Improving the Stability of Silicon Nanowires During Photoelectrochemical Hydrogen Generation with Zinc 1T-Phase Molybdenum Disulfide

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Semiconductor photoelectrodes directly convert sunlight into stored chemical energy. In photoelectrochemical (PEC) devices, this photoconversion process relies on the junction between the semiconductor and catalyst to drive charge separation and generate electron/hole charge carriers. The growth of native oxides (SiO\textsubscript{x}) on the surface of semiconductors during device operation induces charge carrier recombination and photodegradation, which limit the operation lifetime of PEC devices. Likewise, the commercialization of photoelectrochemical devices is hindered by the use of expensive, rare precious metal catalysts such as platinum to enhance hydrogen evolution kinetics. This work demonstrates how drop casting zinc 1T-phase molybdenum disulfide (Zn 1T-MoS\textsubscript{2}) onto silicon nanowires (SiNWs) generates an interface that overcomes these challenges. This Zn 1T-MoS\textsubscript{2}/SiNWs junction drives hydrogen evolution under acidic conditions (0.5 M H\textsubscript{2}SO\textsubscript{4}) comparably to platinum-modified SiNWs (Pt/SiNWs) with a positive overpotential of 164 mV at 10 mA cm\textsuperscript{-2} and low Tafel slope of 42 mV dec\textsuperscript{-1}. Compared to the bare SiNWs, the Zn 1T-MoS\textsubscript{2}/SiNWs junction retains roughly 66% more photocurrent density and reduces SiO\textsubscript{x} growth by 16% after 24 h of continuous electrolysis. By developing a deep understanding of the catalyst-semiconductor interface, photoelectrochemical devices may be effectively designed to maintain their stability over a lifetime of operation.

1. Introduction

As unprecedented worldwide economic growth induces an upsurge in global energy demand, the need for an efficient, renewable replacement for fossil fuel-driven energy generation has never been more prevalent. Hydrogen (H\textsubscript{2}) is recognized as an essential global energy carrier because it features the highest energy content per weight and can provide energy in a form that is easily stored and consumed upon demand.[1,2] Likewise, the magnitude of available solar power striking the Earth’s surface is equivalent to 130 million 500 MW power plants, making solar energy a promising alternative to coal-driven energy sources.[3] Hence, commercially employing a photoelectrochemical (PEC) platform that harvests sunlight to convert water into clean fuels such as H\textsubscript{2} is a longstanding objective of research efforts in renewable energy generation.

In the PEC H\textsubscript{2} generation process, solar irradiation strikes the surface of a semiconductor and generates electron/hole charge carriers. The holes remain in the semiconductor’s valence band, while the free electrons are excited to the semiconductor’s conduction band. In the conduction band, the electrons transfer to the semiconductor’s surface, reduce adsorbed hydrogen ions (H\textsuperscript{+}) and generate H\textsubscript{2} (Scheme S1, Supporting Information).[4,5]

Although semiconductors collect solar energy proficiently, they lack efficiency in selectively catalyzing HER.[6] As a consequence, semiconductors usually need to be coupled with an H\textsubscript{2} evolution catalyst to facilitate HER kinetics and interfacial charge transfer processes. To date, the most common H\textsubscript{2} evolution catalysts are noble metals, specifically platinum (Pt), due to its thermoneutral Gibbs energy of hydrogen adsorption (\(\Delta G^\ddagger_\text{H} = 0\) eV).[7–10] For a heterogeneous catalyst, this implies that binding and releasing adsorbed H\textsuperscript{+} on the catalyst’s surface are both equally facile, which is a requirement for fast electron transport and H\textsubscript{2} generation.[11] Pt and other noble metals, however, are expensive and rare. To reduce device costs without sacrificing performance,
MoS\textsubscript{2} is a 2D layered nanomaterial composed of an atomic layer of molybdenum (Mo) atoms sandwiched between two atomic layers of sulfur (S) atoms via strong interplanar covalent bonding.\cite{13} Stacked layers of MoS\textsubscript{2} are held together by weak out-of-plane van der Waals forces.\cite{14} In nature, MoS\textsubscript{2} primarily exists in its semiconducting 2H phase (2H-MoS\textsubscript{2}). 2H-MoS\textsubscript{2} has trigonal prismatic crystal symmetry, hexagonal layer symmetry, and is stable and semiconducting due to the paired electrons inhabiting the 4d valence orbitals of the Mo\textsuperscript{4+} atoms.\cite{13,15} Primitive unit cells of 2H-MoS\textsubscript{2} exhibit two layers of MoS\textsubscript{2} stacked atop each other. Therefore, available HER active sites that facilitate \( \text{H}_2 \) evolution reactions (HER) in 2H-MoS\textsubscript{2} are limited to positions along the Mo and S edges.\cite{13,16} One may increase the exposure of active sites in MoS\textsubscript{2} by conversion to the metallic 1T phase (1T-MoS\textsubscript{2}). 1T-MoS\textsubscript{2} has octahedral crystal symmetry and distorted tetragonal layer symmetry.\cite{15} In 2H-MoS\textsubscript{2}, the trigonal prismatic crystal symmetry allows the positions of the top and bottom S atom planes to be aligned with one another. In 1T-MoS\textsubscript{2}, the octahedral crystal symmetry causes the bottom plane of S atoms to be rotated by 180° with respect to the upper plane.\cite{17} Therefore, whereas in 2H-MoS\textsubscript{2} the layer of S atoms sandwiching the Mo atomic layer is stacked, the top and bottom layers of S atoms are staggered in 1T-MoS\textsubscript{2}. This change in layer symmetry increases the exposure of S atoms, which in turn increases electronic conductivity and enables fast electron transport for HER.\cite{11,18} This symmetric distortion, along with the intercalation of transition metals, increases the interlayer spacing between adjacent layers of MoS\textsubscript{2} and exposes the large density of active sites on the basal plane that previously were unattainable.\cite{7,19} Furthermore, the staggered S atoms bring the Mo atoms closer to the surface of the catalyst-liquid interface, thus increasing the 2D material’s hydrophilicity by increasing the 2D material’s hydrophilicity by increasing the number of accessible hydrophilic surface sites.\cite{20} Although the metastable nature of 1T-MoS\textsubscript{2} limits catalytic performance, several publications have demonstrated how modifying MoS\textsubscript{2} with various transition metals may increase HER performance and stability.\cite{13,15,21,23} Liang et al. proposed the ability of Zn\textsuperscript{2+} ions to increase interlayer spacing and hydrophilicity in MoS\textsubscript{2} by forming strong interactions with surrounding water molecules and diffusing through the interlayer spacing as a hydrated Zn\textsuperscript{2+} complex.\cite{20} In light of this, we incorporated Zn\textsuperscript{2+} ions into 1T-MoS\textsubscript{2} to determine whether this modification enables an increase in the amount of \( \text{H}_2 \) generated by our PEC device.

Another major challenge to commercializing PEC \( \text{H}_2 \) generation is directly related to the instability of the semiconductor employed. Generally, silicon (Si) is one of the most commonly used semiconductors for PEC water splitting because its conduction band straddles the overpotential required to drive HER.\cite{5} However, the amount of \( \text{H}_2 \) produced by Si semiconductor materials tends to decline over time due to charge recombinaction and material degradation at the semiconductor-liquid junction.\cite{24,25,26} A key parameter that affects the operation lifetime of Si semiconductors is the intrinsic instability of the Si surface due to oxidation.\cite{25,26} Here, to increase the amount of surface area available for light absorption, metal-assisted chemical etching (MACE) was employed to fabricate silicon nanowires (SiNWs). Unfortunately, employing the MACE process to increase the surface area escalates the growth of native oxides (SiO\textsubscript{x}), which further prevents charge transfer across the semiconductor-liquid junction.\cite{26} Often, protection layers are deposited onto Si surfaces to limit further growth of SiO\textsubscript{x} during photoelectrosynthesis. Without a protective layer, photocorrosion will hasten the deterioration of the device’s performance and substantially limit operation lifetime.\cite{25}

In this work, thiocetamide was hydrothermally reacted with an Anderson-type polyoxometalate precursor (\((\text{NH}_4)_4[\text{ZnMo}_6\text{O}_{24}\text{H}_4] \cdot 5\text{H}_2\text{O}\)) to synthesize Zn 1T-MoS\textsubscript{2}. To expedite charge transfer kinetics and protect the electrode from photocorrosion, Zn 1T-MoS\textsubscript{2} was drop casted onto SiNWs (Zn 1T-MoS\textsubscript{2}/SiNWs) to form a catalyst-semiconductor interface. Results were compared to the HER performance of Pt-coated SiNWs (Pt/SiNWs) to evaluate whether Zn 1T-MoS\textsubscript{2} is an adequate HER catalyst replacement for Pt. The PEC performance was analyzed under acidic conditions (0.5 M H\textsubscript{2}SO\textsubscript{4}) and demonstrated a PEC performance comparable to Pt-coated SiNWs (Pt/SiNWs) under the same conditions. After 24 h of continuous electrolysis, the Zn 1T-MoS\textsubscript{2}/SiNWs retained 66% more photocurrent density than the bare SiNWs. Evidence from this work indicates that drop-casting Zn 1T-MoS\textsubscript{2} along the SiNWs surface provides a layer of protection from surface oxidation, which results with a significant improvement in the SiNWs stability. Research efforts to have demonstrated how modifying 1T-MoS\textsubscript{2} with transition metals enhances electrochemical \( \text{H}_2 \) generation.\cite{19,27,28,34} However, investigations of the PEC performance and junction formed between nanostructured Si semiconductors and 1T-MoS\textsubscript{2} catalysts modified with transition metals remain scarce. Therefore, this work seeks to not only determine the feasibility of Zn 1T-MoS\textsubscript{2} as a replacement catalyst for noble metals in PEC systems but also to understand the interfacial phenomena driving PEC performance and stability. In doing so, interfaces may be constructed to maintain their stability over a lifetime of operation. By replacing expensive precious metals with equally efficient low-cost materials, this research provides an opportunity to generate clean energy from natural resources that are abundant and decentralized.

2. Results and Discussion

2.1. Structural Analysis of Zn 1T-MoS\textsubscript{2}/SiNWs

Surface and cross-sectional scanning electron microscopy (SEM) imaging with corresponding energy-dispersive X-ray (EDX) elemental mappings of both the bare SiNWs and Zn 1T-MoS\textsubscript{2}/SiNWs indicate the following results (Figure 1). The surface and cross-sectional images of the bare SiNWs show their customary vertical alignment and uniformity in terms of density, size, and shape, with each NW between 7 and 9 \( \mu \)m in length (Figure 1a, b, and Figure S1, Supporting Information). Slight agglomeration is visible near the tips of the SiNWs, which is an inherent side effect of van der Waals forces and capillary forces induced by the wet chemical etching process.\cite{25,26} The octahedrally coordinated atoms observed by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) EDX elemental mappings of both the bare SiNWs and Zn 1T-MoS\textsubscript{2}/SiNWs.
Microscopy confirm the successful synthesis of MoS$_2$ in the 1T phase (Figure S2, Supporting Information). The surface and cross-sectional images of the Zn 1T-MoS$_2$/SiNWs show that Zn 1T-MoS$_2$ distributes uniformly across the SiNWs surface (Figures 1c, d). Further cross-sectional SEM and EDX profiling of the Zn 1T-MoS$_2$/SiNWs indicate that the majority of the deposited Zn 1T-MoS$_2$ remains near the SiNWs surface (Figure S3, Supporting Information). This may be attributed to the longitudinal direction of growth that is characteristic to 2D nanosheets. Finally, the EDX elemental maps confirm the presence and uniform distribution of the Zn atoms, along with the other elements, throughout the catalyst material (Figure 1e).

Surface analysis of the electronic effects that arise from modifying 1T-MoS$_2$ with Zn atoms was performed by characterizing both Zn 1T-MoS$_2$ and 1T-MoS$_2$ by X-ray photoelectron spectroscopy (XPS) (Figures 2, S4, and S5, Supporting Information). Experimental peak values and assignments are provided in Table S1, Supporting Information. Peak positions identified in the Zn 2p spectrum correspond to the Zn$^{2+}$ oxidation state (Figure S4, Supporting Information). Both samples show two sets of doublet peaks in the Mo 3d, S 2s (Figures 2a,c), and S 2p (Figures 2b,d) spectra.$^{[37]}$ The purple peaks displayed in the Mo 3d spectra represent Mo$^{6+}$ and confirm the presence of stoichiometric 1T-phase MoS$_2$. The presence of the minor Mo 3d peaks shown in orange indicates that an oxidized Mo$^{6+}$ species exists along the surface of both samples.$^{[37]}$ These results indicate that both 1T-MoS$_2$ and Zn 1T-MoS$_2$ are primarily composed of stoichiometric MoS$_2$ with a region of S depleted MoS$_x$ along the surface.$^{[38]}$ In both samples, associated S 2p doublets are present for both MoS$_2$ and MoS$_x$ (Figures 2b,d). While a shift is not observed for peaks present in the S 2p and O 1s spectra, the Mo 3d and S 2s peaks in Zn 1T-MoS$_2$ demonstrate an upshift of 0.1–0.3 eV compared to 1T-MoS$_2$ (Table S1, Supporting Information). Observed upshifts up to 0.1 eV fall within the step size employed during XPS data collection (step size = 0.100 eV per step) and are therefore considered negligible. However, the Mo 3d$_{3/2}$ peak assigned to MoS$_x$ in Zn 1T-MoS$_2$ is upshifted by 0.3 eV compared to the Mo 3d$_{3/2}$ peak assigned to MoS$_x$ in 1T-MoS$_2$. This shift to a higher binding energy indicates that the incorporation of Zn increases the electron density of the d orbitals represented by the 3d$_{3/2}$ peak in MoS$_x$. Fundamentally, weak interactions between atoms do not alter electron distribution sufficiently enough to change binding energy values significantly.$^{[39]}$ Thus, since binding energy shifts were not observed for stoichiometric MoS$_2$, bonding interactions between Zn and 1T-MoS$_2$ are unlikely and the structure of 1T-MoS$_2$ remains unchanged. Conversely, the binding energy shifts observed for MoS$_x$ suggests that covalent bonding interactions occur between Zn and S depleted MoS$_x$ near the catalyst surface where HER occurs.

Raman spectra were collected for 2H-MoS$_2$, 1T-MoS$_2$, and Zn 1T-MoS$_2$ to elucidate the structural changes that arise from modifying 1T-MoS$_2$ with Zn (Figure S6a, Supporting Information). Associated Raman peak assignments are provided in Table S2, Supporting Information. Peaks arising from transverse acoustic phonon modes at the M point of the first Brillouin zone (TA), longitudinal acoustic phonon modes at the X point of the first Brillouin zone (LA), and the zone-center optical phonon modes are observed for both 2H-MoS$_2$ and 1T-MoS$_2$. Upon Zn incorporation, a significant upshift in the Raman peak positions is observed, indicating a change in the interlayer spacing of the catalyst material. This upshift is consistent with the increased electron density resulting from Zn incorporation, which would result in a reduction in lattice parameters due to the decrease in electron–phonon coupling. The observed upshift in the Raman peaks further supports the notion of covalent bonding interactions between Zn and S depleted MoS$_x$ near the catalyst surface, which is consistent with the XPS results.
modes at the M point of the Brillouin zone (LA), and the $J_1$, $J_2$, and $J_3$ phonon modes are all observed for both 1T-MoS$_2$ and Zn 1T-MoS$_2$. The $J_1$, $J_2$, and $J_3$ modes occur as a result of superlattice distortion in the basal plane.\[40\] The presence of these five modes arise from symmetry-induced defects, are indicative of the formation of 1T-MoS$_2$, and are not present in 2H-MoS$_2$.\[14,41,42\] $E_{1g}$ modes present in both 1T-MoS$_2$ and Zn 1T-MoS$_2$ correspond to the in-plane relative vibration of S atoms.\[17\] 2H-MoS$_2$ exhibits peaks assigned to the in-plane $E_{12g}$, out-of-plane $A_{1g}$, and 2LA phonons, respectively, customary to what is seen in the literature.\[17,41\] $E_{12g}$ modes arise from in-plane lattice vibrations of S atoms moving in the same direction, opposite of the direction of vibration experienced by the Mo atoms they are bonded to.\[40\] The $A_{1g}$ modes indicate out-of-plane lattice vibrations of Mo-bound S atoms moving in opposite directions.\[40\] Further investigation of $E_{12g}$ and $A_{1g}$ modes provides insight into the amount of strain and layer thickness present within the MoS$_2$ samples.\[14,41,42\] The change in intensity of the $E_{12g}$ peak with respect to the $A_{1g}$ peak is associated with a decrease in layer thickness and is a typical sign of structural defects in the material’s crystal structure.\[40,44\] Furthermore, it provides additional evidence that the bulk catalyst material is dominated by the 1T-phase of MoS$_2$.\[45\] XRD peak broadening is characteristic of nanomaterials and reveals the high concentration of defects in both samples.\[46\] This result is in agreement with the presence of oxidized Mo$^{6+}$ in the XPS spectra (Figure 2). Minor peaks present at $2\theta = 28.7^\circ$ and $47.6^\circ$ in the Zn 1T-MoS$_2$ XRD spectrum are assigned to ZnS (PDF #00-001-0792). ZnS is an expected side product formed by Zn$^{2+}$ ions that react either with excess thioacetamide or the S atoms released upon S vacancy formation in the reaction chamber during hydrothermal synthesis (see Materials and Methods section for Zn 1T-MoS$_2$ synthesis). Similar results have been previously reported.\[8,28\] Both XRD and Raman spectroscopy are bulk characterization techniques, whereas XPS and SEM are surface-sensitive techniques. The minor presence of ZnS in the XRD spectrum that is absent in the XPS and Raman spectra indicates that some ZnS is likely present in the bulk region of the powder sample, but not on the surface where HER occurs. Thus, the ZnS phase is not considered to catalytically contribute to Zn 1T-MoS$_2$ or facilitate HER. In summary, structural characterizations provided by the SEM, EDX, XPS, Raman, and XRD data all prove the existence of Zn$^{2+}$ atoms in IT-MoS$_2$. 

Figure 2. X-ray photoelectron spectroscopy (XPS) of 1T-MoS$_2$ a,b) and Zn 1T-MoS$_2$ c,d). The purple and orange peaks are assigned to MoS$_2$ and an oxidized MoS$_x$ species, respectively. a,c) Mo 3d and S 2s spectra. b,d) S 2p spectra.
2.2. Photoelectrochemical HER Performance

Resulting PEC analysis of HER performance under acidic conditions of bare SiNWs, Pt/SiNWs, and Zn 1T-MoS 2/SiNWs is provided in Figure 3. To determine the best catalyst concentration for optimal PEC performance, the Zn 1T-MoS 2/SiNWs were investigated with the following concentrations: 1, 5, 10, and 15 mg mL ⁻¹. Resulting onset potentials (E° onset), overpotentials (η), saturated potentials (E° sat), and maximum photocurrent densities (J max) extracted from the linear sweep voltammograms (LSVs) shown in Figure 3a are provided in Table S3, Supporting Information. The results show that as the catalyst concentration of the Zn 1T-MoS 2/SiNWs samples increased, E° onset and E° sat both became more positive and J max decreased (see the Experimental Methods section for parameters used to define E° onset and E° sat). Of the electrodes tested, the electrode with 1 mg mL ⁻¹ catalyst concentration (Zn 1T-MoS 2(1 mg mL ⁻¹)/SiNWs) produced the most comparable E° onset (425 mV), E° sat (−302 mV), and J max (36.5 mA cm ⁻²) values to those of the Pt/SiNWs electrode (355 mV, −277 mV, and 37.2 mA cm ⁻², respectively). When high concentrations of catalytic material are employed in a PEC device, the distance between metal centers within the catalyst decreases, and the generated electron/hole pairs suffer from charge recombination, causing the decrease in PEC efficiency observed as the catalyst concentration increased. Work published by Qian et. al. demonstrated the ability to lower the Tafel slope of MoSe 2 from 92 mV dec ⁻¹ to 58 mV dec ⁻¹ by doping Zn into the MoSe 2 lattice.[49] Liu et. al. reported a 35 mV dec ⁻¹ Tafel slope for Zn-MoS 2 and concluded that HER follows the Volmer–Heyrovsky mechanism, where electrochemical desorption is the rate-limiting step, in agreement with our results.[28] Shi et. al. reported a 51 mV dec ⁻¹ Tafel slope for Zn-doped 2H-MoS 2, concluding that the rate-limiting step involves the recombination of two adsorbed H atoms and the presence of Zn makes HER more favorable.[27] Theoretical calculations predict 1T-MoS 2’s Tafel slope to be 60 mV dec ⁻¹.[50] However, this prediction is based on the assumption that the HER-facilitating active sites are restricted to the edge sites in 1T-MoS 2. Voiry et al. reported a 41–46 mV dec ⁻¹ Tafel slope before iR correction for 1T-MoS 2 nanosheets under acidic conditions.[51] In this work, the lower Tafel slope is attributed to the participating HER active sites located along the basal plane of 1T-MoS 2. To evaluate the performance of 1T-MoS 2 on SiNWs against that of Zn 1T-MoS 2, 1 mg mL ⁻¹ of 1T-MoS 2 was drop cast onto SiNWs (1T-MoS 2/SiNWs) and analyzed by LSV. Compared to the E° onset
The theoretical Tafel slope for Pt(100) is equal to 118 mV dec\(^{-1}\). In a previous HER kinetics study, the Pt/SiNWs Tafel slope reported (118 mV dec\(^{-1}\)) is much higher than Tafel slopes for Pt/C (≈30 mV dec\(^{-1}\)) most commonly reported in similar studies. \(^{[52]}\) Deviation of experimental Tafel slopes from theoretical predictions tends to occur for reasons related to the solvent environment, surface defects, finite coverage of adsorbed H atoms, potential-induced changes in the reaction mechanism, interactions between the electrode’s surface and the adsorbed species, and/or variation in experimental conditions. \(^{[52]}\) In a previous HER kinetics study using the same electrolyte (0.5 H\(_2\)SO\(_4\)), Pt(100) was confirmed to exhibit two Tafel slopes: ≈37 mV dec\(^{-1}\) at low overpotentials and ≈112 mV dec\(^{-1}\) at high overpotentials. \(^{[53]}\) Additionally, the Pt(100) surfaces were reported to follow the Volmer–Heyrovsky HER mechanism. Here, we postulate that the Pt deposited on the Pt/SiNWs may be similar to the (100) phase. Theoretical Tafel (100) slopes are known to follow the linear relationship described in Equation 1: \(^{[53]}\)

\[
b = 2 \left( \frac{2.3RT}{F} \right)
\]

where \(R\) is the gas constant, \(T\) is the temperature, and \(F\) is Faraday’s constant. By this relationship (Equation 1), the theoretical Tafel slope for Pt(100) is equal to 118 mV dec\(^{-1}\), which is in agreement with the experimental Tafel slope reported for the Pt/SiNWs.

Nyquist plots were collected to compare limitations caused by charge and mass transport experienced by the various concentrations of Zn 1T-MoS\(_2\)/SiNWs and Pt/SiNWs (Figure 3c). All results were fitted to an equivalent circuit (inset of Figure 3c). The decreasing trend in the semicircle radius is proportional to the decreasing concentration of Zn 1T-MoS\(_2\) and indicates a decrease in charge and mass transport limitations. Corresponding calculated charge-transfer resistance (\(R_\text{ct}\)) results demonstrate the same trend (Table S5, Supporting Information). The lowest \(R_\text{ct}\) is produced by the Pt/SiNWs, as expected. Of the various catalyst concentrations studied, the Zn 1T-MoS\(_2\)(1 mg mL\(^{-1}\))/SiNWs experience the least charge transport limitations and yield the most comparable results to the Pt/SiNWs, in agreement with the LSV results.

The incident photon-to-current efficiency (IPCE) of the Zn 1T-MoS\(_2\)(1 mg mL\(^{-1}\))/SiNWs electrode was measured to understand how efficiently this PEC device converts incident light into electrical energy across the near-ultraviolet (UV) to the near-infrared (IR) wavelength range (Figure 3d and Table S6, Supporting Information). Maximum IPCE values of ≈60% are achieved at the near-IR range (850–900 nm), which is comparable to the IPCE values of previously reported studies involving SiNWs. \(^{[54,55]}\) While an ideal IPCE plot will show a square curve with near 100% efficiency, most devices cannot achieve this ideal conversion performance due to carrier recombination effects. When incident photons strike a semiconductor’s surface, charge carriers are generated, which consist of majority and minority carriers. Since the SiNWs in this study are fabricated from \(p\)-type Si, the minority carriers here are electrons and the majority carriers are holes. The photo-generated minority carriers must travel a distance equivalent to the absorption depth of the incident photons to reach the conduction band and react with available H\(^+\) ions to generate H\(_2\). If the minority carrier diffusion length and bandgap between the valence and conduction bands are shorter than the incident photon’s absorption depth, the photoexcited charge carriers will recombine and the IPCE will decrease. \(^{[56]}\) Thus, the decrease in efficiency shown in the lower wavelength region is an indication of charge recombination limiting device efficiency. Previously, a study by He et al. revealed the indirectly proportional relationship between SiNWs length and IPCE at lower wavelengths. \(^{[54]}\) Therein, the enhanced aggregation experienced in longer SiNWs resulted in greater charge recombination losses across lower wavelength regions. In this work, the fabricated SiNWs maintained lengths ranging from 75 to 9 \(\mu\)m (Figure S1, Supporting Information). Light traveling at shorter wavelengths cannot reach the junction and achieve charge separation if the diffuse distance is too long. When this occurs, carriers recombine instead of reacting with H\(^+\) ions. Likewise, the occurrence of bunching at the tips of the SiNWs (Figure 1b) also limits photon absorption by reducing the amount of exposed semiconductor surface area to an extent. On the other hand, the current generation with wavelengths above 1100 nm is limited by Si’s 1.12 eV bandgap. \(^{[53]}\) Overall, the PEC performance and IPCE indicate that the Zn 1T-MoS\(_2\)(1 mg mL\(^{-1}\))/SiNWs experience some charge recombination but still provide a competitive, low-cost catalyst-semiconductor interface for effective PEC H\(_2\) generation.

### 2.3. Stability Performance

To evaluate the stability performance over long-term operation, the bare SiNWs and Zn 1T-MoS\(_2\)(1 mg mL\(^{-1}\))/SiNWs were each subjected to 24 h of continuous electrolysis in acidic media (Figure 4). Resulting 24h electrolysis under both light and dark conditions demonstrates the photocatalytic activity of Zn 1T-MoS\(_2\)(1 mg mL\(^{-1}\))/SiNWs (Figure S9, Supporting Information). After 24 h electrolysis, the bare SiNWs and Zn 1T-MoS\(_2\)(1 mg mL\(^{-1}\))/SiNWs retained approximately 20% and 85% of their photocurrent densities, respectively. XPS evaluation before and after electrolysis demonstrates an 18% increase in SiO\(_2\) content for the bare SiNWs (Figures S10a,b, Supporting Information), whereas the Zn 1T-MoS\(_2\)(1 mg mL\(^{-1}\))/SiNWs exhibit a 2% increase in SiO\(_2\) growth (Figures S10c,d, Supporting Information). Although the slight loss of catalyst is experienced during electrolysis, retention of the catalyst-semiconductor interface is evidenced by the presence of Mo and S along the SiNWs surface, as determined by postelectrolysis cross-sectional SEM and EDX analysis (Figure S11, Supporting Information). Based on these results, the improvement in SiNWs operation lifetime is ascribed to the reduced growth of SiO\(_2\), witnessed when Zn 1T-MoS\(_2\) is drop casted along the SiNWs surface. Upon drop casting Zn 1T-MoS\(_2\) onto the SiNWs, the catalyst primarily deposits across the top of the SiNWs (Figure 1d, Figure S3, Supporting Information). Doing so allows the layer of Zn 1T-MoS\(_2\) to passivate dangling...
bonds along the SiNWs surface that would otherwise be oxidized into insulating SiOx when exposed to water.\[25\] As a result, Zn 1T-MoS2 slows oxidation of the SiNWs surface which in turn extends the photocathode’s operation lifetime.

The H2 evolution and Faradaic efficiency plots (Figure S12, Supporting Information) show a 2.44 µmol min\(^{-1}\) H2 generation rate with high catalytic selectivity for HER. These results suggest that this catalytic system can efficiently and selectively use the supplied electrical energy for HER. Calculations of turnover frequency (TOF) and turnover number (TON) to determine the amount of H\(_2\) able to be catalytically generated per active site per second are provided in the Supporting Information. The resulting values include a 0.53 s\(^{-1}\) TOF and 45792 TON for Zn 1T-MoS2. These values are indicative of the high catalytic activity and selectivity Zn 1T-MoS2 exhibits towards HER.

LSVs before and after 24 h electrolysis for each sample tested were collected to unveil more insight into the changes occurring to the catalyst-semiconductor interface over time (Figure S13, Supporting Information). Experimental values of \(E_{\text{onset}}\), \(E_{\text{sat}}\), and \(J_{\text{max}}\) before and after 24 h electrolysis for each electrode are provided in Table S7, Supporting Information. The bare SiNWs (Figure S13a, Supporting Information) experienced an almost complete loss in \(J_{\text{max}}\) and an increase of 223 mV versus RHE in \(E_{\text{onset}}\). \(E_{\text{sat}}\) after electrolysis was unable to be determined because the electrode’s potential would not saturate. The major decline in photocurrent density demonstrates the instability of the liquid-semiconductor interface when the bare SiNWs surface is directly exposed to the electrolyte. In contrast, the Zn 1T-MoS2/SiNWs (Figure S13b, Supporting Information) lost \(\approx20\%\) of the initial \(J_{\text{max}}\) measured, \(E_{\text{onset}}\) increased by 143 mV versus RHE, and \(E_{\text{sat}}\) negatively shifted by 89 mV versus RHE. The smaller shift in \(E_{\text{onset}}\) for the Zn 1T-MoS2(1 mg mL\(^{-1}\))/SiNWs demonstrates the ability of Zn 1T-MoS2 to protect Si nanostructures from HER performance degradation over extended operation lifetimes. Overall, these findings not only highlight how catalytically active, selective, and stable the Zn 1T-MoS2/SiNWs interface is towards HER, but also validate its potential for successful long-term PEC H\(_2\) generation.

3. Conclusion

The research presented attempts to mitigate the two major challenges experienced by PEC H\(_2\) generation devices. First, is the need to discover an Earth-abundant catalyst with a catalytic performance comparable to Pt. Second, developing a catalyst-semiconductor interface that reduces the growth of SiOx on SiNWs and improves PEC operation lifetimes. The resulting evaluation of PEC performance indicates that Zn 1T-MoS\(_2\)(1 mg mL\(^{-1}\))/SiNWs perform comparably to Pt/SiNWs in terms of onset potential and maximum photocurrent density. Furthermore, Zn 1T-MoS2(1 mg mL\(^{-1}\))/SiNWs produces a smaller Tafel slope than the Pt/SiNWs (42 mV dec\(^{-1}\) compared to 118 mV dec\(^{-1}\)). The reduction in SiOx growth when Zn 1T-MoS2 is drop casted onto SiNWs was determined to enable the SiNWs to retain 66% more photocurrent after 24 h of electrolysis. Current and future applications of semiconductor devices demand high-performance systems that prevent the accumulation of insulating oxide layers and fast charge transfer kinetics. Here, how modifying SiNWs interfaces is demonstrated with Zn 1T-MoS2 provides a potential solution to simultaneously achieve the aforementioned goals.

4. Experimental Section

**Chemicals:** Ammonium heptamolybdate tetrahydrate ([NH\(_4\)]\(_6\)Mo\(_7\)O\(_24\)·4H\(_2\)O, 99%, Alfa Aesar) and thioacetamide (C\(_2\)H\(_5\)NS, 99%, Acros Organics) were used without further purification.

**1T-MoS\(_2\) Synthesis:** 1T-MoS\(_2\) nanosheets were synthesized hydrothermally according to the following procedure. First, 50 mg of (NH\(_4\))\(_6\)Mo\(_7\)O\(_24\)·4H\(_2\)O (Mo\(_7\)) and 80 mg of C\(_2\)H\(_5\)NS were added together in a 25 mL autoclave, diluted with 10 mL of deionized water, and sonicated for 30 min. The mixture was then heated at 180 °C for 3 d to enable the SiNWs to retain 66% more photocurrent after 24 h of electrolysis. Current and future applications of semiconductor devices demand high-performance systems that prevent the accumulation of insulating oxide layers and fast charge transfer kinetics. Here, how modifying SiNWs interfaces is demonstrated with Zn 1T-MoS2 provides a potential solution to simultaneously achieve the aforementioned goals.

**ZnMo\(_6\) precursor:** ZnMo\(_6\) precursor was prepared in accordance with previous publications.\[29\,58\] In brief, 6180 mg Zn(NO\(_3\))\(_2\)·6H\(_2\)O (Zn(NO\(_3\))\(_2\)) was prepared in accordance with previous publications.\[29\,38\] In detail, 6180 mg Zn(NO\(_3\))\(_2\)·6H\(_2\)O (Zn(NO\(_3\))\(_2\)) was dissolved into 80 mL of DI water under bath sonication, then heated to 100 °C. 1487 mg Zn(NO\(_3\))\(_2\)·6H\(_2\)O (Zn(NO\(_3\))\(_2\)) was dissolved into 20 mL of DI water by bath sonication, then added to the Mo\(_7\) solution under vigorous magnetic stirring. Heating and stirring of the mixture were maintained for 2 h until the crude product was obtained. After, the crude product was isolated by filtration and purified by recrystallizing twice in hot water maintained at 80 °C. The final product was dried in a vacuum oven at 50 °C for 24 h to obtain the desired ZnMo\(_6\) precursor, which was stored under ambient conditions.
Zn 1T-MoS₂ Synthesis: Zn 1T-MoS₂ nanosheets were synthesized hydrothermally according to the following procedure. First, 50 mg of Zn(NO₃)₂ and 80 mg of C₆H₇NS were added together in a 25 mL autoclave, diluted with 10 mL of deionized water, and sonicated until fully dissolved. Afterward, the autoclaves were sealed within a hydrothermal reactor and heated at 180 °C for 24 h. Once heating ceased and reactors cooled down to room temperature, the catalyst solution was transferred to 14 mL vials, washed, and centrifuged six times: twice with deionized water, twice with 200 proof ethanol alcohol, and twice with acetone. The supernatant layer was removed from the vials after each centrifugation step. Upon completion of washing, the catalyst material was dried at ~100 °C for 24 h, finely ground into a powder, and stored under ambient conditions. A dopant concentration of 6.24% Zn in Zn 1T-MoS₂ was confirmed by inductively coupled plasma optical emission spectrometry.

Silicon Nanowires Fabrication: 525 µm of (100)-oriented p-type boron-doped Si wafers with resistivity $\approx 3-5$ Ω cm (WaferPro LLC) were used. Prior to fabrication, each Si wafer was cut into quarters using a scorer for facile handling during SiNWs synthesis, followed by covering their backside with Kapton tape for protection. To clean the Si wafers, they were sonicated first in acetone for 5 min, then in DI water for 5 min. The SiNWs were prepared at room temperature, without stirring, using a modified adaption of a previously published MACE procedure.[59] Between each step during the MACE process, exposure to air was minimized as much as possible. Likewise, the wafers were laid flat in each solution to ensure the vertical growth of SiNWs. First, the Si wafer was immersed in 5 wt% HF for 90 s to remove native Si oxides, followed by a quick dip in DI water. Next, the wafer was immersed in 0.02 M AgNO₃/10 wt% HF solution for 60 s to grow metallic silver (Ag) nanoparticles onto the Si surface via electroless Ag deposition, followed by a quick dip in DI water. After, the wafer was transferred to a burial solution [10 wt% (5 M) HF to 30 wt% H₂O₂ to produce a volumetric ratio of 10:1] for 10 min, allowing the Ag nanoparticles to bury into the Si wafer and create the nanowires, followed by a quick dip in DI water. The wafer was then moved to a 35 wt% HNO₃ solution for 15 min to remove the Ag nanoparticles, followed by a quick dip in DI water. The resulting SiNWs were carefully dried with a Kimwipe and allowed to dry under air.

Photoelectrode Fabrication: After removing the Kapton tape from the SiNWs, the fabricated SiNWs were cut into appropriately sized pieces (0.1–0.3 cm²). The backside of the SiNWs was washed with DI water and etched in 5 wt% HF for 30 s to remove surface oxides. Next, a thin layer of commercial Ga-In eutectic alloy was applied to the backside to create an ohmic contact. Then, the sample’s backside was carefully pressed onto a spiral copper (Cu) wire coated with conductive Ag paint. Contact with the sample’s surface was minimized as much as possible to avoid damaging the nanowires. Afterward, the Cu wire’s tail was passed through a glass tube to provide a mechanically stable body, leaving the spiral Cu wire holding the sample head assembly outside of the glass tube. The resulting electrode assembly was electrically insulated by covering any exposed Cu wire/Ag paint and the junction between the electrode’s head and glass tube with Loctite E-120 HP epoxy adhesive. The second layer of epoxy was added after drying for 24 h. After the addition of the second layer of epoxy and prior to employment in any electrochemical experiments, the electrodes were dried for another 48 h under ambient conditions. Resulting electrodes all had exposed volumetric areas between 0.1 and 0.3 cm². Surface areas were measured using Image J software (https://imagej.nih.gov/ij/).

Pt Nanoparticle deposition: Electrodes were first etched in 5 wt% HF for 30 s, rinsed with DI water, and dried with N₂. Electrodes were then immersed in 5 mM K₂PtCl₆/1 wt% HF solution for 30 s, washed with DI water, then dried with N₂.

1T-MoS₂ and Zn 1T-MoS₂ Deposition: Electrodes were first etched in 5 wt% HF for 30 s, rinsed with DI water, and dried with N₂. One drop of Zn 1T-MoS₂ was then drop cast onto the electrode’s surface using a 200 µL pipette and laid flat to dry for 5 min. This process was repeated twice for all electrodes employed herein unless otherwise stated. All electrochemical measurements were conducted immediately after the catalyst was deposited onto the electrodes.

Structural Characterization: SEM images and energy-dispersive X-ray (EDX) analyses were collected using the FEI Quanta 450 FEG SEM at 20 eV. The same EDX operating conditions with the best achievable spatial and energy resolution were employed to acquire all elemental mappings reported. High-angle angular dark-field scanning transmission electron microscopy (HAADF-STEM) images were acquired by a convergence semilune of 22 mrad and inner and outer collection angles of 83 and 165 mrad, respectively. XPS spectra were collected using the Kratos AXIS Supra equipped with a monochromatic Al Kα X-ray source, ran at 300 W, and operated at 15 kV. All XPS samples were measured within a 300 × 700 µm² spot size and operated at <10⁻¹⁰ torr chamber pressure. The C 1s peak for aliphatic hydrocarbons at a binding energy of 284.8 eV was used as an internal binding energy reference. XPS spectra were fitted with XPSPEAK 4.1 software and the baseline was fitted to a Shirley background. 80% Lorentzian–Gaussian parameters were employed for all peak analyses and χ² was maintained below 5.0 for all spectra analyzed.[60] Raman spectra were recorded using a Thermo Scientific DXR Raman microscope, employing an Ar-ion laser operating at 532 nm. Fourier transform infrared (FTIR) spectra were measured using a PERKIN ELMER FTIR spectrometer. Powder XRD characterizations were performed on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å).

Photoelectrochemical Measurements: All PEC measurements were conducted in 0.5 M H₂SO₄ electrolytic solution using a standard three-electrode configuration. A CHI 660E Electrochemical Workstation was used to perform all electrochemical testing, a visible light shortpass filter (FESH0750, Thor labs), and a steady DC-powered 150 W Xe arc lamp (Newport) light source calibrated to 100 mW cm⁻² using a Si photodiode provided one sun’s illumination for accurate analysis. Comparative AM 1.5 and Xe Arc lamp power profiles are provided in our previously reported work.[61] Pt wire and Ag/AgCl (3 M NaCl, BASI) were employed as the counter and reference electrodes, respectively. Preparation of working electrodes employed the drop-casting method to load catalyst material onto the semiconductor substrate (the SiNWs). Catalyst concentrations were prepared by diluting Zn 1T-MoS₂ with the volume of acetone appropriate for each desired concentration. All potentials reported were calibrated with respect to the Ag/AgCl reference electrode in acidic media (pH = 0) using Equation (2):

$$E \text{(RHE)} = E \text{(Ag/AgCl)} + 0.241 + 0.059pH$$

(2)

LSVs were conducted under ambient conditions from 0.4 to −1.4 V under the following parameters: scan rate = 0.1 V s⁻¹, sample interval = 0.001 V, and sensitivity = 0.001 A V⁻¹. Electrochemical impedance measurements for the reported Nyquist plots were performed at −0.05 V, with 0.005 V variation in the frequency range of 1–10² Hz and 12 steps per decade. Onset potentials were extracted from the LSV tests, defined as the potential at which the photocurrent began to increase (0.05 mA cm⁻²). The saturation potential was defined as the potential at which the photocurrent value was saturated and ceased increasing.

Stability Testing: The stability tests were conducted in 0.5 M H₂SO₄ electrolytic solution using a split electrochemical cell with three-electrode configuration. Ag/AgCl was used as the reference electrode. To avoid the risk of Pt leaching during electrolysis, the half cells were separated by a Nafion 211 (purchased from Fuel Cell Store) semi-permeable membrane and a graphite rod was employed as the counter electrode. Stability tests were conducted at each photocathode’s saturated potential (bare SiNWs = −0.8 V; Zn 1T-MoS₂ (1 mg mL⁻¹)/SiNWs = −0.6 V) using the amperometric technique and 0.001 A V⁻¹ sensitivity.

Incident Photon-to-Current Efficiency (IPCE) Measurements: All IPCE measurements were performed in a 0.5 M H₂SO₄ electrolytic solution using a standard three-electrode configuration. The chronoamperometric i-t technique using a CHI 660E Electrochemical Workstation and steady DC-powered 150 W Xe arc lamp (New Port) light source calibrated to 100 mW cm⁻² using a Si photodiode was employed for all IPCE measurements. Zn 1T-MoS₂ (1 mg mL⁻¹)/SiNWs was used as the working electrode, Pt wire was used as the counter
electrode, and Ag/AgCl (3 M NaCl, BASI) was used as the reference electrode. An applied bias of –0.4 V was employed for all IPCE measurements. 10 nm bandpass filters centered at 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950, 1000, and 1050 nm were used to limit wavelength ranges from the light source during the IPCE measurements. Photocurrent density at each irradiation intensity (ΔJi) was monitored by finding the difference between the dark and irradiated photocurrent densities at a given applied voltage bias. The total photon flux (I) was measured at each wavelength using an Si photodiode placed at a distance equivalent to the working electrode’s position. IPCE (%) for monochromatic light at each wavelength measured was calculated using Equation (3):

\[
IPCE = \left( \frac{1240 \times \Delta J_i}{\lambda (\text{nm}) \times 1000} \right) \times 100% \tag{3}
\]

All tabulated values are provided in Table S4, Supporting Information.

**Gas Chromatography and Faradaic Efficiency:** H2 concentrations were calibrated and measured with a Shimadzu GC-2010 Plus Tracer equipped with a Molecular Sieve 5 Å capillary column and a barrier ionization discharge (BID) detector. 99.9999% He was used as the carrier gas. Split temperature was maintained at 200 °C and the split ratio was set to 2.5 (split vent flow = 20.58 mL min⁻¹); column gas flow = 8.22 mL min⁻¹; purge flow = 0.5 mL min⁻¹). The column (0.53 mm, RT-Msieve 5A) temperature was maintained at 40 °C and the BID temperature was maintained at 235 °C. The BID detector gas flow rate was set to 50 mL min⁻¹. All calibration and sample gases were collected immediately prior to an injection using a 50 µL Hamilton gas-tight syringe. For H2 calibrations, high purity sodium was reacted with deionized water in a septum-sealed glass vial to produce 1500 ppm of H2 gas. The Faradaic efficiency (FE) for H2 generation was calculated using Equation (4):

\[
\text{FE}_{\text{H2}} = \frac{\text{number of H2 molecules} \times 2}{\text{total current (A)} \times \text{time (s)}} \times 100% \tag{4}
\]

**Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES):** Sample compositions were quantified by an inductively coupled plasma optical emission spectrometer (Perkin Elmer Optima 3000 DV). Commercially available Zinc standard solutions (1000 mg L⁻¹ in nitric acid, Sigma–Aldrich) were used for calibration. The standards were diluted to 1000 ppb (ng g⁻¹), 500 ppb, 100 ppb, 50 ppb, and 1 ppb, respectively, by the mixed acid solutions (5 vol. % HCl + 5 vol. % HNO₃) to establish the calibration curves. The correction coefficient of the as-established calibration curves is 99.96% for Zn. All samples were dissolved in concentrated HNO₃ then diluted to a concentration of 5% with DI water, and finally, Zn concentration was diluted ~25 times using the 5% HNO₃ for measurements.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

2D materials, artificial photosynthesis, catalysis, hydrogen generation, molybdenum disulfide, photoelectrochemical water splitting, silicon nanowires

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