

Electronic Supplementary Information

Hydrogen evolution catalyzed by MoS₃ and MoS₂ particles

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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 cm²) 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.

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

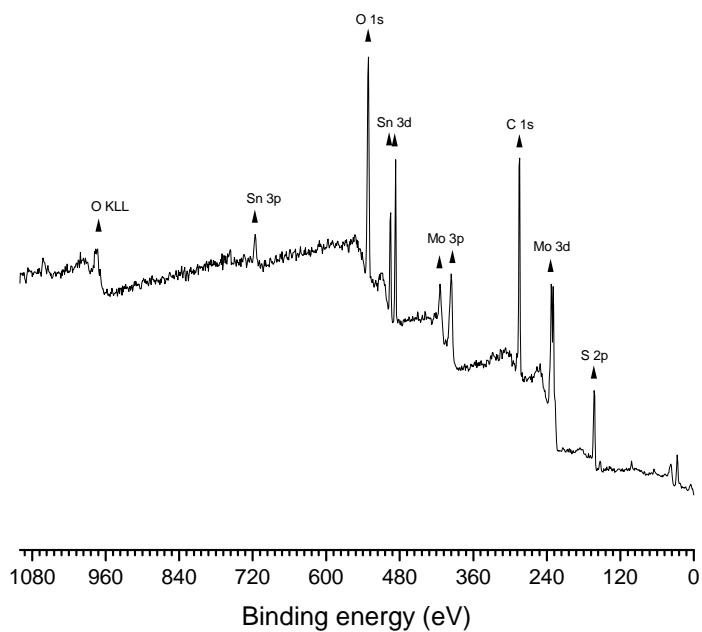
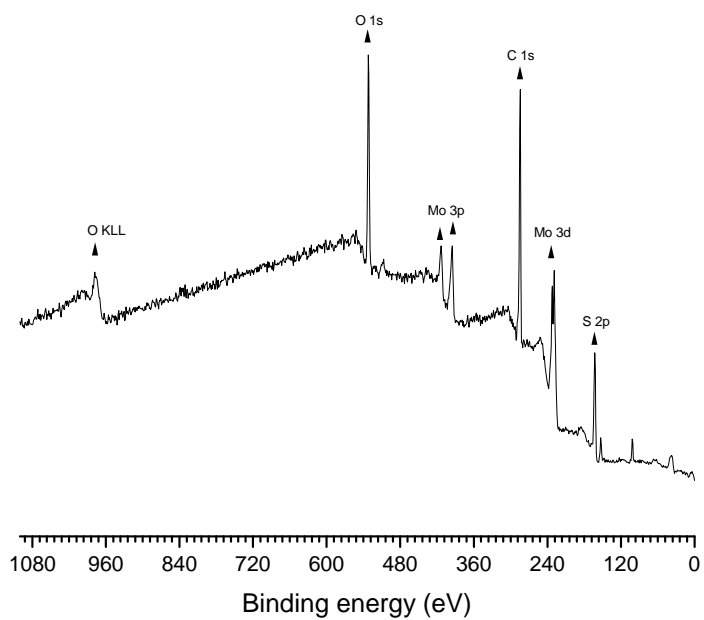


Fig. S1. XPS survey spectra of the MoS₃ particles before (top) and after (bottom) polarization.

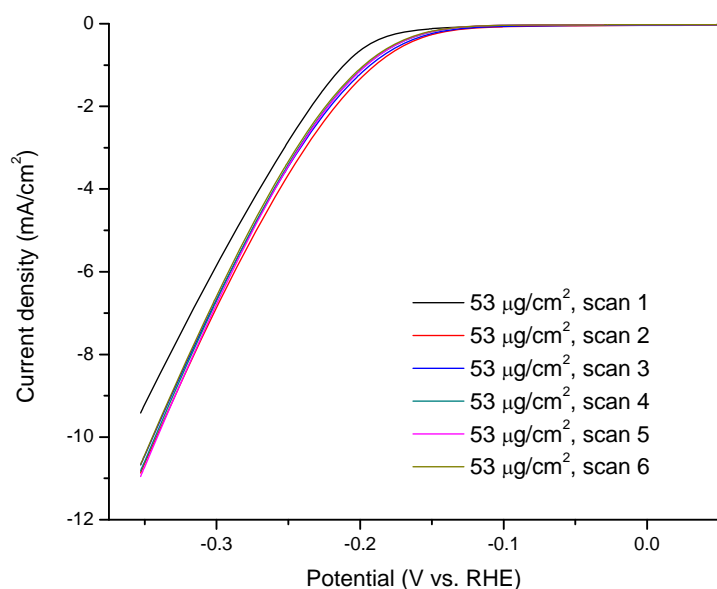


Fig. S2. Consecutive polarization curves of a freshly prepared MoS₃-modified FTO electrode (drop casting) recorded at pH = 0 (1.0 M H₂SO₄); scan rate: 5 mV/s.

Table S1. HER activity of drop-casted MoS₃-modified FTO electrodes according to polarization measurements.

Loading (µg/cm ²)	log j ₀ (log[mA/cm ²])	Tafel Slope (mV/decade)	j _{η=150} (mA/cm ²)	j _{η=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 MoS₃-modified FTO electrodes according to polarization measurements.

Loading ($\mu\text{g}/\text{cm}^2$)	$\log j_0$ ($\log[\text{mA}/\text{cm}^2]$)	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 $\eta = 146 - 186$ mV; ^b Determined at $\eta = 109 - 145$ mV; ^c Determined at $\eta = 110 - 134$ mV; ^d Determined at $\eta = 98 - 125$ mV; ^e Determined at $\eta = 97 - 124$ mV.

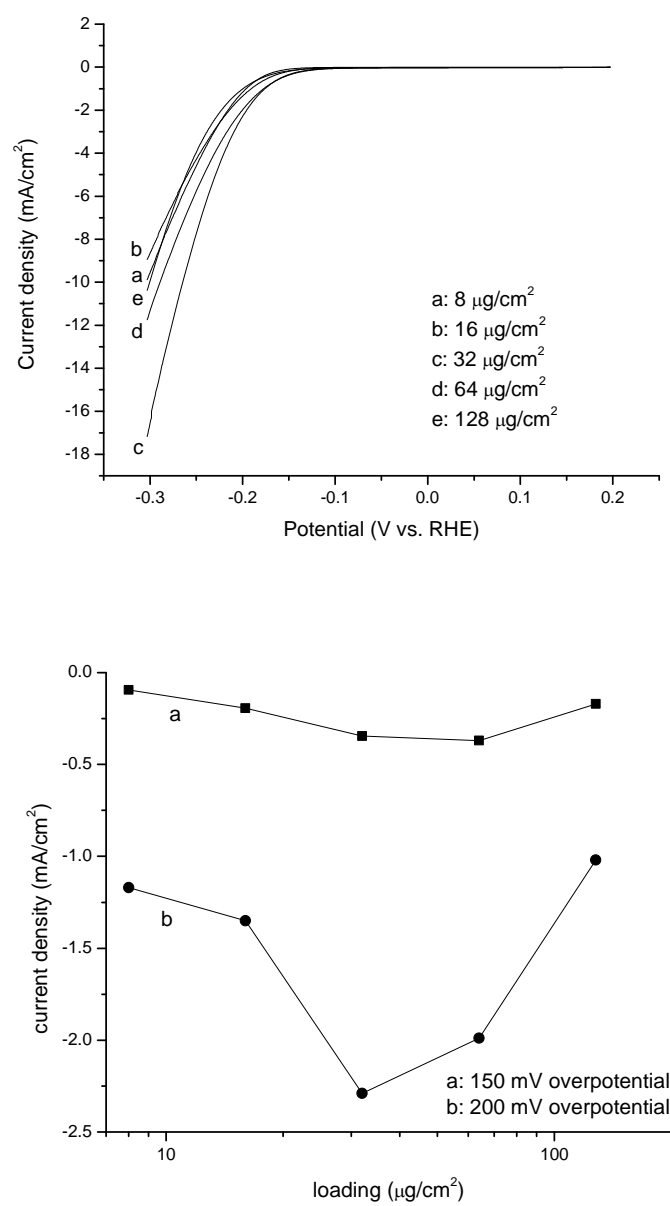


Fig. S3 (Top) Polarization curves of spray-casted MoS₃-modified glassy carbon electrodes recorded at pH = 0 (1.0 M H₂SO₄); scan rate: 5 mV/s. (Bottom) Loading-dependence of current densities.

Table S3. HER activity of spray-casted MoS₃-modified glassy carbon electrodes according to polarization measurements.

Loading (μg/cm ²)	log j ₀ (log[mA/cm ²])	Tafel Slope (mV/decade)	j _{η=150} (mA/cm ²)	j _{η=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.

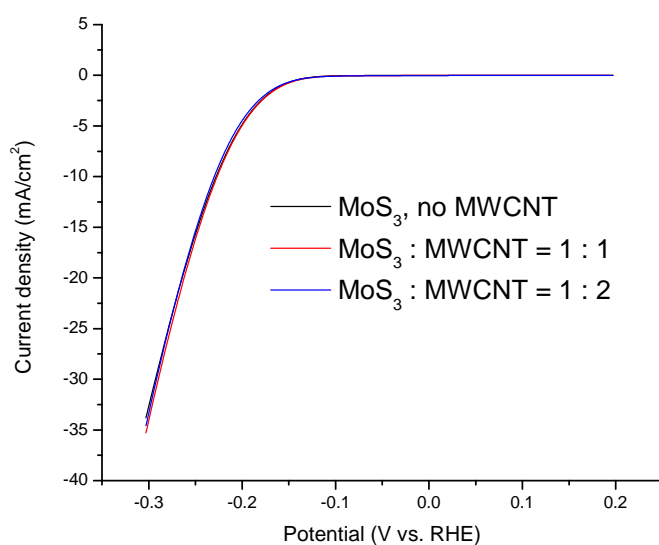


Fig. S4 Polarization curves of spray-casted MoS₃-modified glassy carbon electrodes, with MWCNT as additive, recorded at pH = 0 (1.0 M H₂SO₄); scan rate: 5 mV/s. The loading of MoS₃ is always 130 μg/cm².

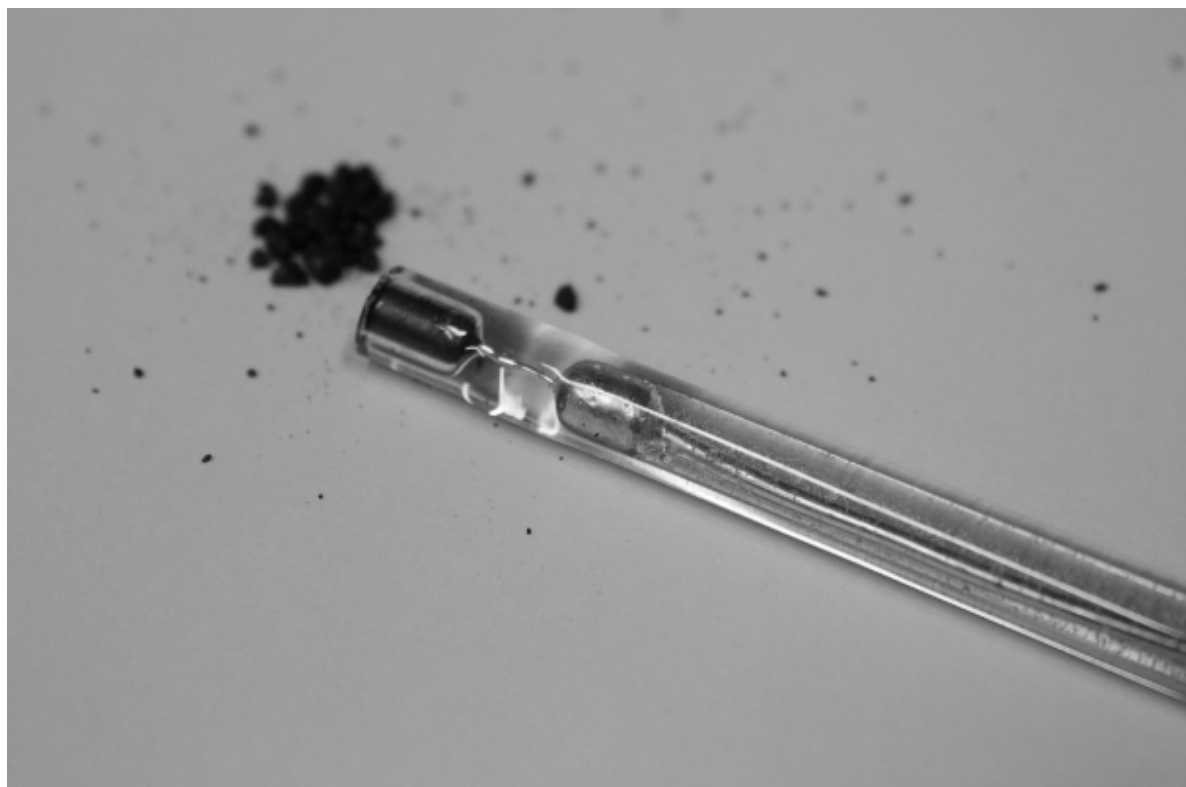


Fig. S5 The home-made working electrode filled with conductive graphite powder.

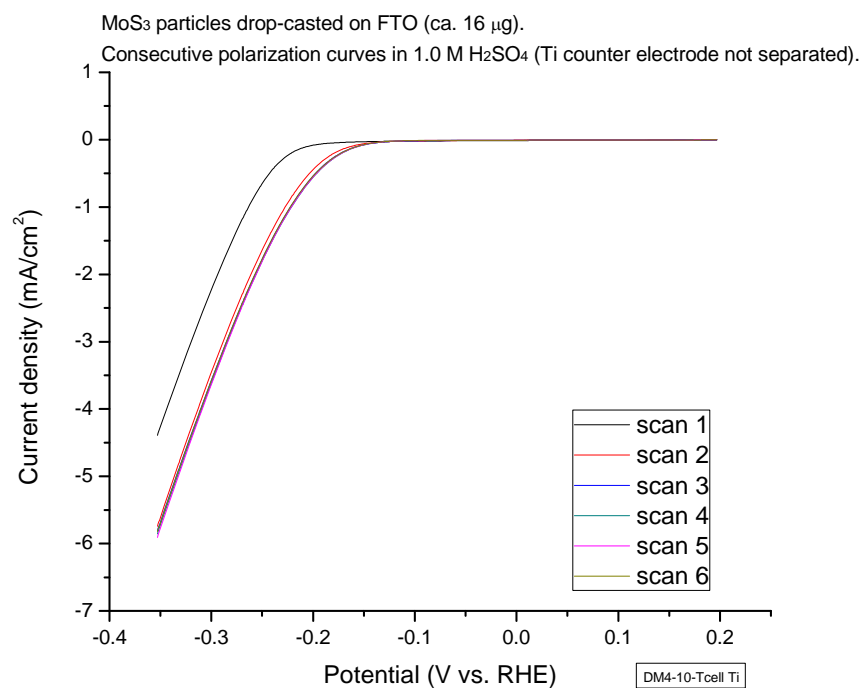


Fig. S6 Consecutive polarization curves of a freshly prepared MoS₃-modified FTO electrode (drop casting) recorded at pH = 0 (1.0 M H₂SO₄); scan rate: 5 mV/s. Ti electrode was used as a counter electrode.

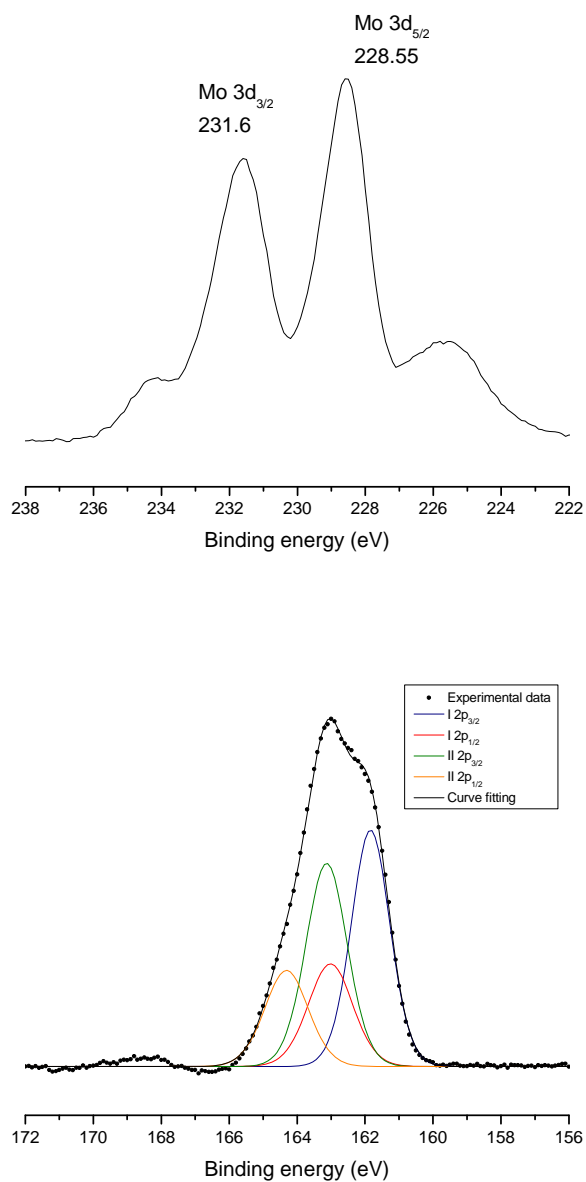


Fig. S7 XPS spectra of the MoS₃-modified electrode after five minutes of electrolysis. (Top) Mo spectrum; (bottom) S 2p spectrum.

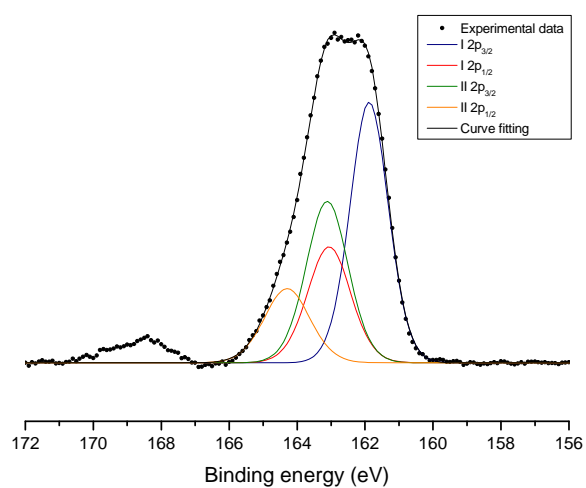
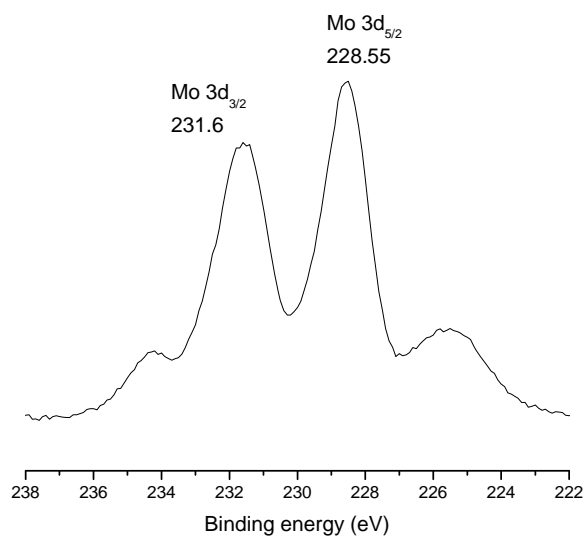


Fig. S8 XPS spectra of the MoS₃-modified electrode after ten minutes of electrolysis. (Top) Mo spectrum; (bottom) S 2p spectrum.

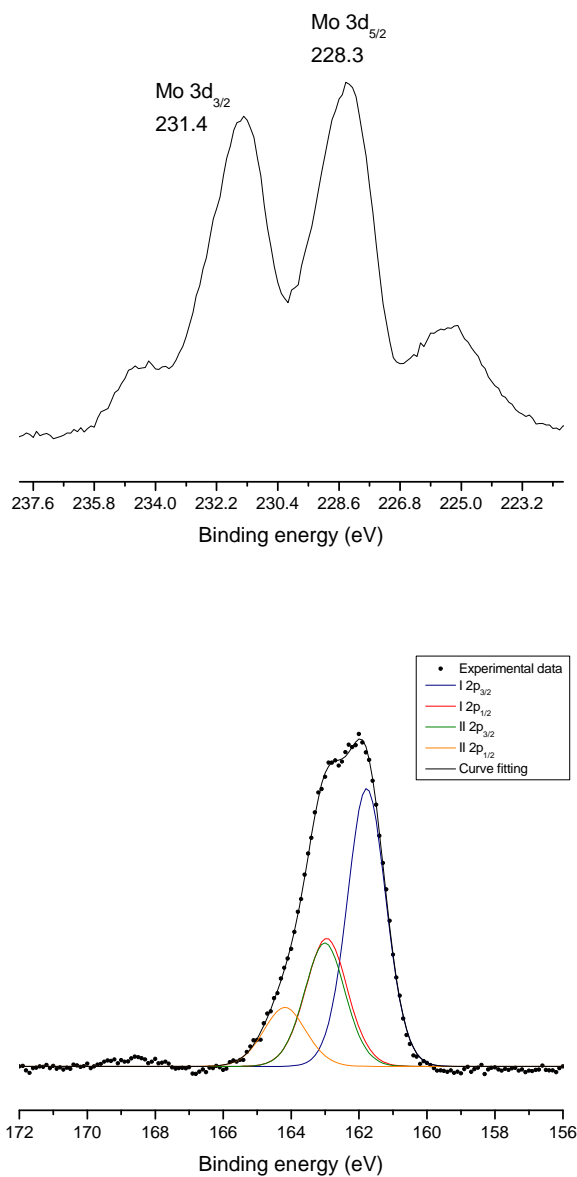


Fig. S9 XPS spectra of the MoS_x species prepared by reduction of MoS₃ with NaBH₄. (Top) Mo spectrum; (bottom) S 2p spectrum.

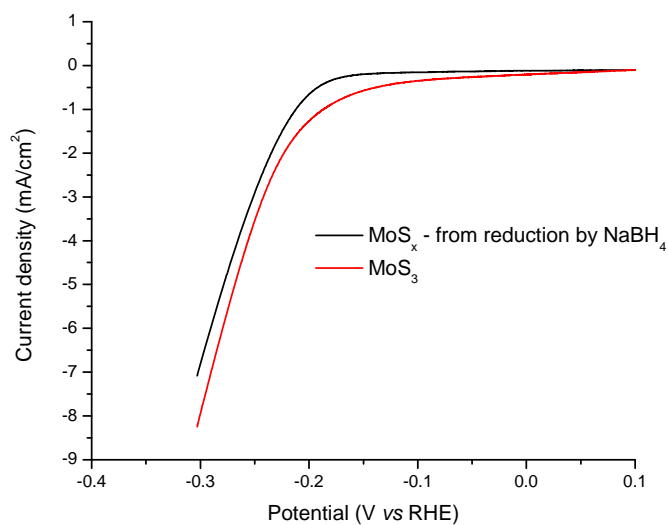
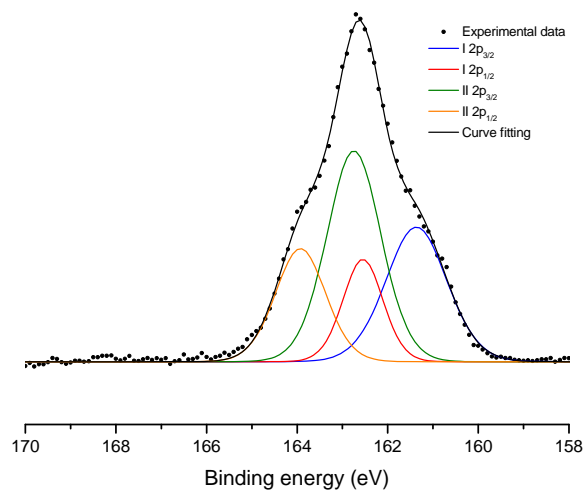
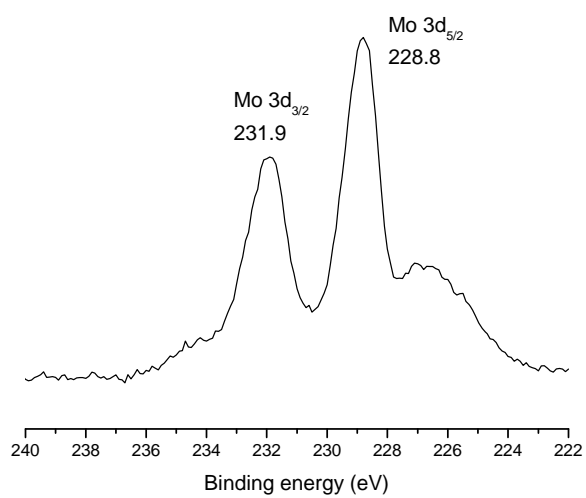


Fig. S10 Polarization curves of FTO electrodes modified by MoS_x species prepared by reduction with NaBH₄, and by MoS₃ particles recorded at pH = 0 (1.0 M H₂SO₄); scan rate: 5 mV/s. The electrodes were made using the same loading of catalysts and drop casting.



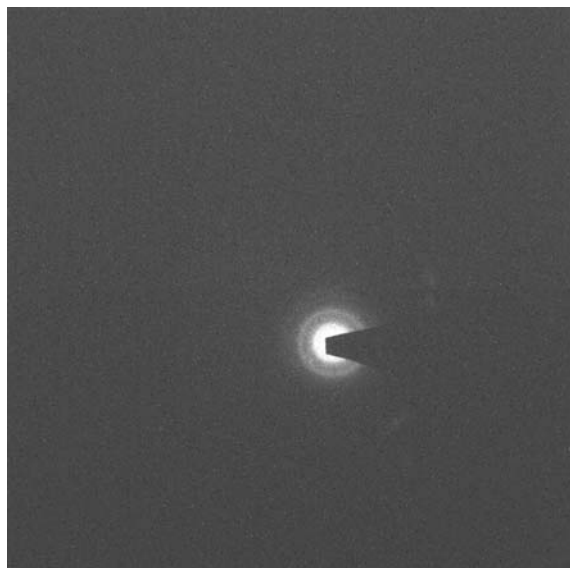
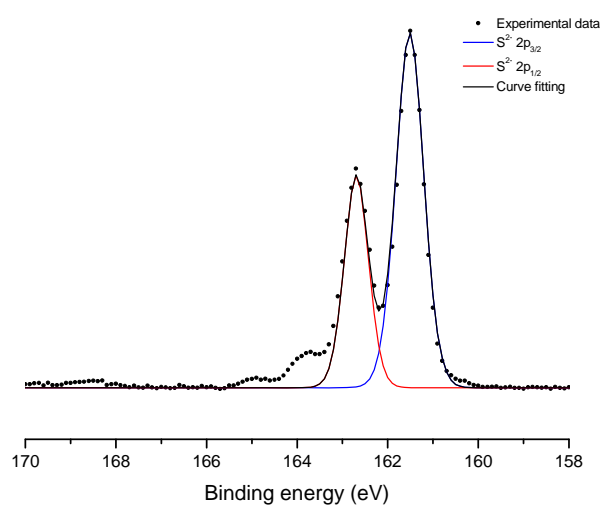
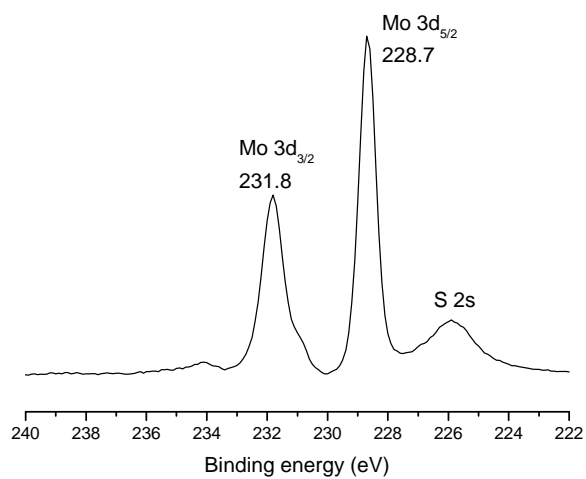


Fig. S11 XPS spectra and electron diffraction pattern of the MoS₃-350 particles. The Mo/S ratio is 1:3.1. For S 2p region; binding energies (eV): doublet I: 2p_{3/2}, 162.0; 2p_{1/2}, 163.2; doublet II: 2p_{3/2}, 163.3; 2p_{1/2}, 164.5.



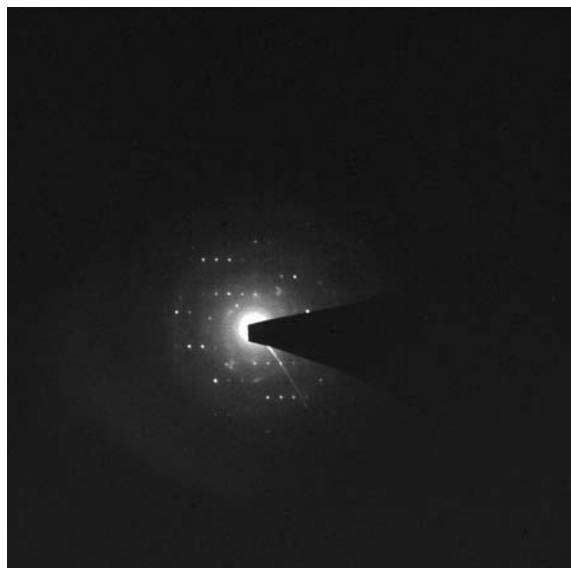
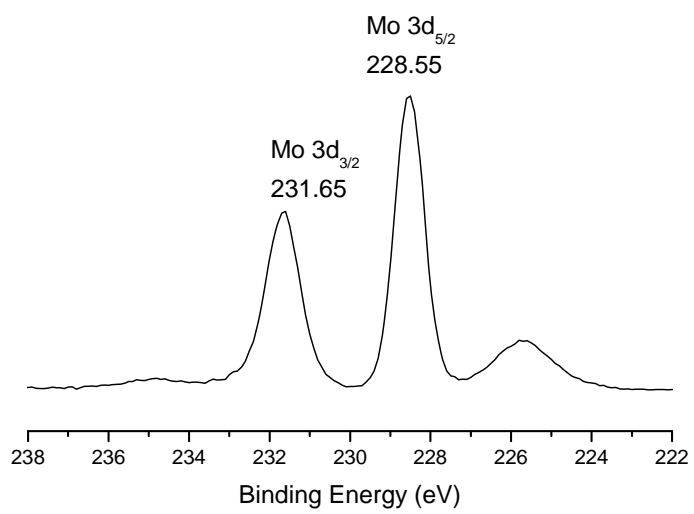
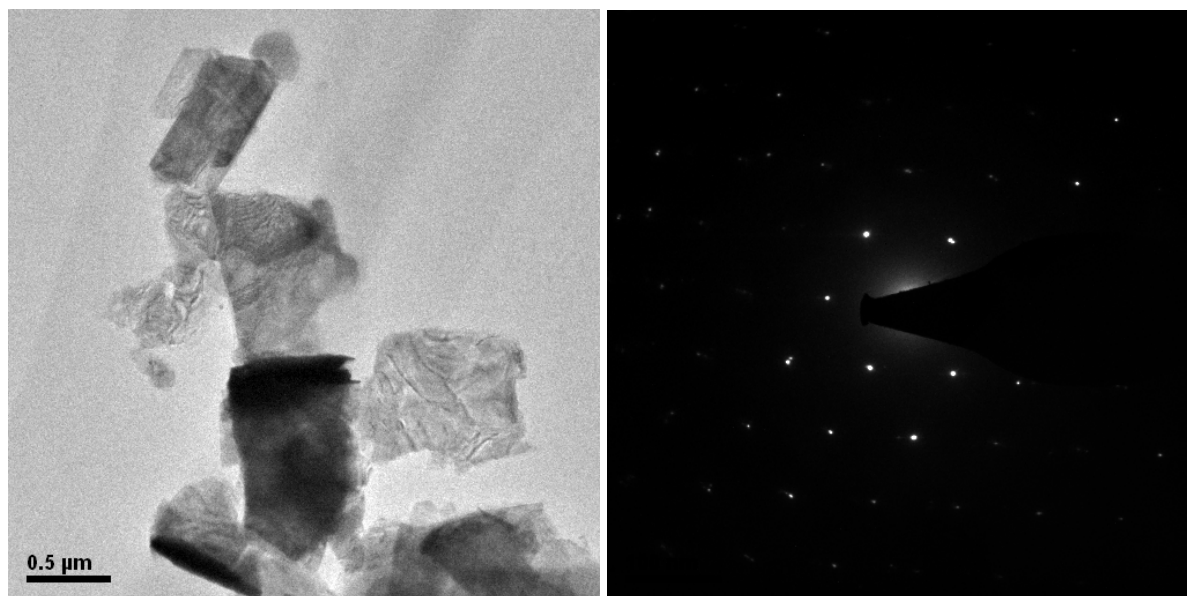


Fig. S12 XPS spectra and electron diffraction pattern of the MoS₂-650 particles. The Mo/S ratio is 1:2.



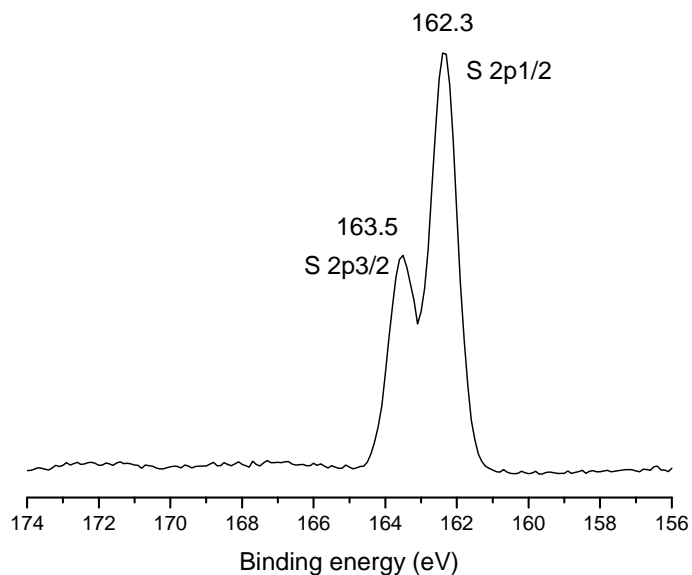


Fig. S13 (Top) TEM image (left) and electron diffraction pattern of commercial MoS₂ particles. (Middle) XPS Mo spectrum of commercial MoS₂ particles. The spectrum shows a peak at lower binding energies, which is the S 2s peak. (Bottom) XPS S spectrum of commercial MoS₂ particles. The S/Mo ratio is 2.1 for MoS₂ particle.