

Surface-anchoring and modification of molecular $[\text{Mo}_3\text{S}_{13}]^{2-}$ cluster co-catalysts for photocatalytic water splitting

Samar Batool, Sreejith P. Nandan, Stephen Nagaraju Myakala, Ashwene Rajagopal, Jasmin S. Schubert, Pablo Ayala, Shaghayegh Naghdi, Johannes Bernardi, Carsten Streb, Alexey Cherevan and Dominik Eder

Efficient conversion of solar energy to hydrogen fuel by visible light-driven water splitting has been a challenging task for the scientists. Photocatalysis is a promising strategy to generate hydrogen from renewable sources, such as water and sunlight. However, the efficiencies of contemporary photocatalytic systems are not yet enough to contribute substantially to the world energy demand. One important issue that requires urgent attention is the design of earth-abundant, tunable and selective co-catalyst.

Among various candidates, transition-metal-based metal sulfides – such as those from the MoS_x -family – have shown excellent co-catalytic properties due to the presence of suitable active sites for electrochemical H_2 production. More recently, thiomolybdates – such as $[\text{Mo}_3\text{S}_{13}]$ molecular clusters deposited on carbonaceous supports – have demonstrated superior electrochemical hydrogen generation efficiency associated with the presence of abundant and exposed sulfur ligands [1]. Compared to other co-catalysts reported elsewhere, such clusters feature well-defined molecular structures, compositions, and geometries, which may allow for in-depth studies and understanding of the active sites, reaction mechanisms, and dynamic nature of the catalytic processes.

In this work [2], we bridge the homogenous and heterogeneous photocatalysis by immobilizing the noble-metal- and carbon-free thiomolybdate $[\text{Mo}_3\text{S}_{13}]^{2-}$ clusters – as molecular co-catalysts – onto photoactive metal oxide supports via covalent linkage for the application of photocatalytic water splitting. We elaborate that $[\text{Mo}_3\text{S}_{13}]^{2-}$ clusters attach strongly to the oxide surfaces. This attachment is limited to the support surface and involves the loss of the majority of the terminal S_2^{2-} groups, which results in the formation of Mo-O-Ti bonds with the hydroxyl groups of TiO_2 surface. The $[\text{Mo}_3\text{S}_{13}]^{2-}$ clusters heterogenized onto TiO_2 are shown to be highly active and stable co-catalysts for light-driven hydrogen evolution reaction (HER) with a comparable performance to that of a benchmark Pt. These co-catalysts show optimal HER activity at 2 wt.% cluster loadings, which is attributed to the availability of support surface required for scavenging holes efficiently. We further investigate the active sites taking part in the HER by applying heat treatments in air and N_2 . Our data suggest that bridging S_2^{2-} as well as vacant coordination sites at the Mo centers are possible HER active sites, which highlight the importance of the trinuclear core of the $[\text{Mo}_3\text{S}_{13}]^{2-}$ cluster. This work provides a prime example for the successful heterogenization of an inorganic molecular cluster as a co-catalyst for light-driven HER and gives the incentive to explore other thio(oxo)metalates.

References

1. Kibsgaard et al., Building an appropriate active-site motif into a hydrogen-evolution catalyst with thiomolybdate $[\text{Mo}_3\text{S}_{13}]^{2-}$ clusters. *Nature Chemistry*, 6, 248–253 (2014)
2. Batool et al., Surface-anchoring and modification of molecular $[\text{Mo}_3\text{S}_{13}]^{2-}$ cluster co-catalysts for photocatalytic water splitting. *ACS Catalysis*, submitted.