Developing Nano-Structured MoS₂ Electro catalysts for Renewable, Sustainable H₂ Production

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Introduction
Electrocatalyst development has become increasingly important as a number of energy technologies rely upon electrochemical conversion reactions.¹,² Electrocatalytic hydrogen production by water splitting is one example; this process could potentially address the needs for the sustainable production of fuels and for solar energy storage in a manner that is renewable and carbon-free.²,³ In contrast to widely utilized steam reformed hydrogen, electrocatalytically produced hydrogen offers much lower carbon monoxide content, which can mitigate the poisoning effect that often decreases operational activity of platinum-based catalysts currently used in hydrogen fuel cells.⁴,⁵ Several device configurations can potentially enable solar driven water electrolysis, including coupled photovoltaic (PV) electrolyzers, integrated PV-electrolyzers, and photoelectrochemical (PEC) water splitting cells.⁶,⁷ The hydrogen evolution catalyst is a key component which needs to be able to drive current densities that match the solar photon flux at low overpotentials while remaining stable in the chosen electrolyte. In this work, we describe our efforts to develop active, stable, earth-abundant hydrogen evolution electrocatalysts based on nanostructured MoS₂.

Materials and Methods
The electrochemical measurements were carried out in a three-electrode electrochemical compression cell using a Bio-Logic VSP potentiostat. Nanostructured MoS₂ samples served as the working electrode (WE) with a graphite foil (Alfa) as counter electrode (CE) and a Hg/Hg₂SO₄ (in saturated K₂SO₄) reference electrode (RE) (Hach). All cyclic voltammograms of the HER activity were conducted using 0.5 M H₂SO₄ electrolyte under continuous sparging with 99.999% H₂ (Praxair).

Results and Discussion
At the nanoscale, MoS₂ exhibits excellent turnover frequencies for the hydrogen evolution reaction (HER) due to the presence of undercoordinated edge sites with high catalytic activity. In order to achieve high electrode current densities, the density of these edge sites must be increased and vertically integrated into a conductive architecture. However, simply creating high surface area morphologies of nanostructured MoS₂ will often yield sub-optimal results since the formation of highly energetic and catalytically active edge sites is thermodynamically unfavorable compared to the formation of extended non-active basal planes. Herein, we show how engineering nanostructured morphologies of MoS₂ can produce desired atomic-scale surface structures with high catalytic activity and stability. Four general nanostructured morphologies will be presented: nanoparticles, nanowires, thin films, and mesoporous structures.⁸,⁹ Among these morphologies, we present core-shell architectures of MoS₂ that simultaneously eliminates charge transport limitations and produces a protecting effect for underlying supports, enabling such structures to drive highly efficient HER over thousands of simulated diurnal cycles and demonstrating its viability for integration into a solar water splitting device. The approaches highlighted in this work serve as guiding principles for the development of novel electrocatalysts through morphological control at the nanoscale.⁹

Significance
Nano-structured morphologies of MoS₂ are being developed as active, stable, earth-abundant electrocatalysts for H₂ evolution; a process that could potentially address the needs for the sustainable production of fuels and for solar energy storage in a manner that is renewable and carbon-free.

Figure 1. MoS₂ nanostructures for electrocatalytic H₂ evolution.

References