Photoelectrolysis

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Hydrogen Production Using a Molybdenum Sulfide Catalyst on a Titanium-Protected n^{+}p-Silicon Photocathode**

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Producing solar fuels is envisioned to be one of the key challenges in switching the world's energy consumption to renewable resources.[1,2] Among these fuels hydrogen is one of the most simple as the molecule only consists of two electrons and two protons. Furthermore, H_2 is an important bulk chemical[3] and has the potential to become an important future energy carrier. This work focuses on the photoelectrocatalytic H_2 evolution reaction (HER) from water.

Platinum is the archetypical catalyst for the HER, but it is scarce and expensive,[4] thus making it commercially unfeasible and demonstrating the need for a catalyst made of abundantly available materials.[5] Using a biomimetic strategy based on the nitrogenase enzyme, DFT studies[6] showed the molybdenum edges of MoS_2 triangular nanoplatelets to be highly electrochemically active for the HER. Subsequent STM and electrochemical measurements[7] verified this experimentally in dark electrolysis. It was also shown that molecular molybdenum sulfides in the form of $Mo_3S_4^{4+}$ (called a cubane) could also be effective for the H_2 evolution reaction.[8] A cubane analogue has been applied to a p-type silicon wafer for the purposes of photocatalytic HER and achieved an IPCE (incident photon to current efficiency) of 47% at 0 V versus the reversible hydrogen electrode (RHE).[9]

By using p-type Si with a high level of surface n-doping, the research group of Lewis[10] showed that the HER onset could be improved by about 250 mV in accordance with earlier findings.[11] This n^{+}p-Si structure allowed for a higher open circuit voltage relative to a p-Si–liquid device by effectively decoupling the band bending in the p-Si from the semiconductor–liquid junction. In other words, the n^{+}-layer provided a built-in depletion region which was independent of the semiconductor–liquid junction. This overcame the inherent limitation of a p-Si–liquid device, namely its low flatband potential.

In our previous work[9] using cubanes on p-Si, the electron Fermi level for p-type Si was high enough, even at flatband conditions, to overcome the overpotential of the cubanes (about 400 mV). This effectively meant that the cubane–p-Si system was not limited by catalysis (interfacial electron transfer) despite the possible 400 mV overvoltage of the cubanes, but rather by the flatband potential of p-Si in an aqueous electrolyte. The cubanes were effectively a "good enough" catalyst for the p-Si electrodes. Using n^{+}p-Si overcomes the flatband potential limitation, but exposes the cubane's large overpotential. Thus a new, nonprecious metal catalyst must be found for the n^{+}p-Si system. The research group of Lewis has recently demonstrated that alloys of nickel and molybdenum (NiMo) may work as non-precious HER catalysts for this system. However, this system has stability issues in acid, which limits the pH to values above 4.[12]

On the other hand, great progress has recently been made on a MoS_x catalyst,[4,13] which is known to be stable in an acidic medium. For instance, the research group of Li[14] has shown that MoS_2 on CdS nanoparticles (NPs) are more efficient for the H_2 evolution than Pt on CdS NPs. They attribute this to a favorable interaction between CdS and MoS_2. The research of Hu's group on electrodeposition of porous, amorphous MoS_x[15] is also quite promising. This material showed an onset potential of 150 mV versus RHE, a Tafel slope of 39 mV dec^{-1}, and has been shown to be relatively stable over a 1 h test period. This MoS_x catalyst was electrodeposited by taking an $(NH_4)_2MoS_4$ precursor to oxidative potentials to produce an amorphous MoS_3 material, and then cycling the potentials back to reductive potentials. By varying the cycles, a controlled amount of MoS_x could be deposited. The research group of Hu has also shown that it is possible to prepare amorphous MoS_3 in powder form, albeit at a slightly lower activity.[16] The research group of Alivisatos[17] has started investigating a microwave-deposited MoS_3 on CdSe-seeded CdS nanorod photoabsorbers. They showed that initially MoS_3 was as active as platinum for the HER, but the activity was reduced as MoS_3 was reduced to MoS_2 over time.

A problem shared by many of the potential low-bandgap photocathodes with a conduction band high enough for H_2 evolution (CdS, Si, and GaP) is that they are readily oxidized. We have found previously that to prevent silicon oxidation during H_2 evolution, the dissolved O_2 concentrations must be < 15 ppb, which is commercially unfeasible in a water-splitting device.[9] A process which electrodeposits at oxidative potential such as the MoS_x catalyst developed by Hu's

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research group[15], would have almost no chance of working effectively since the photoabsorber would be oxidized during the deposition process. This demonstrates that the instability of many photoabsorbers seriously constrains the ability to attach a catalyst and to sustainably evolve H_2.

In this work we resolve this issue by depositing a thin layer of Ti on Si to act as a conductive protection layer, thus drastically enhancing the stability. The conductivity through the composite is optimized by the thin tunnel barrier due to the high level of n-doping in the surface layer of Si and the low Ti-TiO_x barrier (as discussed in the Supporting Information).

We then demonstrate the electrode's stability by scanning to oxidative potentials to electrodeposit MoS_x on an n^+p-Si electrode. Thus we form a MoS_x-Ti-n^+p Si composite photocathode (Figure 1). Using this catalyst we produce photocurrents at bias voltages which are unprecedented for a non-Pt catalyst in strongly acidic media.

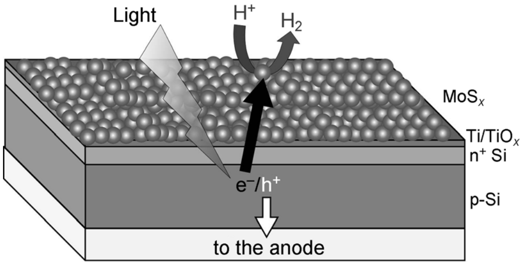

Figure 1. Scheme of a MoS_x-Ti-n^+p-Si electrode showing how photo-irradiated electrons reacts with protons to evolve H_2. e^- and h^+ refer to the photogenerated electron and hole pair, respectively.

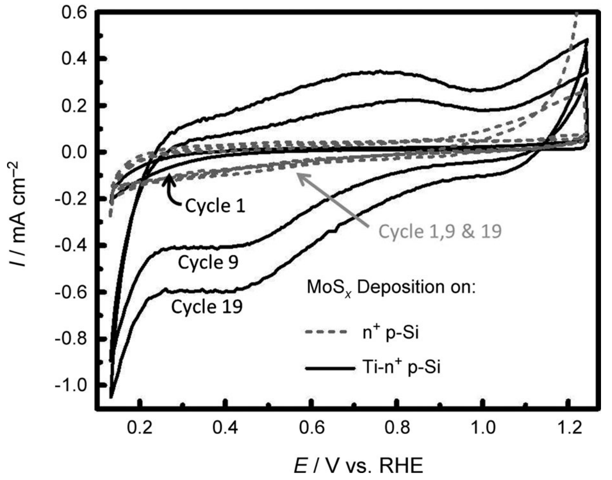

Figure 2. Cyclic voltammetry scans of the photo-electrodeposition of MoS_x onto n^+p-Si and Ti-protected n^+p-Si electrodes.

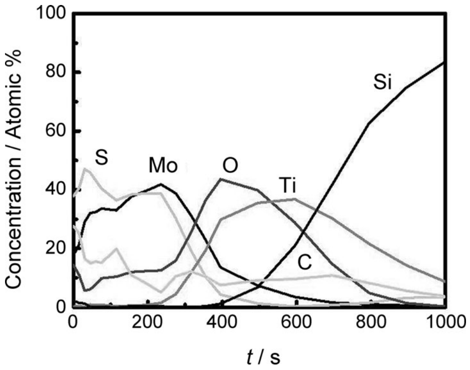

Figure 3. X-ray photoelectron spectroscopy depth profile of a MoS_x-Ti-n^+p-Si electrode.

Initially, we illustrate the problem that occurs without a corrosion protection layer. Due to the low number of charge carriers in Si in the dark, the deposition was done under irradiation. The irradiation of n^+p-Si resulted in a photovoltage of about 0.50 V.[10] Hence, the applied potentials were shifted from between −0.363 and 0.747 V versus RHE[15] to 0.137 and 1.247 V versus RHE, thus allowing the electrodeposition to take place. MoS_x was deposited directly on H-terminated n^+p-Si by cycling 19 times ending at the cathodic potential (Figure 2). The intial scan shows a very small reductive peak similar to the catalyst made by the research group of Hu,[15] but succesive scans do not show an increased peak. This was attributed to the aforementioned oxidation of the silicon surface and the loss of conductivty going through the SiO_x insulating layer. To resolve this issue, a 9 nm layer of Ti was sputtered on a freshly hydrogen-terminated n^+p-Si electrode. Figure 2 shows the photo-electrodepositon of the MoS_x catalyst on the Ti-protected Si (Ti-n^+p-Si). These cycles show clear reduction and oxidation peaks that closely resemble the cyclic voltammograms (CVs) reported by the research group of Hu. Once the CVs were completed, it could visually be seen that a uniform catalyst layer had been deposited on the electrode.

A depth profile of the MoS_x-Ti-n^+p-Si catalyst was created by X-ray photon spectroscopy (XPS) through an argon sputtering procedure. Figure 3 shows the results of this depth profile. This figure clearly shows that there is an initial MoS_x layer followed by a titanium layer and finally by a Si layer. It should be mentioned that the XPS of the as-prepared samples show a Mo:S ratio similar to that determined by the research group of Hu. Another interesting observation is that while a quick glance at the XPS reveals the MoS_x and Ti layers to be approximately of equal thickness, SEM images show (see Figure S2 in the Supporting Information) that the MoS_x and Ti layers are 35 nm and 9 nm, respectively. This can most likely be attributed to the porous nature of the MoS_x[15] allowing for deeper sputtering in a given time interval and differences in sputter yield. The discrepancy in the apparent thickness from the XPS versus the SEM-verified thickness demonstrates that XPS depth profiling is good for a qualitative analysis, but does not allow for a quantitative analysis (e.g. the Mo:S ratio) without calibration.

The goal of these electrodes is to be used in a two-photon water-splitting device.[9] In this device a high-bandgap photoanode would absorbs light at short wavelengths while long wavelengths pass through and are absorbed at the photocathode. Due to the advances in proton exchange membranes (PEM),[18] it is assumed that a PEM will transfer protons from the anode to the cathode, thus acidifying the local environment. Hence to accurately test the efficiency of the electrodes, cyclic voltammograms of the H_2 evolution were measured in an H_2 saturated acidic solution (1.0 M $HClO_4$) using long wavelength light (> 635 nm) with an overall intensity adjusted to approximate the red part of the solar spectrum (AM1.5-G as shown in Ref. [9]). Figure 4 shows the cyclic voltamograms of the MoS_x photocathodes with and without the Ti-protective layer as well as some important standards. While the n^+p-Si and Ti-n^+p-Si standards are self-explanatory, the Pt-Ti-n^+p-Si electrode was produced by dropcasting (5 µg) of a Pt salt on the electrode. By scanning the electrode starting from the most negative potential, the salt was photoreduced to the metal. The exact experimental details for all these electrodes can be found in the Supporting Information.

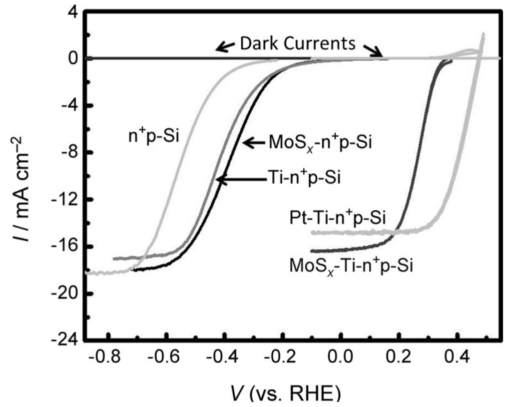

Figure 4. Cyclic voltammetry of the photoelectrocatalytic HER of various n^+p-Si electrodes. The samples were irradiated with red light (AM1.5 cut-off < 635 nm, 38.6 mW cm^{-2}) and scanned at 50 mV s^{-1}.

Figure 4 also shows that the HER activity of the MoS_x-n^+p-Si electrode is noticeably better than a pure n^+p-Si electrode indicating that there is some catalytic effect from MoS_x. When the MoS_x was deposited on a Ti-protected n^+p-Si electrode, the onset of the photocurrent shifted substantially to more positive potentials (0.33 V vs. RHE), which approaches the efficiency of the Pt electrode (0.47 V vs. RHE). Without the Ti protection layer reductive electrons need to tunnel through an insulating SiO_2 surface layer, but with the Ti protection layer the Si surface is protected from oxidation. It should be noted that the Ti surface will also oxidize, but this will form the semiconducting TiO_2 rather than the insulating SiO_2. The Ti-n^+p-Si standard shows that Ti provides a small increase in efficiency relative to the n^+p-Si electrode, but this electrode is still largely unreactive relative to the MoS_x-Ti-n^+p Si electrode. This helps to verify that the Ti is acting more as a protection layer rather than assisting the catalytic reaction. It should be noted that the higher current obtained for the MoS_x-Ti-n^+p Si electrode relative to the Pt electrode at the limiting cathodic current is due to light absorption of the catalyst, rather than any catalytic effect.

The comparison of this MoS_x catalyst to the catalyst produced by Hu's research group[15] is not straightforward because of the voltage added from the photovoltaic effect. However, it is well-known[19] that Pt has an almost negligible overpotential for the evolution of H_2, and thus the Ti-n^+p-Si electrode with MoS_x can be compared to the Pt electrode to get an estimate of how it compares. By applying this technique, a Tafel slope of 39 mV dec^{-1} and an onset potential (U@1 mA cm^{-2}) of 145 mV more cathodic than Pt, were found (see Figure S3 in the Supporting Information). These photo-electrochemical results are quite similar to the electrochemical results found by Hu's research group.[15] This demonstrates that by attaching a protective Ti layer, even quite complex catalysts can be deposited on a photocathode and produce the same results as would be expected in an electrochemical cell. Figure 4 also shows that this is clearly not the case without the Ti-protective layer.

While Ti does an effective job at protecting the Si from oxidation, it also blocks the Si from absorbing light. This effect explains the slight decrease in the saturation currents from the Ti-coated samples in Figure 4. The Ti thickness must be thick enough so that pinholes in the surface do not lead to oxidation, but thin enough to allow light to pass through. In this work Si was irradiated from the front side, but in any final two-photon device, the Si photocathode will be attached to the backside of a photoanode, thus allowing for backside illumination. In that case the protective layer will have no effects on the light absorption and it could therefore be much thicker if needed.

A long-term test was performed to prove both that H_2 was produced as well as to determine the long-term stability of the electrode. A H_2 evolution cyclic voltammogram was taken of the electrode initially, and then the electrode was run at a potential of +200 mV versus RHE for 1 h. The current remained stable at 12 mA cm^{-2} throughout the 1 h run, and produced an amount of H_2 (measured by GC) roughly corresponding to the current passed through the cell (see Figure S4). Directly after the 1 h run, another H_2 evolution cyclic voltammogram was taken. Figure 5 displays both the initial and the 1 h tested H_2 evolution cyclic voltammograms, which shows the relative stability of this catalyst. While the saturation current slightly decreased in this instance, there have been other instances where it slightly increased. Thus no conclusive evidence can be derived from this slight shift. When these cells were run for many hours they would sometimes degraded abruptly, which was attributed to inconsistencies in the protection layer. Currently, we are working

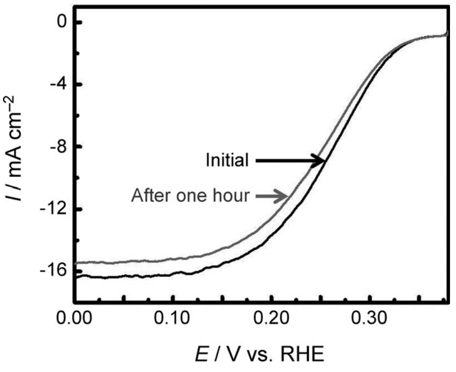

Figure 5. Photocurrent before and after a 1 h chronoamperometry test at +200 mV versus RHE.

on making this layer more consistent and durable using other techniques.

In summary, we have demonstrated that a Ti protection layer on a Si electrode allows for the possibility to take the Si to highly oxidizing conditions without oxidation of the Si. We have taken advantage of this fact by depositing MoS_x on n^+p-Si and have shown an unprecedented anodic onset of the HER for a non-Pt catalyst in acidic medium. The Ti layer is the key component, which allows the production of H_2 without oxidation of the photoabsorber.

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