Electronic Supplementary Material (ESI) for Energy & Environmental Science

Electronic Supplementary Information

Hydrogen evolution catalyzed by MoS_3 and MoS_2 particles

Heron Vrubel, Daniel Merki and Xile Hu*

Laboratory of Inorganic Synthesis and Catalysis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), SB-ISIC-LSCI, BCH 3305, Lausanne, CH 1015, Switzerland

* To whom correspondence should be addressed. E-mail: xile.hu@epfl.ch

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):

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

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 $1/j$.

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

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.

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

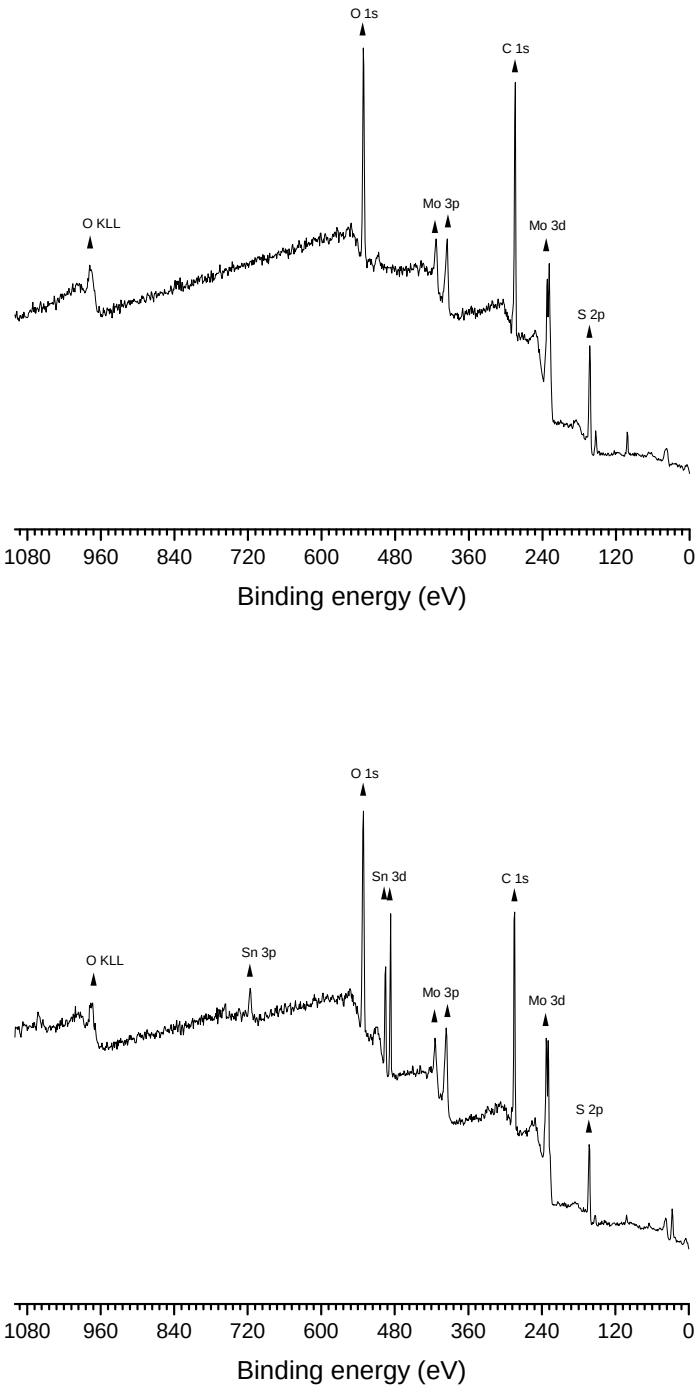


Fig. S1. XPS survey spectra of the MoS_3 particles before (top) and after (bottom) polarization.

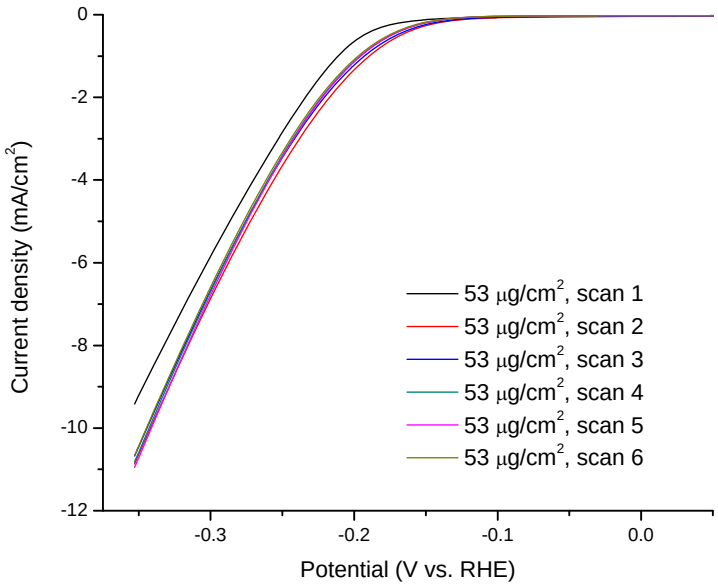


Fig. S2. Consecutive polarization curves of a freshly prepared MoS_3-modified FTO electrode (drop casting) recorded at pH = 0 (1.0 M H_2SO_4); scan rate: 5 mV/s.

Table S1. HER activity of drop-casted MoS_3-modified FTO electrodes according to polarization measurements.

Loading ($\mu g/cm^2$)	log j_0 (log[mA/cm^2])	Tafel Slope (mV/decade)	$j_{\eta=150}$ (mA/cm^2)	$j_{\eta=200}$ (mA/cm^2)
13	-4.0	60[a]	-0.019	-0.14
27	-4.0	52[b]	-0.056	-0.49
40	-3.7	53[c]	-0.13	-0.79
53	-3.4	56[d]	-0.18	-1.1
75	-2.9	61[e]	-0.22	-1.0

[a] Determined at η = 140 – 196 mV; [b] Determined at η = 140 – 190 mV; [c] Determined at η = 119 – 158 mV; [d] Determined at η = 119 – 166 mV; [e] Determined at η = 112 - 158 mV.

Table S2. HER activity of spray-casted MoS_3-modified FTO electrodes according to polarization measurements.

Loading ($\mu g/cm^2$)	log j_0 (log[mA/cm^2])	Tafel Slope (mV/decade)	$j_{\eta=150}$ (mA/cm^2)	$j_{\eta=200}$ (mA/cm^2)
18	-4.8	45[a]	0.040	0.47
100	-4.4	38[b]	0.40	2.8
200	-3.8	40[c]	0.73	3.6
300	-3.3	44[d]	1.02	3.9
400	-3.2	45[e]	1.03	3.9

[a] Determined at η = 146 - 186 mV; [b] Determined at η = 109 - 145 mV; [c] Determined at η = 110 - 134 mV; [d] Determined at η = 98 - 125 mV; [e] Determined at η = 97 - 124 mV.

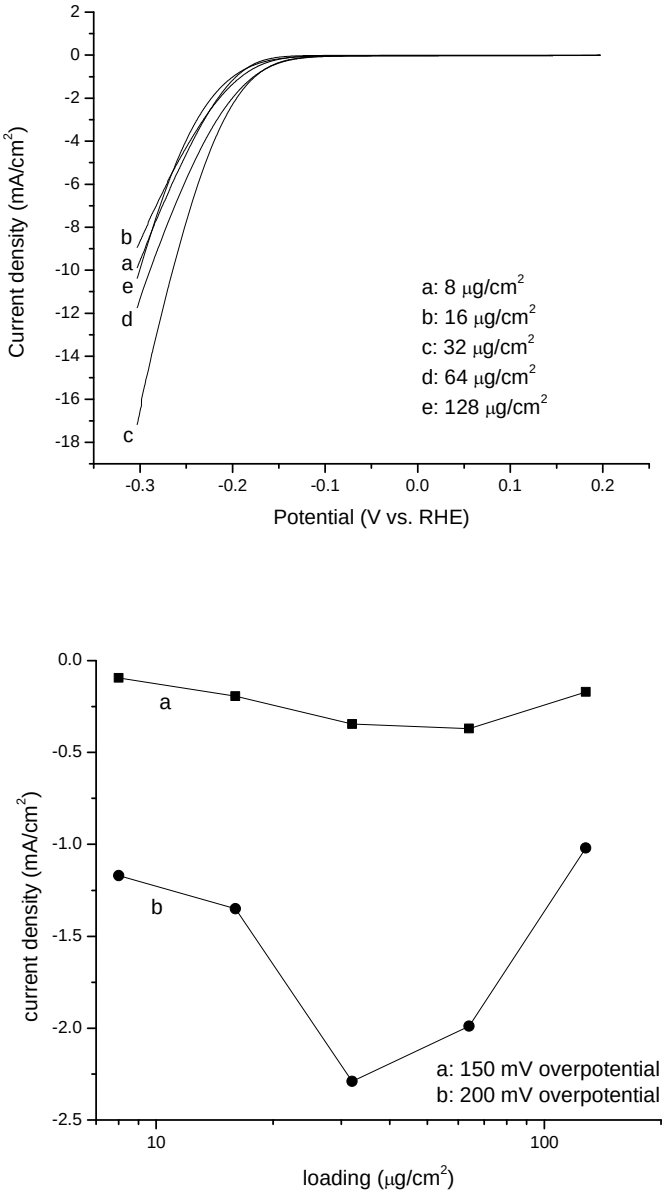


Fig. S3 (Top) Polarization curves of spray-casted MoS_3-modified glassy carbon electrodes recorded at pH = 0 (1.0 M H_2SO_4); scan rate: 5 mV/s. (Bottom) Loading-dependence of current densities.

Table S3. HER activity of spray-casted MoS_3-modified glassy carbon electrodes according to polarization measurements.

Loading ($\mu g/cm^2$)	log j_0 (log[mA/cm^2])	Tafel Slope (mV/decade)	$j_{\eta=150}$ (mA/cm^2)	$j_{\eta=200}$ (mA/cm^2)
26	-4.6	43[a]	0.083	0.95
77	-4.4	40[b]	0.26	2.5
129	-4.2	39[c]	0.48	4.4
180	-4.1	39[d]	0.49	4.1
231	-3.9	41[e]	0.58	3.5

[a] Determined at η = 139 - 175 mV; [b] Determined at η = 125 - 159 mV; [c] Determined at η = 112 - 153 mV; [d] Determined at η = 113 -151 mV; [e] Determined at η = 107 - 144 mV.

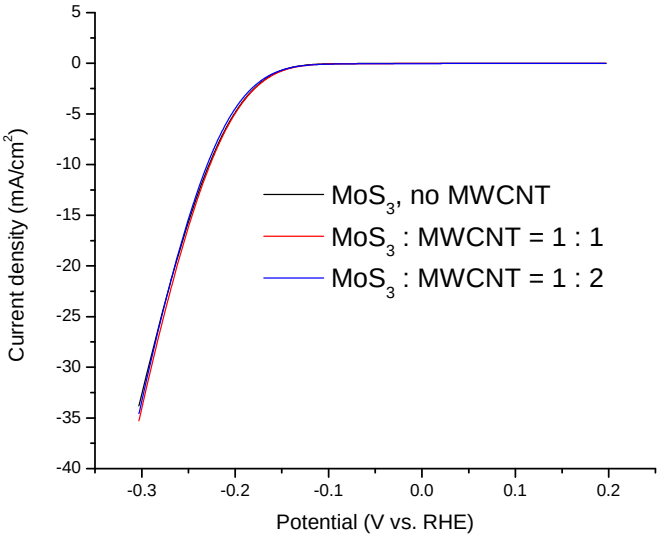


Fig. S4 Polarization curves of spray-casted MoS_3-modified glassy carbon electrodes, with MWCNT as additive, recorded at pH = 0 (1.0 M H_2SO_4); scan rate: 5 mV/s. The loading of MoS_3 is always 130 $\mu g/cm^2$.

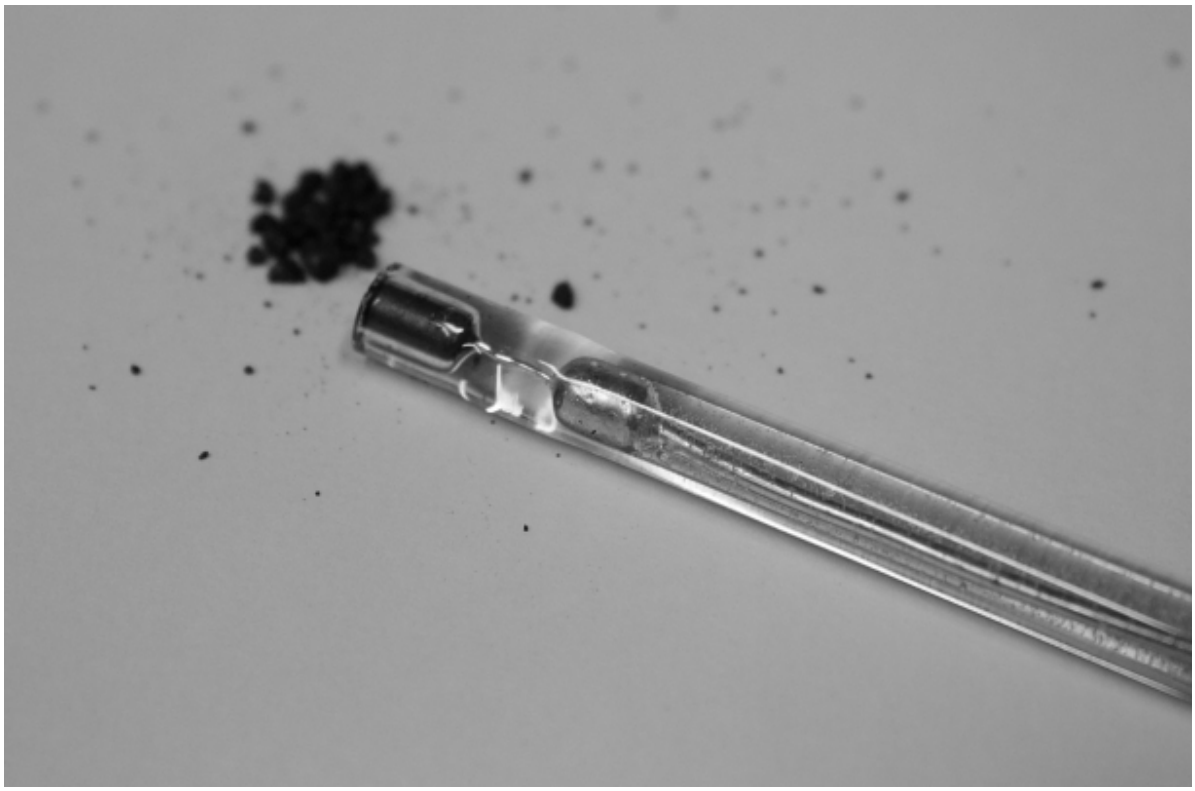


Fig. S5 The home-made working electrode filled with conductive graphite powder.

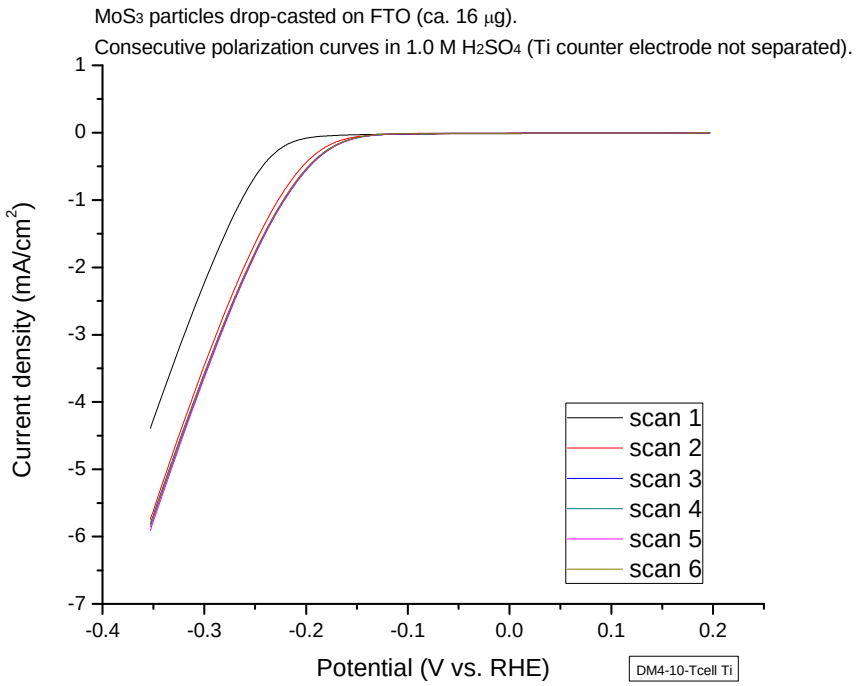


Fig. S6 Consecutive polarization curves of a freshly prepared MoS_3-modified FTO electrode (drop casting) recorded at pH = 0 (1.0 M H_2SO_4); scan rate: 5 mV/s. Ti electrode was used as a counter electrode.

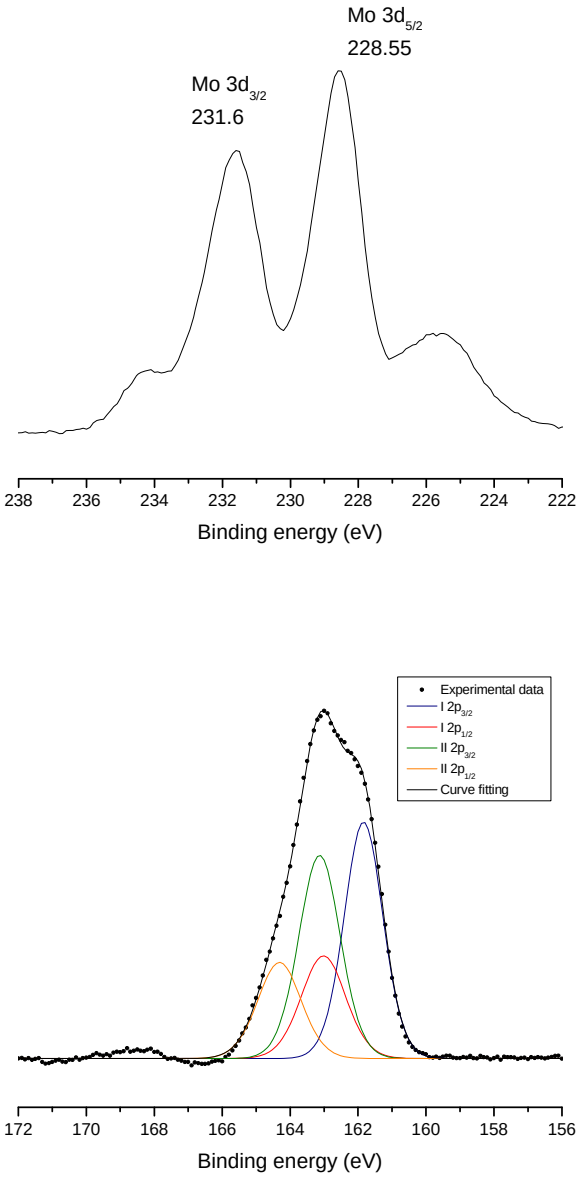


Fig. S7 XPS spectra of the MoS_3-modified electrode after five minutes of electrolysis. (Top) Mo spectrum; (bottom) S 2p spectrum.

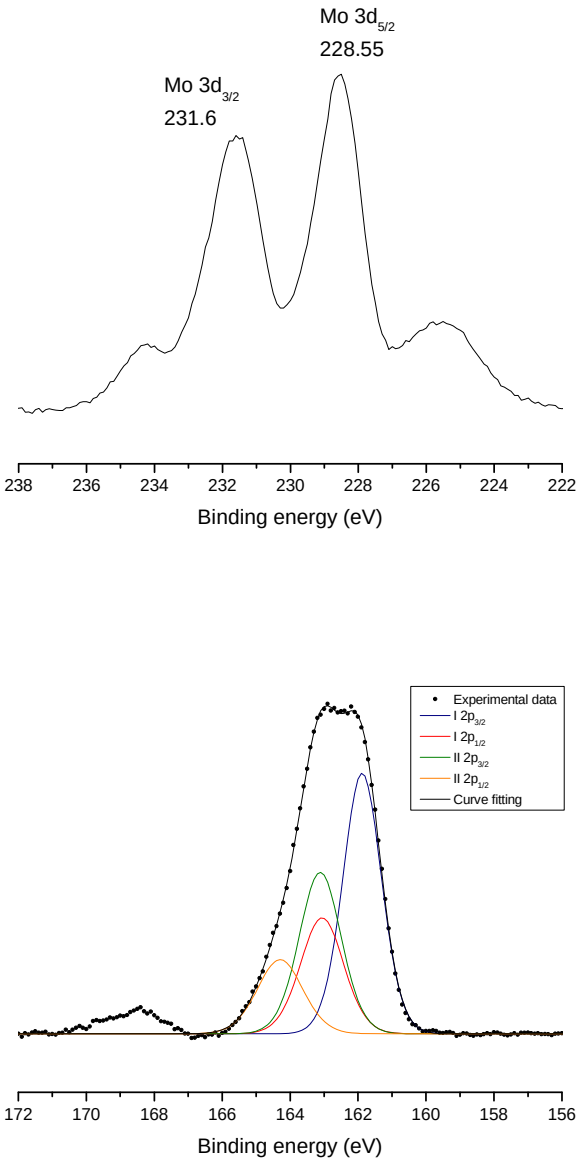


Fig. S8 XPS spectra of the MoS_3-modified electrode after ten minutes of electrolysis. (Top) Mo spectrum; (bottom) S 2p spectrum.

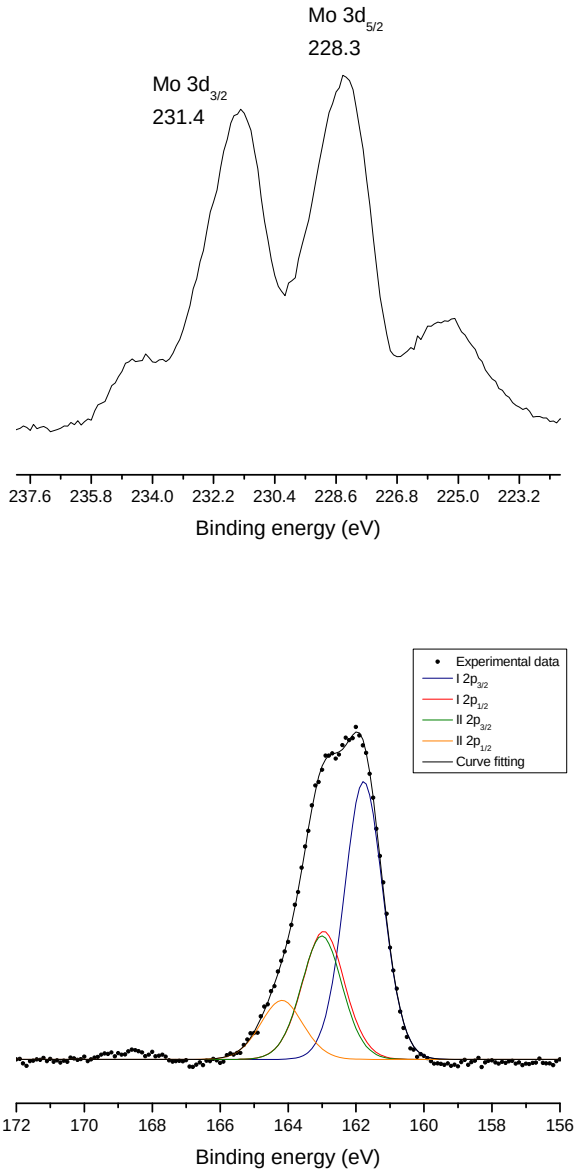


Fig. S9 XPS spectra of the MoS_x species prepared by reduction of MoS_3 with $NaBH_4$. (Top) Mo spectrum; (bottom) S 2p spectrum.

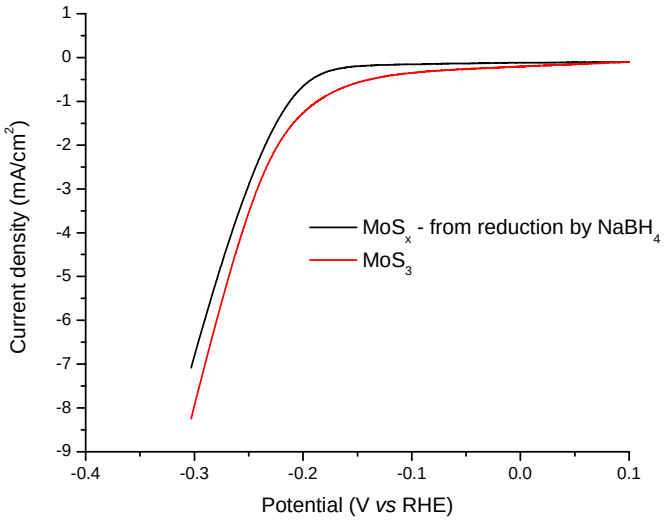
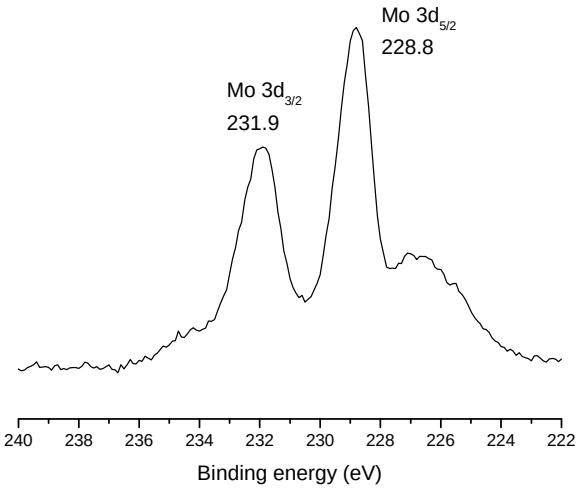
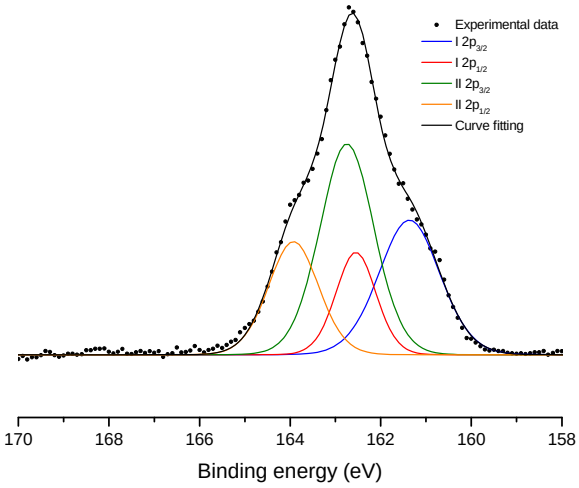


Fig. S10 Polarization curves of FTO electrodes modified by MoS_x species prepared by reduction with $NaBH_4$, and by MoS_3 particles recorded at pH = 0 (1.0 M H_2SO_4); scan rate: 5 mV/s. The electrodes were made using the same loading of catalysts and drop casting.





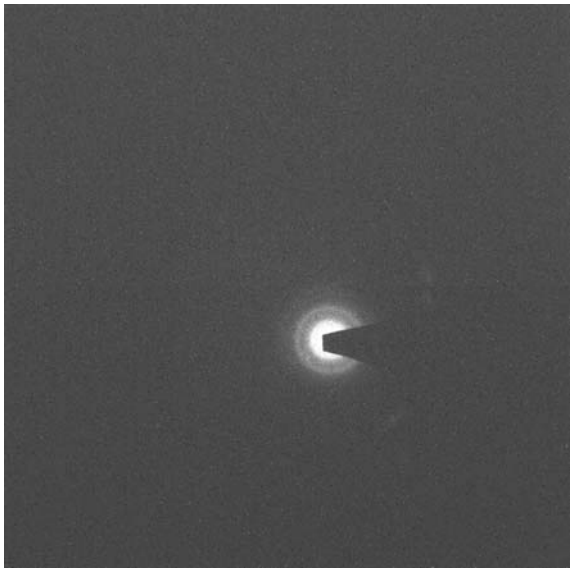
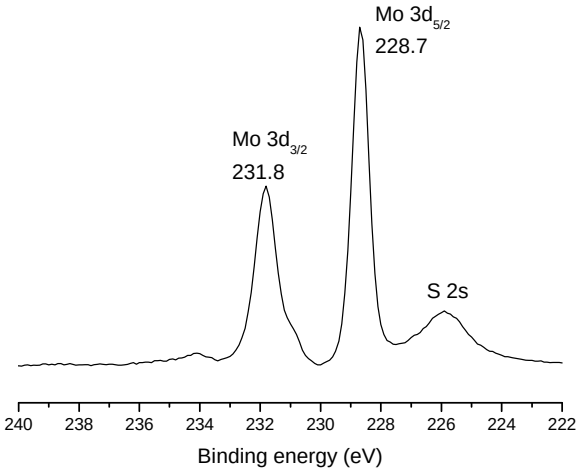
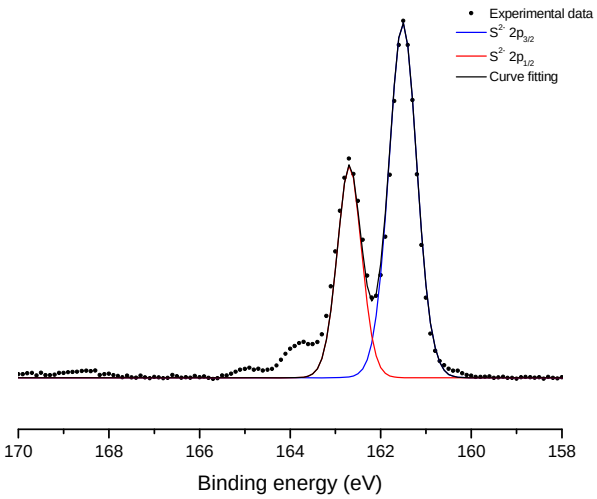


Fig. S11 XPS spectra and electron diffraction pattern of the MoS_3-350 particles. The Mo/S ratio is 1:3.1. For S 2p region; binding energies (eV): doublet I: $2p_{3/2}$, 162.0; $2p_{1/2}$, 163.2; doublet II: $2p_{3/2}$, 163.3; $2p_{1/2}$, 164.5.


Mo 3d5/2
228.7
Mo 3d3/2
231.8
S 2s
240
238
236
234
232
230
228
226
224
222
Binding energy (eV)


Experimental data
S2- 2p3/2
S2- 2p1/2
Curve fitting
170
168
166
164
162
160
158
Binding energy (eV)

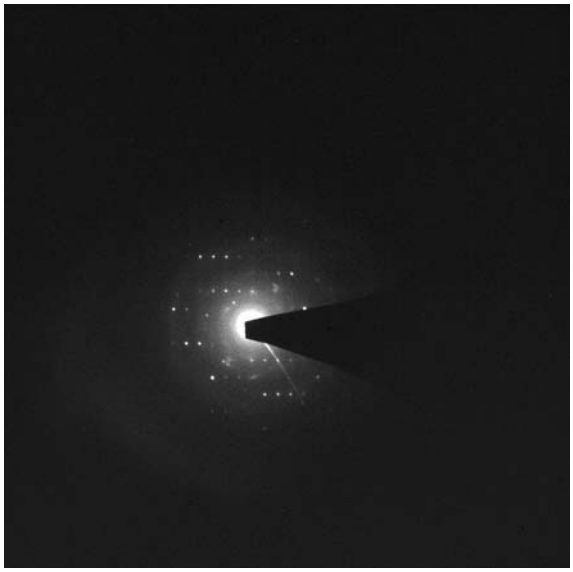
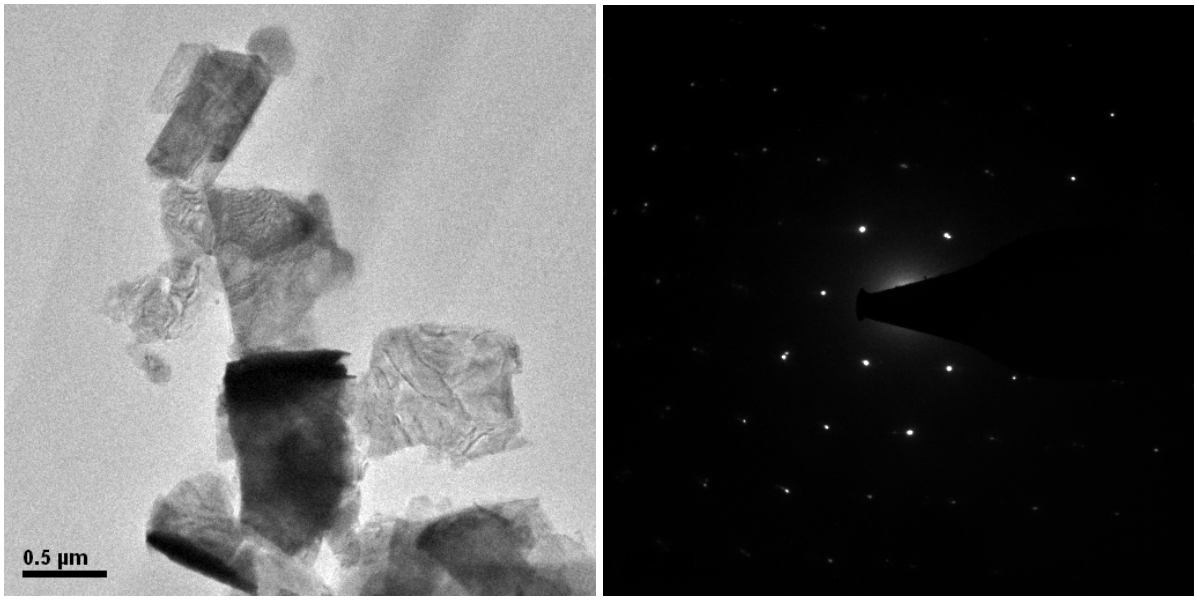
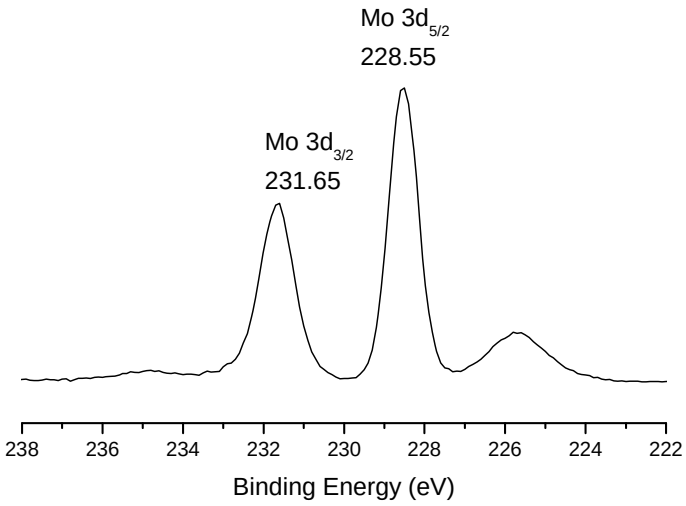


Fig. S12 XPS spectra and electron diffraction pattern of the MoS_2-650 particles. The Mo/S ratio is 1:2.





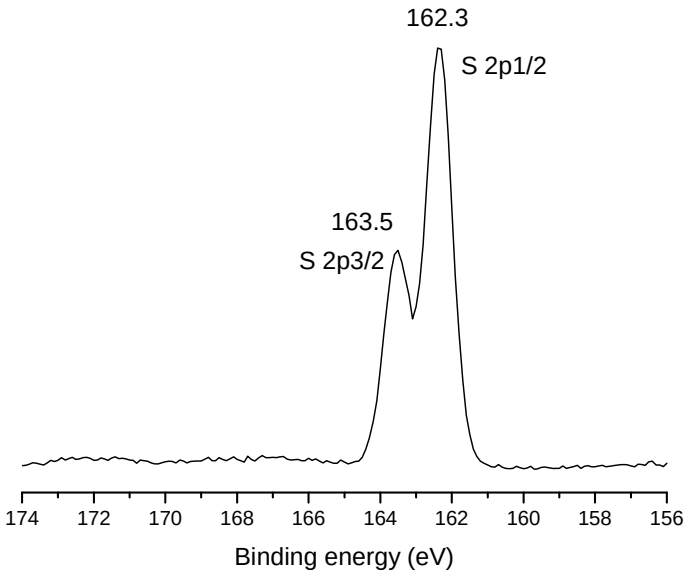


Fig. S13 (Top) TEM image (left) and electron diffraction pattern of commercial MoS_2 particles. (Middle) XPS Mo spectrum of commercial MoS_2 particles. The spectrum shows a peak at lower binding energies, which is the S 2s peak. (Bottom) XPS S spectrum of commercial MoS_2 particles. The S/Mo ratio is 2.1 for MoS_2 particle.