Molybdenum Sulfides Materials as Hydrogen Evolution Catalysts and Surface Protecting Layers for Highly Active and Stable Silicon-Based Water Splitting Photocathodes

Jesse D. Benck, Jakob Kibsgaard,
and Thomas F. Jaramillo
Stanford University Dept. Chemical Engineering
381 North-South Axis, Stanford, CA 94305

Photoelectrochemical (PEC) water splitting could provide a sustainable means of hydrogen fuel production.[1] Recent research in PEC water splitting has focused on developing materials suitable for application in a dual-absorber device configuration due to the high solar-to-hydrogen efficiencies tandem devices could enable.[2, 3]

Silicon is a promising candidate photocathode material for a tandem PEC device due to its abundance, relatively low cost, excellent charger carrier transport, and near-ideal band structure.[4-9] However, several challenges must be addressed to make silicon-based photocathodes efficient and economical. The surface of the silicon must be protected to prevent the formation of an insulating SiO_2 layer, which can degrade device performance.[8] The silicon must also be combined with an active catalyst to reduce the kinetic overpotential necessary to drive the hydrogen evolution reaction (HER) at the photocathode surface.[4-9]

Previous reports have demonstrated that high-quality SiO_2 tunneling layers or conductive TiO_2 layers can protect silicon photocathode surfaces.[8, 9] When combined with platinum catalysts, these photocathodes demonstrate excellent activity and stability on the order of days. Si photocathodes incorporating catalyst materials based on earth-abundant elements such as NiMo and Mo_3S_4 cubanes have also been demonstrated, but significant improvements in the activity and stability of these precious-metal free devices are necessary to match the performance of Pt/Si structures.[4, 6]

Molybdenum sulfide materials offer a promising solution to these challenges. Nanostructured, crystalline MoS_2 HER catalysts possess excellent activity and stability.[10, 11] We show that MoS_2 can also confer these benefits of high activity and stability to silicon photocathodes. We fabricate conformal coatings of MoS_2 on silicon using a simple thermal synthesis. This technique yields silicon photocathodes that remain highly active after more than 24 hours of continuous operation. While the stability of this structure is among the best reported for silicon photocathodes, but the low density of HER-active MoS_2 edge sites at the electrode/electrolyte interface limits the voltage generated by this device. As illustrated in the figure below, we incorporate additional molybdenum sulfide HER catalysts such as $[Mo_3S_{13}]^{2-}$ clusters[12] to increase the density of active site densities and improve the photocurrent onset voltage to within ~150 mV of the best reported Pt/Si photocathodes.

Our results demonstrate that molybdenum sulfides can be employed as multifunctional coatings for silicon photocathodes, serving as both catalysts and protecting layers. Based on our findings, we propose strategies for further improving the performance of molybdenum sulfide/silicon photocathodes.

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