

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

Xiao-Qing Bao,[†] Dmitri Y. Petrovykh,[†] Pedro Alpuim,[†] Daniel G. Stroppa,[†] Noelia Guldreis,[†] Helder Fonseca,[†] Margaret Costa,[†] Joao Gaspar,[†] Chuanhong Jin,[‡] Lifeng Liu^{†,}*

[†]International Iberian Nanotechnology Laboratory (INL), Av. Mestre Jose Veiga, 4715-330 Braga, Portugal

[‡]State Key Laboratory of Silicon Materials, Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, and Department of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, P.R. China

*E-mail: lifeng.liu@inl.int (L.F. Liu)

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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 molybdenum oxysulfide (MoO_xS_y) as both a hydrogen evolution catalyst and a passivation layer. The MoO_xS_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_xS_y catalyst loadings ($\text{Si-MWs@MoO}_x\text{S}_y$) 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 $\text{Si-MWs@MoO}_x\text{S}_y$ cathodes toward water reduction is investigated and compared with that of platinum nanoparticle decorated Si-MW array electrodes (Si-MWs@PtNPs). An optimized $\text{Si-MWs@MoO}_x\text{S}_y$ 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, $\text{Si-MWs@MoO}_x\text{S}_y$ 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 demonstrated photoelectrochemical performance, the $\text{Si-MWs@MoO}_x\text{S}_y$ arrays reported here hold substantial promise for use as low-cost and efficient photocathodes for water reduction.

1. 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 ($E_g = 1.12$ 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 (V_{on}) and a limited photocurrent density ($J_{V=0}$) under short-circuit conditions [15-17, 19-21, 27]. To increase the V_{on} and $J_{V=0}$, Lewis's group and Chorkendorff's group have introduced a n^+ -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 V_{on} 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 V_{on} of 0.46 V and a $J_{V=0}$ of 9.1 mA cm⁻² [38]. Hou and co-workers first demonstrated that bioinspired cubane-like Mo₃S₄ 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 Pt catalysts.

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 Mo₃O₆⁻ clusters, compared with Mo₃S₆⁻ counterparts, can absorb water more strongly [44], thereby facilitating reduction of water. Experimentally, Sinaim *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 MoS₂ nanosheets in HER and demonstrated dramatically enhanced HER catalytic activity delivered by the oxygen-incorporated MoS₂ [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 MoO₃ 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_xS_y) catalysts toward HER, when attached onto Si-MW arrays as photocathodes for water reduction (denoted as Si-MWs@MoO_xS_y hereafter). We have comprehensively

investigated the microstructure and PEC performance of the Si-MWs@MoO_xS_y photocathodes with different MoO_xS_y loadings (i.e., MoO_xS_y layer thicknesses), and demonstrated that the photocathodes with an optimal MoO_xS_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_xS_y photocathodes appreciably outperform the Si-MWs@PtNPs electrodes in terms of both HER activity and stability.

2. Materials and methods

2.1 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 M Ω cm), and then dried in a nitrogen flow. Subsequently, a 1 μ m thick SiO₂ 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 surface of SiO₂, and a well-ordered hole array with a designed diameter of 1 μ m and a center-to-center spacing of 2 μ m was patterned by direct write laser lithography (Heidelberg DWL 2000). The pattern was then developed and transferred into the underlying SiO₂ layer by reactive ion etching (RIE, SPTS APS ICP) to form a SiO₂ mesh 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 SiO₂ 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 $^{\circ}$ 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 $2.7 \times 2.7 \text{ cm}^2$ by a dicing saw (DISCO DAD 3350). On each piece, a circular area of $\sim 2.5 \text{ cm}^2$ (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 test. 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 nitrogen flow. The Ohmic contact between the Al layer and the Si wafer was achieved by thermally annealing the wafer at 400 $^\circ\text{C}$ in high-purity nitrogen (99.999%) for 1 min.

2.2 Fabrication of Si-MWs@MoO_xS_y and Si-MWs@Pt arrays: The amorphous MoO_xS_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 Na₂MoO₄ (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 – -0.2 V vs. Hg/HgSO₄ reference electrode (MSE, saturated K₂SO₄), 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_xS_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_xS_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 ($\text{Ni@MoO}_x\text{S}_y$).

To compare the PEC performance of the $\text{Si-MWs@MoO}_x\text{S}_y$ electrodes with that of the Si-MWs@Pt 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_2PtCl_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 nitrogen 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 electrodes is shown in Figure S3 (SI).

2.3 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 keV). 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_α X-ray source. The standard analysis spot of ca. $900 \times 600 \mu\text{m}^2$ 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 $<5 \times 10^{-10}$ mbar; the charge neutralization device produced ca. 2×10^{-7} mbar partial pressure of Ar during measurements. The energy of the monochromated Al K_α X-ray source was measured to be within <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_xS_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_xS_y samples were acquired on a Bruker VERTEX 80v FT-IR spectrometer in the range 1000–370 cm^{-1} in absorbance mode. A spatula tip of the sample was mixed with 200 mg of KBr, and the powder was pressed at 10 tons for 2 min to obtain a transparent pellet. Spectra were recorded at 1.66 hPa with 32 scans and 4 cm^{-1} resolution using DTGS (Deuterated triglycine sulfate) detector. The empty holder at 1.66 hPa was used as background, and baseline correction was applied to the spectrum.

2.4 Electrocatalytic and photoelectrochemical (PEC) tests: The electrocatalytic performance of the Ni@MoO_xS_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 K₂SO₄ ($\geq 99\%$, Sigma-Aldrich) buffered at pH = 1 using sulfuric acid (95-98%, Sigma-Aldrich), which was bubbled with high-purity nitrogen 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 K₂SO₄ buffered at pH = 1, or to a 1.0 M

potassium phosphate solution buffered at pH = 7 (exposed area: 2.5 cm²). 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 nitrogen gas was flowed through the cell for 5 min. The sample temperature was maintained at 23±1 °C during the test by employing 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 estimated to be 60 mW cm⁻².

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

$$V_{\text{RHE}} = V_{\text{MSE}} + 0.654 + 0.059 \text{ pH} \quad (1)$$

3. Results and discussion

3.1 Morphology and microstructure

Figure 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_xS_y catalysts were grown on the Si-MW surface by photo-assisted CV electrodeposition in an aqueous solution of 10 mM Na_2MoO_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_xS_y (representative CV profiles are shown in **Figure S5**, SI). We note that illumination plays an important role in the deposition of MoO_xS_y on Si-MWs, because the photo-generated electrons at the Si-MW surface can facilitate the reduction of $[\text{MoO}_4]^{2-}$ 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_xS_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 $[\text{MoO}_4]^{2-}$ 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_xS_y . The overall content of sulfur (S) in our MoO_xS_y deposits, however, is low (< 5 at%) according to the energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) analyses, indicating that the incorporation of S is not a dominant process during our CV deposition process.

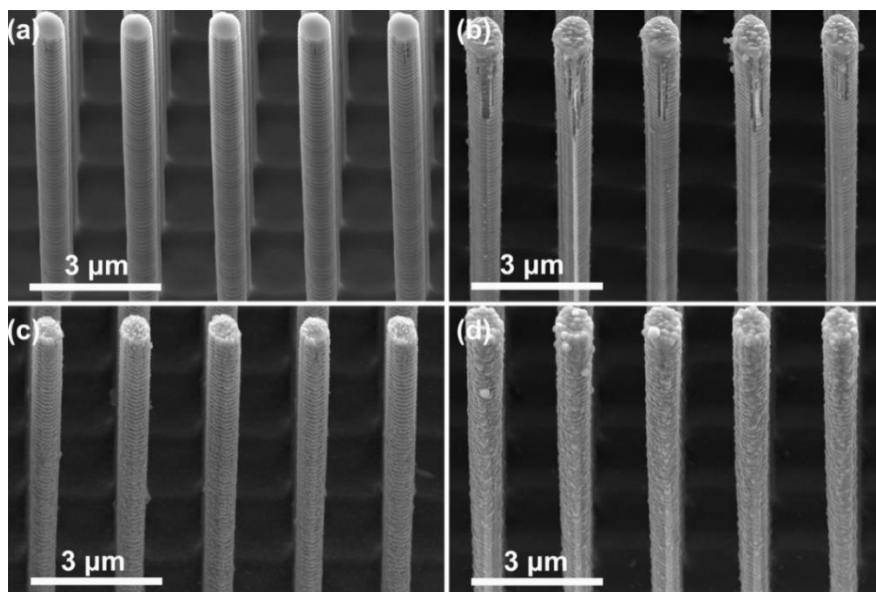


Figure 1. Representative SEM images showing the morphology of the Si-MW arrays (a) before the CV deposition of MoO_xS_y catalysts and after the deposition for (b) 10, (c) 30, and (d) 50 cycles.

The morphology of the Si-MW arrays after the CV deposition for 10, 30, and 50 cycles, respectively (hereafter denoted as $\text{Si-MWs@MoO}_x\text{S}_y\text{-10}$, $\text{Si-MWs@MoO}_x\text{S}_y\text{-30}$, and $\text{Si-MWs@MoO}_x\text{S}_y\text{-50}$), is illustrated by representative scanning electron microscopy (SEM) images in **Figure 1b – 1d**. The appearance of the $\text{Si-MWs@MoO}_x\text{S}_y\text{-10}$ 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_xS_y NPs greatly increases and these NPs tend to interconnect, forming a continuous layer (**Figure 1c**). Increasing the cycle number to 50 results in the formation of a continuous MoO_xS_y layer conformally covering the entire surface of the MWs, as can be seen in **Figure 1d**. Further increase in the deposition cycles (e.g., to 100 cycles) makes the MoO_xS_y layer thicker, but produces cracks, which likely form due to the mismatch in the thermal expansion coefficients of Si and amorphous MoO_xS_y and/or due to the strain induced in a thick MoO_xS_y layer (**Figure S7, SI**).

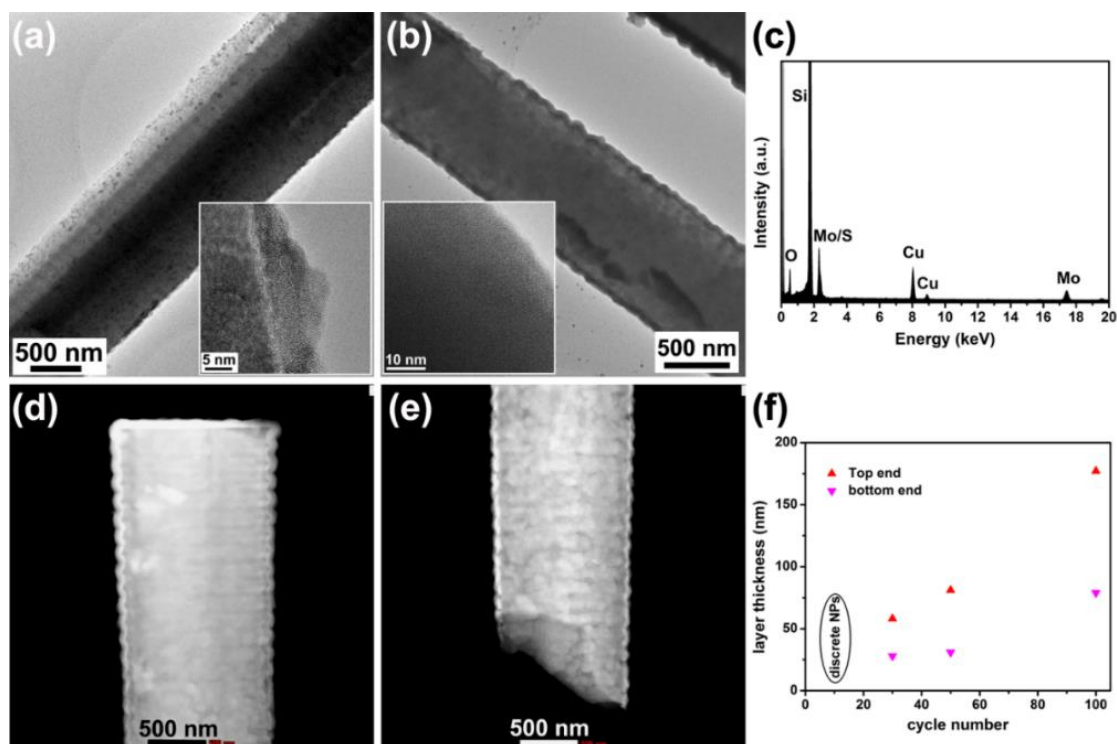


Figure 2. TEM micrographs of (a) Si-MWs@MoO_xS_y-10 and (b) Si-MWs@MoO_xS_y-50. (c) A typical EDX spectrum. (d) HAADF-STEM micrographs taken at (d) the top end and (e) the bottom end of an individual Si-MW coated with a MoO_xS_y catalyst layer (50 cycles). (f) Variation of the deposited MoO_xS_y catalyst layer thickness with the CV deposition cycle numbers.

The distribution and microstructure of the MoO_xS_y NPs and films on Si-MWs@MoO_xS_y electrodes were examined in more detail by extensive transmission electron microscopy (TEM) imaging. A typical TEM image of a Si-MWs@MoO_xS_y-10 sample reveals discrete NPs distributed on the MW surface (**Figure 2a**). High-resolution TEM (HR-TEM) analysis confirms that these NPs are amorphous and intimately adhere to the MWs (**Figure 2a**, inset). The presence of discrete MoO_xS_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_xS_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_xS_y-50 sample in **Figure 2b**, in agreement with the above SEM observation. Extensive EDX analyses reveal that the electrodeposit consists of Mo and O as the major components, as shown in **Figure 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 ($E_{\text{Mo-L}} = 2.292 \text{ eV}$, $E_{\text{S-K}} = 2.307 \text{ eV}$) so that it is not well distinguishable. Nevertheless, quantitative EDX analysis reveals that there is only ca. 5 % S in the deposits. As discussed previously, the small amount of S likely stems from the deposition of S²⁻, which was introduced into the electrolyte by the cathodic decomposition of TU [50].

Despite being continuous, MoO_xS_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_xS_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 **Figures 2d** and **2e**. 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_xS_y layer thickness, and thereby the loading of the MoO_xS_y catalyst, increases with the CV deposition cycle number (**Figure 2f**), allowing us to investigate the loading-dependent PEC performance of Si-MWs@MoO_xS_y photocathodes.

The continuous and conformal character of the MoO_xS_y layers is confirmed by the elemental distribution maps (**Figure 3**) for a representative Si@MoO_xS_y MW shown in **Figure 2d**. Both Mo and O characteristic of the MoO_xS_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 photoelectrodes. The map of S is not presented in **Figure 3** because of the

aforementioned difficulty in deconvolution of S-*K* edge from Mo-*L* edge. This continuous and conformal MoO_xS_y catalyst layer also protects the Si-MWs from photo-oxidation during HER, as will be discussed in more detail in a later section.

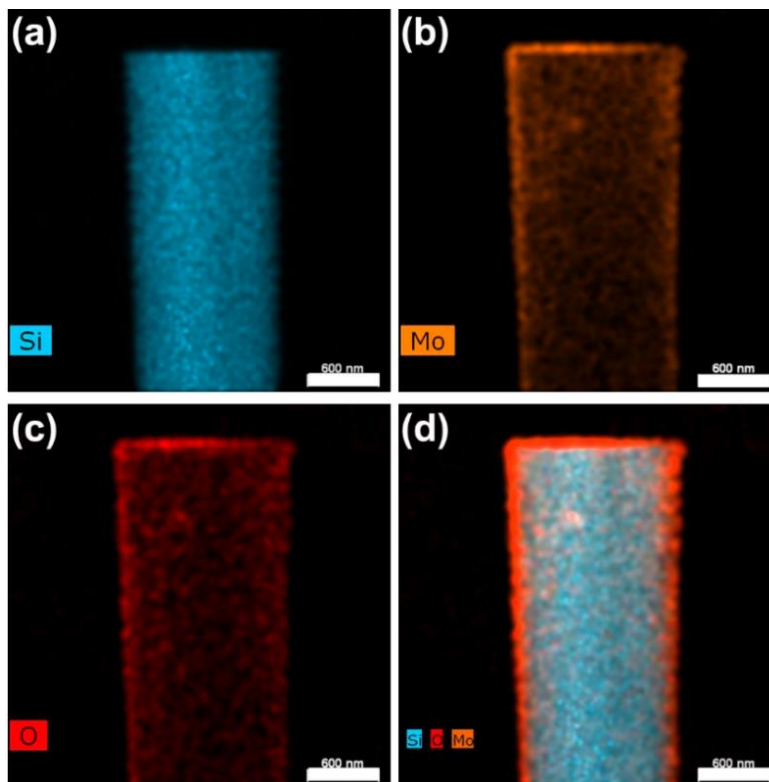


Figure 3. The elemental maps of (a) Si, (b) Mo, and (c) O. (d) The overlap map of elements.

The mapping was carried out with the sample Si-MWs@ MoO_xS_y -50 shown in Figure 2d. Scale bars: 600 nm.

3.2 Spectroscopic characterization of the deposited MoO_xS_y catalysts

To quantitatively investigate the chemical composition of the deposited MoO_xS_y layer, we analyzed these samples using XPS. **Figure 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@ MoO_xS_y -10, -30, and -50 electrodes,

respectively. The peak position and full width at half-maximum (FWHM) information is summarized in **Table S1** (SI).

The fits shown in **Figure 4** indicate the presence of four major components in Mo 3d spectra; for clarity, only the 3d_{5/2} components are shown explicitly, while contributions from 3d_{3/2} 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 3d_{5/2} 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 3d_{5/2} at 231.7 eV, red in **Figure 4** and in **Figure S10**, SI) is a surprising observation, apparently unique to our MoO_xS_y materials. Its uniqueness is highlighted by comparing to a recent study of electrochemically deposited MoS_x [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 (**Figure 4** and **Figure S10**, SI), the oxidation state corresponding to this component is speculative, but it likely corresponds to a MoO_xS_y material phase/structure with an effective oxidation state of ca. 5.5+. In all the samples, predominant Mo oxidation states are reduced relative to that of the precursor material (i.e., 6+ in Na₂MoO₄). As the band structure of MoO₃ is highly dependent on the Mo cation oxidation state [47], the prevalence of reduced Mo oxidation states (i.e., 5.5+, 5+ and 4+) indicates that the Mo d-band has been partially filled, implying enhanced electronic conductivity in the deposited MoO_xS_y [48].

In addition to the multiple Mo oxidation states, **Figure 4** also reveals that the S content in our MoO_xS_y layers is low, as evidenced by the minimal intensity of the S 2s peak relative to the Mo 3d peak. The low S content is consistent with our EDX results. 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_xS_y deposits (i.e., Si-MWs@MoO_xS_y-30 and Si-MWs@MoO_xS_y-50, see **Table S2**, 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 MoS₂) [50, 52]. Notably, no sulfur oxidation was observed in the deposited MoO_xS_y layers, as indicated by the absence of any S 2p features above 166 eV.

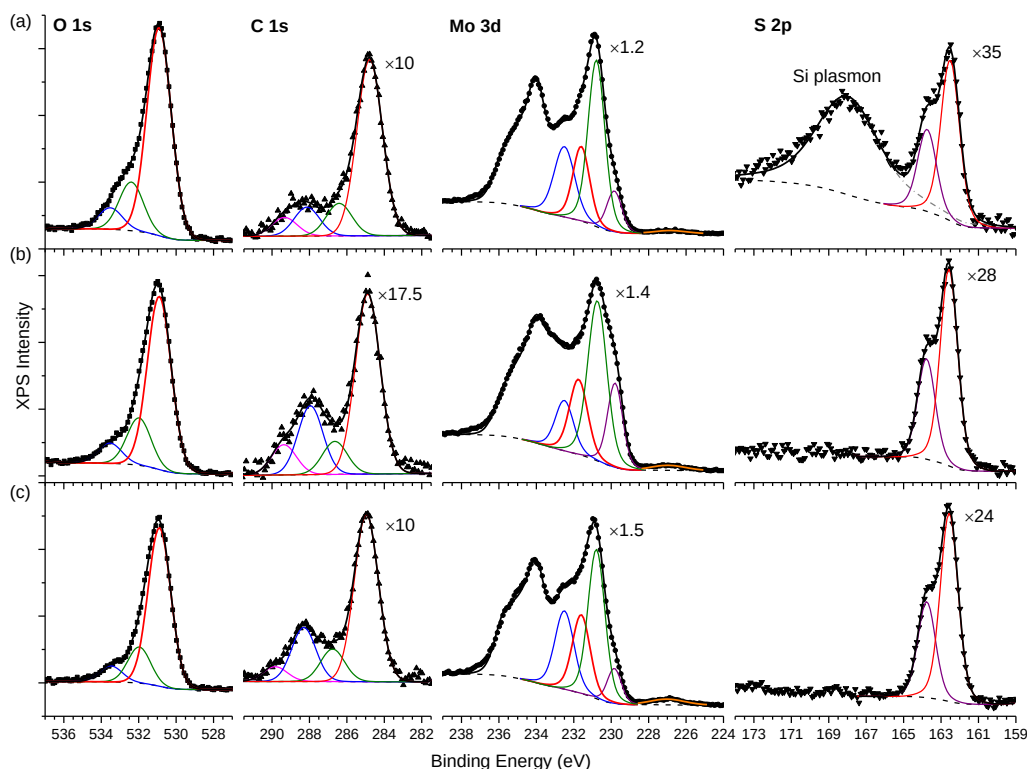


Figure 4. High-resolution XPS data for MoO_xS_y samples. The O 1s, C 1s, Mo 3d (S 2s), and S 2p regions are shown for (a) Si-MWs@MoO_xS_y-10, (b) Si-MWs@MoO_xS_y-30 and (c) Si-MWs@MoO_xS_y-50 electrodes. The intensity of the O 1s peak was the highest among all the peaks and nearly constant among the samples, making it a convenient approximate reference for comparison; signals in all the other regions have been scaled, as indicated. For clarity, in Mo 3d region, only the 3d_{5/2} components are shown; the total fit curves include both 3d_{5/2} and 3d_{3/2} components (complete fits are shown in **Figure S9**, SI). Low-intensity S 2s peaks are indicated in

Mo 3d region at ca. 227 eV. Symbols: experimental data; thick lines: total fit curves; dashed line: background; thin colored lines: fit components.

To further investigate the molecular structure of the deposited MoO_xS_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 oxysulfide [54]. This indicates that the deposited MoO_xS_y is not a simple blend of molybdenum oxides and sulfides. We presume that the MoO_xS_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.

3.3 Photoelectrochemical performance toward water reduction

Before testing the PEC performance of the Si-MWs@ MoO_xS_y photocathodes, the electrocatalytic properties of the deposited MoO_xS_y was examined by linear scan voltammetry (LSV, **Figure S12**, SI) using the Ni@ MoO_xS_y electrodes in N_2 -saturated 0.5 M K_2SO_4 solution (pH = 1). The MoO_xS_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_3/CNT composites reported recently in the literature [62, 63], illustrating that the deposited MoO_xS_y is electrocatalytically active toward HER.

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

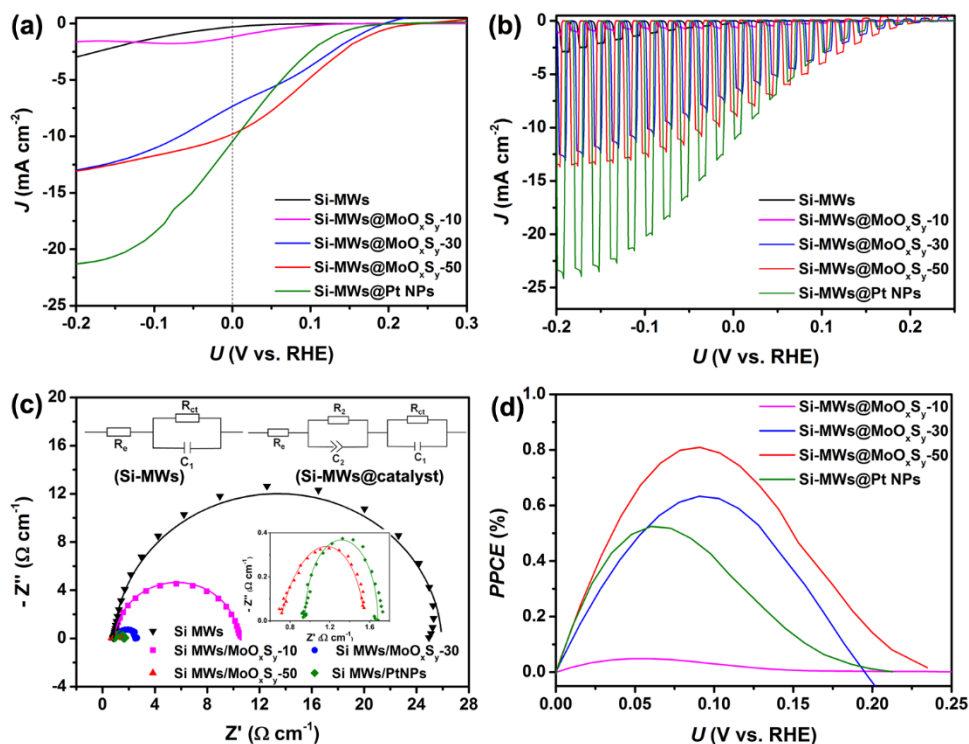


Figure 5. (a) J - U profiles of the Si-MWs@MoO_xS_y photocathodes with different MoO_xS_y catalyst loadings. For comparison, the J - U profiles of Si-MWs and Si-MWs@PtNPs are also given. Scan rates: 50 mV s⁻¹. (b) J - U profiles of the Si-MWs@MoO_xS_y photocathodes measured under chopped illumination (0.5 Hz). (c) Nyquist plots of the Si-MWs@MoO_xS_y photocathodes recorded at 0 V vs. RHE. Inset: Zoomed view for the Si-MWs@MoO_xS_y-50 and Si-MWs@PtNPs electrode (middle) and the equivalent circuit models (top). (d) Photo-conversion efficiency vs. the applied potential. All the measurements were done in 0.5 M K₂SO₄ solution buffered at pH = 1 under illumination of 100 mW cm⁻².

Figure 5a shows the current density – potential (J - U) profiles of the Si-MWs@MoO_xS_y photocathodes with different loadings of the MoO_xS_y catalysts, measured in a pH = 1 buffer

solution under constant illumination of 100 mW cm^{-2} (Tungsten light, Zahner). For comparison, the $J-U$ curves of the bare Si-MW and Si-MWs@PtNPs arrays are also presented. As seen in **Figure 5a**, the bare Si-MW array electrode reveals a negligible photocurrent of 0.31 mA cm^{-2} at 0 V vs. RHE (i.e. $J_{V=0}$), and its V_{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_xS_y , both the V_{on} and $J_{V=0}$ of the electrodes increase, indicating that the amorphous MoO_xS_y has a strong electrocatalytic effect toward HER. The V_{on} of the Si-MWs@ MoO_xS_y -10, Si-MWs@ MoO_xS_y -30, and Si-MWs@ MoO_xS_y -50 photocathodes are 0.15, 0.20, and 0.24V, respectively; while the $J_{V=0}$ of these electrodes amount to 1.28, 7.35, and 9.83 mA cm^{-2} , respectively. Compared with the Si-MWs@PtNPs electrode having a V_{on} of 0.21V and $J_{V=0}$ of 10.5 mA cm^{-2} , the Si-MWs@ MoO_xS_y -50 photocathode exhibits a slightly more positive V_{on} and a similar $J_{V=0}$.

Further increase in the MoO_xS_y layer thickness (i.e., by increasing the CV deposition cycles) results in a decrease in $J_{V=0}$, for example, the $J_{V=0}$ of the Si-MWs@ MoO_xS_y -100 is reduced to 8.60 mA cm^{-2} (**Figure S13**, SI). The reduced photocurrent may, on the one hand, result from the enhanced light absorption by the thick catalyst layer in Si-MWs@ MoO_xS_y -100 sample, similar to the case of amorphous molybdenum sulfide coated Cu_2O photocathode reported before [64]; on the other hand, the reduced photocurrent is probably associated with the increased electron-transport resistance in the thick amorphous layer and/or the loose electrical contact between the thick MoO_xS_y layer and Si-MWs due to the induced stress, as evidenced by the cracks observed in the Si-MWs@ MoO_xS_y -100 electrode (**Figure S7**, SI).

Figure 5b shows the $J-U$ curves of the Si-MWs@ MoO_xS_y photocathodes measured under chopped illumination at a frequency of 0.5 Hz: the Si-MW, Si-MWs@ MoO_xS_y , and Si-MWs@PtNPs electrodes all show well-defined photo-response. Moreover, no sharp current spikes

are observed upon the illumination, indicating that the MoO_xS_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 molybdenum sulfide catalysts, electrocatalysis of the HER based on molybdenum oxides and MoO_xS_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, ΔG_{H} , is a primary descriptor of the HER activity [66, 67]. The closer the ΔG_{H} to $\Delta G_{\text{H}} \approx 0$, 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 ΔG_{H} for the amorphous MoO_xS_y would not significantly deviate from $\Delta G_{\text{H}} \approx 0$, given the high electrocatalytic and photoelectrocatalytic activities delivered by the $\text{Ni@MoO}_x\text{S}_y$ and $\text{Si-MWs@MoO}_x\text{S}_y$ electrodes, respectively. Moreover, we presume 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]. Furthermore, we believe that the amorphous nature of the MoO_xS_y layer may allow more active sites to be exposed to the electrolyte, in analogy with previous reports for the amorphous MoS_x catalysts [41]. Besides, our XPS analysis reveals predominantly reduced Mo oxidation states in the MoO_xS_y catalyst layer, indicating that the Mo 3d band is partially filled and that the electronic conductivity could be improved [47, 48]. Indeed, the conductive nature of the deposited MoO_xS_y layers was confirmed by the small equivalent series resistance of the $\text{Si-MWs@MoO}_x\text{S}_y$ electrodes measured by EIS (e.g., only $0.71 \, \Omega \, \text{cm}^{-2}$ for $\text{Si-MWs@MoO}_x\text{S}_y\text{-50}$), which will be shown below.

Figure 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_e represents the overall resistance arising from the electrode materials, electrical contacts, and the electrolyte, the R_{ct} -C₁ 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 -C₂ simulates the charge transfer at the Si/catalyst interface and transport in the catalyst layer. As can be seen from **Figure 5c** and the fitting results shown in **Table S3** (SI), the R_e for all the electrodes is very similar, approximately $0.8 \Omega \text{ cm}^{-2}$, indicating that the deposition of the MoO_xS_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_xS_y or Pt catalysts, with a fit charge transfer resistance R_{ct} of $16.19 \Omega \text{ cm}^{-2}$, indicating unfavorable charge transfer kinetics. In contrast, the R_{ct} of the Si-MWs@ MoO_xS_y photocathodes is significantly smaller and decreases with the increasing MoO_xS_y layer thickness, following the order: Si-MWs@ MoO_xS_y -10 > Si-MWs@ MoO_xS_y -30 > Si-MWs@ MoO_xS_y -50. Notably, the R_{ct} of the Si-MWs@ MoO_xS_y -50 electrode is found to be as small as that of the Si-MWs@Pt, at only around $0.42 \Omega \text{ cm}^{-2}$. This trend suggests that the deposited MoO_xS_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_xS_y array photocathodes is also evaluated by the **photopower conversion efficiency (PPCE)** of the cells (η) defined by the following equation [5]:

$$\eta = \frac{U_{app} - U(H^+/H_2)}{I_0} \times 100\% \quad (2)$$

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. It is found that the Si-MWs@MoO_xS_y-50 exhibits a maximum η 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_xS_y-30 and Si-MWs@PtNPs, respectively, and much higher than the 0.05% delivered by the Si-MWs MoO_xS_y-10 electrode. The η of the Si-MWs@MoO_xS_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.

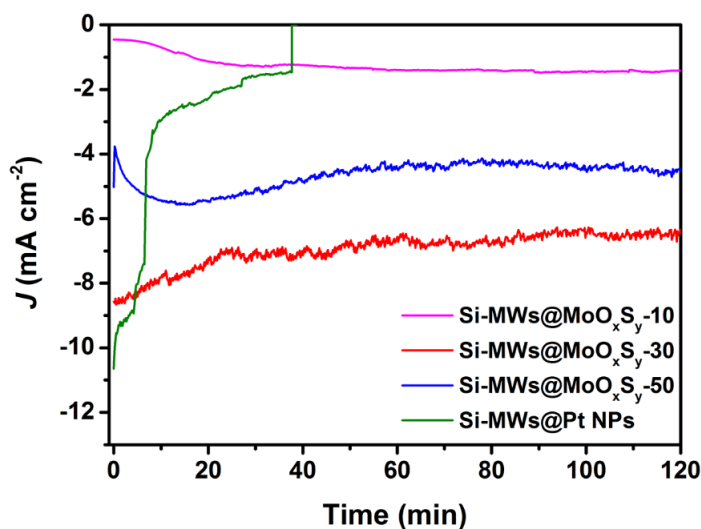


Figure 6. Stability test of the Si-MWs@MoO_xS_y photocathodes at 0 V vs. RHE under constant illumination of 100 mW cm⁻² in 0.5 M K₂SO₄ solution (pH = 1).

The stability of the Si-MWs@MoO_xS_y photocathodes was tested at 0 V vs. RHE under constant illumination in a pH = 1 buffer solution. **Figure 6** shows the chronoamperometric (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_xS_y-50 photocathode first goes down and then gets stabilized after a 30-min test at ~ 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_xS_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_xS_y catalyst layer not only offers high catalytic activity toward HER, but also effectively protects the Si-MWs from oxidation.

Although MoO₃ was previously reported to be soluble in strong acids [42], the oxygen-rich MoO_xS_y we deposited was found to be acid-stable. The underlying reason for this acid-stability remains unclear. Presumably, the cyclic or linear oligomers of MoO_xS_y are intertwined together by sulfur bridging (i.e., Mo-S-Mo, evidenced in **Figure S11a**) during repetitive cathodic and anodic sweeping upon the CV electrodeposition. The presence of Mo-S bonds that inter-link the MoO_xS_y oligomers would help to stabilize the material in acid medium. Further mechanistic discussion about the stability of MoO_xS_y is out of scope of the present work.

Similar to Si-MWs@MoO_xS_y-50, the Si-MWs@MoO_xS_y-10 and Si-MWs@MoO_xS_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_xS_y catalysts.

The PEC performance of Si-MWs@MoO_xS_y photocathodes was also tested in a neutral phosphate buffer solution (pH = 7.0). The *J-U* plots in **Figure 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_xS_y-50 (i.e., 2.25 mA cm⁻²), but is higher than that of Si-MWs@MoO_xS_y-30 (i.e., 0.85 mA cm⁻²). The photo-stability of the benchmark Si-MWs@PtNPs cathode has been dramatically improved to ca. 2 h in the neutral electrolyte (**Figure 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_xS_y-50 electrode only decreases in the beginning of the *J-t*

test and then gets stabilized at $\sim 0.75 \text{ mA cm}^{-2}$ for up to 5 h. Notably, the photocurrent generated by the Si-MWs@MoO_xS_y-30 electrode gradually increases over time within 5 h, rather than just initially, as observed at pH = 1 in **Figure 6**.

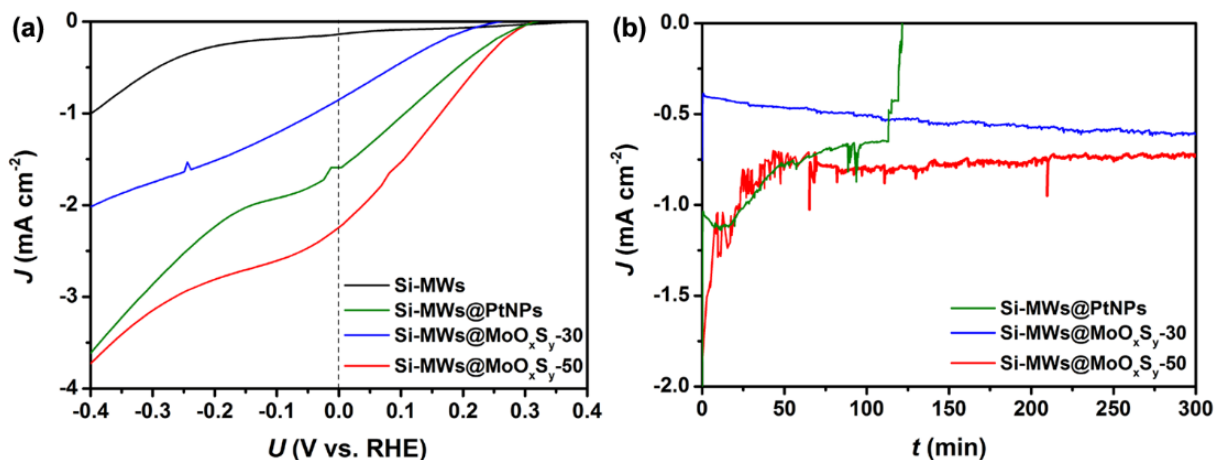


Figure 7. PEC performance of the Si-MWs@MoO_xS_y photocathodes measured in a neutral phosphate buffer solution (pH = 7.0) under illumination. (a) J - U profiles. Scan rate: 50 mV s^{-1} . (b) J - t profiles recorded at 0 V vs. RHE.

Overall, the photocurrent density of the Si-MWs@MoO_xS_y electrodes measured in the neutral solution was found to be smaller than that measured in the acidic solution (**Figure 5**). On the one hand, this likely arises from the drastically reduced proton concentration in the neutral electrolyte; on the other hand, the decrease in photocurrent density is associated with 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.

4. Conclusions

In summary, p-Si microwire array photocathodes coupled with electrodeposited amorphous MoO_xS_y catalysts have been fabricated. The morphology, structure and photoelectrochemical

performance toward water reduction of the as-obtained Si-MWs@MoO_xS_y electrodes with varying MoO_xS_y loadings have been comprehensively investigated. The Si-MWs@MoO_xS_y photocathodes with an optimal MoO_xS_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 an acidic electrolyte. In neutral electrolyte, the optimized Si-MWs@MoO_xS_y electrode outperforms the Si-MWs@PtNPs electrode in terms of both activity and stability. **The excellent catalytic performance of MoO_xS_y may arise from low free energy of hydrogen adsorption on the catalyst, the amorphous nature of MoO_xS_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_xS_y layers. Given the well-established fabrication procedure for Si microwires and the easy deposition of MoO_xS_y catalytic layers through photo-assisted cyclic voltammetry, the Si-MWs@MoO_xS_y electrodes reported here hold substantial promise for use in low-cost and durable photoelectrochemical water splitting cells.

Supporting Information. XPS analysis, Raman and FTIR spectra, Si-MW array fabrication scheme, additional TEM images and STEM elemental maps, EDX spectra, photoelectrochemical characterization, and spectra of the light source. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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