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Accelerating the photocatalytic water splitting in catalyst-dye complexes

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Citation

Shao, Y. (2021, February 24). *Accelerating the photocatalytic water splitting in catalyst-dye complexes*. Retrieved from <https://hdl.handle.net/1887/3147173>

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Issue date: 2021-02-24

Summary

By utilizing freely available sunlight, DS-PEC devices split water into molecular oxygen, protons and electrons via four consecutive PCET steps at the photoanode, which combines sensitizers for visible light absorption and efficient WOCs for catalytic water splitting. The photocatalytic four-photon water oxidation half-reaction is a chemical challenge and often limit over the entire water splitting cycle. Better understanding of the catalytic mechanisms at the molecular level and in-depth exploration of the factors affecting the PCET processes are urgently needed at present in the field of artificial photosynthesis and will provide guidelines for engineering and optimization of high-performance DS-PEC devices for solar-driven water splitting. Computational simulations provide a powerful technique for the collection of convincing microscopic chemical engineering paradigms ahead of their experimental realization.

The whole photocatalytic water splitting cycle performed by a WOC–dye supramolecular complex in explicit water solvent is systematically explored in **Chapter 2**. The results indicate that the selected NDI dye is able to drive the whole catalytic cycle after photooxidation when properly coupled to the Ru-based catalyst. The first three catalytic PCET steps are all exothermic and the fourth catalytic step is barrier-less. The third catalytic step involving the O–O bond formation is confirmed to be the rate-limiting step because of the high activation energy barrier. For this step antiparallel spin alignment of unpaired electrons on the WOC and dye appears essential for the reaction to proceed well. The microscopic details provide strong evidence for the significant role of the rearrangement of solvent water molecules in facilitating the catalytic PCET processes. The in-depth insight in the photocatalytic water oxidation mechanism provides guidelines for the design and optimization of efficient photoanodes for DS-PEC devices.

Considering that the O–O bond formation process represents a thermodynamic and kinetic bottleneck in photocatalytic water oxidation, it is essential to find

strategies to lower the activation free energy barrier of the third catalytic step. **Chapter 3** elucidates how and to what extent the O–O bond formation process can be facilitated by tuning the solvent environment. The introduction of an additional OH[−] group as a proton acceptor in the hydration shell near the active site induces a cooperative event proceeding via a concerted PCET mechanism, which dramatically lowers the activation free energy barrier, and thus significantly accelerates the O–O bond formation. The mechanistic insight provides a flexible and simple strategy for facilitating the photocatalytic water oxidation and for improving the efficiency of DS-PEC devices.

To understand if and how nonadiabatic factors accelerate the PCET rate of the O–O bond formation, a series of WOC–dye supramolecular complexes functionalized with different alkyl groups on the catalyst component are investigated in **Chapter 4**. The structural modifications modulate not only the value of the dihedral angle at the WOC–dye linkage, but also the electronic structure of the supramolecular complexes and the characteristic frequencies associated with the electron transfer dynamics and the torsional motion around this link. These structural modifications then lead to tunable thermodynamic driving forces, PCET rates, and vibronic coupling with specific resonant torsional modes. Such resonant coupling between electronic and nuclear motions turns out to facilitate the crossing of catalytic barriers in PCET reactions by enabling semiclassical coherent conversion of a reactant into a product. These results provide a general and rational approach on how to engineer efficient WOC–dye supramolecular complexes for high-performance DS-PEC devices from a structural design perspective.

In **Chapter 5**, the photocatalytic water oxidation process driven by a dye–WOC–dye supramolecular complex in explicit water solvent is investigated. The introduction of the second NDI dye provides an extra electron-transfer channel, *i.e.* a two-channel model for ET, allowing for the concurrent transfer of two electrons in different directions from the WOC to the two oxidized dyes separately. The third and fourth catalytic steps are observed to proceed consecutively without stable intermediates in between, leading to a five-step catalytic cycle. The total spin $S = 1$ is conserved during the catalytic process, and the system proceeds from the Ru=O intermediate to the final Ru–O₂ intermediate with a triplet molecular O₂ ligand that is eventually released into the environment.