How First Row Transition Metal Complexes Can Be Utilized to Improve Water Oxidation in (Photo)Electrocatalytic Hybrid Systems?

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Hydrogen is a promising chemical energy carrier that can be generated in a pure form relying on renewable energy sources by the splitting of water. The oxygen evolution reaction (OER), $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$, is arguably the most challenging process of the overall water splitting. Encouraging results were published about carefully designed Ru and Ir containing molecular water oxidation catalysts (WOCs) that combine unpaired efficiency with robustness. On the other hand, low-cost, robust and effective WOCs would rather require the use of the more abundant first row transition metals. While the high abundance and low cost of these metals is appealing, insufficient stability often hurdles their utilization.

Another important aspect is the immobilization of WOCs on (photo)electrodes aiming to create advanced hybrid systems that can combine efficient solar energy harvesting with high catalytic effectiveness. Grafting molecules to the surface through covalent interactions is typically achieved by synthetic modification steps that introduce anchoring groups on both sides. However, one needs to consider that structural changes are not always viable and may severely affect the overall performance, too. On the other hand, non-covalent immobilization through self-assembly and surface precipitation of the precursors, physical confinement, or electrostatic interactions represent alternatives that are worth considering.

In the presentation a few examples will be discussed on Cu- and Fe-based molecular WOC/semiconductor hybrids that are fabricated by simple and scalable methods. Ad-layers of the molecular WOCs can be made by exploiting hydrophobic interactions between the surface and the water-insoluble molecules. While this strategy is successful for a number of compounds, experimental results suggest that the composition of the ancillary ligand plays crucial role in determining the stability, activity and light-response properties of the assemblies. It will be discussed that water-insoluble ancillary ligands are able to aid the immobilization of molecular WOC candidates, but these ad-layers can behave very differently under the conditions of (photo)electrocatalysis in aqueous buffer.

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