

Electronic Supplementary Information

Amorphous Molybdenum Sulfide Films as Catalysts for Electrochemical Hydrogen Production in Water

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Chemicals and Reagents

All manipulations were carried out under an inert N₂(g) atmosphere using glovebox techniques unless otherwise mentioned. Unless noted, all other reagents were purchased from commercial sources and used without further purification.

Physical methods

GC measurement was conducted on a Perkin-Elmer Clarus 400 GC with a FID detector a TCD detector and a 5 Å molecular sieves packed column with Ar as a carrier gas. UV-Vis measurements were carried out using a Varian Cary 50 Bio Spectrophotometer controlled by Cary WinUV software. SEM secondary electron (SE) images were taken on a Philips (FEI) XLF-30 FEG scanning electron microscope. XRD measurements were carried out on a PANalytical X'Pert PRO diffractometer using Cu K_{α1} radiation (0.1540 nm). Electrochemical measurements were recorded by an IviumStat electrochemical analyzer or an EG&G Princeton Applied Research Potentiostat/Galvanostat model 273. A three-electrode configuration was used. For polarization and electrolysis measurements, a platinum wire was used as the auxiliary electrode and an Ag/AgCl (KCl saturated) electrode was used as the reference electrode. The reference electrode was placed in a position very close to the working electrode with the aid of a Luggin tube. For rotating disk measurements, an Autolab Rotating Disk Electrode assembly was used. Potentials were referenced to reversible hydrogen electrode (RHE) by adding a value of (0.197 + 0.059 pH) V. The polarization curves measured under one atmosphere of H₂ are nearly identical to those collected in the absence of external H₂, indicating that the potentials measured in the latter experiments are close to the thermodynamically-calibrated values. Ohmic drop correction was done prior to Tafel analysis. Film thickness was measured using an Alpha Step

500 (KLA-Tencor) stylus-based surface profiler. Pressure measurements during electrolysis were performed using a SensorTechnics BSDX0500D4R differential pressure transducer. Both current and pressure data were recorded simultaneously using an A/D Labjack U12 interface with a sampling interval of one point per second. X-ray photoelectron spectroscopy (XPS) data were collected by Axis Ultra (Kratos analytical, Manchester, UK) under ultra-high vacuum condition ($<10^{-8}$ Torr), using a monochromatic Al K_{α} X-ray source (1486.6 eV), in the Surface Analysis Laboratory of CIME at EPFL. The source power was maintained at 150 W (10 mA, 15kV). Gold (Au $4f_{7/2}$) and copper (Cu $2p_{3/2}$) lines at 84.0 and 932.6 eV, respectively, were used for calibration, and the adventitious carbon 1s peak at 285 eV as an internal standard to compensate for any charging effects. For quantification, relative sensitivity factors from the supplier were used. The XPS samples were placed inside an antechamber which was then evacuated by an independent turbomolecular pump. The inner door of the antechamber was then opened and the samples were introduced to the main chamber of XPS analysis.

Deposition of films

I. On glassy carbon electrodes

A 3 mm diameter glassy carbon rotating disk working electrode from *Autolab* (6.1204.300 GC) and a 3 mm diameter glassy carbon working electrode from *CH Instruments* (CHI 104) were used.

The electrodes were polished with two different Alpha alumina powder (1.0 and 0.3 micron from *CH Instruments*) suspended in distilled water on a Nylon polishing pad (*CH Instruments*) and with Gamma alumina powder (0.05 micron from *CH Instruments*) suspended in distilled water on a Microcloth polishing pad (*CH Instruments*). Before going to the next smaller powder size and at the end of polishing, the electrodes were thoroughly rinsed with distilled water.

Deposition of MoS₃-CV: The modification was carried out in a glove box under nitrogen. The freshly polished electrode was immersed into a 2 mM solution of (NH₄)₂[MoS₄] in 0.1 M NaClO₄ in water (8 mL). Both chemicals were used as received (*Aldrich*). Thirty consecutive cyclic voltammograms were carried out on an Ivium Stat potentiostat (*Ivium Technologies*) with a saturated silver/silver chloride reference electrode (separated by a porous vycor tip) and a titanium wire counter electrode. The cyclic voltammograms were performed between +0.1 and -1.0 V vs. Ag/AgCl (sat.) and a scan rate of 0.05 V/s was employed. Finally, the modified electrode was rinsed with distilled water.

II. On FTO-coated glass plates

On FTO-coated glass plates: FTO-coated glass was cut down to rectangular plates of 9 x 25 mm. The plates were cleaned in a bath of 1 M KOH in ethanol and washed with ethanol, water and acetone. An adhesive tape with a hole of 5 mm diameter was attached on each plate in such a way that a circle of 5 mm diameter in the bottom part and a small strip at the top of the plate remained uncovered. The plate will be modified in the area of the circle only and the uncovered strip serves as electrical contact.

Depositions of MoS₃-CV: The modification was carried out in a glove box under nitrogen. The freshly prepared FTO electrode was immersed into a 2 mM solution of (NH₄)₂[MoS₄] in 0.1 M

NaClO₄ in water (6 mL). Both chemicals were used as received (*Aldrich*). Fifteen, twenty-five or thirty-five consecutive cyclic voltammograms were carried out on an Ivium Stat potentiostat (*Ivium Technologies*) with a saturated silver/silver chloride reference electrode (separated by a porous vycor tip) and a platinum wire counter electrode. The cyclic voltammograms were performed between +0.1 and -1.0 V vs. Ag/AgCl (sat.) and a scan rate of 0.05 V/s was employed. Finally, the modified electrode was rinsed with distilled water.

Note: to ensure that the catalytic properties of the MoS₃-CV films are not due to Pt particles that can be accidentally deposited during film formation, we also deposited MoS₃-CV films using Ti as the counter electrode. The polarization curves of these films were measured using Ti as the counter electrode as well. At overpotentials below 300 mV, the polarization curves are nearly identical to those measured using Pt as the counter electrode. Some discrepancy was found at higher overpotentials, probably because the Ti counter electrode is not able to supply enough current at those potentials. These results rule out the possibility of Pt contamination.

Deposition of MoS₂-CV film: Same procedure as described for MoS₃-CV film, but the cyclic voltammograms were performed between -1.0 and +0.1 V vs. Ag/AgCl (sat.), i.e. they started and ended at -1.0 V vs. Ag/AgCl (sat.).

Deposition of MoS₃-AE: Same conditions as described above, but instead of consecutive cyclic voltammograms, a constant potential of +0.3 V vs. Ag/AgCl (sat.) was applied for 70 s.

Deposition of MoS₂-CE film: Same conditions as described above, but instead of consecutive cyclic voltammograms, a constant potential of -1.3 V vs. Ag/AgCl (sat.) was applied for 160 s.

Ohmic drop correction:

The ohmic drop correction of polarization curves has been performed according to the method given in the literature [1-3]. The overpotential η (V) observed during an experiment is given by equation (1):

$$\eta = a + b \ln j + jR \quad (1)$$

where a (V) is the Tafel constant, b (V dec⁻¹) is the Tafel slope, j (A cm⁻²) is the current density and R (Ω cm⁻²) is the total area-specific uncompensated resistance of the system, which is assumed to be constant. The derivative of Eq. (1) with respect to current density gives Eq. (2) from which b and R can be easily obtained by plotting $d\eta/dj$ as a function of $1/j$.

$$\frac{d\eta}{dj} = \frac{b}{j} + R \quad (2)$$

The estimation of R allows correcting the experimental overpotential by subtracting the ohmic drop jR according to equation (3):

$$\eta_{corr} = \eta - jR \quad (3)$$

During the calculations, the derivative $d\eta/dj$ was replaced by their finite elements $\Delta\eta/\Delta j$ estimated from each pair of consecutive experimental points.

Bulk Electrolysis

Electrolysis experiments were performed in an H shape cell (Fig. S1). The platinum counter electrode was separated from the solution through a porous glass frit (porosity 3) and this whole assembly inserted into one side of the H cell. The modified working electrode was inserted in the

other side of the cell, together with a magnetic stirring bar and a Luggin capillary. Two small inlets were present in the cell allowing the connection to the pressure monitoring device and the other kept closed by a septum for sampling of the gas phase. The whole cell apparatus is gas-tight and the pressure increase is proportional to the gases generated ($H_2 + O_2$). It is assumed that for 2 moles of H_2 generated in the working electrode, 1 mole of O_2 is generated in the counter electrode. Prior to each experiment, the assembled cell was calibrated by injecting known amounts of air into the closed system and recording the pressure change, after the calibration the cell was purged with nitrogen for 20 minutes and the measurements were performed.

Control experiments were performed using platinum as a working electrode and a quantitative Faraday yield was obtained by measuring the pressure (97-102 %) and confirmed by GC analysis of the gas in the headspace (92-96 %) at the end of the electrolysis. For the electrochemical modified electrodes the films were deposited on glassy carbon electrodes and electrolysis carried out during 60 minutes. At the end the current efficiency was determined by the pressure change in the system and confirmed by GC analysis.

Calculation of active sites

The MoS_3 -CV film was deposited as described above during a certain number of consecutive cyclic voltammograms in a solution of $(NH_4)_2MoS_4$ in pH = 7 phosphate buffer (modification cycles). After 6, 9, 12, 15 and 18 modification cycles, cyclic voltammetry measurements were carried out in pH = 7 phosphate buffer only (blank measurements). The potential window and scan rate applied for these blank measurements were the same as those applied for the modification cycles.

Later, the absolute components of the voltammetric charges (cathodic and anodic) reported during one single blank measurement were added. Assuming a one electron redox process, this absolute charge was divided by two. The value was then divided by the Faraday constant to get the number of active sites of the film.

Following this procedure, the number of active sites (in mol) after 6, 9, 12, 15 and 18 modification cycles was determined.

Determination of the turnover frequency (TOF)

When the number of active sites is known, the turnover frequencies (in s^{-1}) were calculated with

the following equation:
$$\text{TOF} = \frac{I}{Fn} \frac{1}{2}$$

I: Current (in A) during the linear sweep measurement after 6, 9, 12, 15 or 18 modification cycles, respectively.

F: Faraday constant (in C/mol).

n: Number of active sites (in mol) after 6, 9, 12, 15 or 18 modification cycles, respectively.

The factor $\frac{1}{2}$ arrives by taking into account that two electrons are required to form one hydrogen molecule from two protons.

Reference

- [1] D.M. Schub, M.F. Reznik, *Elektrokhimiya*, 21 (1985) 937
- [2] N. Krstajic, S. Trasatti, *Journal of Applied Electrochemistry*. 28 (1998) 1291
- [3] L.A. De Faria, J.F.C. Boodts, S. Trasatti, *Journal of Applied Electrochemistry*, 26 (1996) 1195

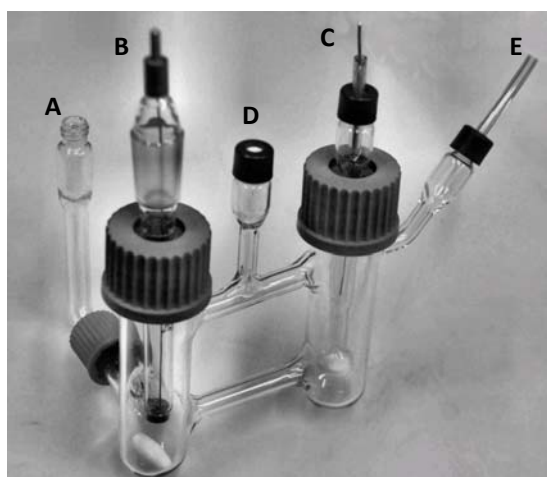
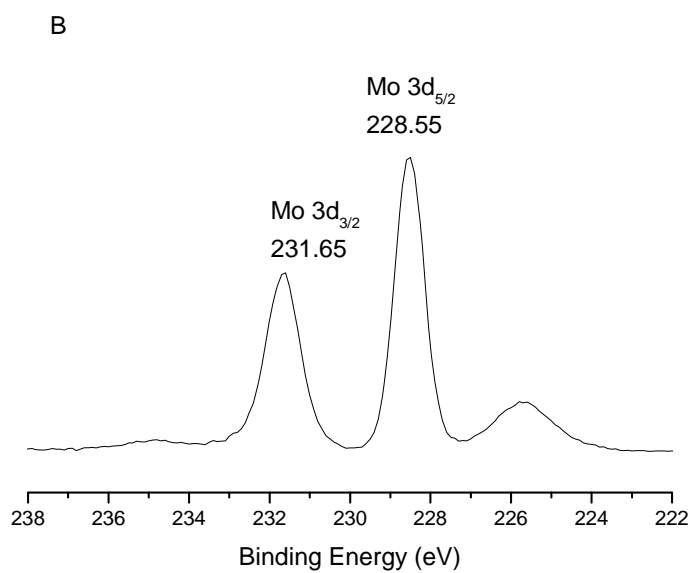
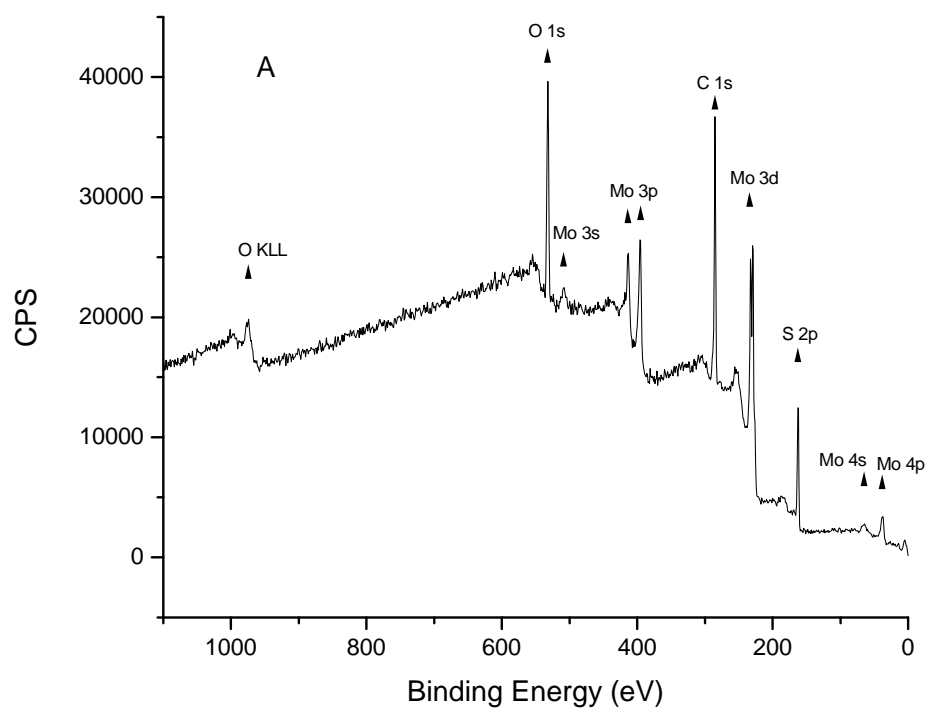


Fig. S1 Cell used for electrolysis experiments. (A) Insert on the Luggin capillary for the reference electrode, (B) 6 mm diameter glassy carbon working electrode, (C) Platinum wire counter electrode, (D) Septum closed inlet, (E) PVC tubing connecting the cell to the pressure meter.



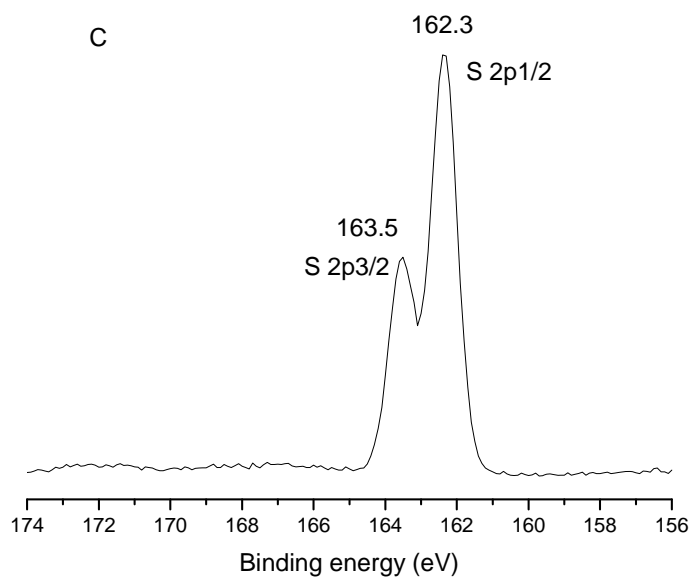
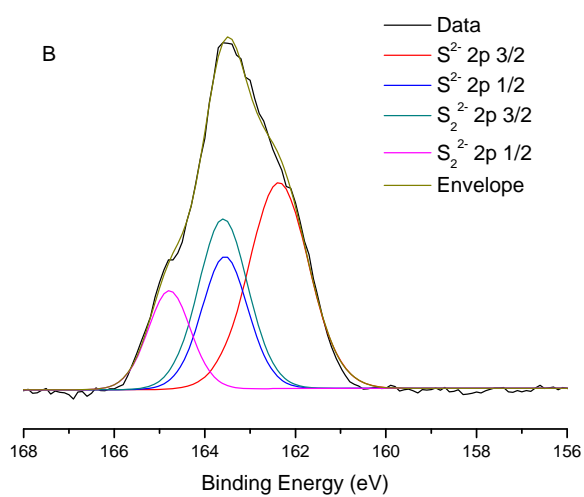
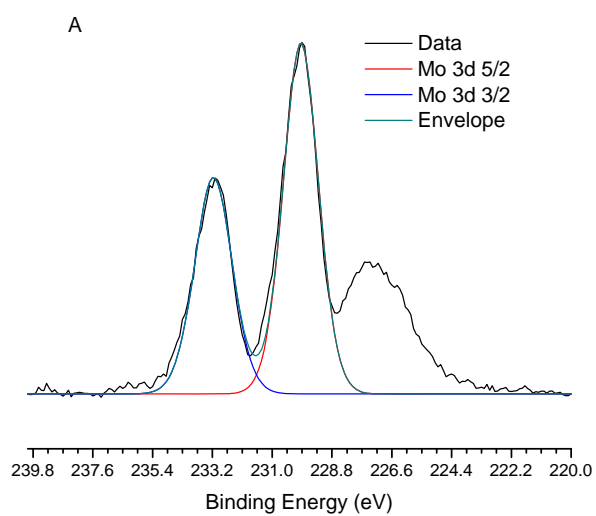


Fig. S2 (A) XPS survey spectrum of the MoS₃-CV film. (B) XPS Mo spectrum of commercial MoS₂ particles. The spectrum shows a peak at lower binding energies, which is the S 2s peak. (C) XPS S spectrum of commercial MoS₂ particles. The S/Mo ratio is 2.1 for MoS₂ particle.



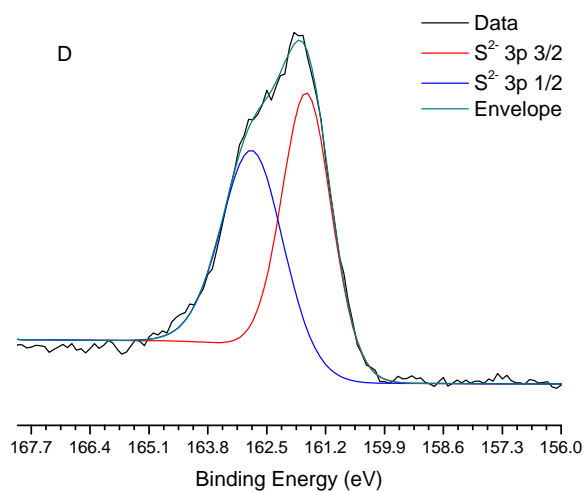
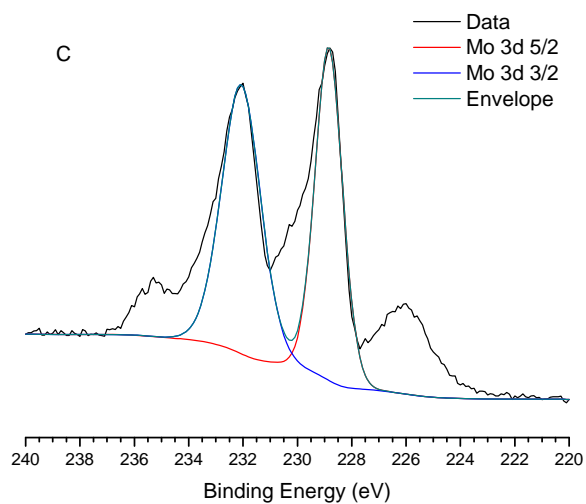


Fig. S3 (A) XPS Mo spectrum of the MoS₃-AE film. (B) XPS S spectrum of the MoS₃-AE film.
(C) XPS Mo spectrum of the MoS₂-CE film. (D) XPS S spectrum of the MoS₂-CE film.

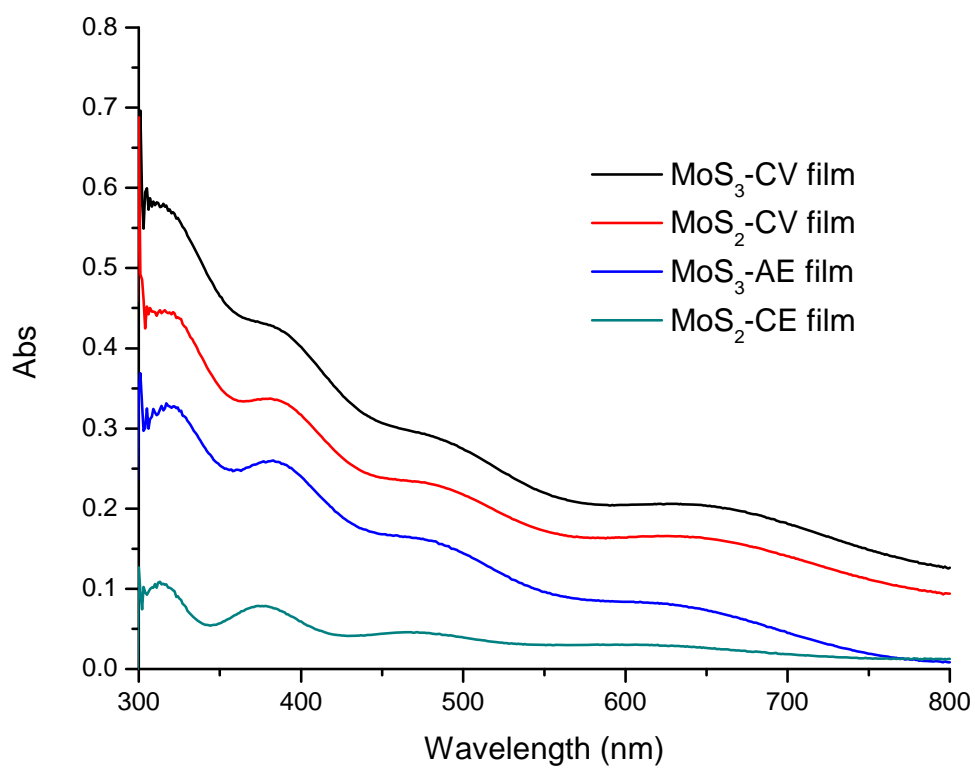
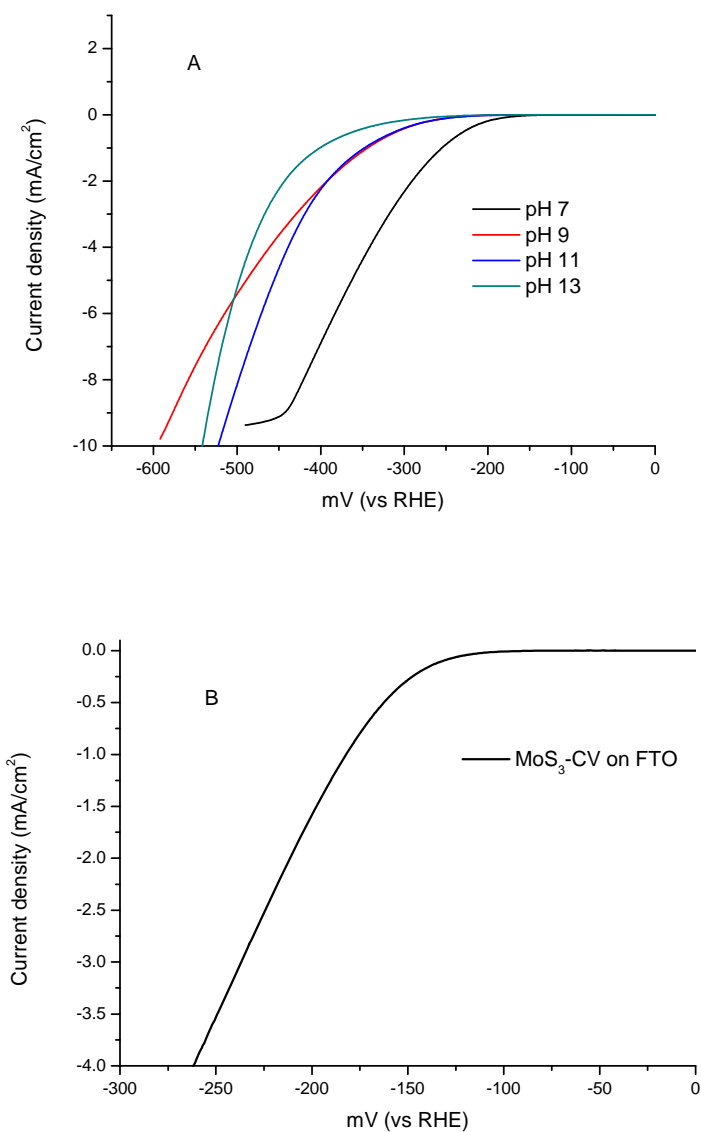


Fig. S4 UV-vis absorption spectra of the freshly prepared MoS_x films: MoS₃-CV, MoS₂-CV, MoS₃-AE, and MoS₂-CE.



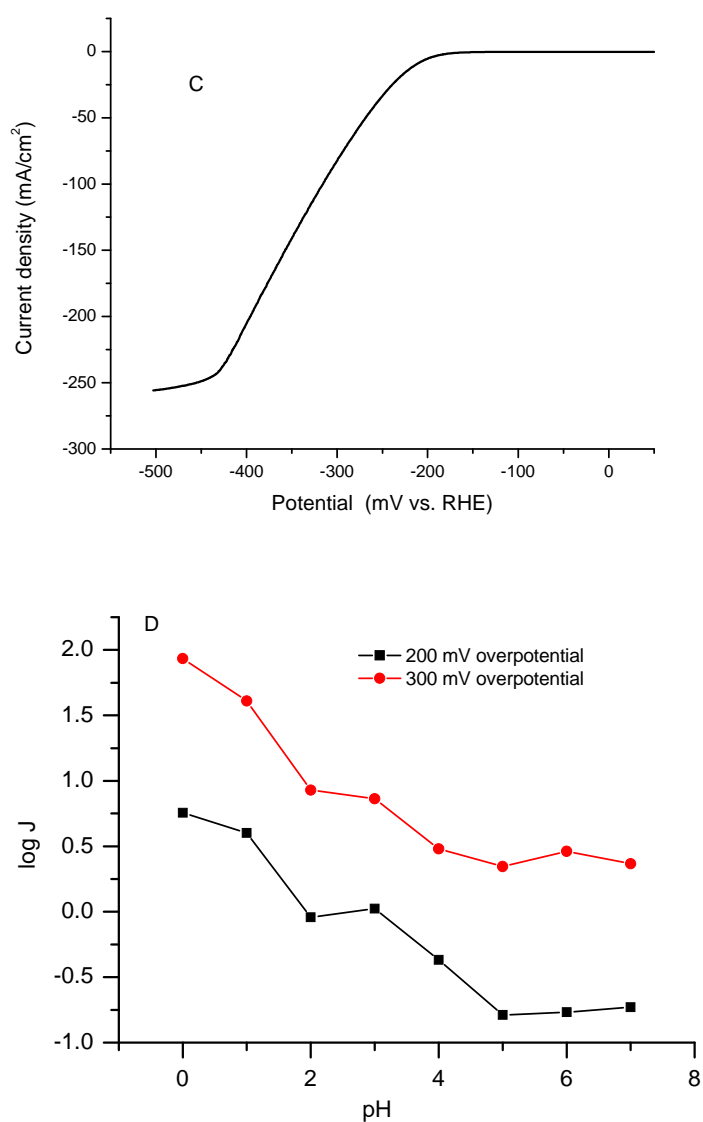
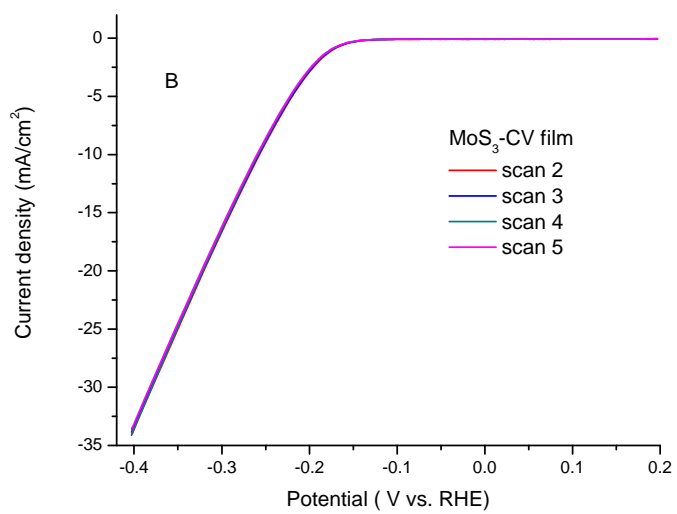
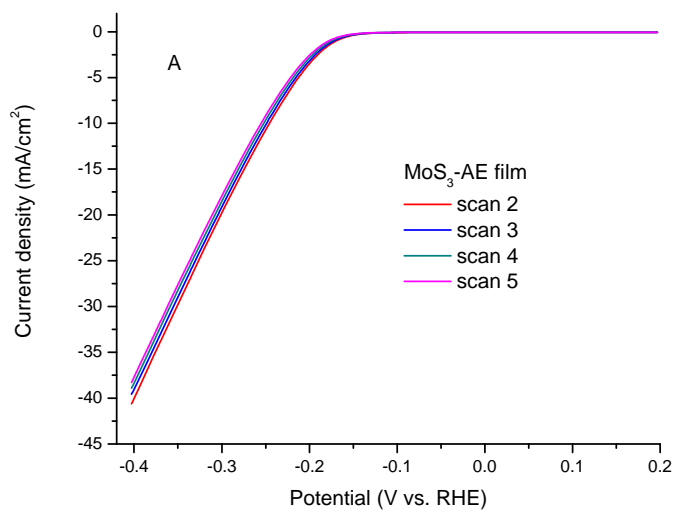


Fig. S5 (A) Polarization curves of MoS₃-CV film on a rotating glassy carbon electrode recorded at pH = 7, 9, 11, and 13. Scan rate: 2 mV/s; rotating rate: 4500 rpm. (B) Polarization curves of MoS₃-CV film on FTO recorded at pH = 2. Scan rate: 2 mV/s (C) Polarization curve of MoS₃-CV film on a rotating glassy carbon electrode recorded at pH = 0 showing response at a current higher than 100 mA/cm². Scan rate: 2 mV/s; rotating rate: 4500 rpm. (D) Dependence of log j over the pH values for MoS₃-CV film at 200 and 300 mV overpotential.



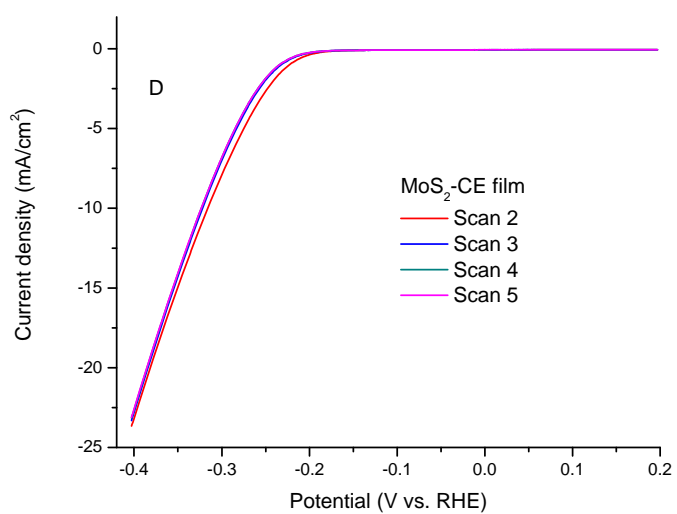
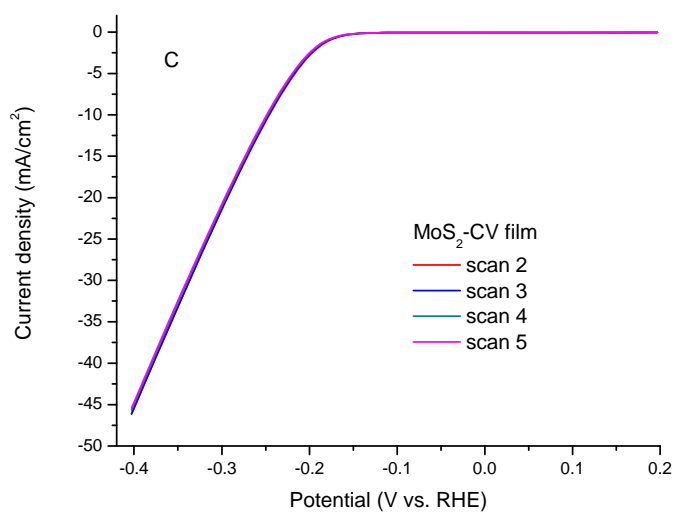


Fig. S6 Consecutive polarization curves of MoS_x films on FTO at pH = 0: MoS₃-AE (A), MoS₃-CV (B), MoS₂-CV (C), and MoS₂-CE (D).

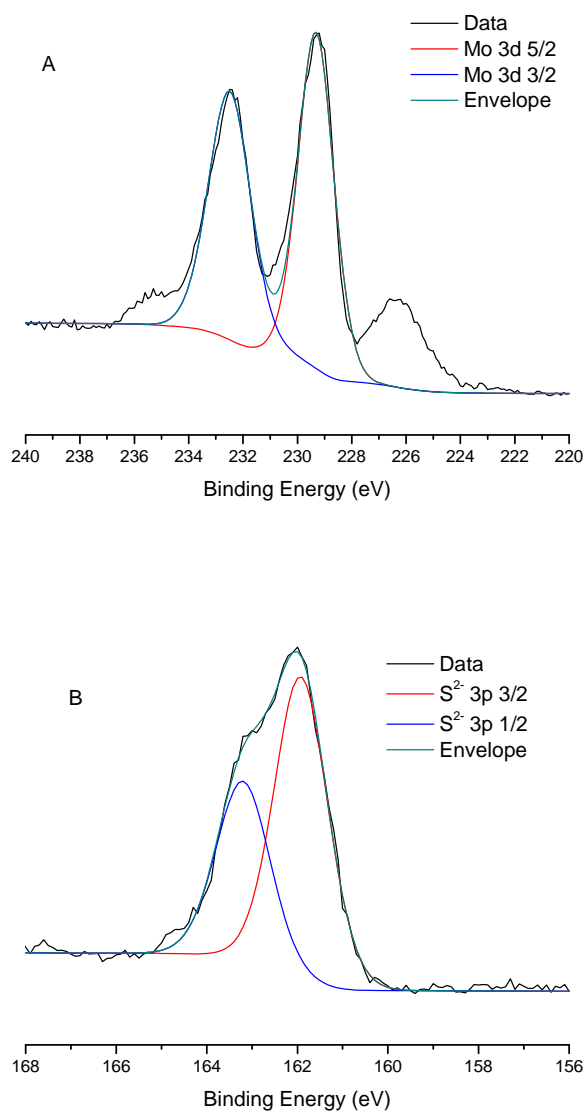


Fig. S7 (A) XPS Mo spectrum of the MoS₃-CV film after 10 polarization measurement at pH = 0. (B) XPS S spectrum of the MoS₃-CV film after 10 polarization measurement at pH = 0.

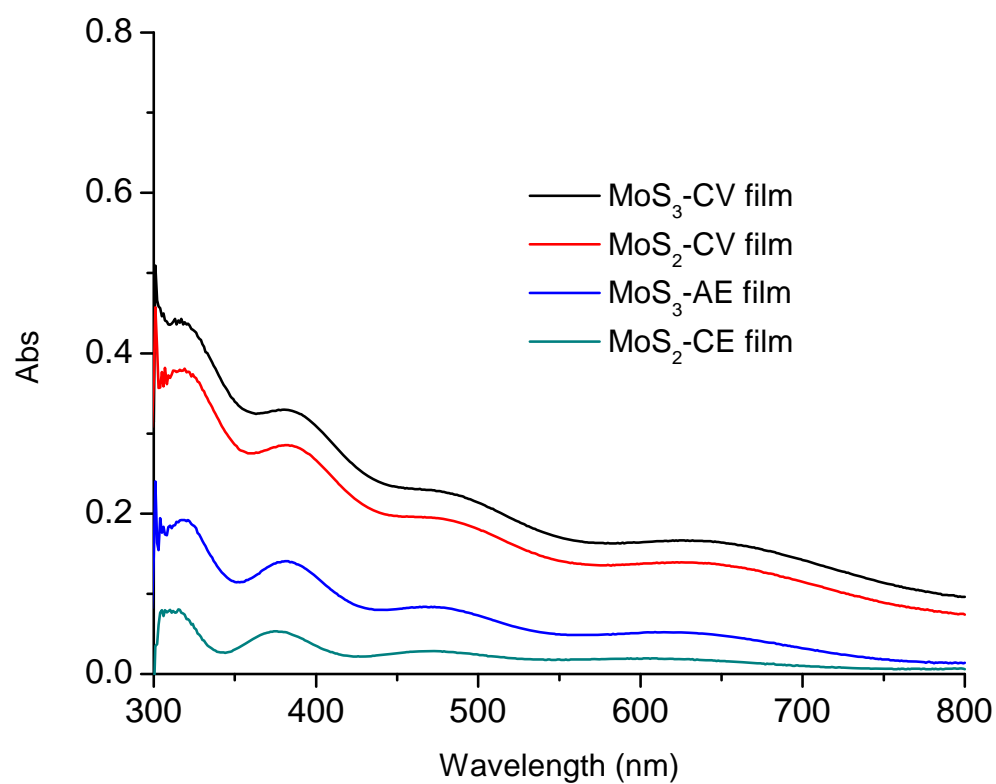


Fig. S8 UV-vis absorption spectra of the MoS_x films after 5 polarization cycles: MoS₃-CV, MoS₂-CV, MoS₃-AE, and MoS₂-CE.

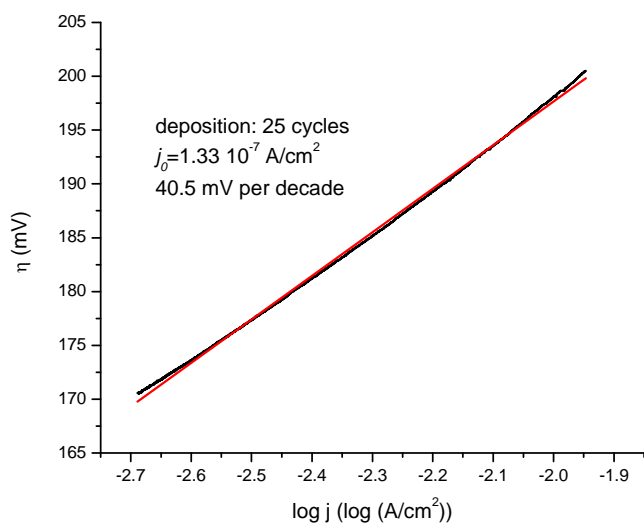


Fig. S9 Tafel analysis of the polarization curve at $\eta = 170$ to 200 mV for MoS_3 -CV film on glassy carbon at $\text{pH} = 0$. The film was made with 25 scanning cycles. Scan rate for polarization: 1 mV/s .

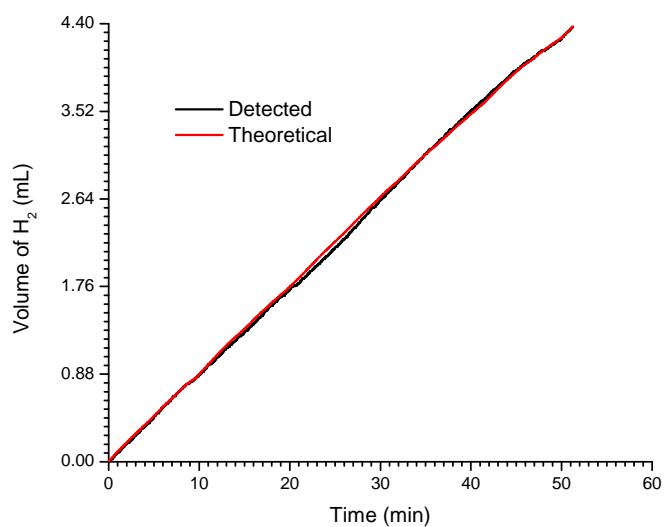


Fig. S10 Current efficiency for H₂ production catalyzed by a MoS₃-CV film on glassy carbon at pH = 0 and 300 mV overpotential. The theoretical line was calculated according to the cumulative charge, assuming a 100% Faraday's yield for H₂ production.

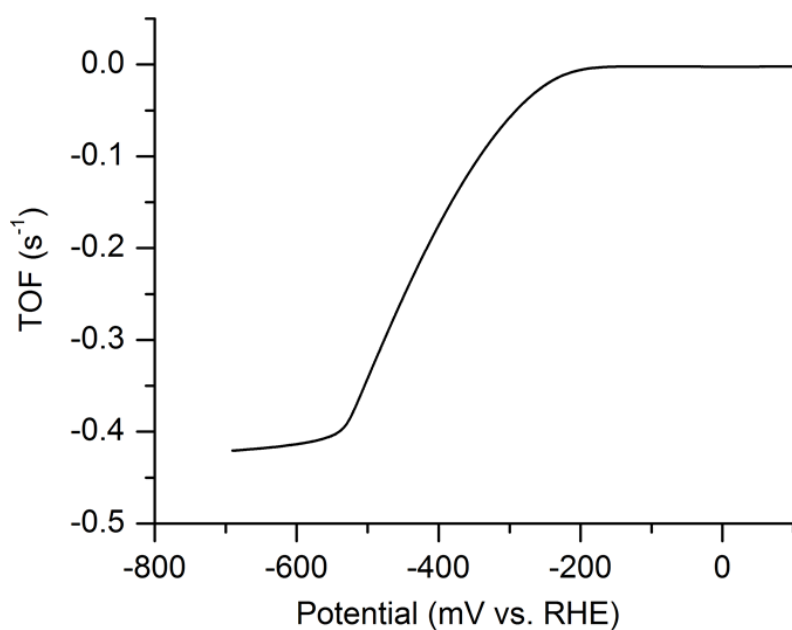


Fig. S11 Calculated TOFs for MoS₃-CV as a function of potential at pH = 7. The polarization curves were recorded on films deposited on a rotating glassy carbon electrode. Scan rate: 2 mV/s; rotating rate: 6000 rpm.