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Amorphous oxygen-rich molybdenum oxysulfide Decorated p-type silicon microwire Arrays for efficient photoelectrochemical water reduction

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Abstract

We report the fabrication of p-type silicon (Si) photocathodes consisting of well-ordered Si microwire (Si-MW) arrays coupled with non-precious and earth-abundant amorphous oxygen-rich molybdenum oxysulfide (MoO\textsubscript{x}S\textsubscript{y}) as both a hydrogen evolution catalyst and a passivation layer. The MoO\textsubscript{x}S\textsubscript{y} is conformally grown on the Si-MW surface through photo-assisted cyclic voltammetric (CV) deposition. By adjusting the cycle numbers of the CV deposition, Si-MW array electrodes with different MoO\textsubscript{x}S\textsubscript{y} catalyst loadings (Si-MWs@MoO\textsubscript{x}S\textsubscript{y}) have been obtained and comprehensively characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Raman and Fourier-transform infrared spectroscopies. The photoelectrochemical performance of the Si-MWs@MoO\textsubscript{x}S\textsubscript{y} cathodes toward water reduction is investigated and compared with that of platinum nanoparticle decorated Si-MW array electrodes (Si-MWs@PtNPs). An optimized Si-MWs@MoO\textsubscript{x}S\textsubscript{y} photocathode is found to exhibit activity comparable to that of the Si-MWs@PtNPs one, with a much better stability in acidic medium. In neutral electrolyte, Si-MWs@MoO\textsubscript{x}S\textsubscript{y} outperforms Si-MWs@PtNPs in terms of both activity and stability. Given the low materials cost, easy and well-established electrode fabrication procedure, and high...
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Determined photoelectrochemical performance, the Si-MWs@MoO3Sx arrays reported here hold substantial promise for use as low-cost and efficient photocathodes for water reduction. © 2015 Elsevier Ltd. All rights reserved.

Introduction

Photoelectrochemical (PEC) water splitting using semiconductor photoelectrodes is broadly considered as a promising approach for direct conversion of solar energy into renewable and storable chemical energy [1,2]. As an essential component of a PEC water splitting cell, the semiconductor photoelectrode plays a crucial role in governing the solar-to-fuel conversion performance. For efficient harvesting and conversion of solar energy, the semiconductor material of the photoelectrode should not only have a suitable band gap to absorb incident light and appropriate energy-band positions to drive water reduction and oxidation, but also render fast charge-transfer kinetics to suppress recombination at the electrode/electrolyte interface [1,2]. In addition, the material itself must be stable enough in aqueous solution under PEC operation conditions. So far, the challenge of developing a single semiconductor that can meet all these requirements remains out of reach. To simplify the challenge, a strategy to decouple the requirements has been proposed, whereby water splitting is realized using tandem cells consisting of a photocathode in a series with a photoanode [3].

P-type silicon (p-Si), among other semiconductors investigated to date [4,5], has long been of interest as a photocathode material because it offers many advantageous properties for PEC water reduction [6–28]. Specifically, p-Si has a narrow band gap (Eg=1.12 eV) enabling a broad light absorption over the solar spectrum; the typically long mean free path of charge carriers in single-crystalline Si can enhance charge collection [29]; furthermore, Si is earth-abundant, and the processing techniques for Si-based materials are well established. Particularly, recent progress in fabricating Si micro-/nanostructure arrays has opened up new opportunities for improving the PEC performance of p-Si photocathodes. Vertically aligned arrays of p-Si microwires (Si-MWs) [9,11,12,15,26], nanowires (Si-NWs) [10,16,17,19–21], and tilted p-Si nanobelts (Si-NBs) [27,28] have been demonstrated to exhibit enhanced performance toward PEC hydrogen evolution reaction (HER), due primarily to the significantly increased electrode/electrolyte contact area and the unique light harvesting capability that enables the decoupling of light capture and charge carrier collection. In addition to their HER performance, the operational stability of both planar Si [18,22,23,30–32] and Si nanostructure array photoelectrodes [28,33] also has been recently improved to a remarkable extent.

Though the band-bending in illuminated p-Si is favorable for HER, the reaction at the p-Si/electrolyte interface is kinetically slow at zero overpotential (i.e., 0 V vs. RHE) if no catalysts are present. As a result, pristine p-Si photocathodes including the advanced ones composed of MW or NW arrays, only exhibit a small positive, or sometimes even negative [17], HER onset voltage (Von) and a limited photocurrent density (Jv=0) at 0 V vs. RHE [15–17,19–21,27]. To increase the Von and Jv=0, Lewis’s group and Chorkendorff’s group have introduced a n–p-Si layer on the surface of planar p-Si or p-Si-MWs to form a homojunction to promote the charge separation at the electrode/electrolyte interface, which appreciably improved the water reduction performance [11,12,18,22,23]. A positive shift of the Von as high as 600 mV relative to that of pristine p-Si also has been achieved for p-Si/n-ZnO heterojunctions [34,35]. Efforts on homo- and hetero-junctions notwithstanding, electrocatalysts are generally indispensable for efficiently reducing water with p-Si photocathodes, and can substantially help to increase the fill factor [1]. Platinum (Pt) is the best and most commonly used electrocatalyst for PEC hydrogen evolution [8,14–17,19,22,23,27,36,37], but Pt is precious and scarce and therefore cannot be deployed practically in PEC devices on a large scale. Accordingly, recent efforts have been focused on developing earth-abundant and non-precious HER catalysts attached to p-Si photocathodes. For example, Warren et al. reported the fabrication of NiMo-coated radial-junction n–p-Si-MW array photocathodes, the best of which exhibited a Von of 0.46 V and a Jv=0 of 9.1 mA cm−2 [38]. Hou and co-workers first demonstrated that bioinspired cubane-like Mo5S4 clusters decorated on p-Si pillars are highly efficient for HER, revealing an efficiency comparable to that achieved by Pt-modified p-Si [15]. Following their work, molybdenum sulfide (Mo(S)-) based catalysts synthesized by different methods have been extensively studied for use together with p-Si photocathodes to catalyze HER [16,18,20,39], and their photocatalytic performance is reported to be comparable to that of Si/Pt electrodes.

While intensive research efforts have been dedicated to Mo-S catalysts [15,16,18,20,39–41], very little attention was paid to molybdenum oxides (Mo-O), likely because MoO3 is known to be soluble in acidic solutions [20,42]. Molecular Mo-oxo complexes, however, have been recently reported to show high stability and activity for HER [43]. A subsequent computational analysis also revealed that MoO3 clusters, compared with Mo5S4 counterparts, can absorb water more strongly [44], thereby facilitating reduction of water. Experimentally, Sinan et al. have reported that α-MoO3 nanobelts synthesized by a hydrothermal method exhibited reasonably high electrocatalytic activity toward HER in acids [45]. Very recently, Xie and co-workers confirmed the important role of oxygen incorporated into MoO3 nanosheets in HER and demonstrated dramatically enhanced HER catalytic activity delivered by the oxygen-incorporated MoO3 [46]. Though not commonly reported, using Mo-O, particularly those containing reduced Mo oxidation states, as HER catalysts would be potentially favorable because the well-known metallic nature of MoO2 or oxygen-
deficient MoO$_3$ could help to improve charge-transfer kinetics during HER [47,48].

Here, we report the first demonstration of the effectiveness of oxygen-rich molybdenum oxysulfide (MoO$_x$S$_y$) catalysts toward HER, when attached onto Si-MW arrays as photocathodes for water reduction (denoted as Si-MWs@MoO$_x$S$_y$ hereafter). We have comprehensively investigated the microstructure and PEC performance of the Si-MWs@MoO$_x$S$_y$ photocathodes with different MoO$_x$S$_y$ loadings (i.e., MoO$_x$S$_y$ layer thicknesses), and demonstrated that the photocathodes with an optimal MoO$_x$S$_y$ catalyst loading exhibit HER activity comparable to that of Pt-nanoparticle (NP) decorated electrodes (Si-MWs@PtNPs) in an acidic solution (pH=1), yet showing much better stability. Notably, under neutral conditions (pH=7), the optimized Si-MWs@MoO$_x$S$_y$ photocathodes appreciably outperform the Si-MWs@PtNPs electrodes in terms of both HER activity and stability.

Materials and methods

Fabrication of Si-MW arrays

The fabrication procedure of Si-MW arrays is schematically illustrated in Figure S1 in the Supporting Information (SI). Briefly, a 8-inch p-type Si (100) wafer (B-doped, 8–30 Ω cm, LG Siltron) was cleaned by ultrasonication in acetone for 5 min, rinsed sequentially by isopropanol and deionized (DI) water (≥ 18 MΩ cm), and then dried in a nitrogen (N$_2$) flow. Subsequently, a 1 μm thick SiO$_2$ film was deposited on the polished side of the Si wafer by plasma-enhanced chemical vapor deposition (SPTS MPX CVD). Afterwards, a 600 nm thick layer of AZ1505 photoresist was spin-coated onto the polished side of the SiO$_2$ film, and a well-ordered hole array with a designed diameter of 1 μm and a center-to-center spacing of 2 μm was patterned by direct write laser lithography (Heidelberg DWL 2000). The pattern was then developed and transferred into the underlying SiO$_2$ layer by reactive ion etching (RIE, SPTS APS ICP) to form a SiO$_2$ mask for the subsequent deep RIE process (SPTS Pegasus IDP) to obtain Si-MW arrays. After that, the resist was dissolved by acetone and the exposed SiO$_2$ was then removed through hydrofluoric (HF) vapor etching (SPTS μ etch module) followed by the evaporation of the HF etching-induced skeleton on a hotplate at 300 °C for 3 min. We noted that the cross-section shape of the resulting MWs became elliptical because the DWL laser writer was operating at its resolution limit.

The front side of the as-fabricated MW array was then protected by a 2 μm thick AZ1505 photoresist, and a 300 nm aluminum (Al) film was sputtered on the backside of the wafer (Singulus FTM magnetron sputtering tool). The 8-inch wafer was subsequently cut into small pieces with an area of 2.7×2.7 cm$^2$ by a dicing saw (DISCO DAD 3350). On each piece, a circular area of 2.5 cm$^2$ (1.8 cm in diameter) where the Si-MWs are fabricated is defined at its center (Figure S2, SI), which will be exposed to the electrolyte during the PEC tests. After cutting, the photoresist layer on the front side was removed by rinsing the wafer sequentially in acetone and DI water, followed by drying it in a high-purity N$_2$ flow. The Ohmic contact between the Al layer and the Si wafer was achieved by thermally annealing the wafer at 400 °C in high-purity N$_2$ (99.999%) for 1 min.

Fabrication of Si-MWs@MoO$_x$S$_y$ and Si-MWs@Pt arrays

The amorphous MoO$_x$S$_y$ and MoO$_x$ catalysts were decorated on the Si-MW surface by photo-assisted cyclic voltammetric (CV) electrodeposition in a mixed aqueous solution of 10 mM Na$_2$MoO$_4$ (Sigma) with and without 0.75 M thiourea (TU, Sigma-Aldrich) as additive, respectively. The deposition was carried out under illumination of 100 mW cm$^{-2}$ (tungsten lamp WOW01, Zahner) in a potential range of −1.6 to −0.2 V vs. Hg/HgSO$_4$ reference electrode (MSE, saturated K$_2$SO$_4$), with the Si-MW arrays as the working electrode and a Pt coil as the counter electrode. The scan rate was 50 mV s$^{-1}$. In order to investigate the effect of MoO$_x$S$_y$ loading on the PEC performance of the photocathodes, the CV electrodeposition was performed for various numbers of cycles (10, 30, 50, and 100). After CV deposition, the electrode was thoroughly cleaned with copious DI water and then immediately used in the PEC test. To confirm that the deposited MoO$_x$S$_y$ are electrocatalytically active, CV deposition was also carried out under the same conditions as mentioned above using a nickel foam as the working electrode (Ni@MoO$_x$S$_y$).

To compare the PEC performance of the Si-MWs@MoO$_x$S$_y$ electrodes with that of the Si-MWs@PtNPs electrode, Pt NPs were impregnated onto the surface of Si MWs by soaking the Si MWs in a solution of 0.4 M HF (Sigma) and 1 mM K$_3$PtCl$_6$ (Sigma) for 3 min according to the previous report [17], during which the backside of the wafer (i.e., the Al layer) was well protected by a Teflon tape. After Pt impregnation, the wafer was rinsed with copious DI water and dried in a N$_2$ flow. This impregnation process was repeated 5 times in order to increase the Pt loading to achieve optimized PEC performance. Prior to the Pt impregnation, the Si-MWs were immersed into a 2.5 wt% HF solution for 5 min to remove the native oxide layer. Typical morphology of the Si-MWs@PtNPs electrode is shown in Figure S3 (SI).

Structural and spectroscopic characterization

The morphology and microstructure of the samples were examined by scanning electron microscopy (SEM, FEI Quanta FEG 650) and aberration-corrected transmission electron microscopy (TEM, FEI Titan ChemiSTEM 80-200, operating at 200 kV). For TEM investigation, the wires were scratched off the Si substrate and directly dispersed on a carbon-coated copper grid. The grid was then placed in a vacuum oven at 110 °C for 2 h before being mounted on the TEM sample stage.

The X-ray photoelectron spectroscopy (XPS) measurements were performed with freshly prepared samples using an ESCALAB 250 XI system (Thermo Scientific) equipped with a monochromated Al K$_\alpha$ X-ray source. The standard analysis spot of ca. 900×600 μm$^2$ was defined by the microfocused X-ray source. The measurements were carried out at room temperature in an ultra-high vacuum chamber with the base pressure <5×10$^{-10}$ mbar; the charge neutralization device produced ca. 2×10$^{-7}$ mbar partial pressure of Ar during...
measurements. The energy of the monochromated Al Kα X-ray source was measured to be within \( \pm 0.2 \) eV from 1486.6 eV.

Raman scattering measurements were carried out on an alpha300 R confocal Raman microscope (WITec) using a 532 nm Nd:YAG laser for excitation. The system was operated with a low output laser power of 0.1 mW, and the laser beam was focused on the Si-MWs@MoO\(_x\)S\(_y\) samples by a \( \times 100 \) Zeiss lens with a numerical aperture (NA) of 0.9. The spectra were collected using a 1800 grooves/mm grating for 10 acquisitions with integration time of 5 s.

Fourier-transform infrared (FTIR) spectra of the MoO\(_x\)S\(_y\) samples were acquired on a VERTEX 80v FT-IR spectrometer (Bruker) in absorbance mode. A spatula tip of the sample was mixed with 200 mg of KBr (FTIR grade), and the powder was pressed at 10 t for 2 min to obtain a transparent pellet. Spectra were recorded using DTGS (Deuterated triglycine sulfate) detector the system evacuated to 1.7 hPa; 32 scans were acquired in the range of 1000–370 cm\(^{-1}\) with 4 cm\(^{-1}\) resolution. A background spectrum was acquired with an empty holder in the system evacuated to 1.7 hPa. Baseline correction was applied to the spectra.

Electrocatalytic and photoelectrochemical (PEC) tests

The electrocatalytic performance of the Ni@MoO\(_x\)S\(_y\) electrode was evaluated using a three-electrode configuration with a graphite plate as the counter electrode and a MSE as the reference. The electrolyte consisted of 0.5 M K\(_2\)SO\(_4\) (\( \geq \) 99%, Sigma-Aldrich) buffered at pH=1 using sulfuric acid (95–98%, Sigma-Aldrich), which was bubbled with high-purity N\(_2\) gas (99.999%) during the tests. The PEC tests were carried out in a commercially available thin Teflon cell (PECC2, Zahner) [27]. A Pt coil and a MSE electrode were used as counter and reference electrodes, respectively. The Si photocathode was exposed to an electrolyte consisting of 0.5 M K\(_2\)SO\(_4\) buffered at pH=1, or to a 1.0 M potassium phosphate solution buffered at pH=7 (exposed area: 2.5 cm\(^2\)). A calibrated tungsten lamp (WOW01, Zahner) was used as the light source and controlled by an external potentiostat (Zahner PP211). A photo-sensor (EPIGAP EPD-470-5-0.5 based on GaP doping) and a feedback loop circuit were employed to detect and tune the light intensity (Zahner). The J-U, EIS, and J-t plots were recorded by a Zennium electrochemical workstation (Zahner). The EIS measurements were performed in the frequency range of 0.1 Hz - 100 kHz at a fixed potential of 0 V vs. RHE under nominal illumination of 100 mW cm\(^{-2}\), with an AC voltage amplitude of 10 mV. Prior to each measurement, high-purity N\(_2\) gas was flowed through the cell for 5 min. The sample temperature was maintained at 23 ± 1 °C during the test using a home-made cooling unit connected with a refrigerated chiller (HAAKE Phoenix II, Thermo Scientific). For each measurement, the tungsten lamp was first calibrated at 100 mW cm\(^{-2}\) and then an IR filter (Newport, 20HMS-O hot mirror) was placed perpendicularly to the light path. The spectra of the tungsten lamp recorded without and with the IR filter are shown in Figure S4 (SI). The intensity of the incident light hitting on the photocathode (i.e., IR filtered) is calculated to be 60 mW cm\(^{-2}\) by integrating the intensity in the range of 300-1000 nm.

Unless otherwise stated, all potentials are reported versus reversible hydrogen electrode (RHE) by converting the potentials measured versus MSE through the following equation:

\[
V_{\text{RHE}} = V_{\text{MSE}} + 0.654 + 0.059 \text{pH} \tag{1}
\]

Results and discussion

Morphology and microstructure

Fig. 1a shows the typical morphology of as-fabricated Si-MW arrays: ca. 8-μm long wire are oriented perpendicularly to
the Si substrate and arranged with an inter-wire distance of 2 μm (center-to-center). DWL working at its resolution limit, slightly deviated from the nominal wire diameter of 1 μm, and produced an elliptical cross-section with long and short axes of 1.2 μm and 0.9 μm, respectively. Regularly distributed threads, which resulted from well-known Bosch process during the RIE, are also observed on the surface of these wires.

The MoO$_x$S$_y$ catalysts were grown on the Si-MW surface by photo-assisted CV electrodeposition in an aqueous solution of 10 mM Na$_2$MoO$_4$ mixed with 0.75 M TU. The deposition was carried out for different number of cycles (10, 30, 50, and 100) to tune the loading of the MoO$_x$S$_y$ (representative CV profiles are shown in Figure S5, SI). We note that illumination plays an important role in the deposition of MoO$_x$S$_y$ on Si-MWs, because the photo-generated electrons at the Si-MW surface can facilitate the reduction of [MoO$_4$]$^{2-}$ anions [16]. When the CV electrodeposition is performed in darkness, the cathodic deposition current becomes very small, implying an ineffective deposition (Figure S5, SI). Although Seger et al. argued that direct electrodeposition on p-Si surface would cause oxidation of Si [18], CV deposition did not noticeably degrade the PEC performance of our Si-MWs@MoO$_x$S$_y$ electrodes. We also note that the addition of TU plays a critical role in achieving good PEC performance, as evidenced by the relatively poor HER activity of the electrodes prepared without adding TU during the CV electrodeposition (Figure S6, SI). Being often used as an additive that helps the formation of uniform electrodeposits [49], TU may serve as a complexing agent to facilitate the reduction of [MoO$_4$]$^{2-}$ on the Si surface. In principle, TU itself could also be reduced in the cathodic process, producing $S^2-$, which could then be incorporated into the catalyst layer [50], forming MoO$_x$S$_y$. The overall content of sulfur (S) in our MoO$_x$S$_y$ deposits, however, is low (< 4 at%) according to the X-ray photoelectron spectroscopy (XPS) analyses (Table S1, SI), indicating that the incorporation of S is not a dominant process during our CV deposition process.

The morphology of the Si-MW arrays after the CV deposition for 10, 30, and 50 cycles, respectively (hereafter denoted as Si-MWs@MoO$_x$S$_y$-10, Si-MWs@MoO$_x$S$_y$-30, and Si-MWs@MoO$_x$S$_y$-50), is illustrated by representative scanning electron microscopy (SEM) images in Figs. 1b – d. The appearance of the Si-MWs@MoO$_x$S$_y$-10 indicates that the CV deposition initially occurs predominantly at the top end of the wires, accompanied by only sparsely distributed NPs on the side walls. This preferential deposition pattern could result from a relatively poor mass transport of the electrolyte inside MW arrays. After a CV deposition for 30 cycles, the density of the MoO$_x$S$_y$ NPs greatly increases and these NPs tend to interconnect, forming a continuous layer (Fig. 1c). Increasing the cycle number to 50 results in the formation of a continuous MoO$_x$S$_y$ layer conformally.

Fig. 2 TEM micrographs of (a) Si-MWs@MoO$_x$S$_y$-10 and (b) Si-MWs@MoO$_x$S$_y$-50. (c) A typical EDX spectrum. (d) HAADF-STEM micrographs taken at (d) the top end and (e) the bottom end of an individual Si-MW coated with a MoO$_x$S$_y$ catalyst layer (50 cycles). (f) Variation of the deposited MoO$_x$S$_y$ catalyst layer thickness with the CV deposition cycle numbers.
covering the entire surface of the MWs, as can be seen in Fig. 1d. Further increase in the deposition cycles (e.g., to 100 cycles) makes the MoO$_x$S$_y$ layer thicker, but produces cracks, which likely form due to the mismatch in the thermal expansion coefficients of Si and amorphous MoO$_x$S$_y$, and/or due to the strain induced in a thick MoO$_x$S$_y$ layer (Figure S7, SI).

The distribution and microstructure of the MoO$_x$S$_y$ NPs and films on Si-MWs@MoO$_x$S$_y$ electrodes were examined in more detail by extensive transmission electron microscopy (TEM) imaging. A typical TEM image of a Si-MWs@MoO$_x$S$_y$-10 sample reveals discrete NPs distributed on the MW surface (Fig. 2a). High-resolution TEM (HR-TEM) analysis confirms that these NPs are amorphous and intimately adhere to the MWs (Fig. 2a, inset). The presence of discrete MoO$_x$S$_y$ NPs distributed on the Si-MW surface was also corroborated by elemental mapping in scanning transmission electron microscopic (STEM) mode (Figure S8, SI). When the CV deposition is performed for 30 cycles or more, a continuous amorphous MoO$_x$S$_y$ layer forms over the entire surface of the Si-MWs and conformally covers the MWs, as illustrated by a representative TEM micrograph of a Si-MWs@MoO$_x$S$_y$-50 sample in Fig. 2b, in agreement with the above SEM observation. Extensive EDX analyses reveal that the electrodeposited layer consists of Mo and O as the major components, as shown in Fig. 2c. A peak assigned to sulfur K edge (S-K) by the software also appears in the spectrum, but the corresponding peak completely overlaps with the Mo-L edge ($E_{Mo-L}=2.292$ eV, $E_{S-K}=2.307$ eV) so that it is not well distinguishable. Nevertheless, quantitative XPS analysis reveals that there is only ca. 3-4% S in the deposits (Table S1, SI). As discussed previously, the small amount of S likely stems from the deposition of S$^2$-, which was introduced into the electrolyte by the cathodic decomposition of TU [50].

Despite being continuous, MoO$_x$S$_y$ layers deposited after 30 or more CV deposition cycles are not uniformly thick over the length of the wire, in agreement with indications from SEM images. Specifically, a thicker MoO$_x$S$_y$ layer is deposited at the top end of a MW and becomes progressively thinner toward the bottom, as can be clearly seen from the high-angle annular dark field (HAADF) STEM images shown in Figs. 2d and e. This top-to-bottom variation likely arises from the variation in electrolyte concentration that forms due to a limited mass diffusion during the CV deposition. Variation along the MW notwithstanding, the overall MoO$_x$S$_y$ layer thickness, and thereby the loading of the MoO$_x$S$_y$ catalyst, increases with the CV deposition cycle number (Fig. 2f), allowing us to investigate the loading-dependent PEC performance of Si-MWs@MoO$_x$S$_y$ photocathodes.

The continuous and conformal character of the MoO$_x$S$_y$ layers is confirmed by the elemental distribution maps (Fig. 3) for a representative Si@MoO$_x$S$_y$ MW shown in Fig. 2d. Both Mo and O characteristics of the MoO$_x$S$_y$ catalyst layer are conformally distributed over the MW surface, indicating that CV electrodeposition is effective for catalyst loading onto high aspect-ratio MW/NW

Fig. 3 The elemental maps of (a) Si, (b) Mo, and (c) O. (d) The overlap map of elements. The mapping was carried out with the sample Si-MWs@MoO$_x$S$_y$-50 shown in Fig. 2d. Scale bars: 600 nm.
photoelectrodes. The map of S is not presented in Fig. 3 because of the aforementioned difficulty in deconvolution of S-K edge from Mo-L edge. This continuous and conformal MoO₅Sₓ catalyst layer also protects the Si-MWs from photooxidation during HER, as will be discussed in more detail in a later section.

**Spectroscopic characterization of the deposited MoO₅Sₓ catalysts**

To quantitatively investigate the chemical composition of the deposited MoO₅Sₓ layer, we analyzed these samples using XPS. Fig. 4 shows the high-resolution XPS data acquired in the O 1s, C 1s, Mo 3d (S 2s), and S 2p regions from Si-MWs@MoO₅Sₓ-10, -30, and -50 electrodes, respectively. The peak position and full width at half-maximum (FWHM) information is summarized in Table S2 (SI).

The fits shown in Fig. 4 indicate the presence of four major components in Mo 3d spectra; for clarity, only the 3d₅/₂ components are shown explicitly, while contributions from 3d₃/₂ components are included in the total fit curves and shown explicitly in Figure S9 (SI). The assignments are clear from the literature for three out of four Mo 3d components that we observe for our samples: the Mo 3d₅/₂ components at 229.8, 230.7, and 232.5 eV can be assigned as Mo⁴⁺, Mo⁵⁺, and Mo⁶⁺ oxidation states, respectively [51-53]. The fourth component (Mo 3d₅/₂ at 231.7 eV, red in Fig. 4 and in Figure S10, SI) is a surprising observation, apparently unique to our MoO₅Sₓ materials. Its uniqueness is highlighted by comparing to a recent study of electrochemically deposited MoSₓ [53], where a clear gap in the binding energy range around 231.5 eV was observed in Mo 3d spectra. Being clearly distinct from and positioned between the known Mo⁵⁺ and Mo⁶⁺ states (Fig. 4 and Figure S10, SI), the oxidation state corresponding to this component is speculative, but it likely corresponds to a MoO₅Sₓ material phase/structure with an effective oxidation state of ca. 5.5+.

In addition to the multiple Mo oxidation states, Fig. 4 also reveals that the S content in our MoO₅Sₓ layers is low, as
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evidenced by the minimal intensity of the S 2s peak relative to the Mo 3d peak. The amount of S can be quantitatively determined from the S 2p spectra to be at the level of 3-4 at % for the continuous MoO$_x$S$_y$ deposits (corresponding to x ≈ 2 and y ≈ 0.15 for Si-MWs@MoO$_x$S$_{y-30}$ and Si-MWs@MoO$_x$S$_{y-50}$, see Table S1 and estimates in the SI). A single sharp S 2p doublet with the S 2p$_{3/2}$ binding energy at 162.5 eV indicates that the S exists in a well-defined sulfide chemical state (similar to that in MoS$_2$) [50,52]. Notably, no sulfur oxidation was observed in the deposited MoO$_x$S$_y$ layers, as indicated by the absence of any S 2p features above 166 eV.

To further investigate the molecular structure of the deposited MoO$_x$S$_y$, Raman and FTIR measurements were performed. The Raman spectrum shown in Figure S11a confirms the presence of bridged oxygen and bridged sulfur bonds (i.e., Mo-O-Mo and Mo-S-Mo) as well as the O-Mo-S bonds [54]; while the FTIR spectrum verifies the presence of terminal oxygen (i.e., Mo=O, Figure S11b, SI) [55]. Notably, both Raman and FTIR spectra are distinctly different from those of MoO$_3$ [56-58], MoO$_2$ [58,59], and MoS$_2$ [60,61] reported in the literature, showing some unique characteristics of reduced oxy sulfide [54]. This indicates that the deposited MoO$_x$S$_y$ is not a simple blend of Mo oxides and sulfides. We hypothesize that the MoO$_x$S$_y$ microscopically may consist of cyclic or linear oligomers that are intertwined together by sulfur or oxygen bridging, which forms by repetitive cathodic and anodic sweeping during the photo-assisted CV deposition.

**Photoelectrochemical performance toward water reduction**

Before testing the PEC performance of the Si-MWs@MoO$_x$S$_y$ photocathodes, the electrocatalytic properties of the deposited MoO$_x$S$_y$ was examined by linear scan voltammetry (LSV, Figure S12, SI) using the Ni@MoO$_x$S$_y$ electrodes in N$_2$-saturated 0.5 M K$_2$SO$_4$ solution (pH=1). The MoO$_x$S$_y$ shows an HER onset potential of −135 mV and needs an overpotential of 285 mV to afford a current density of 10 mA cm$^{-2}$, whose performance is comparable to that of MoS$_2$ nanoflowers and MoS$_2$/CNT composites recently reported in the literature [62,63], illustrating that the deposited MoO$_x$S$_y$ is electrocatalytically active toward HER.

The PEC performance of the Si-MWs@MoO$_x$S$_y$ electrodes toward water reduction has been evaluated by LSV, electrochemical impedance spectroscopy (EIS) and chronocamperometry in both acidic (pH=1) and neutral (pH=7) solutions.

Fig. 5a shows the current density-potential (J-U) profiles of the Si-MWs@MoO$_x$S$_y$ photocathodes with different loadings of the MoO$_x$S$_y$ catalysts, measured in a pH=1 buffer solution under constant illumination of 60 mW cm$^{-2}$ (Tungsten lamp, Zahner, IR-filtered). For comparison, the J-U curves of the bare Si-MW and Si-MWs@PtNPs arrays are also presented. As seen in Fig. 5a, the bare Si-MW array electrode reveals a negligible photocurrent of 0.31 mA cm$^{-2}$ at 0 V vs. RHE (i.e. J$_{\nu_0}$), and its $V_{\text{on}}$ (defined as the potential where the generated photocurrent density is 0.5 mA cm$^{-2}$) is only 0.05 V. After modifying the Si-MW arrays with amorphous MoO$_x$S$_y$, both the $V_{\text{on}}$ and $J_{\nu_0}$ of the electrodes increase, indicating that the amorphous MoO$_x$S$_y$ has a strong electrocatalytic effect toward HER. The $V_{\text{on}}$ of the Si-MWs@MoO$_x$S$_{y-10}$, Si-MWs@MoO$_x$S$_{y-30}$, and Si-MWs@MoO$_x$S$_{y-50}$ photocathodes are 0.15, 0.20, and 0.24 V, respectively; while the $J_{\nu_0}$ of these electrodes amount to 1.28, 7.35, and 9.83 mA cm$^{-2}$, respectively. The Si-MWs@MoO$_x$S$_{y-50}$ photocathode exhibits the highest photocurrent at 0 V, likely because the higher loading of amorphous MoO$_x$S$_y$ catalysts on this electrode offers more electrocatalytically active sites, compared to that of Si-MWs@MoO$_x$S$_{y-10}$ and Si-MWs@MoO$_x$S$_{y-30}$ electrodes (Fig. 2f). This is consistent with previous reports on amorphous MoS$_x$ catalysts where a higher MoS$_x$ loading gave rise to a higher HER current [41,53]. Compared with the Si-MWs@PtNPs electrode having a $V_{\text{on}}$ of 0.21 V and $J_{\nu_0}$ of 10.5 mA cm$^{-2}$, the Si-MWs@MoO$_x$S$_{y-50}$ photocathode exhibits a slightly more positive $V_{\text{on}}$ and a similar $J_{\nu_0}$.

Further increase in the MoO$_x$S$_y$ layer thickness (i.e., by increasing the CV deposition cycles) results in a decrease in $J_{\nu_0}$, for example, the $J_{\nu_0}$ of the Si-MWs@MoO$_x$S$_{y-100}$ is reduced to 8.60 mA cm$^{-2}$ (Figure S13, SI). The reduced photocurrent may result from the enhanced light absorption by the thick catalyst layer in Si-MWs@MoO$_x$S$_{y-100}$ sample, similar to the case of amorphous Mo-S coated Cu$_2$O photocathode reported before [64]. Other factors that may contribute to the reduced photocurrent include the increased electron-transport resistance in the thick amorphous layer and/or the loose electrical contact between the MoO$_x$S$_y$ layer and Si-MWs due to the induced stress, as evidenced by the cracks observed in the Si-MWs@MoO$_x$S$_{y-100}$ electrode (Figure S7, SI).

Fig. 5b shows the J-U curves of the Si-MWs@MoO$_x$S$_y$ photocathodes measured under chopped illumination at a frequency of 0.5 Hz: the Si-MW, Si-MWs@MoO$_x$S$_{y-30}$, and Si-MWs@PtNPs electrodes all show well-defined photoresponse. Moreover, no sharp current spikes are observed upon the illumination, indicating that the MoO$_x$S$_y$ catalyst facilitates the rapid electron transfer to the electrolyte, thus suppressing the charge recombination on the MW surface [65].

In contrast to previous detailed investigations of Mo-S catalysts, electrocatalysis of the HER based on Mo oxides and MoO$_x$S$_y$ is rarely documented. It is well known that the difference between the free energy of hydrogen adsorption at the catalyst surface and that of the reactant or product, $\Delta G_{\text{H}}$, is a primary descriptor of the HER activity [66,67]. The closer the $\Delta G_{\text{H}}$ to $\Delta G_{\text{H}}$ cis 0, the more active the catalysts. According to the density functional theory (DFT) calculations, the differential free energy of adsorption of hydrogen bound to sulfur at S-Mo-S sites is 0.1 eV, assuming a hydrogen coverage of above 0.25 [66]. Therefore, only a low overpotential of the order 0.1 V is needed for MoS$_2$ to catalyze the HER. We speculate that $\Delta G_{\text{H}}$ for the amorphous MoO$_x$S$_y$ would not significantly deviate from $\Delta G_{\text{H}}$ cis 0, given the high electrocatalytic and photoelectro catalytic activities delivered by the Ni@MoO$_x$S$_y$ and Si-MWs@MoO$_x$S$_y$ electrodes, respectively. Moreover, we hypothesize that proton reduction would take place at bridged/terminal oxygen and bridged sulfur sites, as recent DFT calculations point out that both sulfur and oxygen sites are preferential for hydrogen atom adsorption [44,66,68]. The number of active sites exposed to the electrolyte may be further increased by the amorphous nature of the MoO$_x$S$_y$ layer, in analogy with previous reports for the amorphous MoS$_x$.
catalysts [41]. Besides, our XPS analysis reveals predominantly reduced Mo oxidation states in the surface layers of MoO$_x$S$_y$ catalysts, indicating that the Mo 3d band is partially filled and that the electronic conductivity could be enhanced [47, 48]. Indeed, the conductive nature of the deposited MoO$_x$S$_y$ layers was confirmed by the small equivalent series resistance measured by EIS (e.g., only 1.7 $\Omega$ for Si-MWs@MoO$_x$S$_y$-50), which will be shown below.

Fig. 5c displays the Nyquist plots of the bare Si-MWs and Si-MWs@catalyst photocathodes, which have been fitted with the two equivalent circuit models shown in the inset. The equivalent series resistance $R_s$ represents the overall resistance arising from the electrode materials, electrical contacts, and the electrolyte, the $R_{ct}$-C$_1$ stands for the charge transfer process at the Si/electrolyte interface for the bare Si-MW electrode and at the catalyst/electrolyte interface for the Si-MWs@catalyst electrodes, and the $R_2$-C$_2$ simulates the charge transfer at the Si/catalyst interface and transport in the catalyst layer. As can be seen from Fig. 5c and the fitting results shown in Table S3 (SI), the $R_s$ for all the electrodes is very similar, approximately 2.0 $\Omega$, indicating that the deposition of the MoO$_x$S$_y$ layer does not introduce extra electrical resistance. The semicircle of the bare Si-MWs photocathode is much larger than that of the electrode modified with either MoO$_x$S$_y$ or Pt catalysts, with a fit charge transfer resistance $R_{ct}$ of 40.48 $\Omega$, indicating unfavorable charge transfer kinetics. In contrast, $R_{ct}$ of the Si-MWs@MoO$_x$S$_y$ photocathodes is significantly smaller and decreases with the increasing MoO$_x$S$_y$ layer thickness, following the order: Si-MWs@MoO$_x$S$_y$-10 > Si-MWs@MoO$_x$S$_y$-30 > Si-MWs@MoO$_x$S$_y$-50. Notably, the $R_{ct}$ of the Si-MWs@MoO$_x$S$_y$-50 electrode is found to be as small as that of the Si-MWs@Pt, at only around 1.07 $\Omega$. This trend suggests that the deposited MoO$_x$S$_y$ catalysts significantly accelerate the electron-transfer rate from Si to the electrolyte, to the extent that the charge transfer outruns the surface recombination.

The PEC performance of the Si-MWs@MoO$_x$S$_y$ array photocathodes is also evaluated by the photopower conversion efficiency (PPCE) of the cells ($\eta$) defined by the following equation [5]:

$$\eta = \frac{J (U_{app} - U(H^+/H_2))}{I_0} \times 100\%$$
Amorphous oxygen-rich molybdenum oxy sulfide Decorated p-type silicon microwire Arrays for efficient photoelectrochemical water reduction

Where $I_0$ is the power density of the light incident to the test cell, which is 60 mW cm$^{-2}$ in our case (with IR filter, Figure S4, SI), $U_{app}$ is the applied bias, $U(H^+/H_2)$ is the potential of the redox couple, and $J$ is the photocurrent density. It is found that the Si-MWs@MoO$_{S_y}$-50 exhibits a maximum $\eta$ of 0.82% at a potential of 0.09 V vs. RHE, which is higher than 0.63% and 0.53% achieved by the Si-MWs@MoO$_{S_y}$-30 and Si-MWs@PtNPs, respectively, and much higher than the 0.05% delivered by the Si-MWs MoO$_{S_y}$-10 electrode. The $\eta$ of the Si-MWs@MoO$_{S_y}$-50 electrode is found to be higher than that of the Ni-Mo modified p-Si MW arrays (0.22%) [38]. If a $n^-$-Si layer could form on the MW surface, a higher efficiency would be expected.

The stability of the Si-MWs@MoO$_{S_y}$ photocathodes was tested at 0 V vs. RHE under constant illumination in a pH=1 buffer solution. Fig. 6 shows the chronoelectrochemical water reduction (J-t) curves of the tested electrodes. The photocurrent of the Si-MWs@PtNPs electrode first sharply and then gradually decreases over time, and finally reduces to ca. zero in about 40 min. The failure may arise from the oxidation of the Si-MWs, as verified by EDX analysis (Figure S14, SI) and previous observations [28]. In contrast, the photocurrent of the Si-MWs@MoO$_{S_y}$-50 photocathode first goes down and then gets stabilized after a 30-min test at $\sim$6.8 mA cm$^{-2}$ for up to 2 h. In order to check if the Si core was oxidized upon the extended J-t test, we performed TEM investigation for the Si-MWs@MoO$_{S_y}$-50 electrode being tested for 2 h. As shown in the elemental map in Figure S15 (SI), no oxygen was observed in the Si core, indicating that the MoO$_{S_y}$ catalyst layer not only offers high catalytic activity toward HER, but also effectively protects the Si-MWs from oxidation.

The stability of our oxygen-rich MoO$_{S_y}$ films in acidic solutions is most likely related to their unique chemistry and structure. While determining the exact origin of this aciddensity would require a dedicated systematic study that falls beyond the scope of the current work, we can hypothesize about the following contributing factors. For Mo oxides, for example, solubility in acid strongly depends on the Mo oxidation state: while MoO$_3$ is soluble in a variety of aqueous solutions, including acidic and basic ones, MoO$_2$ is only slightly soluble or insoluble in common acidic or basic solutions. The unique combination of Mo oxidation states (between Mo$^{4+}$ and Mo$^{6+}$, Fig. 4) in our MoO$_{S_y}$ films, therefore, may contribute to their acid-stability. Furthermore, molybdate salts would be expected to readily produce $-Mo-O-$ networks [69] under the repetitive cathodic and anodic sweeping during CV electrodeposition; these O-based networks and chains are likely stabilized by sulfur bridging (i.e., Mo-S-Mo indicated by both XPS and Raman data). Additional stabilization of $-Mo-O-$ networks may be provided by incorporation of ammonium ligands [69], the presence of which would be consistent with XPS data (Table S1, SI).

Similar to Si-MWs@MoO$_{S_y}$-50, the Si-MWs@MoO$_{S_y}$-10 and Si-MWs@MoO$_{S_y}$-30 electrodes also show markedly improved stability in the acidic electrolyte, though the photocurrents they generated are lower. Interestingly, for these two samples, the photocurrent increases with time at the beginning of the J-t test, before it eventually stabilizes; this behavior may result from a progressive activation or surface re-arrangement of the MoO$_{S_y}$ catalysts.

The PEC performance of Si-MWs@MoO$_{S_y}$ photocathodes was also tested in a neutral phosphate buffer solution (pH=7.0). The J-U plots in Fig. 7a show that at 0 V vs. RHE the photocurrent generated by Si-MWs@PtNPs is 1.58 mA cm$^{-2}$, which is lower than that of Si-MWs@MoO$_{S_y}$-50 (i.e., 2.25 mA cm$^{-2}$), but is higher than that of Si-MWs@MoO$_{S_y}$-30 (i.e., 0.85 mA cm$^{-2}$). The photocurrent of the benchmark Si-MWs@PtNPs cathode has been dramatically improved to ca. 2 h in the neutral electrolyte (Fig. 7b). Nevertheless, the Si-MWs@PtNPs electrode eventually failed, probably due to the gradual oxidation of the Si-MWs [28]. In contrast, the photocurrent of the Si-MWs@MoO$_{S_y}$-50 electrode only decreases in the beginning of the J-t test and then gets stabilized at $\sim$0.75 mA cm$^{-2}$ for up to 5 h. Notably, the photocurrent generated by the Si-MWs@MoO$_{S_y}$-30 electrode gradually increases over time within 5 h, rather than just initially, as observed at pH=1 in Fig. 6.

Overall, the photocurrent density of the Si-MWs@MoO$_{S_y}$ electrodes measured in the neutral solution was found to be smaller than that measured in the acidic solution (Fig. 5). Two major factors may contribute to this reduction of the photocurrent density: the drastically reduced proton concentration in the neutral electrolyte and the substantially decreased electrical conductivity of the electrolyte (from 146 mS cm$^{-1}$ for the acidic electrolyte to 9 mS cm$^{-1}$ for the neutral electrolyte).

Conclusions

In summary, p-Si microwave array photocathodes coupled with electrodeposited amorphous MoO$_{S_y}$ catalysts have been fabricated. The morphology, structure and photoelectrochemical performance toward water reduction of the as-obtained Si-MWs@MoO$_{S_y}$ electrodes with varying MoO$_{S_y}$ loadings have been comprehensively investigated. The Si-MWs@MoO$_{S_y}$ photocathodes with an optimal MoO$_{S_y}$ loading are found to exhibit activity toward hydrogen evolution comparable to that of the Pt nanoparticle decorated Si microwire array electrodes, but having much better
stability in acidic electrolyte. In neutral electrolyte, the optimized Si-MWs@MoO$_x$S$_y$ electrode outperforms the Si-MWs@PtNPs electrode in terms of both activity and stability. The excellent catalytic performance of MoO$_x$S$_y$ may arise from low free energy of hydrogen adsorption on the catalyst, the amorphous nature of MoO$_x$S$_y$ that allows more active sites to be exposed to the electrolyte, and the predominance of reduced Mo oxidation states that give rise to high electrical conductivity, which helps to accelerate charge-transfer kinetics; while the extended stability is believed to result from the effective passivation of the Si microwire arrays by continuous and conformal MoO$_x$S$_y$ layers. Given the well-established fabrication procedure for Si microwires and the easy deposition of MoO$_x$S$_y$ catalytic layers through photo-assisted cyclic voltammetry, the Si-MWs@MoO$_x$S$_y$ electrodes reported here hold substantial promise for use in low-cost and durable photoelectrochemical water splitting cells.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2015.06.014.

References

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Noelia Guldris received her MSc degree (2013) in Advanced Chemistry from the University of Santiago de Compostela, Spain, where she conducted research on the synthesis of dendritic block copolymers and their application as drug delivery systems. She is currently working as a PhD student under the supervision of Prof. Jose Rivas at INL on multifunctional systems based on magnetic nanoparticles as contrast agents for Magnetic Resonance Imaging.

Helder Fonseca is a Cleanroom engineer at INL since 2009. His tasks are mainly dedicated to microfabrication processing where he is responsible for the systematic development, monitoring and maintenance of several dry etching and chemical vapor deposition tools / processes. In the past, he worked at Portuguese Technological Centre for Textile Industries where he participated in several product development projects and provided technical consulting to companies. He received a Degree and Master in Materials Engineering from University of Minho in 2005, where he developed research work in the field of thin films deposition by PVD.

Margaret Costa is integrated in the Cleanroom Department of INL being responsible for Lithography processes. Margaret works actively in the management of the cleanroom facility, specifically in the components of process development, technology and quality assurance with responsibilities that involve the definition of procedures and methodologies, continuous process improvement, new products and materials qualification and resources management. Prior to joining INL, Margaret worked in a large semiconductor manufacturing plant as a process integrator for the Wafer Level Package Area. Margaret received both Degree and Master in Chemical Engineering from the University of Porto and is currently pursuing a PhD in Technological Physics Engineering from IST, Lisbon. Her work aims the Integration of Hybrid Spintronic and MEMS devices with CMOS technology.

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Lifeng Liu received his PhD degree in Condensed Matter Physics in 2007 from the Institute of Physics, Chinese Academy of Sciences. Afterwards, he joined the Max Planck Institute of Microstructure Physics, first working as a postdoc researcher and then as a staff scientist and group head. He moved to the International Iberian Nanotechnology Laboratory (INL) in 2011 and set up a group where his research is presently focused on the development of nanomaterials for use in energy storage and conversion devices including photoelectrochemical cells, lithium-ion batteries, supercapacitors and fuel cells.
Supporting Information for

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

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**XPS analysis of the Si-MWs@MoO$_2$S$_x$ 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$_{3/2}$.$^1$

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,$^2$ and effective attenuation lengths for photoelectrons from the standard TPP-2M formalism.$^3$ 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$^{4-9}$ 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.$^{4,6,8,9}$ 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 the 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 Figures 4 and S9 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 the literature for similar materials.89

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$_x$S$_y$ 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 Mo$^{5+}$ and Mo$^{6+}$ oxidation states (green and blue, respectively, in Figures 4 and S10) is unambiguously confirmed by its appearance in reference spectra obtained for control samples that underwent an intentional oxidation (Figure S10); 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.
The stoichiometry of our MoO$_x$S$_y$ materials can be estimated from the data in Table S1. The Si-MWs@MoO$_x$S$_y$-10 film is not continuous, as evidenced by the strong Si signal that originates from the substrate; the O signal that originates from the Si oxide will, therefore, result in underestimating the Mo:O ratio for that sample. For the thicker and continuous Si-MWs@MoOxSy-30 and -50 films, the apparent elemental ratios should be more representative of the real stoichiometry of their surfaces. The most conservative estimate would include only the O signal that is unambiguously associated with a metal oxide, i.e., the component at ca. 530.9 eV$^{54,56,58,59}$ following this approach we observe Mo:O ratios of ca. 1:1.8 for both MoO$_x$S$_y$-30 and -50 films. The Mo:S ratios for these films are unambiguous at ca. 0.13 and 0.18, respectively. These values suggest an overall stoichiometry for our materials of MoO$_{2y}$S$_y$, where $y$ is between 0.1 and 0.2. We note, however, that this MoO$_{2y}$S$_y$ formula represents an oversimplified view of our materials for two important reasons. First, multiple oxidation states of Mo clearly observed in Figure S9 unambiguously indicate that the material is not simply mostly MoO$_2$ in terms of composition. Second, some of the O 1s components with BEs above 531 eV (green and blue lines in O 1s fits in Figure 4) may correspond to O incorporated into MoO$_x$S$_y$ materials; the total amount of O provides a lower limit on Mo:O ratios at ca. 1:2.4 for these samples, but at least some of the total O signal is associated with the organic carbonaceous material (C 1s components above 286 eV BE in Figure 4). Accordingly, we retain the MoO$_x$S$_y$ notation in the text, to avoid a misleading oversimplification; as briefly explained above, the apparent values of $x$ and $y$ are in the ranges of 1.8–2.4 and 0.1–0.2, respectively.
Supplementary Figures:

**Figure S1.** Fabrication procedure of the Si-MW arrays.
Figure S2. A digital photo showing the as-fabricated Si-MWs@MoO₃Sₓ photocathodes. The circular area at the center is the active area exposed to the light, which is ~2.5 cm².
**Figure S3.** SEM image showing the morphology of the 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$_x$S$_y$. Working electrode: p-Si-MW array electrode; counter electrode: Pt wire; reference electrode: Hg/HgSO$_4$ (sat. K$_2$SO$_4$). The deposition was performed at a scan rate of 50 mV s$^{-1}$ under illumination of a tungsten lamp (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$_x$S$_y$-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@MoOₓSᵧ-100 sample (i.e., subjected to 100 CV deposition cycles) showing the cracks across the electrodeposited thick MoOₓSᵧ 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@MoOₓSᵧ-100.
Figure S8. (a) HAADF-STEM micrograph of the electrodeposited MoO$_x$S$_y$ nanoparticle decorated Si-MWs (Si-MWs@MoO$_x$S$_y$-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$_S$$_Y$ samples. The fits in Mo 3d (S 2s) region are shown for (a) Si-MWs@MoO$_S$$_Y$-10, (b) Si-MWs@MoO$_S$$_Y$-30 and (c) Si-MWs@MoO$_S$$_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 MoOₙSₚ samples that were intentionally oxidized in air for one month. The Mo 3d₅/₂ 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$_x$S$_y$ sample. (c) Schematic representation of chemical structures that may be present in MoO$_x$S$_y$ oligomers.
Figure S12. A representative polarization curve of the Ni foam supported MoO$_x$S$_y$ catalysts (Ni@MoO$_x$S$_y$). For comparison, the polarization curve of a bare Ni foam is also presented. The measurements were performed in N$_2$-bubbled 0.5 M K$_2$SO$_4$ solution (pH = 1) at a scan rate of 10 mV s$^{-1}$. 
Figure S13. $J$-$U$ profiles of the Si-MWs@MoO$_x$S$_y$ photocathodes with different MoO$_x$S$_y$ 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$_x$S$_y$-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. XPS analysis of elemental and chemical composition of Si-MWs@MoO$_x$S$_y$ samples.

<table>
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<th>Element Component</th>
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<td>B</td>
<td>8.8</td>
<td>10.7</td>
<td>9.1</td>
</tr>
<tr>
<td>C</td>
<td>4.0</td>
<td>4.8</td>
<td>5.1</td>
</tr>
<tr>
<td>D</td>
<td>4.6</td>
<td>3.2</td>
<td>5.4</td>
</tr>
<tr>
<td>O</td>
<td>50.9</td>
<td>56.3</td>
<td>51.6</td>
</tr>
<tr>
<td>Mo–O</td>
<td>38.1</td>
<td>40.5</td>
<td>38.8</td>
</tr>
<tr>
<td>high BE</td>
<td>12.8</td>
<td>15.8</td>
<td>12.8</td>
</tr>
<tr>
<td>S</td>
<td>1.6</td>
<td>3.0</td>
<td>3.8</td>
</tr>
<tr>
<td>C</td>
<td>13.5</td>
<td>12.0</td>
<td>19.2</td>
</tr>
<tr>
<td>C–C</td>
<td>9.3</td>
<td>6.9</td>
<td>12.0</td>
</tr>
<tr>
<td>high BE</td>
<td>4.2</td>
<td>5.1</td>
<td>7.2</td>
</tr>
<tr>
<td>Si$^a$</td>
<td>12.1</td>
<td>2.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Na$^b$</td>
<td>2.0</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>N$^c$</td>
<td></td>
<td>≤ 4</td>
<td></td>
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</table>

$^a$ Si signal includes both metallic Si and SiO$_x$ for the Si-MWs@MoO$_x$S$_y$-10 and Si-MWs@MoO$_x$S$_y$-30, and only SiO$_x$ for Si-MWs@MoO$_x$S$_y$-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) – Mo$^{4+}$; Mo (B) – Mo$^{5+}$; Mo (C) – new chemical state (Mo$^{5.5+}$); Mo (d) – Mo$^{6+}$
**Table S2.** Peak parameters from fits to XPS data in Figure 4

<table>
<thead>
<tr>
<th>Region</th>
<th>O 1s</th>
<th>Mo 3p&lt;sub&gt;3/2&lt;/sub&gt;</th>
<th>C 1s</th>
<th>Mo 3d&lt;sub&gt;5/2&lt;/sub&gt;</th>
<th>S 2s</th>
<th>S 2p&lt;sub&gt;3/2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Component</strong></td>
<td>Mo–O</td>
<td>C–C</td>
<td>D</td>
<td>C</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>BE,&lt;sup&gt;a&lt;/sup&gt; (eV)</td>
<td>530.9</td>
<td>397.0±0.2</td>
<td>284.9</td>
<td>232.5</td>
<td>231.7</td>
<td>230.7</td>
</tr>
<tr>
<td>FWHM,&lt;sup&gt;a&lt;/sup&gt; (eV)</td>
<td>1.5</td>
<td>4.3±0.5</td>
<td>1.5</td>
<td>1.2</td>
<td>1.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

<sup>a</sup> Peak parameters for consistent fits to all Si-MWs@MoO<sub>x</sub>S<sub>y</sub> 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<sub>5/2</sub> region: A – Mo<sup>4+</sup>
- B – Mo<sup>5+</sup>
- C – new chemical state (Mo<sup>5.5+</sup>)
- D – Mo<sup>6+</sup>
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$^2$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_e$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$C_1$ (µF)</th>
<th>$R_2$ (Ω)</th>
<th>$C_2$ (µF)</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-MWs</td>
<td>2.15</td>
<td>40.48</td>
<td>90.03</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Si-MWs@Pt NPs</td>
<td>2.37</td>
<td>1.05</td>
<td>108.60</td>
<td>0.78</td>
<td>131.50</td>
<td>1.00</td>
</tr>
<tr>
<td>Si-MWs@MoO$_x$S$_y$-10</td>
<td>1.86</td>
<td>22.97</td>
<td>60.79</td>
<td>1.06</td>
<td>99.92</td>
<td>0.61</td>
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<tr>
<td>Si-MWs@MoO$_x$S$_y$-30</td>
<td>2.03</td>
<td>3.39</td>
<td>67.36</td>
<td>0.97</td>
<td>32.42</td>
<td>0.71</td>
</tr>
<tr>
<td>Si-MWs@MoO$_x$S$_y$-50</td>
<td>1.77</td>
<td>1.07</td>
<td>82.33</td>
<td>1.05</td>
<td>54.24</td>
<td>0.74</td>
</tr>
</tbody>
</table>
References and notes


