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Linking Molybdenum—Sulfur Clusters for Electrocatalytic Hydrogen Evolution

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Background



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Building an appropriate active-site motif into a hydrogen-evolution catalyst with thiomolybdate $[Mo_3S_{13}]^{2-}$ clusters

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Dimeric $[Mo_2S_{12}]^{2-}$ Cluster: A Molecular Analogue of MoS_2 Edges for Superior Hydrogen-Evolution Electrocatalysis

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Relevance to the group:

We are trying to synthesize new gold and silver clusters and trying to crystalize them. We can try to synthesis this kind of M-X clusters (M = Mo, W and X = S, Se etc).

Introduction

- Hydrogen production through water splitting is envisioned to satisfy the global demand for clean and sustainable energy. To facilitate the implementation of this technology on a wide scale, great efforts have been devoted to identifying efficient and cheap catalysts for the hydrogen evolution reaction (HER).
- MoS₂ represents a promising non-noble-metal-based candidate as an alternative to the precious metal platinum which shows one of the best-known hydrogen evolution activities in acidic media.
- The edges of this layered structure act as active sites, while the basal planes are inert. To maximize the number of catalytically active sites within the material on the electrode surface, bulk MoS₂ can be downsized to nanoparticles and even discrete clusters.

Synthesis



^aColor code for ball-and-stick models: Mo, blue; Br, orange; S, yellow; R group, purple.





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Figure S1. Structure of a molecule of MOS-1. Ellipsoids are plotted with 50% probability. Color code: Mo, dark blue; S, yellow; Br, brownish red; C, gray; H, white.



Figure S7. The structure of MOS-3. (a) Heavy atoms solved from the SXRD data. The position of S atoms matches well with that in *p*-BDT, allowing the simulation of a structural model where a pair of clusters are connected by two linkers in the same way as the MOS-2 dimer structure, and further linked by the third linker into a chain. (b) Top view of the MOS-3 unit cell. (c) Side view of the MOS-3 unit cell. Color code: Mo, blue; Br, orange; S, yellow; C, black.



Scheme 3. Mo₃S₄ Clusters Connected by Linkers into a Dimer and a Cage^a

^aColor code for ball-and-stick models: Mo, blue; Zn, pink; S, yellow; C, gray; N, green; O, red. Color code for topology illustrations: SBUs, blue triangles; linkers, red lines; Zn centers, pink squares; cavity, yellow sphere.



Figure S5. Structure of a molecule of MOS-4. Ellipsoids are plotted with 50% probability. Color code: Mo, dark blue; S, yellow; O, red; C, gray; H, white.



Figure S6. Structure of a molecule of MOS-5. Ellipsoids are plotted with 30% probability. Color code: Mo, dark blue; Zn, dark purple; S, yellow; O, red; N, bluish purple; C, gray; H, white.



Figure 1. HER activities of MOS materials. (a) Polarization curves of thin-layer coverage of $[Mo_3S_7Br_6]^{2-}$, MOS-1, and MOS-3 on FTO. (b) Tafel plots of the polarization curves. (c) Polarization curves of MOS-3 on GC and CFP with various loadings. (d) Comparison between the metrics of Mo–S-based HER catalysts: TOF per Mo at an overpotential (η) of 0.2 V plotted against the overpotential required for a current density of 10 mA cm⁻².^{5-9,14-20} The values optimized independently for these two parameters are taken (section S12). (e) Chronoamperometry of MOS-3 at $\eta = 89$ mV with a loading of 2.7 μ mol cm⁻² on CFP. (f) Initial and postcycling CVs of MOS-3 with a loading of 0.1 μ mol cm⁻² on GC.

Three possible steps has been suggested as elementary steps of HER in acidic medium:

the primary discharge step (Volmer reaction):

 $H_3O^+ + e^- \rightleftharpoons H_{ads} + H_2O$, where H_{ads} denotes an H atom adsorbed on catalyst surface, followed by either an electrochemical desorption step (Heyrovsky reaction): $H_3O^+ + H_{ads} + e^- \rightleftharpoons H_2 + H_2O$ or a recombination step (Tafel reaction): $2 H_{ads} \rightleftharpoons H_2$

- ✤ Tafel slope of 30 mV per decade, which follows the Volmer-Tafel mechanism. This is due to the higher coverage of H_{ads} on the electrode surface, which favors the recombination step.
- On the other hand, Mo-S based materials have been proposed to follow Volmer-Heyrovsky mechanism with a characteristic Tafel slope of 40 mV per decade.
- When the measured Tafel slope goes above 40 mV, it could suggest that after an initial discharge step, a chemical rearrangement takes place before the Heyrovsky reaction and becomes the rate-limiting step. This chemical rearrangement can lead to a Tafel slope of up to 60 mV per decade, as presented in the case of MOS-3.

Conclusion

- They have shown outstanding HER performance to the periodic arrangement of Mo-S clusters on the conductive surface, facilitating the mass transport.
- By exposure of a majority of the active sites to the electrolyte, the catalyst loading at the electrode becomes scalable without sacrificing the performance of each active center.
- The wet chemistry developed here provides a solid material with welldefined structures at the molecular level that is capable of straightforward synthesis and processing onto the electrode.

