

HETEROGENIZATION OF MOLECULAR OXO/THIO METALATE CATALYSTS FOR SOLAR FUEL GENERATION

Sreejith P Nandan^a, Ashwene Rajagopal^b, Alexey Cherevan^{a*}, Carsten Streb^b, Dominik Eder^{a*}

^aE165 Institute of Materials Chemistry, Technical University of Vienna, 1060 Vienna, Austria

^bInstitute of Inorganic Chemistry-1, Ulm University, 89081 Ulm, Germany

INTRODUCTION

One of the main challenges of today's society is the impending energy crisis, which is tightly linked to global warming and ever-increasing greenhouse gas emissions. A strong shift in our political and economic decisions is inevitable, as evidenced by the rapidly growing reliance on renewable energy sources and the corresponding research hype in the field of materials science. One solution for this issue is the concept of solar fuels that can be generated by means of photocatalytic (PC) water splitting and CO₂ reduction, both of which are highly demanding redox reactions that require a delicate design of the PC system (see Figure). To accomplish this multifaceted task, we propose a novel strategy that will complement the advantages of homogeneous and heterogeneous PC and eliminate the drawbacks.

Polyoxometalates (POMs) and polythiometalates (PTMs) have captured the attention of chemists and material scientists over the past decades with their structural and compositional tunability along with their functional properties ^[1]. POMs are basically molecular metal oxide clusters of early transition metals in their high-valent states, while PTMs are molecular metal sulphides that have recently emerged as 0D analogues to low-dimensional MoS₂ nanostructures. Both of them have been studied extensively as versatile catalysts for homogeneous reactions. Most recently, POM and PTM clusters triggered a lot of attention as first fully-inorganic homogeneous water oxidation and water reduction catalysts, respectively ^[2,3]. However, similar to other molecular photocatalysts (PCs), they [A] suffer from rapid self-aggregation that leads to the shielding of active sites. Besides, [B] almost all reported POM/PTM PC systems are not able to complete the light absorption and require the presence of a molecular photosensitizer such as [Ru(bpy)₃]²⁺. These two issues pose a strong limitation hindering the development of the field and its commercialization.

OBJECTIVES

In my Ph.D. project, I aim to address these challenges of *molecular PC* using an innovative approach that takes inspiration from *heterogeneous PC* and combines the advantages of both fields. I am currently on my second year and my project is entitled "Heterogenization of molecular oxo/thio metalate catalysts for solar fuel generation". Briefly, in my project I am wiring the catalytically relevant POM/PTM clusters to high-surface-area semiconducting substrates (shown in Figure) that are capable of complementing the light absorption step (Step 1 in Figure) of a PC process. Besides, we expect this POM/PTM heterogenization approach to provide a better accessibility of the active sites, along with preventing the catalytic species from deactivation.

RESULTS AND DISCUSSION

I have started my work by examining several PTM clusters that have recently been reported to be catalytically active towards HER in homogeneous phase (i.e. their molecular form). I first successfully synthesized various Mo-based PTMs (eg. Na₂[Mo₃S₁₃] clusters) and performed

systematic studies on their electrostatic immobilization on TiO₂ nanoparticles (NPs) chosen here as a model photoactive substrate.

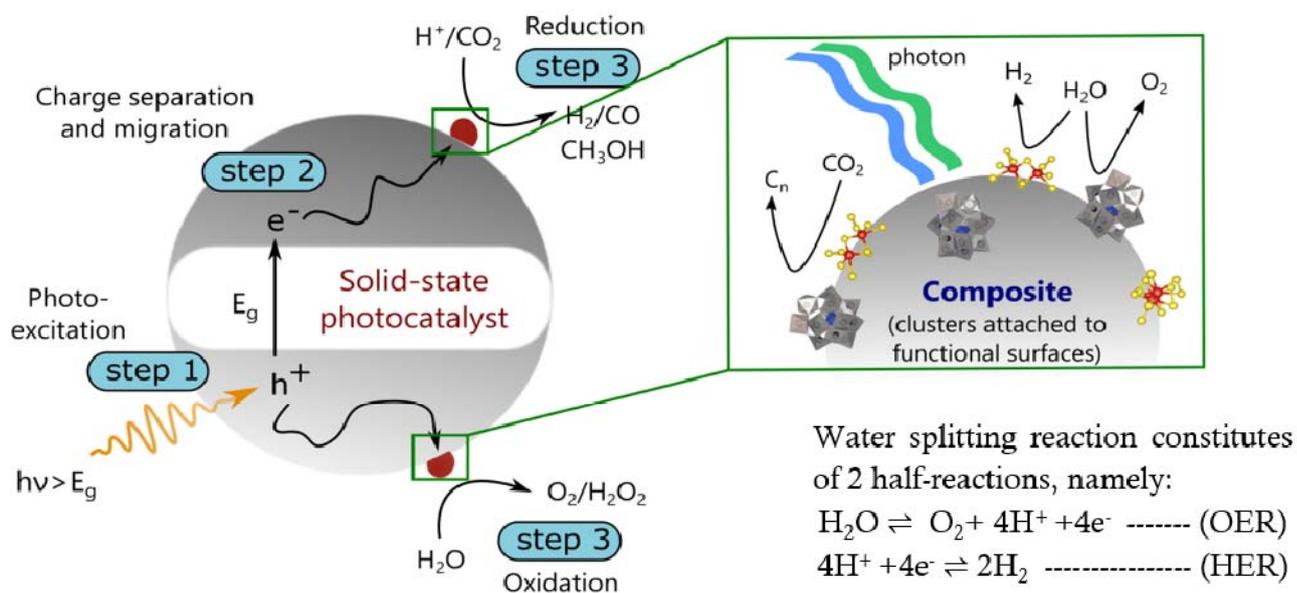


Figure 1: Schematic for heterogeneous photocatalysis and immobilization of the POM/PTM clusters on the surface (zoomed view)

I have carefully optimized immobilization protocols investigating attachment kinetics (how quick does the deposition occur) and loading degree (how much of the PTM can I put on the TiO₂ surface) as a function of solvent and PTM type. In this poster, I will demonstrate various HER experiments and the observation that the PTM-TiO₂ composites show an improved and stable activity towards HER over the benchmark reference TiO₂. These results confirm that functional properties of solid-state substrates (light absorption) and molecular compounds (catalytic activity) can be combined and even lead to synergistic functions (stabilization) demonstrating the feasibility of our approach. Most recently, I have started working on Co-based POMs for oxygen evolution reaction (OER) – necessary step for both CO₂ reduction and water splitting. Due to complex structure of these clusters, I am working on the development of novel attachment protocols to ensure formation of stable POM-substrate composites. I will also present a range of characterization techniques that we applied to study the resulting composites including SEM-EDX, XPS and ICP-OES.

CONCLUSION

Thus, electrostatic immobilization of POM/PTMs on TiO₂ nanoparticles have been accomplished and experimental data is shown on how efficiently these clusters can be utilized as co-catalysts in heterogeneous photocatalytic water splitting reactions. I will further work on (a) developing synthetic protocols for optimised immobilization of molecular oxo/thio clusters on photoactive substrates by covalent approach (b) conducting fundamental studies on interfacial processes and substrate effects, and (c) exploring their potential as high-performance PCs towards solar-to-fuel conversions

REFERENCES

- [1] D. Long et al. *Angew. Chem.*, 2010, 49, 1736
- [2] Q. Yin et al. *Science*, 2010, 328, 342
- [3] J. Kibsgaard et al. *Nat. Chem.*, 2014, 6, 248