

Summary

Dye-sensitized photoelectrochemical cells represent a highly promising technology for the production of solar fuels via light-driven water splitting as an integral part of a carbon-neutral economy. In that context, the design of more performant dye-catalyst assemblies is highly demanded as they should allow to precisely control over the excited state processes, especially ET. However, detailed investigations on the light-induced processes of dyad-sensitized photocathodes under operando conditions are scarce in the literature, and few studies have addressed in depth the degradation processes in those photocathodes.

Therefore, this work aimed at providing a comprehensive understanding of the performances of hydrogen-evolving DSPC based on a series of molecular dye-catalyst assemblies varying by the nature of the dye and the catalyst, including the elucidation of the systems' weak points and bottlenecks for hydrogen production. To this end, a full characterization of the photoelectrochemistry and activity of the photocathodes was combined with the study of the excited state processes both in solution and on films to gain a full understanding of the systems and their performance-limiting factors. Especially important was the determination of the lifetime of the CSS and the kinetics of the ET to the catalyst unit. The mainly studied compounds were a series of four noble-metal free dyads which varied in the nature of the push-pull organic dye (**T1** or **T2R**) and in that of the catalyst for proton reduction (**Co** or **Cat1**). Assessing the activity of all four combinations enabled the determination of each part's contribution to the overall performance and therefore to link the molecular structure to the activity of the system. The elucidation of such a structure-activity relationship is important to be able to rationally improve the molecular structure of the dyads. The best-performing system **T2R-Cat1** was studied in detail, notably including the excited state processes at applied potential by transient absorption spectroelectrochemistry (TA-SEC) and post- and in-operando measurements to determine the deactivation pathways and kinetics. In addition, NiO photocathodes sensitized with a Ruthenium-cobalt dyad were studied by TA-SEC for comparison.

The first important part of the work was to investigate the photophysics of the organic dyes and dyads in solution using TA spectroscopy and TA-SEC, i.e. at different applied potentials. The **T1-Co** dyad showed no excited state electron transfer was observed despite emission quenching and reduced excited state lifetime in the dyad

compared to the dye. The **T2R**-based dyads, in contrast to **T1-Co**, showed rapid



intersystem crossing to the long-lived excited triplet state of the dye, induced by an interaction of the rigid cyclopentadithiophene bridge with the cobalt catalyst. This study showed how the interaction of different structures in a dye-catalyst assembly can lead to unexpected excited-state behaviour, which needs to be taken into account in the design of dye-catalyst dyads.

As part of the work on dye-sensitised photocathodes, NiO films sensitised with **RuCo** were investigated using TA-SEC to study the light-induced processes in the dyad and the potential dependence of the interfacial processes such as hole injection and charge recombination. For this purpose, a special spectroelectrochemistry cell was designed that enabled femtosecond TA experiments on films with a precise applied potential under inert conditions, allowing the analysis of the potential dependence of the interfacial processes and the observation of a dramatic increase in the lifetime of the charge-separated state. In spite of this long-lived state, no electron transfer was observed, which explains the low activity of the system.

The organic dyads with the new **T2R** dye and **Cat1** catalyst showed significantly improved hydrogen production compared to **T1-Co**, which is mainly explained by the higher stability of the catalyst. Post-operando and in-operando measurements showed that the dye decays under operando conditions, and the kinetics of this decay could be determined. TA-SEC measurements showed a similar potential dependence as for **RuCo**, but electron transfer could be observed for this system, confirming the higher activity of the system. However, the electron transfer to the catalyst was not quantitative, leading to charge accumulation on the reduced dye and ultimately to its degradation. Therefore, an improved molecular design of the dyad that ensures rapid and quantitative electron transfer to the catalyst should solve both the problem of low activity and reductive degradation of the dye moiety.

This dissertation thus provides important insights into the light-induced processes in NiO photocathodes sensitised with dye-catalyst dyads and their dependence on the applied bias voltage, together with an evaluation of the photocathode performance and deactivation processes and their kinetics. The knowledge gained about the weak points of the systems, in particular the very inefficient electron transfer from the dye to the catalyst and the reductive degradation of the organic dye units, will help to develop dyads with improved activity and stability.