Building an appropriate active-site motif into a hydrogen-evolution catalyst with thiomolybdate [Mo\textsubscript{3}S\textsubscript{13}]\textsuperscript{2-} clusters - DTU Orbit (16/01/2019)

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Identifying and understanding the active sites responsible for reaction turnover is critical to developing improved catalysts. For the hydrogen-evolution reaction (HER), MoS\textsubscript{2} has been identified as an active non-noble-metal-based catalyst. However, only edge sites turnover the reaction because the basal planes are catalytically inert. In an effort to develop a scalable HER catalyst with an increased number of active sites, herein we report a Mo-S catalyst (supported thiomolybdate [Mo\textsubscript{3}S\textsubscript{13}]\textsuperscript{2-} nanoclusters) in which most sulfur atoms in the structure exhibit a structural motif similar to that observed at MoS\textsubscript{2} edges. Supported sub-monolayers of [Mo\textsubscript{3}S\textsubscript{13}]\textsuperscript{2-} nanoclusters exhibited excellent HER activity and stability in acid. Imaging at the atomic scale with scanning tunnelling microscopy allowed for direct characterization of these supported catalysts. The [Mo\textsubscript{3}S\textsubscript{13}]\textsuperscript{2-} nanoclusters reported herein demonstrated excellent turnover frequencies, higher than those observed for other non-precious metal catalysts synthesized by a scalable route.

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