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Accelerating the photocatalytic water splitting in catalyst-dye complexes

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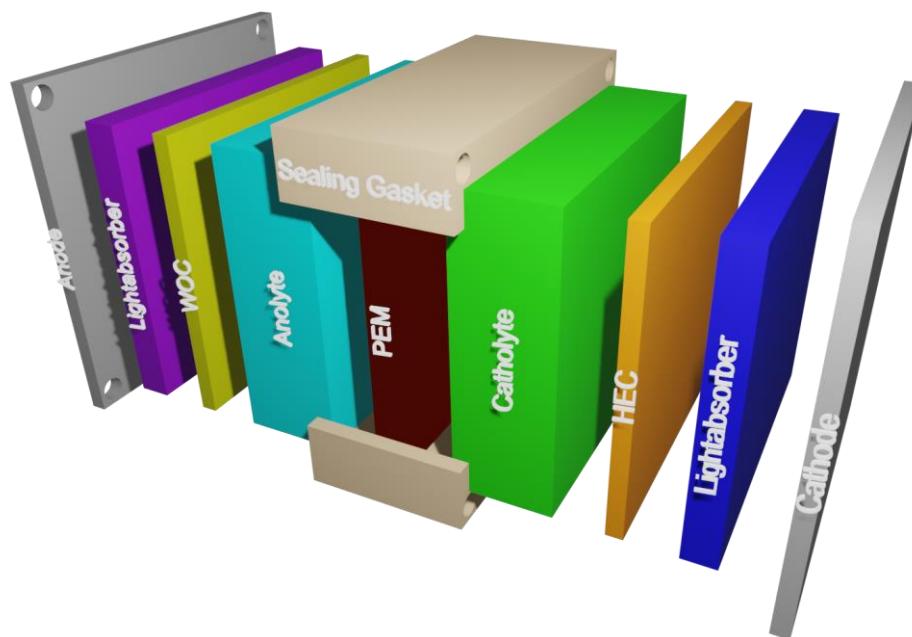
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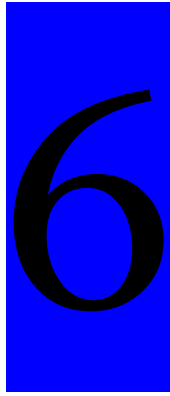
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CHAPTER 6

Conclusions and Outlook





6.1. Conclusions

As a virtually inexhaustible source, solar energy plays a major role in future global energy scenarios. Solar-driven water splitting via DS-PEC devices is a scalable, affordable and sustainable technology of great potential for direct conversion of solar energy into storable chemical fuels to produce clean, cost-efficient and environmentally friendly H₂ or CO₂-derived fuels and thus to contribute to the transformation of a sustainable society from the blueprint to reality. However, to improve the overall yield of the photocatalytic water splitting is a challenge. It is limited by the water oxidation half-reaction, which consists of four catalytic PCET steps. In particular the third PCET step involving the O–O bond formation is difficult, which impedes the development towards commercialization and large-scale terrestrial implementation of DS-PEC devices.

Although rate enhancement has been experimentally realized in catalytic water oxidation to a limited extent via the engineering of novel WOCs, as well as fine-tuning of the solvent environment, the intrinsic mechanisms at the molecular level along the reaction coordinate are obscured in ensemble measurements, in particular for systems driven by WOC–dye supramolecular complexes. To further facilitate the reaction, it is necessary to elucidate beforehand key factors determining the rate of predominant catalytic processes. Computational studies serve as a very useful tool complementary to experiment, play an important role in providing an accurate and detailed microscopic description of the nuclear and electronic dynamics for the catalytic processes along the reaction coordinate, can predict the free energy profile from reactant to product, and provide an in-depth understanding of the intrinsic catalytic mechanisms.

The explicit aim of this thesis is to provide an in-depth understanding of the catalytic mechanisms for the water oxidation half-reaction in WOC–dye supramolecular complexes and to find rational strategies to facilitate the involved catalytic reactions. The computational methods used to reach this goal are DFT calculations and DFT-based molecular dynamics (AIMD) simulations. This thesis is divided into three parts: (i) **Chapter 2** elucidates the catalytic mechanism along the whole photocatalytic water splitting cycle by a Ru-based WOC–dye supramolecular complex; (ii) **Chapters 3** and **4** provide flexible strategies for facilitating the photocatalytic water oxidation, specifically the rate-limiting third catalytic step involving the O–O bond formation; (iii) **Chapter 5** proposes a Ru-

based dye–WOC–dye supramolecular complex with two separate electron-transfer channels for the photoanode of DS-PEC devices and explores the proposed photocatalytic water splitting cycle. More specifically, the rate enhancement in **Chapter 3** is achieved by tuning the solvent environment, whereas in **Chapter 4** by ligand modification on the catalyst component.

An ideal dye should meet the stringent requirements of absorbing a significant fraction of the visible spectrum and having at the same time an appropriate redox potential to drive the whole catalytic water oxidation cycle when coupled with an efficient WOC. In **Chapter 2**, the whole visible light-driven photocatalytic water splitting cycle performed by the WOC–dye supramolecular complex $[\text{Ru}^{\text{II}}(\text{H}_2\text{O})]^{2+}$ –NDI in explicit water solvent is systematically explored by means of CPMD simulations at room temperature, in which we consider all possible spin alignments between unpaired electrons on the WOC and on the oxidized NDI⁺. It is demonstrated that the selected NDI dye is a promising dye sensitizer to integrate in a DS-PEC device since it is able to sufficiently drive the whole catalytic cycle after photooxidation when properly coupled to the Ru-based catalyst. The predicted activation free energy barriers indicate that the first three catalytic PCET steps are all exothermic and the fourth catalytic step is barrier-less after photooxidation of the NDI dye. The third catalytic step involving the O–O bond formation is confirmed to be the rate-limiting step because of its considerably high activation energy barrier. Furthermore, the coupled electron and proton dynamics together with the solvent rearrangement during the cycle are followed to elucidate the catalytic mechanism of the four consecutive catalytic PCET steps. This analysis provides strong evidence for the significant role of spin alignment and solvent rearrangement in facilitating the catalytic PCET processes. The importance of solvent environmental tuning in the acceleration of the third catalytic PCET process is investigated in detail in **Chapter 3**. The results presented in **Chapter 2** expand the current understanding of the photocatalytic water oxidation mechanism and provide guidelines for the optimization of high-performance DS-PEC devices.

Since the O–O bond formation process via water nucleophilic attack (WNA) has emerged in **Chapter 2**, in line with previous literature, as the thermodynamic and kinetic bottleneck in photocatalytic water oxidation, it is of fundamental significance and yet challenging to find strategies to facilitate this reaction.

Motivated by the crucial role of the solvent environment emphasized in **Chapter 2**, one additional charged OH^- group is introduced as a proton acceptor in the hydration shell near the catalytic active site to demonstrate the effect of varying charge and proton chemical potential in **Chapter 3**. In this way it is possible to resolve how and to what extent the O–O bond formation process is facilitated by tailoring the solvent environment. Since the same WOC–dye supramolecular complex considered in **Chapter 2** and **Chapter 3**, the results obtained are quantitatively comparable. The explicit solvent and dynamic description obtained with the adiabatic DFT-MD simulation approach reveals that the presence of a proton acceptor (OH^-) induces a cooperative event proceeding via a concerted PCET mechanism, dramatically lowers the activation free energy barrier, and thus significantly accelerates the O–O bond formation. The mechanistic insight into facilitated O–O bond formation process provides a strategy for the improvement of the performance of DS-PEC devices by straightforward tuning of the environment.

Since coherence in the electronic and nuclear motion has been suggested to play a role in electron transfer processes in both natural and artificial systems, which appears indistinctly in **Chapter 2** as well, it is essential to understand if and how resonant coupling can accelerate the rate-limiting O–O bond formation process in catalytic water oxidation. In **Chapter 4**, structural modifications in a series of WOC–dye supramolecular complexes functionalized with different alkyl groups on the catalyst component are found to modulate the value of the dihedral angle at the WOC–dye linkage. This affects the electronic structure of the supramolecular complexes, the characteristic frequencies associated with the electron transfer dynamics, and the torsional motion around this link. The frequency tuning leads to a resonance condition that increases the coupling between electronic and nuclear motions and facilitates the ET step from the WOC to the oxidized dye in the region of the crossing of reactant and product states. The computed free energy profiles for this PCET reaction show a considerable decrease in activation energy and increase in the driving force. We expect that the in-depth insight into the acceleration of this specific catalytic water oxidation step provides a general and rational engineering approach for the improvement of the performance of DS-PEC devices from a structural design perspective, which can also be achieved by modifying other ligands around the connecting region or

replacing the linker between WOC and dye.

To make the utmost of solar energy, a two-channel model for ET in a dye–WOC–dye supramolecular complex for photocatalytic water splitting is proposed in **Chapter 5**, in which a Ru-based water oxidation catalyst (WOC) is covalently bounded to two NDI dyes. Compared to the one-channel model described in **Chapter 2**, the introduction of the second light-harvesting dye in the dye–WOC–dye complex enables two parallel electron-transfer channels, which theoretically allows for concurrent ET events from the WOC to the two separate oxidized dyes. The realistic and dynamical description of the proposed photocatalytic cycle of the two-channel model obtained with constrained AIMD approach demonstrates that the third and fourth catalytic steps can proceed consecutively without stable intermediates in between, as well as the coupled first and second catalytic steps, leading to a five-step catalytic cycle with three intermediates and two doubly oxidized states, whereas the one-channel model presented in **Chapter 2** follows a nine-step cycle. Two intermediates of the WOC–dye complex in the one-channel model become transients in the two-channel model. In addition, intermediates, oxidized states, and transients for the combined first half and second half of the catalytic cycle are all exhibiting a spin multiplicity of 3, leading to triplet oxygen to be released without the need for *e.g.* intersystem crossing between configurations with different overall spin multiplicity. Thus, electronic spin appears a conserved quantity along the reaction coordinate of the water oxidation process. The in-depth insight into the proposed photocatalytic cycle of the investigated two-channel model provides a strategy for the improvement of the overall efficiency of DS-PEC devices from the perspective of reaction intermediate reassignment, sequence rearrangement and conservation of spin multiplicity.

6.2. Outlook

Thanks to the predictive power of CPMD simulations, the underlying reaction mechanisms of the photocatalytic water oxidation processes have been well elucidated in this thesis, especially for such a large system containing a WOC–dye supramolecular complex and explicit description of the water solvent. Although strategies for facilitating the O–O bond formation in catalytic water oxidation have been provided in **Chapters 3** and **4**, a considerable gap exists between theoretical/experimental proofs and large-scale implementation. Efforts in the development of novel DS-PEC devices will continue in the future with the main focus remaining on the understanding of factors limiting the overall efficiency of solar-to-fuel conversion and the search of rational strategies for accelerating the photocatalytic water oxidation. Luckily, computational techniques will act as a tempting, powerful but inexpensive tool on this long discovery journey from empirical to informed approaches.¹

To achieve the final goal of near-unity yield in photochemical water oxidation, considerable work needs to be done by forthcoming computational studies, part of which is likely to go in several potential directions of great interest and importance:

- I. Charge recombination from the semiconductor into the oxidized dye is a main factor limiting the quantum yield of the whole photocatalytic water splitting process,²⁻³ which is not covered in this thesis. It might be interesting to include the catalytic water oxidation process and at the same time the electron injection in one MD simulation to address the competition between the ET from the WOC to the oxidized dye and the charge recombination from the semiconductor to the oxidized dye, although it is challenging due to the different time scales of the processes occurring upon photoexcitation.⁴
- II. In **Chapter 3**, we specifically use the OH⁻ group as a conceptual example, but this can be easily replaced by other proton acceptors with different proton charge ratio, such as OAc⁻, HPO₄²⁻, PO₄³⁻.⁵⁻⁷ The ones that would be less detrimental to the WOC stability are more desirable. In addition, assembly strategies similar to a solid-state water electrolysis cell with alkaline membranes might be interesting to be employed as a design strategy for a DS-PEC architecture, in which the OH⁻ ions are transported to the catalyst layer

through the anion exchange membrane and act as proton-withdrawing groups to facilitate the O–O bond formation.⁸

- III. Recently, we have found convincing evidence that Nonadiabatic Conversion by Adiabatic Passage involving resonant coupling of reactant and product states is important for energy transfer and separation of charges,^{9–11} which is also corroborated by the results presented in **Chapter 4**. To further unveil the nonadiabatic effects that can accelerate the PCET process in WOC–dye supramolecular complexes in a more direct way, it might be interesting to calculate the nonadiabatic coupling between reactant and product electronic states with existing approaches¹² or methods to be developed to enable quantitative evaluation.
- IV. For an integrated solar-driven DS-PEC device, the overall solar-to-fuel conversion efficiency depends not only on the material properties of all the individual components but also on the device design. Multiphysics simulation software can represent a powerful tool for the prediction of device efficiencies, the operating conditions, and the evaluation of novel device architectures and concepts.^{13–14} A combination of microscopic and macroscopic modelling and simulation might be interesting for the design and improvement of DS-PEC devices, in which DFT and AIMD calculations provide estimates of crucial parameters to be used as input in macroscopic modeling. In these operating conditions one could understand how properties at the molecular level can determine the overall performance of integrated systems at the device level.

6.3. References

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