

## 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 lightinduced 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

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



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

