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Published in:

Journal of the Electrochemical Society

Link to article, DOI:

[10.1149/2.0161412jes](https://doi.org/10.1149/2.0161412jes)

Publication date:

2014

Document Version

Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):

Seger, B., Herbst, K., Pedersen, T., Abrams, B., Vesborg, P. C. K., Hansen, O., & Chorkendorff, I. (2014). Mo₃S₄ Clusters as an Effective H₂ Evolution Catalyst on Protected Si Photocathodes. *Journal of the Electrochemical Society*, 161(12), H722-H724. DOI: 10.1149/2.0161412jes

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Mo₃S₄ Clusters as an Effective H₂ Evolution Catalyst on Protected Si Photocathodes

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This work shows how a molecular Mo₃S₄ cluster bonded to a photoelectrode surface via a phosphonate ligand can be a highly effective co-catalyst in photocathodic hydrogen evolution systems. Using a TiO₂ protected n⁺p Si photocathode, H₂ evolution occurs with an onset of +0.33 V vs. RHE in an acid solution with this precious metal-free system. Using just the red part of the AM1.5 solar spectrum ($\lambda > 635$ nm), a saturation current of 20 mA/cm² is achieved from an electrode containing Mo₃S₄ dropcasted onto a 100 nm TiO₂/7 nm Ti/n⁺p Si electrode.

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Manuscript submitted June 30, 2014; revised manuscript received August 4, 2014. Published August 12, 2014.

It is well established that society cannot indefinitely rely on fossil fuels and must switch to a renewable energy source.¹ Solar fuels such as hydrocarbons from CO₂ reduction and H₂ from the water splitting reaction are highly attractive since these molecular products can be stored indefinitely² and used directly in the transportation infrastructure. Photocatalytic water splitting using a 2-photon device has the potential for much higher efficiency than a 1-photon device.^{3,4} In a 2-photon device the optimal bandgaps for the 2 photoabsorbers are approximately 1.7 eV and 1.0 eV.³⁻⁵ This allows for the large bandgap material to absorb the blue light leaving the red light to be absorbed by the small bandgap material. Silicon is very promising as the small bandgap material since it has a bandgap of 1.1 eV. A major problem with Si and other small bandgap materials is that they have stability problems in a water splitting environment. Recently it was shown that depositing a thin film of TiO₂ mitigates stability issues.⁶⁻⁸ However, the rectifying properties of this film may restrict the ability to electrodeposit catalysts onto the protected photoabsorber surface.^{9,10} Even though the TiO₂ protection layer can be detrimental to certain electrodeposition procedures, it may also open up a new avenue to help improve the stability of molecular catalysts.

Previous work showed molecular clusters such as Mo₃S₄ incomplete cubane clusters to be quite effective as H₂ evolution catalysts,^{11,12} however the materials are also known to be water soluble. This solubility makes it quite difficult to keep these catalysts adsorbed on an electrode surface in a working environment. A previous approach to resolve this issue involved attaching hydrophobic ligands to the clusters.^{13,14} Unfortunately this approach decreased catalytic activity and stability in air. One of the great difficulties in depositing these catalysts was the limited freedom in interacting with the Si surface due to its extreme propensity to oxidize to SiO₂. However with the emergence of TiO₂ as a protection layer, there now is a much larger freedom to design molecular catalysts that can interact with the electrode.

In the present work we investigated attaching a (hydrophilic) molecular linker to help bind Mo₃S₄ clusters to the TiO₂ surface. Previous work showed that phosphonate groups are quite effective at binding to TiO₂ in photocatalytic H₂ evolving systems.¹⁵ Thus a N-(phosphonomethyl)iminodiacetate (Hpmida)-Mo₃S₄ cluster was synthesized and used as a catalyst. Rather than dropcasting the catalyst onto the electrodes, we soaked the electrodes in a solution of the Mo₃S₄-Hpmida overnight. We then thoroughly washed off the electrode with ultrapure water (18 M Ω -cm) to ensure that only bound Mo₃S₄-Hpmida remained on the 100 nm TiO₂/7 nm Ti/n⁺p Si electrodes. This was found to give the same performance as dropcasting,

thus indicating an adsorbed monolayer is all that is needed to maximize catalytic efficiency. A photoirradiated p-n junction was used rather than simply a degenerately doped Si to show that potential photon absorption from Mo₃S₄ clusters is not a significant issue for blocking light to the Si nor in the Mo₃S₄ catalysis of protons to H₂.

Figure 1 shows a cyclic voltammogram (CV) of red light irradiated ($\lambda > 635$ nm) 100 nm TiO₂/7 nm Ti/n⁺p Si photocathodes with either Mo₃S₄-Hpmida or Pt nanoparticles as catalysts. The electrolyte was 1.0 M HClO₄. This material has an onset potential (i.e. at current density of 1 mA/cm²) of +0.32(4) V vs. Reversible Hydrogen Electrode (RHE), which is essentially the same as the +0.33(0) V vs. RHE achieved earlier with a MoS_x catalyst. However, unlike in our previous work using Mo₃S₄ clusters with a hydrophobic ligand,^{13,14} the Mo₃S₄-Hpmida clusters were relatively stable in air, thus no special precautions were necessary to use these materials. It was found that leaving the catalysts in atmospheric conditions for 2 years did result in a slight decrease (~30 mV) in activity. See Supporting Information for details.

Since the Mo₃S₄-Hpmida clusters are water soluble, there is the risk that they dissolve into solution during operation. In previous work, there was substantial current loss after less than 10 scans (corresponding to approximately 5 minutes). To test for durability, a

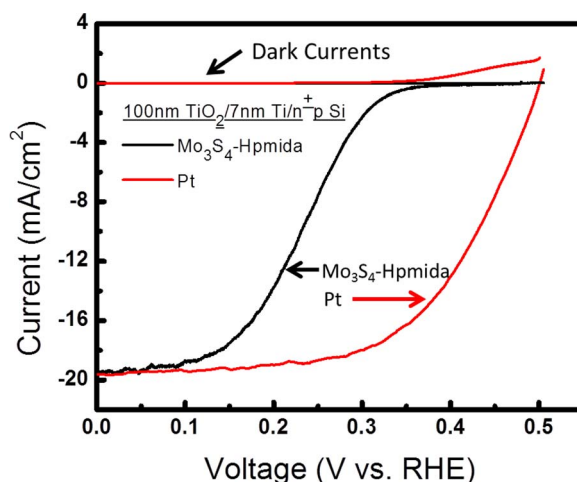


Figure 1. Cyclic voltammograms of either Pt or Mo₃S₄-PMIDA deposited on 100 nm TiO₂ / 7 nm Ti/n⁺p Si electrodes for photocathodic H₂ evolution. These catalysts were deposited via adsorption from a solution containing the catalyst.

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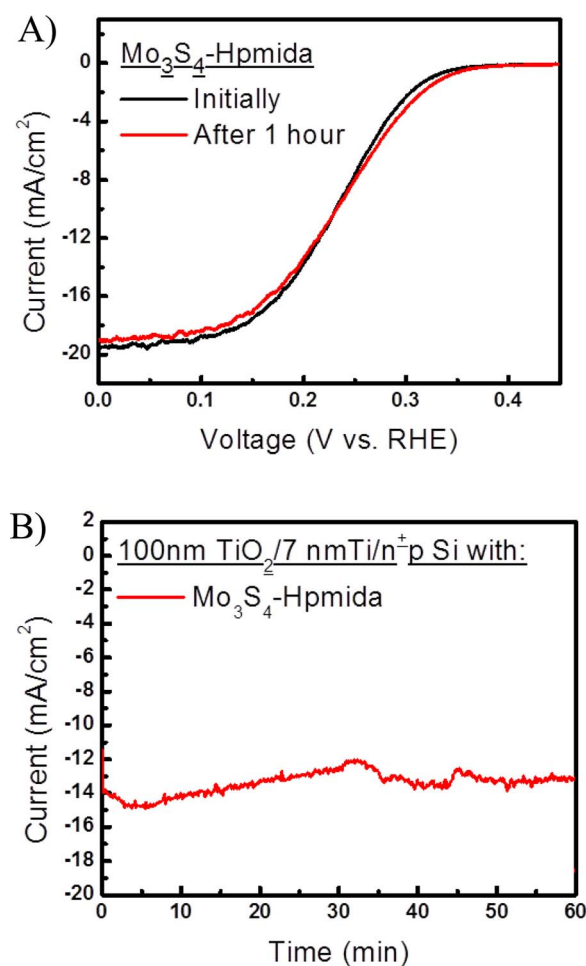


Figure 2. A) Cyclic voltammograms of photoirradiated Mo_3S_4 -Hpimida deposited on 100 nm TiO_2 / 7 nm Ti/n^+p Si electrodes initially and after 1 hour. B) Chronoamperometry test of the photoelectrodes used in part A. These catalysts were deposited via adsorption from a solution containing the catalyst. The electrode was held at +0.2 V vs. RHE during the test.

chronoamperometry test was run. Figure 2A shows a CV before and after a 1 hour chronoamperometry test was ran at a potential of +0.20 V vs. RHE. Figure 2B shows the corresponding 1 hour chronoamperometry test. The variations during the 1 hour chronoamperometry test may be related to mass transfer issues near the catalyst. The CV after 1 hour shows negligible change in catalytic activity. Compared to previous work with water soluble, air stable catalysts,¹¹ the Hpimida functional group greatly stabilized the catalysts. Further long term testing at more reductive potentials show that some cathodic stability issues remain. Since previous results show that TiO_2/Ti is stable,⁶ we attribute these losses to catalyst detachment/deactivation. However, re-deposition of the catalyst allowed for a completely regain in performance (See Supporting Information).

Previous research has shown that Mo_3S_4 entities can easily undergo degradation.^{14,16} To investigate if this could potentially be an issue, the Mo_3S_4 -Hpimida catalyst/100 nm TiO_2 /7 nm Ti/n^+p Si was photoirradiated and cycled to highly oxidative potentials as shown in Figure 3. The scan before and after the oxidation cycle show no difference indicating that anodic corrosion does not occur on the photoelectrode. This inability for the 100 nm TiO_2 /7 nm Ti/n^+p Si to corrode the Mo_3S_4 was actually expected due to the TiO_2 layer forming a depletion layer, which blocks electron transfer.⁹ Previous research has shown that when using moderately doped TiO_2 , anodic electron transfer cannot occur at potentials much more anodic H^+/H_2 redox potential.⁹ In Figure 3 the 5 nm Pt/n^+p Si shows anodic current due

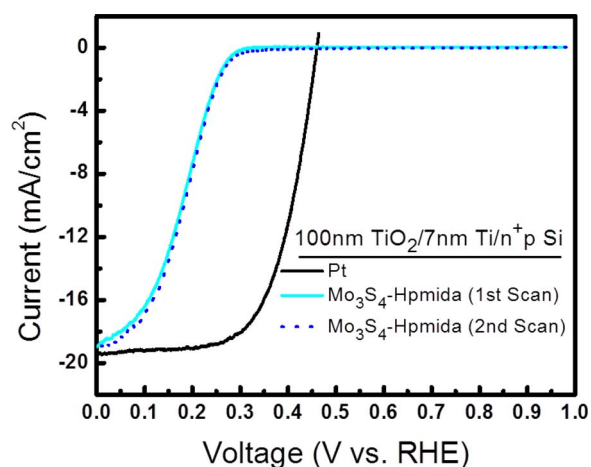


Figure 3. Cyclic voltammograms of Mo_3S_4 -PMIDA deposited on 100 nm TiO_2 / 7 nm Ti/n^+p Si electrodes. These CV's show that the photoelectrode can go to corrosive potentials without corroding the catalyst due to TiO_2 acting as a blocking layer. These catalysts were deposited via dropcasting.

to H_2 oxidation, however Mo_3S_4 cannot oxidize H_2 , thus no current is seen for the Mo_3S_4 -Hpimida/100 nm TiO_2 /7 nm Ti/n^+p Si sample.¹⁶

It should be noted that different Si wafers were used in Figure 1 and Figure 3. Each Si wafer has a slightly different photovoltage, thus accounting for the small difference in onset potentials between Figure 1 and Figure 3. In Figure 1 and Figure 3 the electrode with Pt and the electrode with Mo_3S_4 -Hpimida came from the same wafer so their photovoltages should be equivalent.

While Figure 3 shows that catalyst oxidation is highly unlikely due to blocking action of the TiO_2 layer, there are other potential degradation mechanisms which the catalyst may suffer. In a commercial device, catalysts may degrade by poisoning via electrolyte impurity, mechanical instability, oxidation from oxygen crossover, or many other mechanisms. Thus regeneration/redeposition of the catalyst may be an important process that needs to be taken into consideration. These molecular Mo_3S_4 -Hpimida clusters have the advantage over the typical nanoparticle catalysts in that they are soluble in water, and will adsorb to the TiO_2 surface of the composite photocathode. Thus deposition (and redeposition) is as simple as soaking/wash-coating the photocathode in a solution of catalyst. Nanoparticles must contend with dispersion issues, thus adding an extra step for optimization. While electrodeposition or photoelectrodeposition also typically uses water soluble precursors, an electrical bias needs to be applied, thus adding another step to this procedure as well. While optimization of both nanoparticles and electrodeposited particles is possible, the simplicity of having an aqueous solution of a catalyst adsorb to the semiconductor surface gives molecular catalysts such as cubane clusters a distinct advantage of simplicity.

In summary, this work demonstrates that a Mo_3S_4 -Hpimida/100 nm TiO_2 /7 nm Ti/n^+p Si composite photocathode can produce an onset of +0.32(4) V vs. RHE for H_2 evolution. Importantly, we demonstrate that anchoring the cubane catalyst to the electrode via phosphonate- TiO_2 gives a very significant improvement in the stability of this efficient, molecular H_2 evolution catalyst, although room for improvement remains. Future work will focus on analyzing other potential deactivation mechanisms and designing the photocathodic system to eliminate them.

Experimental

For anchoring on hydroxylated TiO_2 surfaces, the Mo_3S_4 cluster was derivatized with N-(phosphonomethyl)iminodiacetate (Hpimida) ligands. A suspension of the free acid H_4pmida in water was deprotonated by 3 molar equivalents of NaHCO_3 leading to dissolution of the ligand. Dropwise addition of this mixture into an aqueous

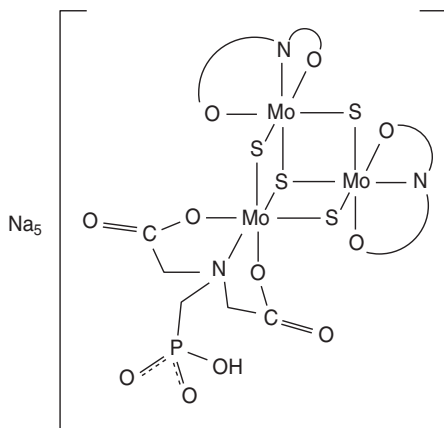
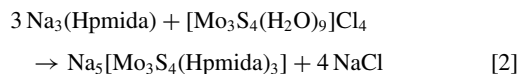
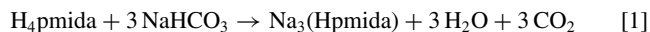


Figure 4. Plot of the $\text{Na}_5[\text{Mo}_3\text{S}_4(\text{Hpmida})_3]$ catalyst structure used in this work as an H_2 evolution catalyst.

solution of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]\text{Cl}_4$ led to a light green solution.¹⁷ From this solution the cluster $\text{Na}_5[\text{Mo}_3\text{S}_4(\text{Hpmida})_3]$ was isolated using slow crystallization after addition of 0.5 vol-eq. of ethanol to the aqueous mixture.

The formation of the new cluster is shown in the reaction scheme below, and simplified formula plots are shown in Figure 4.



The electrodes were made and tested in a manner similar to our previous work.⁹ The exact details are given in the supporting information.

Acknowledgment

We gratefully acknowledge the Danish Ministry of Science for funding the CAtalysis for Sustainable Energy (CASE) initiative, the Danish National Research Foundation for funding The Center for Individual Nanoparticle Functionality-CINF (DNRF54).

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