S nanosheets.

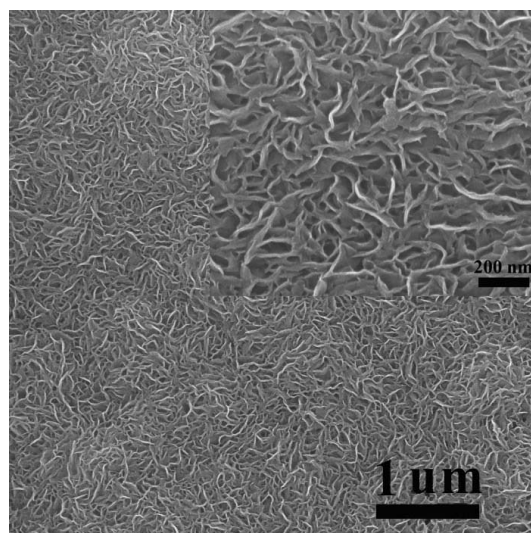


Figure S7. Low-resolution SEM images of MoS₂ nanosheets, (inset) high-resolution SEM images.

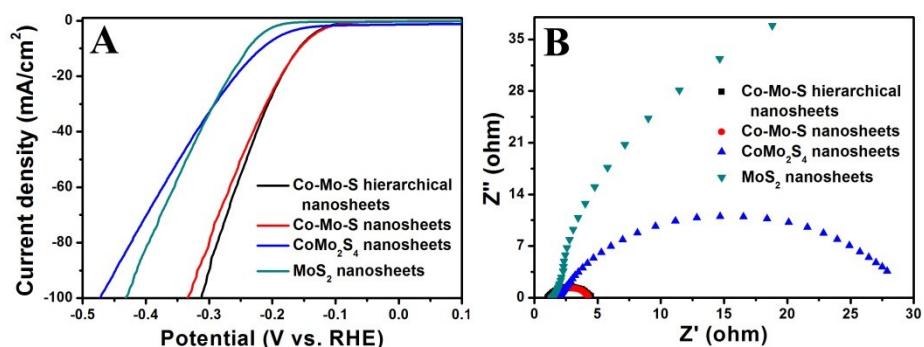


Figure S8. (A) Polarization curves and (B) Nyquist plots of several electrocatalysts as indicated, including Co-Mo-S hierarchical nanosheets, Co-Mo-S nanosheets, CoMo₂S₄ nanosheets and MoS₂ nanosheets.

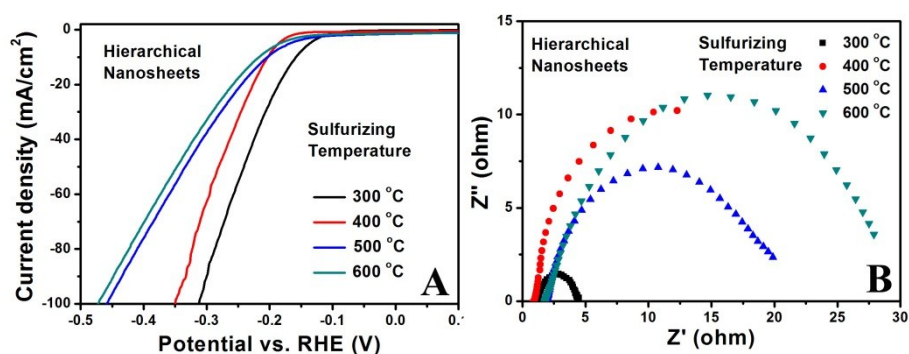


Figure S9. (A) Polarization curves and (B) Nyquist plots of several hierarchical nanosheets electrocatalysts obtained at different sulfurizing temperature.

Table S1. Comparison of HER performances in 0.5 M H₂SO₄ solution for Co-Mo-S nanoarray electrodes with other HER electrocatalysts

Electrocatalyst	Onset potential (mV)	Tafel slope (mV dec ⁻¹)	Overpotential at -10 mA cm ⁻² (mV)	Overpotential at -100 mA cm ⁻² (mV)
Co-Mo-S hierarchical nanosheets/Ti foil, this work	90	53	147	203
Co-Mo-S thin nanosheets/Ti foil, this work	90	54	144	202
CoS ₂ @MoS ₂ nanoarray/Ti foil, ref. 14	44	57.3	111	none
MoS ₂ nanosheet array/Ti foil, ref. 22	150	51	225	272

MoS ₂ @MoO ₃ nanowires/FTO, ref. 27	150	50	260	none
Co-doped MoS ₃ film/GC, ref. 9	135	43	188	none
CoS ₂ nanopyramid array/Ti foil, ref. 28	81	72	193	262
CoS ₂ nanowires/graphite, ref. 16	75	51.6	145	215
CoS ₂ nanoparticles/graphite, ref. 29	50	52	192	none

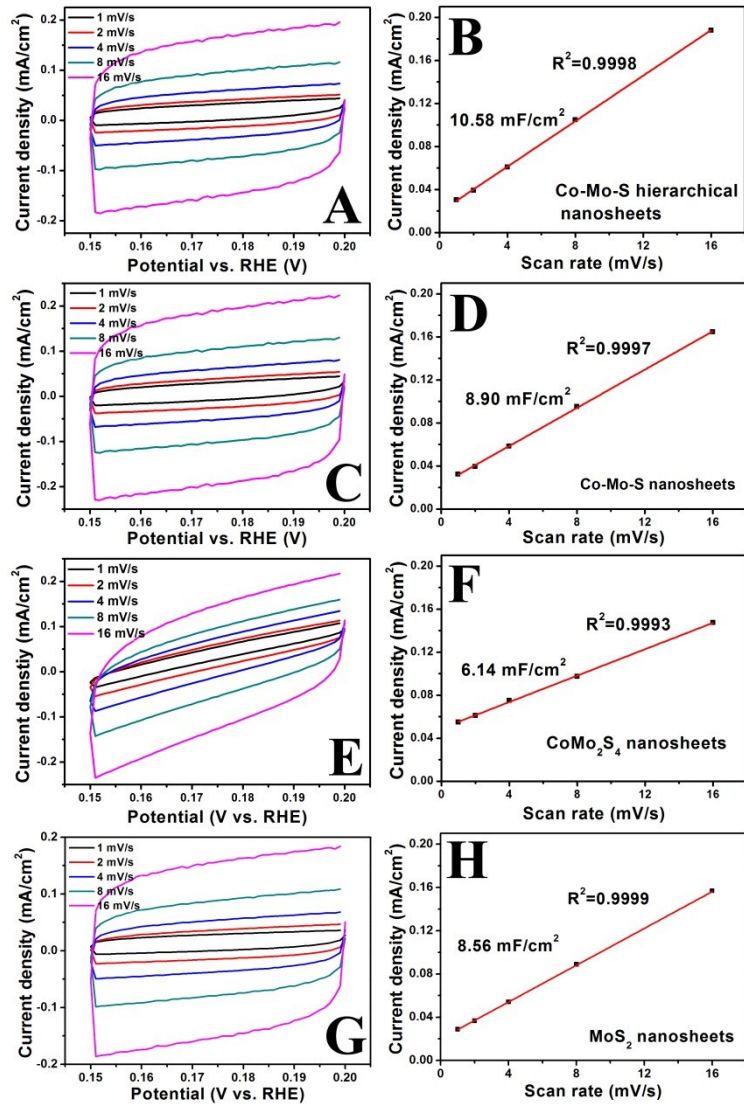


Figure S10. EDLC measurements and the corresponding current density-scan rates curves of several electrocatalysts as indicated, including (A and B) Co-Mo-S hierarchical nanosheets, (C and D) Co-Mo-S nanosheets, (E and F) CoMo₂S₄ nanosheets and (G and H) MoS₂ nanosheets.

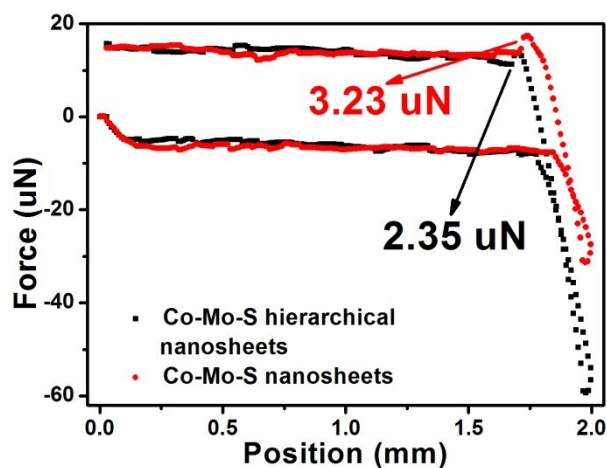


Figure S11. The bubble adhesive forces of the Co-Mo-S hierarchical nanosheets (2.35 uN) and Co-Mo-S nanosheets (3.23 uN).

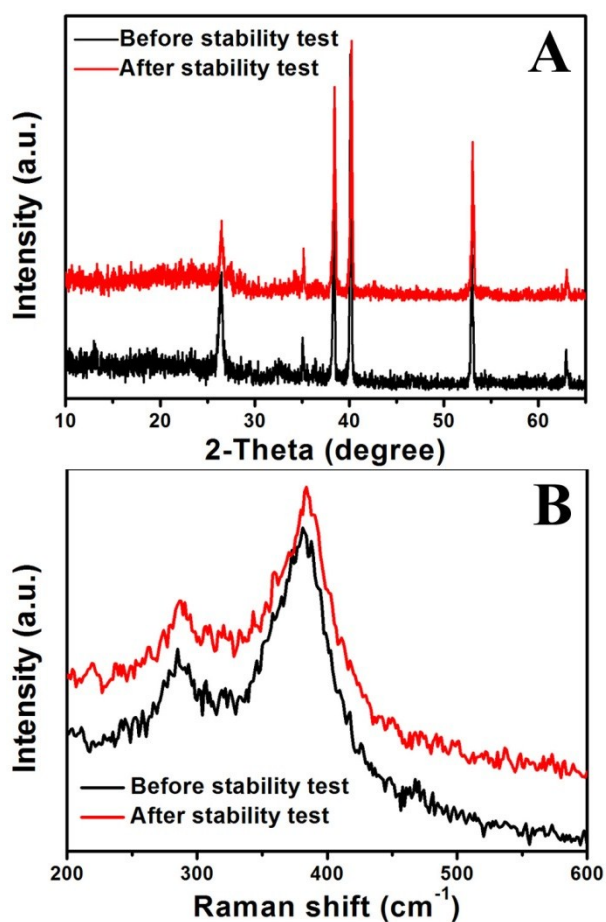


Figure S12. (A) XRD patterns and (B) Raman spectrum of the Co-Mo-S hierarchical nanosheets electrode before and after stability test.