Amorphous Molybdenum Oxysulfide Decorated p-Type Silicon Microwire Arrays for Efficient Photoelectrochemical Water Reduction

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XPS analysis of the Si-MWs@MoO_xS_y electrodes

During the XPS measurements, uniform charge neutralization was provided by beams of low-energy (≤ 10 eV) Ar⁺ ions and low-energy electrons guided by a magnetic lens. All the spectra were acquired in normal emission with an effective analyzer collection angle of ca. 30°. The binding energy (BE) scale of the analyzer was calibrated to produce <50 meV deviations of the three standard peaks from their standard values: 83.98 eV for Au 4f_{7/2}, 368.26 eV for Ag 3d_{5/2}, and 932.67 eV for Cu 2p_{3/2}.^{S1}

Avantage software package (Thermo Fisher Scientific) was used to fit the elemental spectra and to quantify the standard “atomic %” elemental compositions based on calibrated analyzer transmission functions, Scofield sensitivity factors,^{S2} and effective attenuation lengths for photoelectrons from the standard TPP-2M formalism.^{S3} We note that in fits for Mo 3d region the 3d_{5/2} and 3d_{3/2} components partially overlap, accordingly, for clarity, in **Figure 4** only the 3d_{5/2} components are shown explicitly, while the total fit curves represent contributions from both 3d_{5/2} and 3d_{3/2} components; for completeness, fits with both components shown explicitly are presented in **Figure S9**. Spin-orbit splitting of 3.15 ± 0.15 eV and intensity ratio of 0.69 were used in the Mo 3d fits.

The O 1s and C 1s regions presented in **Figure 4** serve as binding energy (BE) references, whereby the positions of the lowest-BE components (corresponding primarily to Mo–O and C–C chemistries, respectively) can be directly compared with previous literature reports^{S4-S9} and used to check for evidence of differential charging that may affect BE values for nanostructured layers. The BEs of Mo–O and C–C components for our samples are ca. 530.9 and 284.9 eV, respectively, consistent with the 530.5–530.8 and 284.6–284.8 eV ranges reported in the literature.^{S4,S6,S8,S9} The ca. 0.1–0.2 eV difference between the BE values in our measurements and the high end of the

literature values is likely due to the combination of the finite conductivity of our p-Si substrates and the ca. 0.1 eV bias applied by the charge neutralization device. Accordingly, for the assignment of the Mo oxidation states, we can directly compare the measured BEs of Mo 3d components to the values reported in literature.

Data fitting in the Mo 3d region was performed with peak positions weakly constrained to ensure non-overlapping components in fits to the data for all the measured samples. The full width at half-maximum (FWHM) values were not constrained, because the common approach of forcing exactly equal FWHM for two or more components resulted in visible fitting artifacts and did not improve the quality of the fits. Nevertheless, the FWHM values in the fits shown for Mo 3d in **Figure 4** do not vary strongly and remain in the 0.9–1.2 eV range (**Table S1**), which is comparable to the FWHM values reported in literature for similar materials.^{S9}

Since the sampling depth of XPS is roughly <10 nm (accurate estimation is difficult because of the nanostructured features on our samples), our data do not provide information on whether the new Mo oxidation state appearing at 231.7 eV (presumably Mo^{5.5+}) extends below the surface of the samples. Nevertheless, this sampling depth already includes a significant fraction of the MoO_xS_y layer that can contribute to the catalytic activity during HER. The presence of the new Mo oxidation state as well as its position and co-existence with components that correspond to Mo⁵⁺ and Mo⁶⁺ oxidation states (green and blue, respectively, in **Figure 4** and **Figure S7**) is unambiguously confirmed by its appearance in reference spectra obtained for control samples that underwent an intentional oxidation (**Figure S7**); the presence and enhancement of this state in reference samples also indicates that the corresponding material phase is likely to be thermodynamically stable rather than transient.

Supplementary Figures:

Figure S1. Fabrication procedure of the Si-MW arrays.

Figure S2. A digital photo showing the as-fabricated Si-MWs@MoO_xS_y photocathodes. The circular area at the center is the active area exposed to the light, which is $\sim 2.5 \text{ cm}^2$.

Figure S3. SEM image showing the morphology of Si-MWs@PtNPs electrodes. Consistent with the literature report [17, 19], the deposited Pt NPs mainly reside on the top part of the Si-MW arrays.

Figure S4. Spectra of the light source (Tungsten lamp WOW01, Zahner) measured with and without an IR filter (Newport, 20HMS-O hot mirror). The dotted line is a transmittance spectrum of the IR filter.

Figure S5. Cyclic voltammograms recorded during the electrodeposition of amorphous MoO_xS_y . Working electrode: p-Si-MW array electrode; counter electrode: Pt wire; reference electrode: Hg/HgSO_4 (sat. K_2SO_4). The deposition was performed at a scan rate of 50 mV s^{-1} under illumination of a tungsten light (100 mW cm^{-2}). Cycle number: 30. For comparison, a CV curve recorded under dark conditions is also presented.

Figure S6. (a) Typical CV curves recorded during the CV electrodeposition in an electrolyte with and without thiourea. A much higher anodic current was observed in the presence of thiourea. (b) Comparison of the PEC performance of the Si-MWs@MoO_xS_y-50 photocathode prepared in an electrolyte with thiourea and the Si-MWs@MoO_x-50 photocathode in an electrolyte without thiourea.

Figure S7. (a) A representative TEM image of the Si-MWs@MoO_xS_y-100 sample (i.e., subjected to 100 CV deposition cycles) showing the cracks across the electrodeposited thick MoO_xS_y layer. Inset: HR-TEM image showing the amorphous nature. (b) HAADF-STEM micrograph and the elemental maps of (c) Si, (d) O, and (e) Mo as well as (f) their overlap of an individual Si-MW@MoO_xS_y-100.

Figure S8. (a) HAADF-STEM micrograph of the electrodeposited MoO_xS_y nanoparticle decorated Si-MWs (Si-MWs@ MoO_xS_y -10). The elemental maps of (b) Si, (c) O and (d) Mo, and (e) their overlap.

Figure S9. High-resolution XPS data in Mo 3d region for MoO_xS_y samples. The fits in Mo 3d (S 2s) region are shown for (a) Si-MWs@ MoO_xS_y -10, (b) Si-MWs@ MoO_xS_y -30 and (c) Si-MWs@ MoO_xS_y -50 electrodes. The indicated scaling factors are the same as those in Figure 4. While in Figure 4 only the $3d_{5/2}$ components are shown, here the $3d_{3/2}$ components have been added as dashed lines with the same color-coding as that of the $3d_{5/2}$ components. Low-intensity S 2s peaks are indicated at ca. 227 eV. Symbols: experimental data; thick lines: total fit curves; dashed line: background; thin colored lines: fit components.

Figure S10. High-resolution Mo 3d XPS data for reference MoO_xS_y samples that were intentionally oxidized in air for one month. The Mo $3d_{5/2}$ component at ca. 531.7 eV (red) clearly dominates in these spectra, providing an unambiguous reference of the presence, BE, and FWHM of this component, as well as of its co-existence with components at ca. 230.7 (green) and 232.5 eV (blue).

Figure S11. Representative (a) Raman and (b) FTIR spectra of the Si-MWs@ MoO_xS_y sample. (c) A typical molecular configuration of MoO_xS_y oligomers among many possible others.

Figure S12. A representative polarization curve of the Ni foam supported MoO_xS_y catalysts (Ni@MoO_xS_y). For comparison, the polarization curve of a bare Ni foam is also presented. The measurements were performed in nitrogen-bubbled 0.5 M K₂SO₄ solution (pH = 1) at a scan rate of 10 mV s⁻¹.

Figure S13. J - U profiles of the Si-MWs@MoO_xS_y photocathodes with different MoO_xS_y catalyst loadings.

Figure S14. The EDX spectra of the Si-MWs@PtNPs electrode before and after ~ 40 min J - t test.

An obvious increase in the O content can be clearly seen after the J - t test.

Figure S15. TEM investigation of the Si-MWs@MoO_xS_y-50 photoelectrode after extended J - t test for 2 h. (a) HAADF-STEM micrograph. The distribution of (b) Si, (c) Mo and (d) O over the MW. (e) The overlap elemental map showing that the Si core was not oxidized.

Table S1. Peak parameters from fits to XPS data in **Figure 4**

Region	O 1s	Mo 3p _{3/2}	C 1s	Mo 3d _{5/2}				S 2s	S 2p _{3/2}
<i>Component</i>	<i>Mo–O</i>		<i>C–C</i>	<i>D</i>	<i>C</i>	<i>B</i>	<i>A</i>		
BE, ^a (eV)	530.9	397.0±0.2	284.9	232.5	231.7	230.7	229.8	226.9	162.5
FWHM, ^a (eV)	1.5	4.3±0.5	1.5	1.2	1.1	1.1	0.9	2.1	1.1

^a Peak parameters for consistent fits to all Si-MWs@MoO_xS_y samples predominantly had variation of ±0.1 eV or below (as indicated by the reported significant digits); for two cases with variation above ±0.1 eV the ranges are specified.

BE: binding energy; FWHM: full width at half-maximum.

Mo 3d_{5/2} region: A – Mo⁴⁺

B – Mo⁵⁺

C – new chemical state (Mo^{5.5+})

D – Mo⁶⁺

Table S2. XPS analysis of elemental and chemical composition of Si-MWs@MoO_xS_y samples.

Element <i>Component</i>	Si-MWs@Mo _x S _y -10 atomic %	Si-MWs@Mo _x S _y -30 atomic %	Si-MWs@Mo _x S _y -50 atomic %
Mo	19.4	23.2	21.4
<i>A</i>	2.0	4.5	1.8
<i>B</i>	8.8	10.7	9.1
<i>C</i>	4.0	4.8	5.1
<i>D</i>	4.6	3.2	5.4
O	50.9	56.3	51.6
<i>Mo–O</i>	38.1	40.5	38.8
<i>high BE</i>	12.8	15.8	12.8
S	1.6	3.0	3.8
C	13.5	12.0	19.2
<i>C–C</i>	9.3	6.9	12.0
<i>high BE</i>	4.2	5.1	7.2
Si ^a	12.1	2.6	1.8
Na ^b	2.0	2.3	2.3
N ^c	≤ 4		

^a Si signal includes both metallic Si and SiO_x for the Si-MWs@MoO_xS_y-10 and Si-MWs@MoO_xS_y-30, and only SiO_x for Si-MWs@MoO_xS_y-50.

^b Na is present as counterions in the electrolyte during photoelectrochemical deposition.

^c N at. % can be estimated only approximately because of an overlap with Mo 3p_{3/2}; this N presumably is produced from the decomposition of thiourea.

BE: binding energy; Mo (A) – Mo⁴⁺; Mo (B) – Mo⁵⁺; Mo (C) – new chemical state (Mo^{5.5+}); Mo (d) – Mo⁶⁺

Table S3. Fitting results of the Nyquist plots for the tested photocathodes obtained using the equivalent circuit models shown in the inset of **Figure 5c**. The electrode area is 2.5 cm^2 .

Samples	R_e ($\Omega \text{ cm}^{-2}$)	R_{ct} ($\Omega \text{ cm}^{-2}$)	C_1 ($\mu\text{F cm}^{-2}$)	R_2 ($\Omega \text{ cm}^{-2}$)	C_2 ($\mu\text{F cm}^{-2}$)	m
Si-MWs	0.86	16.19	36.01	—	—	—
Si-MWs@Pt NPs	0.95	0.42	43.44	0.31	52.60	1.00
Si-MWs@MoO _x S _y -10	0.74	9.19	24.32	0.42	39.97	0.61
Si-MWs@MoO _x S _y -30	0.81	1.36	26.94	0.39	12.97	0.71
Si-MWs@MoO _x S _y -50	0.71	0.43	32.93	0.42	21.70	0.74

References and notes

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