

Molecular and surface-anchored thiomatalate clusters for light driven H₂ generation

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The reaction of water splitting has been investigated widely in literature motivated by the possibility of producing molecular hydrogen (H₂) as a clean, renewable, and abundant source of energy. Photocatalysis is a promising strategy to generate hydrogen from renewable sources, however, the efficiencies of contemporary photocatalytic systems are not yet enough to contribute substantially to the world energy demand. One important issue is the design of earth-abundant and tunable co-catalysts able to perform the desired redox reaction in a stable and selective manner. Among various candidates, transition-metal-based metal sulfides have shown excellent catalytic properties towards electrochemical H₂ production due to the presence of suitable active sites. This work provides a comprehensive insight into potential chalcogenide based molecular clusters as catalysts for both homogeneous and heterogeneous photocatalytic hydrogen evolution reaction. These clusters have well-defined molecular structures and compositions which allow their rational design and additionally makes them ideal candidates to gain in-depth understanding of HER active sites and mechanisms.

In this work, we explored novel Ni-based polyoxometalates molecular clusters as catalysts for photocatalytic hydrogen evolution reaction in the homogeneous phase. These clusters showed exceptional quantum yields up to 10 %. However, the stability of these clusters is questionable in homogeneous HER conditions due to the use of degradable molecular sensitizer. Therefore, we bridge the homogenous and heterogeneous photocatalysis by immobilizing the noble-metal- and carbon-free thiomolybdate [Mo₃S₁₃]²⁻ clusters – as molecular co-catalysts – onto photoactive metal oxide supports via covalent linkage for photocatalytic water splitting. The [Mo₃S₁₃]²⁻ clusters heterogenized onto TiO₂ are shown to be highly active and stable co-catalysts for hydrogen evolution reaction (HER). The absorption of TiO₂ is limited to the UV region of the spectrum which consequently led us to explore other supports capable of absorbing visible light. Therefore, these [Mo₃S₁₃]²⁻ cocatalysts were immobilized onto graphitic carbon nitride to examine their HER performance and to draw a direct comparison of homogeneous and heterogeneous photocatalysis under similar reaction conditions. The heterogenized clusters were shown to be highly stable for long-term, however, the stability of these clusters was compromised over activity under homogeneous HER conditions. 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 oxothiometalates.