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Supporting Information for:

The Direct Hydrothermal Deposition of Cobalt-Doped MoS_2 onto Fluorine-Doped SnO_2 Substrates for Catalysis of the Electrochemical Hydrogen Evolution Reaction†

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Figure S1. Photograph showing the positioning of the FTO substrate inside the Teflon-lined bomb, at 45° to both the walls and base of the vessel. No dependence was observed on whether the conductive side of the FTO substrate faced towards the bottom of the vessel or towards the top.

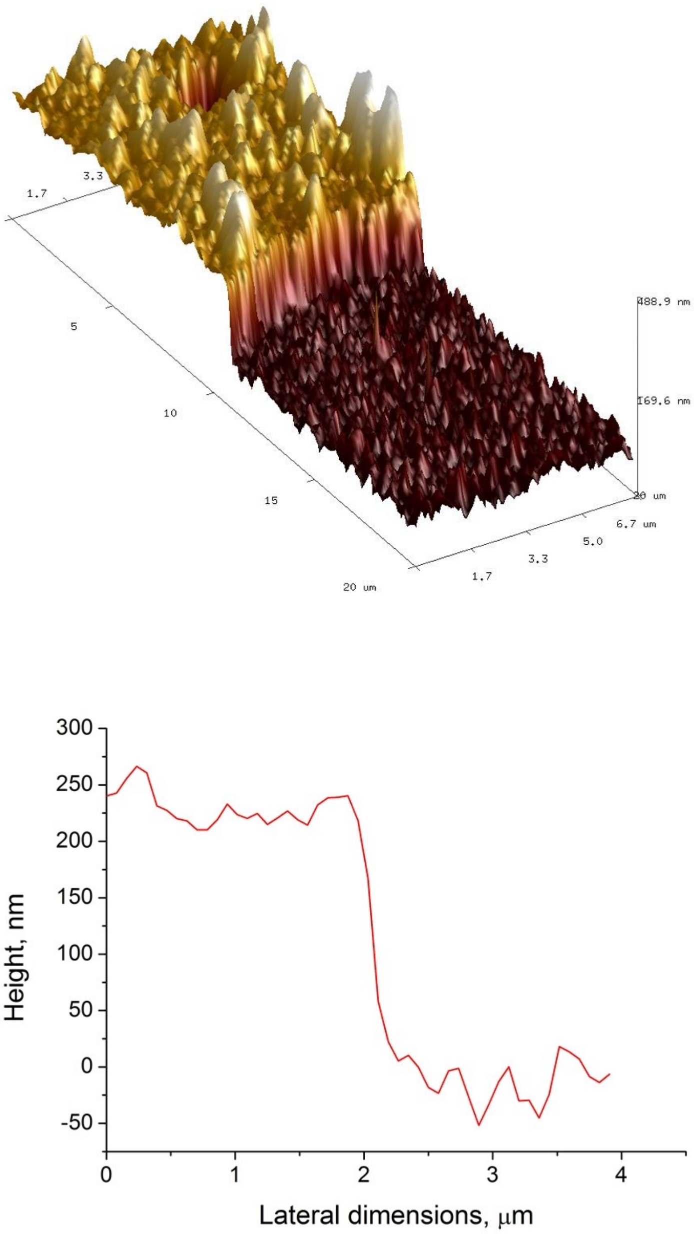

Figure S2. Representative AFM data collected on a film of around 300 nm in thickness. Upper panel: 3D topographical profile of the substrate/deposit step. Lower panel: A line scan showing the variation in height measured over the step shown in the upper panel.

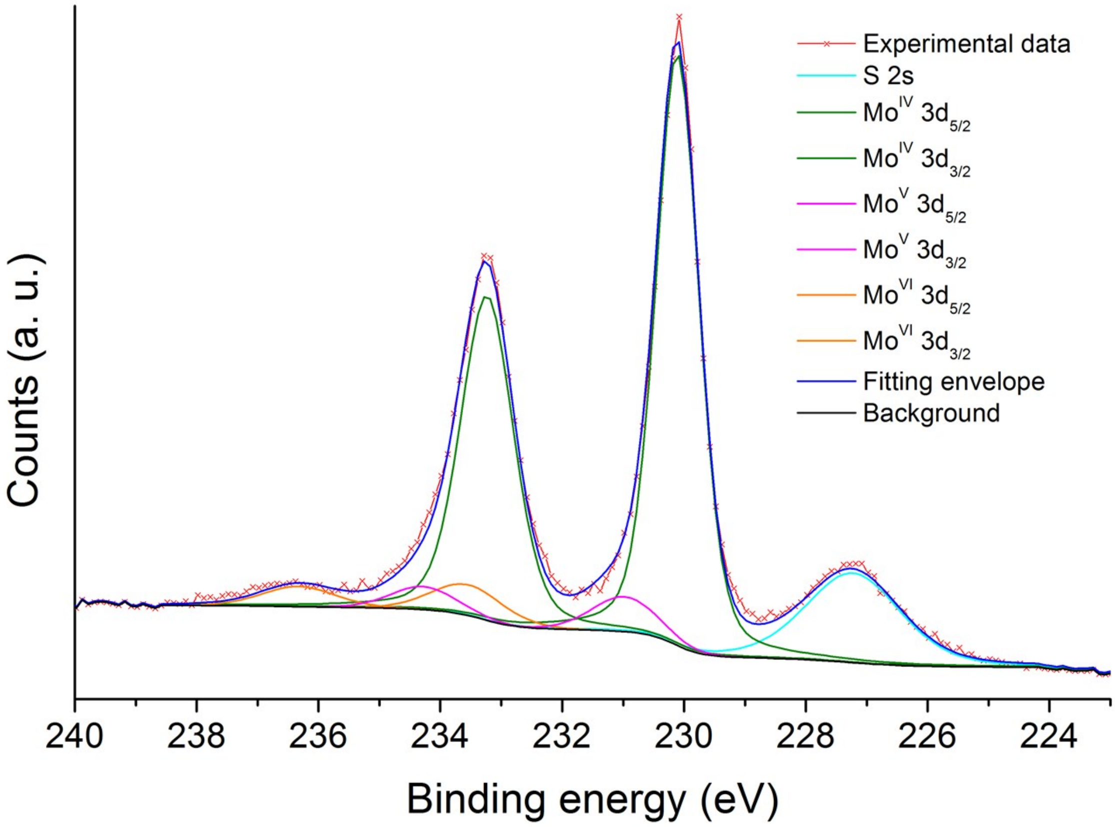

Figure S3. The 3d Mo region and 2s S region of the XPS spectrum for a 600 nm-thick film. The peaks were fitted with a combination of Gaussian-Lorentzian profile functions corresponding to a mixed-valence oxidation state of the molybdenum (Mo^{2+} 87 at. %; Mo^{5+} 6.5 at. % and Mo^{6+} 6.5 at. %).

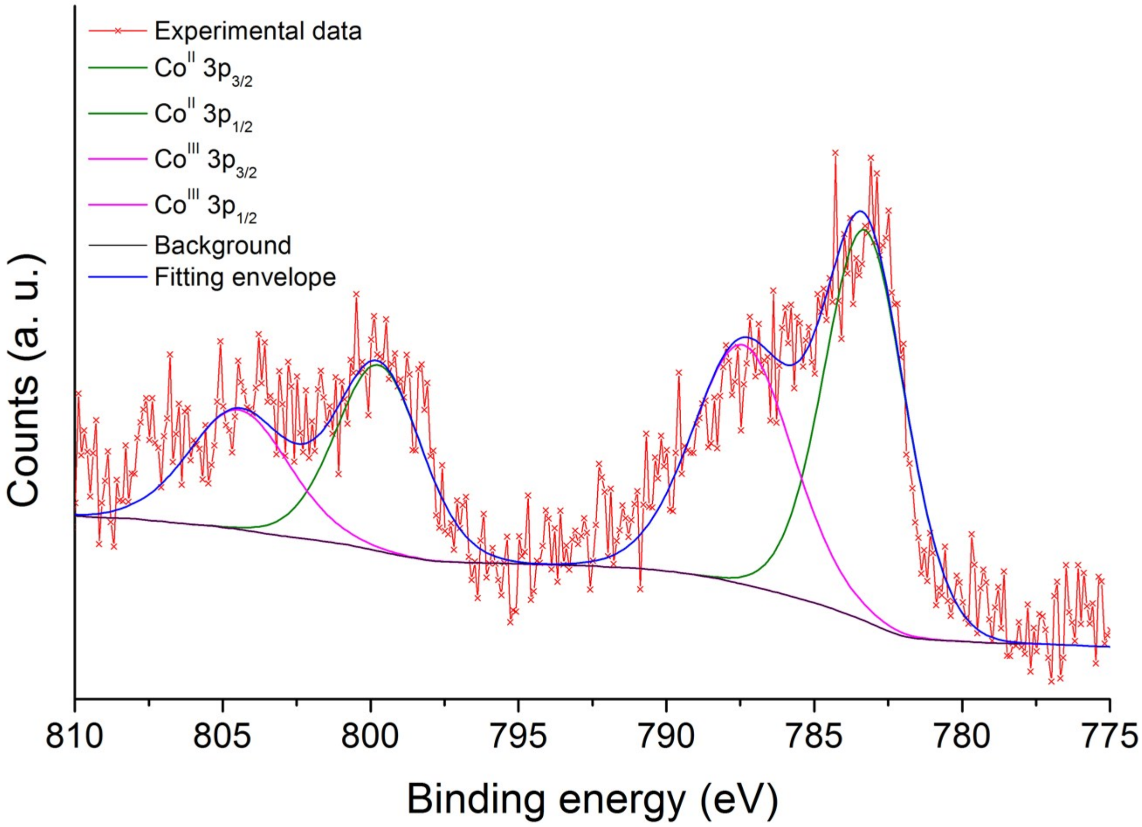

Figure S4. The 3p region of the Co XPS spectrum for a 600 nm-thick film with peaks fitted with a combination of Gaussian-Lorentzian profile functions and representing a mixed-valence oxidation state for cobalt (Co^{2+} 57 at. % and Co^{3+} 43 at. %).

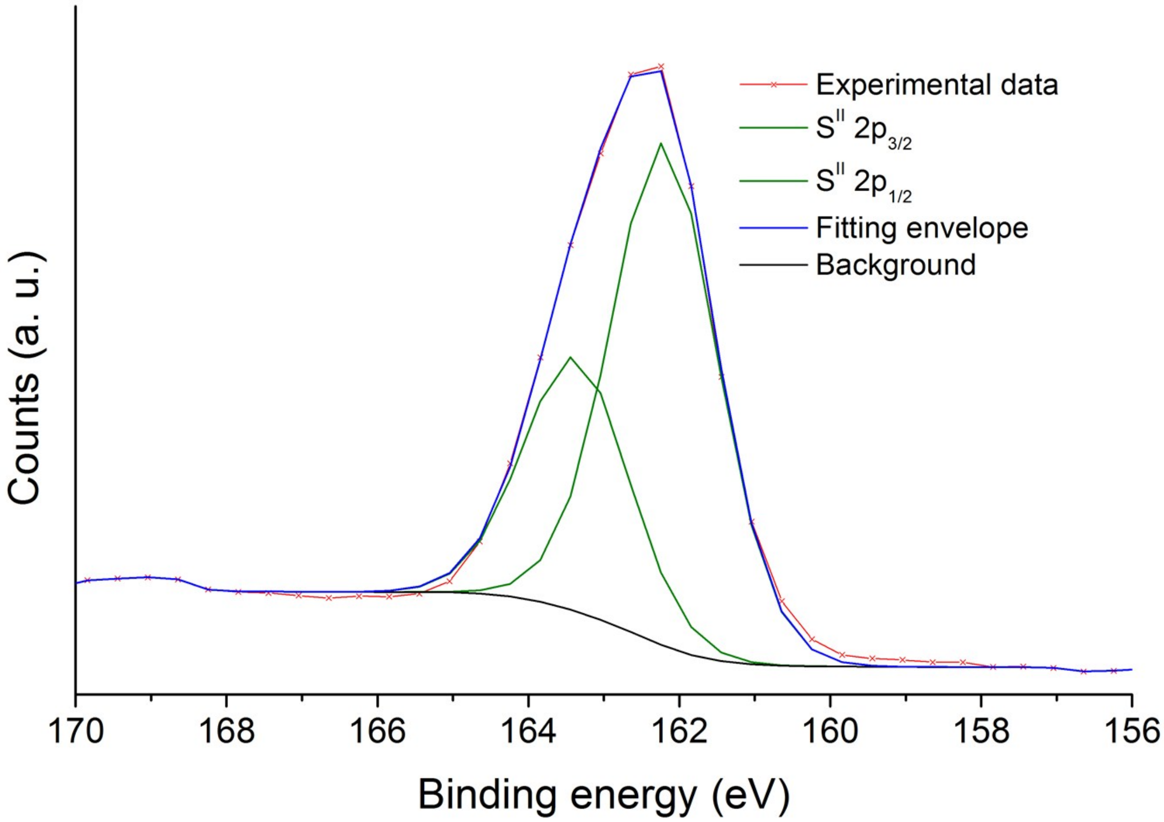

Figure S5. 2p S region of the XPS spectrum for a 600 nm-thick film. The peaks could be fitted with a single doublet using a combination of Gaussian-Lorentzian profiles, attributable to a sole S^{2-} oxidation state within the film.

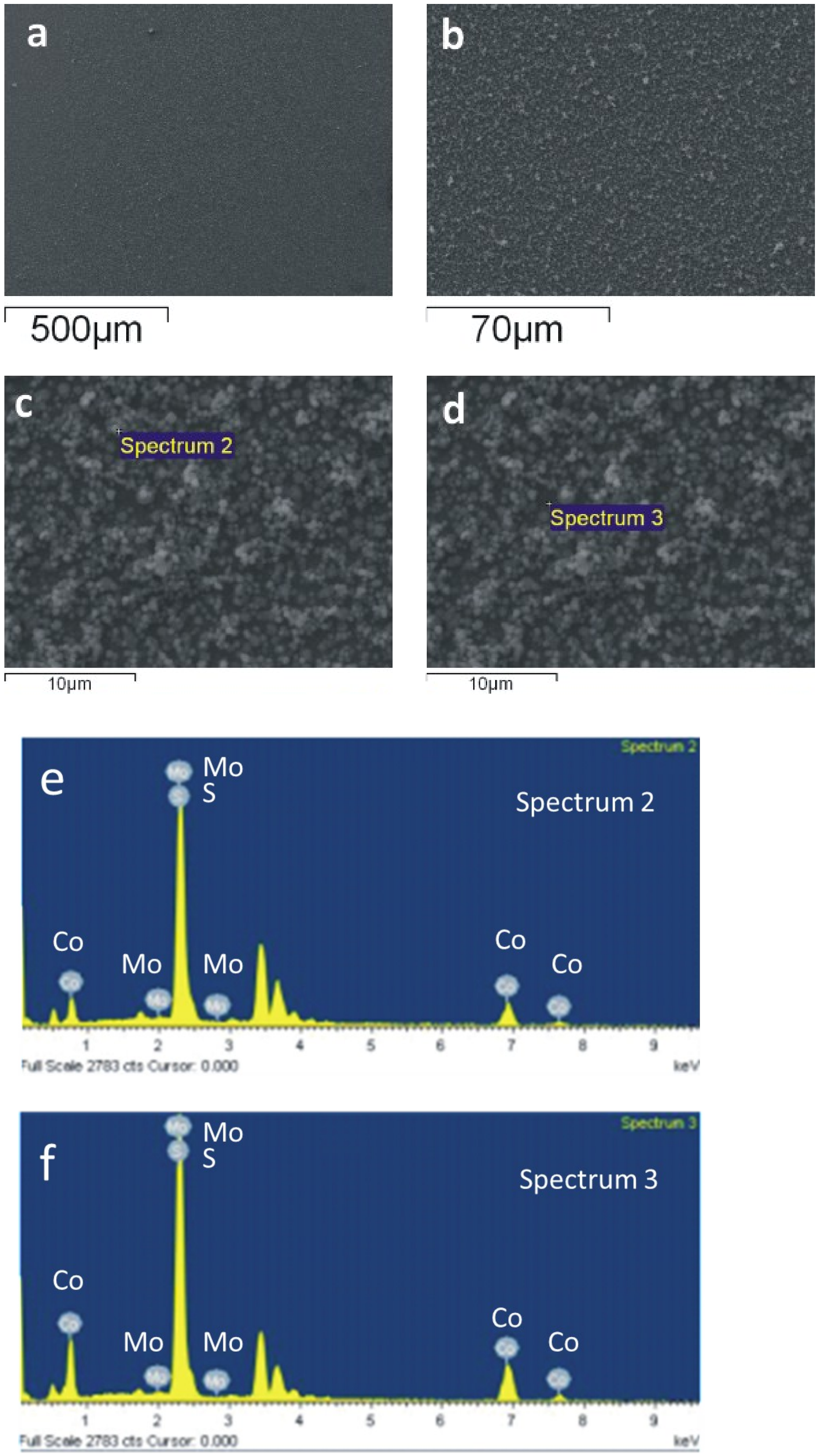

Figure S6. (a-b) SEM images showing the surface of the prepared films various magnifications. (c-d) Magnified region with the probed points and the corresponding EDX spectra (e,f) with

Co, S and Mo peaks marked. The strong triplet of the peaks at 3-4 keV originate from Sn due to the FTO substrate.

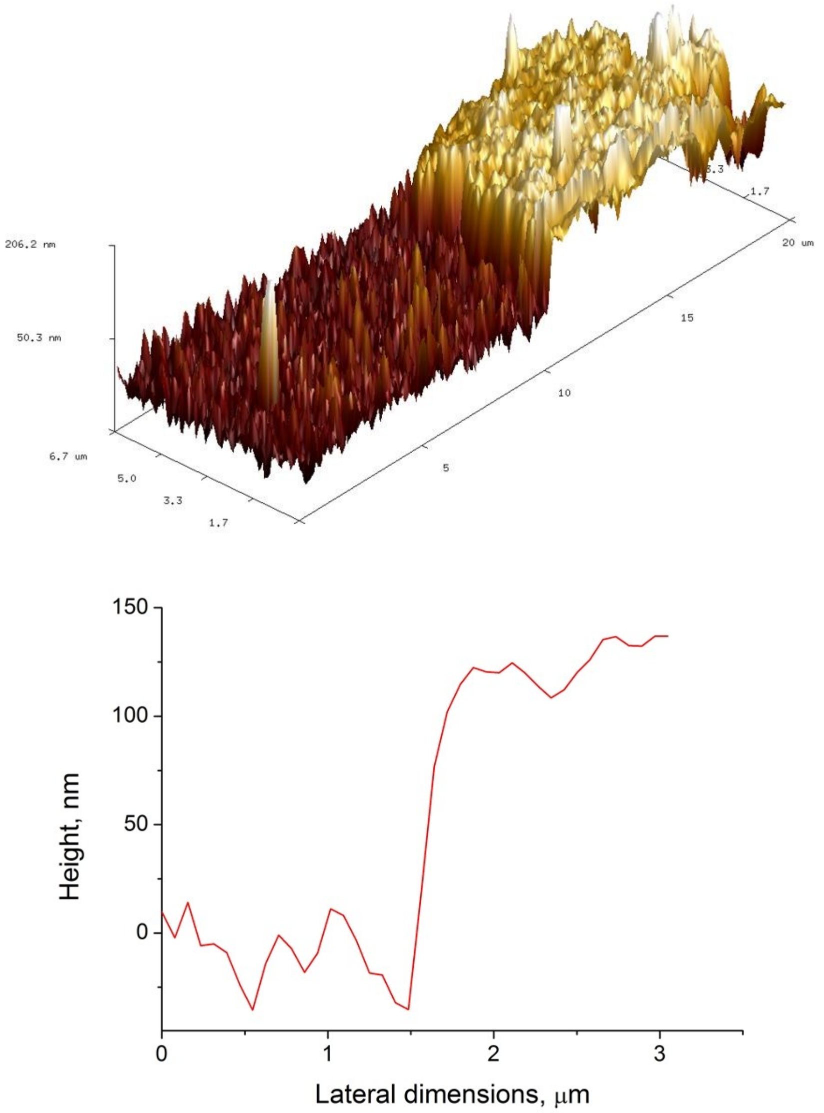

Figure S7. Representative AFM data collected on a film of around 150 nm in thickness. Upper panel: 3D topographical profile of the substrate/deposit step. Lower panel: A line scan showing the variation in height measured over the step shown in the upper panel.

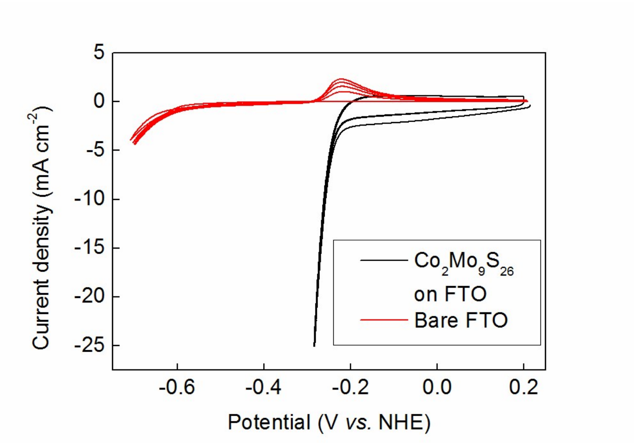

Figure S8. Cyclic voltammograms at room temperature in 0.5 M H_2SO_4 of a Co-doped molybdenum sulfide-on-FTO film (black line) and a bare FTO electrode (red line). All current densities have been corrected for resistance. In both cases, the sweep rate was 100 mV per second. For both traces, the reference electrode used was Ag/AgCl and the counter electrode was carbon felt.

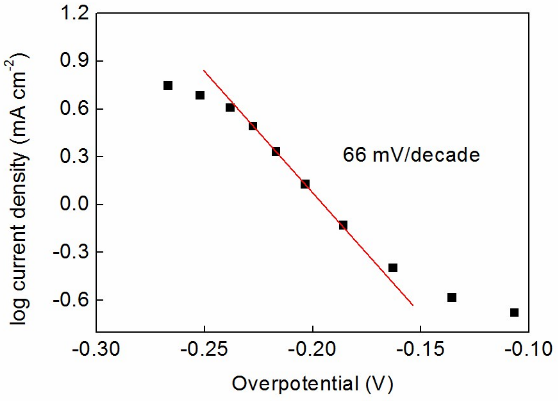

Figure S9. Tafel plot of a 300 nm-thick film collected as per the conditions stipulated in the Experimental Section whereby the current density was recorded after 5 minutes of electrolysis at each of the potentials denoted. A Tafel slope of 66 mV was obtained. Some delamination of the film was observed at overpotentials more negative than 250 mV in this case.

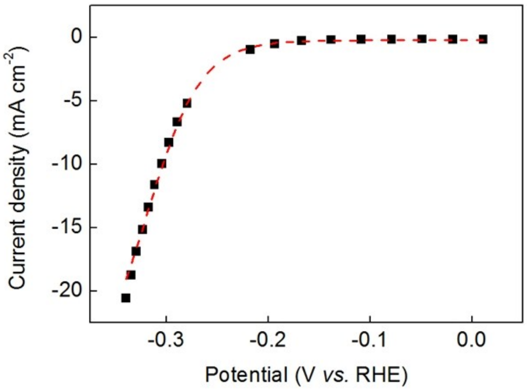

Figure S10. A representative trace showing the current density at pH 0 delivered by a 150 nm-thick $Co_2Mo_9S_{26}$ film prepared by the methods described in the main text on an FTO support. An Ag/AgCl reference electrode and carbon cloth counter electrode were used at room temperature. All current densities have been corrected for resistance. Black squares indicate steady-state current densities obtained after 5 minutes of polarization at the potentials indicated and the red dashed line is provided as a guide to the eye.

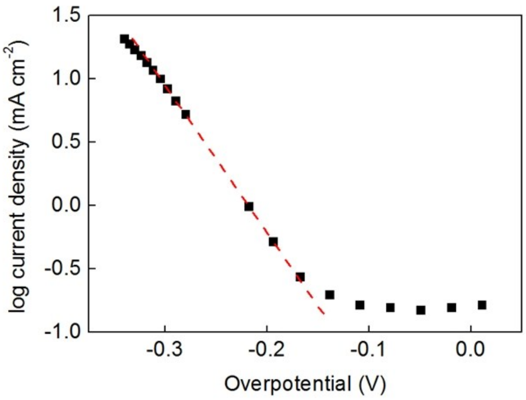

Figure S11. A representative Tafel plot collected for a 150 nm-thick $Co_2Mo_9S_{26}$ film in 0.5 M H_2SO_4 as per the conditions stipulated in the Experimental Section whereby the current density was recorded after 5 minutes of electrolysis at each of the potentials denoted (black squares). A Tafel slope of 85 mV was obtained (indicated by the red dashed line).

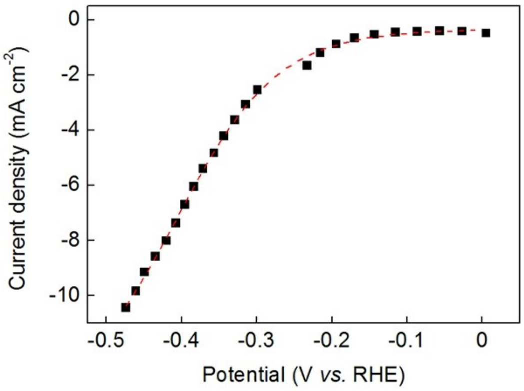

Figure S12. A representative trace showing the current density at pH 7 delivered by a 150 nm-thick $Co_2Mo_9S_{26}$ film prepared by the methods described in the main text on an FTO support. An Ag/AgCl reference electrode and carbon cloth counter electrode were used at room temperature. All current densities have been corrected for resistance. Black squares indicate steady-state current densities obtained after 5 minutes of polarization at the potentials indicated and the red dashed line is provided as a guide to the eye.

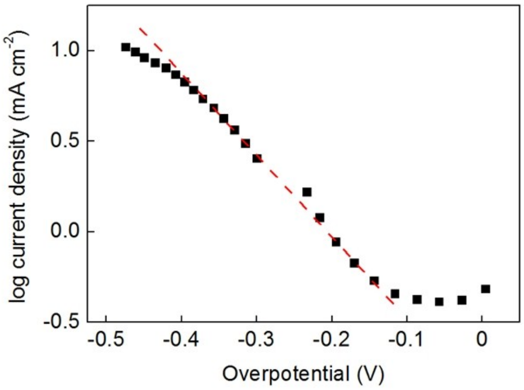

Figure S13. A representative Tafel plot collected for a 150 nm-thick $Co_2Mo_9S_{26}$ film in 0.5 M sodium phosphate buffer as per the conditions stipulated in the Experimental Section whereby the current density was recorded after 5 minutes of electrolysis at each of the potentials denoted (black squares). A Tafel slope of around 220 mV was obtained (indicated by the red dashed line).

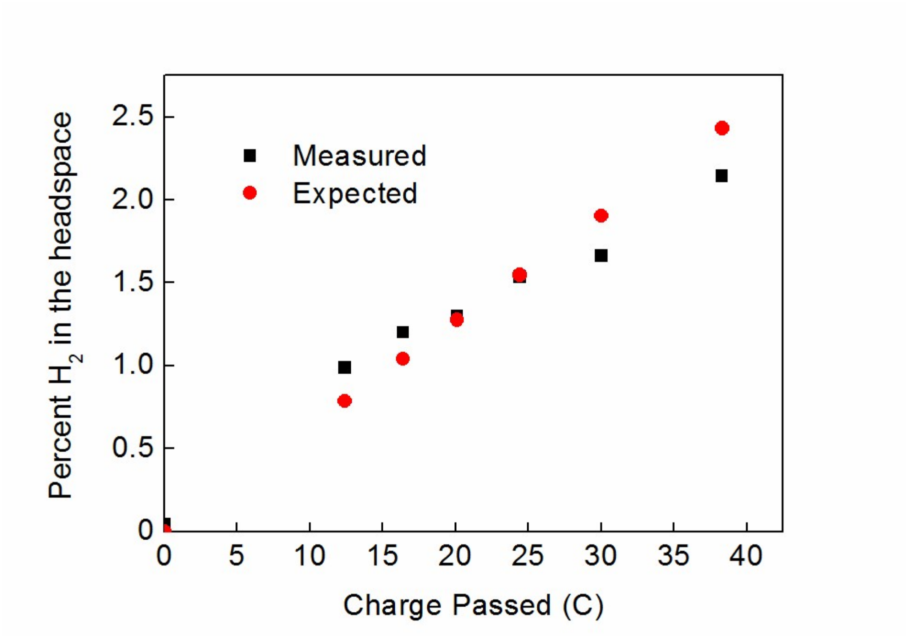

Figure S14. A representative trace showing gas chromatographic analysis of the headspace of airtight cells during electrolysis of a solution of 0.5 M sulfuric acid according to the general procedure given in the main text. An overpotential for proton reduction of 0.25 V was used. The red points indicate the % of hydrogen expected in the cell headspace based on the charge passed during electrolysis (38 C in this case). Black squares indicate actual measurements of the % of H_2 in the cell headspace as determined by gas chromatography.

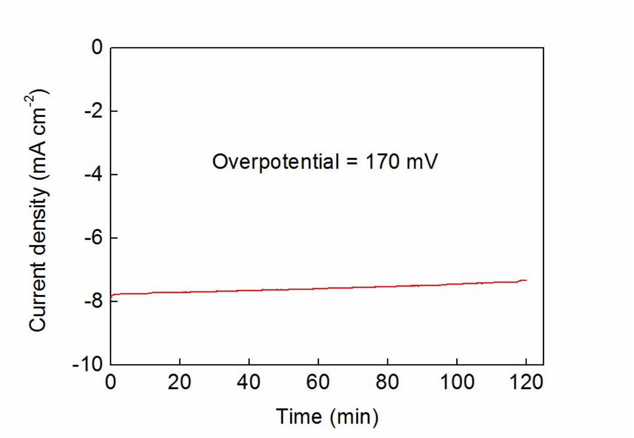

Figure S15. Controlled potential bulk electrolysis of a 300 nm-thick $Co_2Mo_9S_{26}$ film on an indium-tin oxide (ITO) support at a fixed, resistance-corrected overpotential for the hydrogen evolution reaction of 170 mV. The electrolyte was 0.5 M H_2SO_4 and was stirred throughout. ITO-coated plain float electrodes (12-15 ohms per square) were purchased from Optical Filters, and the hydrothermal deposition was carried out on this substrate in the same way as for depositions on FTO substrates (see Experimental Section in main text). A large surface area carbon felt (Alfa Aesar) was used as the counter electrode, and an Ag/AgCl (NaCl, 3 M) reference electrode (RE 5B, BASi) was used. The working electrode was washed with deionized water prior to use and had an area of 1.4 cm^2.

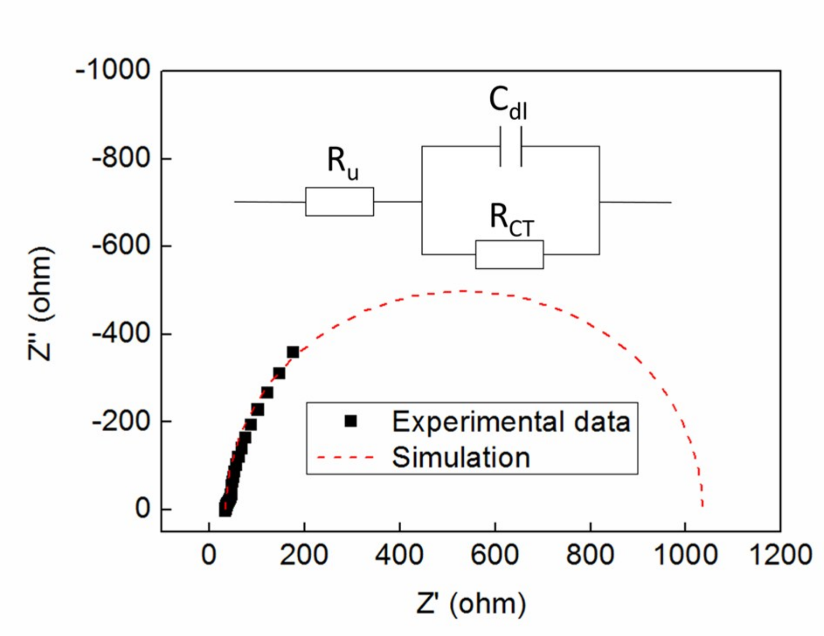

Figure S16. Nyquist plot showing electrochemical impedance spectroscopy (EIS) on a Co-doped molybdenum sulfide-on-FTO film at 0 V *vs.* Ag/AgCl in 0.5 M H_2SO_4. A graphite counter electrode was used. A voltage perturbation of 5 mV was applied with frequencies ranging between 100 kHz and 0.1 Hz and the results were fitted to the simplified equivalent circuit shown in the inset using EC Lab software (V11.01). This gave a value of R_u of 33.3 Ω, in close agreement with that measured using the *iR* test function on the potentiostat (33.4 Ω). Other parameters were fitted as follows: R_{CT} = 1000 Ω, C_{dl} = 1 × 10^{-7} F.

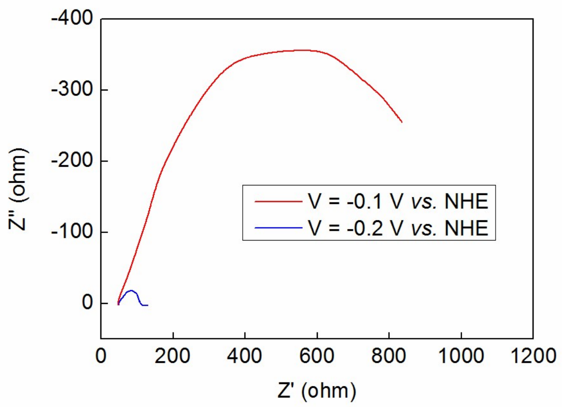

Figure S17. Nyquist plots showing electrochemical impedance spectroscopy (EIS) on a Co-doped molybdenum sulfide-on-FTO film in 0.5 M H_2SO_4 at the potentials indicated. A graphite counter electrode was used. A voltage perturbation of 5 mV was applied with frequencies ranging between 100 kHz and 0.1 Hz. Thus it is apparent that the charge transfer resistance decreases significantly as the overpotential for hydrogen evolution is increased.