Coupled electronic and nuclear dynamics at interfaces of artificial photosynthesis devices

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Chapter 1: Introduction

Solar-to-fuel production stands as a promising strategy to reduce CO_2 emissions from fossil fuel combustion. However, the realization of devices that can effectively store solar energy into chemicals has proven to be difficult. This chapter highlights some of the challenges in this field and places the contents of this dissertation in a broader perspective.

1.1 Dye-Sensitized Photoelectrochemical Cells

Fossil fuel combustion has been identified as a major driver for human-induced global warming, creating urgent need for alternative energy sources and effective means of energy storage.[1–3] Solar light offers an unparalleled energy resource, with an hourly global flux sufficient to meet the world annual energy demand.[4] Over the last decades, highly efficient photovoltaic (PV) cells have been developed[5], which nowadays supply a substantial share of consumed electricity.[3] Nevertheless, the discontinuous supply of solar energy necessitates large-scale energy storage solutions if we aim to fully transition to solar power.

While batteries are promising for many applications, their heavy weight and limited capacity prompt a need for innovative energy storage technologies. One strategy is to perform electrolysis using green electricity to generate hydrogen or carbon-based fuels. However, this decentralized PV plus electrochemical approach is costly and the photon to product yield is intrinsically limited by concentration and overpotential losses.[6,7]

Inspired by natural photosynthesis, researchers have been investigating the possibility of storing solar energy directly into chemical bonds. Ideally, one would like to mimic algae and plants by using sunlight to convert water and carbon dioxide into hydrocarbons with a high energy-density. Through billions of years of evolution, the natural photosynthetic system achieves this transformation with remarkable efficiencies, but reproducing these efficiencies in an artificial setting and at a meaningful scale remains challenging.[4,8]

The first photoelectrochemical cell for water splitting was developed in the early 70s by Fujishima and Honda, who employed TiO_2 as a photoanode.[9] Although their system was capable of driving hydrogen evolution, the wide TiO_2 bandgap of 3 eV firmly restricted the range of the solar spectrum that they could capture, lowering the cells efficiency. In addition, the catalytic activity of TiO_2 towards water oxidation is sluggish compared to molecular catalysts developed in recent years.[10–14]

Nature employs a sophisticated assembly of molecular pigments, proteins, enzymes and co-enzymes, each individually optimized and interlinked to efficiently capture photons and use that energy to oxidize water and reduce CO_2.[15,16] Dye-sensitized photoelectrochemical cells (DS-PEC), mimic this functional separation in specialized units, thereby overcoming some of the fundamental limitations encountered in early water splitting devices. The photon absorption, water oxidation, proton reduction, and charge separation and transport, are addressed by separate chemical components or materials that can be tailored to meet desired criteria.[17] A schematic overview of a DS-PEC is provided in Figure 1.1.

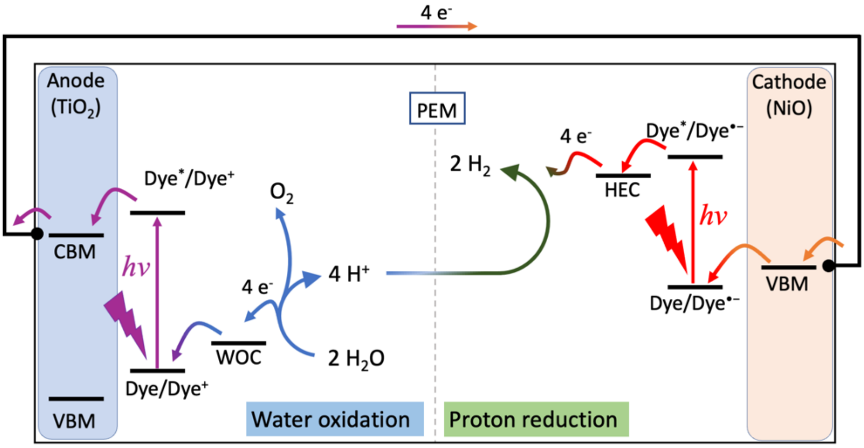

Figure 1.1. *Schematic overview of a tandem dye-sensitized photoelectrochemical cell (DS-PEC) for water splitting. Photoexcitation of the dye at the cell's photoanode results in electron injection into the* TiO_2 *conduction band (CBM stands for conduction band minimum, while VBM stands for valence band maximum) and the resulting hole is used to drive the OER in a water oxidation catalyst (WOC). The obtained protons and electrons are transported to the photocathode through the proton exchange membrane (PEM) and through a conducting medium attached to the* TiO_2*, respectively. Excitation of the photocathode dye generates additional reduction potential, which provides a driving force for the hydrogen evolution catalyst (HEC) to produce hydrogen. For*

clarity, the energy level heights are depicted schematically; however, the actual water-splitting process requires 1.23 eV under standard conditions (pH = 0).

DS-PECs are composed of two compartments separated by a proton-exchange membrane (PEM). These membranes are designed such that they can conduct protons while keeping the produced hydrogen and oxygen separated.[18] At the cell's photoanode, sunlight is absorbed by a dye molecule (see Figure 1.1, purple photon absorption). Upon photoexcitation, an electron is injected from the excited dye (dye*) into the conduction band (CB) of an *n*-type semiconductor, typically TiO_2. This process leaves an electron hole on the oxidized dye (dye$^+$) molecule, which then transfers to a water oxidation catalyst (WOC), where it drives water oxidation. Through four consecutive photoinduced oxidation steps, water is converted into O_2 four protons and a reduction potential in the form of four electrons. The electrons and protons are transferred to the cathode side of the DS-PEC, where they are used to generate hydrogen by a hydrogen evolution catalyst (HEC) or reduce CO_2 to produce carbon-based solar-fuels (Figure 1.1).

Early DS-PEC devices for water splitting employed dark cathodes that do not absorb a second photon to drive the hydrogen evolution reaction (HER). In these cells, solar harvesting is limited to the UV spectrum, and a small additional potential is often required to drive the HER catalysis.[4,19–21] Tandem DS-PECs overcome these limitations by using dye-sensitized p-type semiconductors. Ideally, the cathode dye absorbs at a higher wavelength than the anode dye, thereby capturing a broader range of the solar spectrum (see Figure 1.1, red photon absorption).

Despite the great potential of DS-PECs, current devices are still severely limited in their photon-to-fuel efficiency. A major reason for this poor performance is the considerable energy loss due to electron-hole recombination after photoexcitation of the dye. To have efficient charge separation at the dye-catalyst interface, the catalyst needs to operate at high turnover frequency with low the chemical conversion barriers. Additionally, it is critical that the photoexcited dye* injects charge efficiently into the semiconductor surface. Although these topics are active areas of research, mechanistic insights in these photoinduced processes are still limited for many systems.

The aim of this thesis is to gain insights into charge transfer phenomena at dye-semiconductor and dye-catalyst interfaces and to better understand the catalytic mechanisms of specific WOCs and HECs. The coupling between nuclear and electronic motion is a central and common theme. Several chapters of this thesis include experimental collaborations. The important role of molecular dynamics simulations and density functional theory calculations in complementing and clarifying experimental data is evident. The following section provides an outline of this thesis.

1.2 Outline of the thesis

An extensive theoretical background is provided in **Chapter 2** of this dissertation. Starting from the Born-Oppenheimer approximation, the basic principles of molecular dynamics calculations and thermodynamics are explained. The discourse then extends to excited states, and finally density functional theory (DFT) and time-dependent density functional theory (TD-DFT) are discussed.

Chapter 3 investigates the catalytic cycle of a supramolecular [Ru-bda]-dye complex using DFT-based Born-Oppenheimer molecular dynamics. The performed simulations shed light on the equilibrium dynamics of the low-valent Ru^{III}-bda intermediate and further investigate whether this specific Ru-based WOC is efficient also following the water nucleophilic attack mechanism.

Because the proton-coupled electron transfer (PCET) steps that constitute the photocatalytic water oxidation cycle can involve non-adiabatic effects, it is interesting to investigate these reactions while considering several electronically excited states.[22–24] **Chapter 4** maps out the electronic reactant and product states for two key reaction steps in two supramolecular dye-catalyst complexes. It is shown that these PCET reactions evolve through a reaction path where the two states get very close in energy and are strongly coupled. Based on these results, a strategy is suggested to dramatically accelerate the PCET processes by optically populating a specific electronic state.

Another challenging aspect of DS-PEC's is that the oxygen evolution reaction (OER) and HER typically proceed in acidic and alkaline conditions, respectively. HER catalysts that perform efficiently at high pH conditions are limited, and known examples rely heavily on rare metals such as platinum.[25] Therefore, further research into catalysts based on earth-abundant materials that perform well in alkaline media is warranted.[26,27] **Chapter 5** of this thesis presents a combined theoretical and experimental investigation into photocatalytic hydrogen formation catalyzed by a series of cobalt porphyrin complexes. It was shown that through synthetic modification of the catalyst with electron withdrawing groups, the charge density on the cobalt metal center could be controlled. Interestingly, the catalysts with low electron density on the metal preferred to catalyze the HER via the ligand rather than the metal. In alkaline to neutral conditions, the ligand-based catalysis appears considerably more efficient than the metal-based catalysis, effectively opening a new avenue for HER catalyst design.

As mentioned above, dye-semiconductor interfaces present an important aspect in DS-PEC design. Tandem cells are presently limited by poor hole-conductance of the p-type semiconductor materials. Therefore, insights into the photoinduced hole-injection process, from the dye* into the semiconductor surface, are highly desirable. **Chapter 6** presents a combined theoretical and experimental study into the charge transfer dynamics at the P1/NiO interface, which serves as a benchmark for dye-sensitized photocathodes. Through means of quantum-classical molecular dynamics simulations and transient absorption (TA) spectroscopy, it was shown that the hole-injection dynamics are affected considerably by the thermal nuclear motion of the dye. In addition, two different surface species were identified and tentatively assigned to dye molecules either standing perpendicular or parallel to the surface. These results provide valuable insights that can inform the design of future DS-PECs.

The idea that electronic and nuclear dynamics are strongly coupled is a recurring theme in this dissertation. While the first chapters show that these coupled dynamics are important in the context of artificial photosynthesis, the importance of this coupling emerges also in vibrationally resolved spectroscopy. Low-temperature spectroscopy of single molecules can provide highly resolved spectra with very sharp 0-0 zero phonon lines (ZPL), up to a few tens of megahertz in width. Recently, it was shown that hexagonal boron nitride (hBN) can be used as a host matrix for fluorescence spectroscopy studies of single-molecules of terrylene.[28] Interestingly, a fraction of the molecules displayed considerable redshifts in their 0-0 ZPL and showed very weak vibronic coupling. These features, in combination with the very high sensitivity of these fluorescence spectra to the chemical environment of the dye molecule, render the reported terrylene/hBN system promising for applications in quantum technologies and quantum sensing.[29,30] These promising applications make a deep understanding of the physics behind the observed phenomena highly desirable. **Chapter 7** of this thesis presents a combined theoretical and experimental study of terrylene molecules adsorbed on hBN. It is shown that the redshift of the 0-0 ZPL and the reduced vibronic coupling can be explained by terrylene chemisorption on specific charge donating defect sites in hBN. These insights provide a strategy for the design of material-molecule interfaces which can emit photons with extremely narrow lines at highly specific wavelengths.

Chapter 8 presents an outlook, in which the conclusions of this work are summarized, and future lines of research are suggested. Special emphasis is placed on the systems discussed in chapter 3 and chapter 4 of this thesis. In chapter 4 it was proposed that populating the electronic product state in the studied dye-catalyst complex could accelerate the key catalytic step in the water oxidation cycle. This hypothesis has been further explored through excited state surface-hopping simulations. These simulations show that population of the electronic product state is indeed accompanied by ultrafast proton transfer, suggesting a promising avenue for increasing the rate of water oxidation in dye-catalyst systems.

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