

Summary

This thesis examines the design, construction, and application of novel reactors that merge light, electricity, and flow chemistry as efficient, scalable platforms for producing fine chemicals and fuels. The work can be divided into two main research lines. In the first part (**Chapters 2-3**), the focus is on electrophotocatalytic transformations and the use of the newly built reactor for the synthesis of fine organic molecules. In the second part (**Chapters 4-5**) the reactor is modified into a photoelectrochemical platform for fuel production.

In **Chapter 2**, we reported the successful development of an efficient flow electrophotocatalytic (*f*-EPC) reactor. Unlike earlier designs, our new flow reactor concept simultaneously accommodated photons and electrons in the microchannel, enabling control over short-lived intermediates. The *f*-EPC platform proved compatible with photochemical, electrochemical, and electrophotocatalytic transformations and was particularly effective for forging C(sp³)-N bonds. The synthetic protocol merges hydrogen atom transfer photocatalysis with electrochemically induced radical-polar crossover and operates under remarkably mild conditions, permitting functionalization across a broad substrate scope and enabling late-stage functionalization of drug-like molecules. The electrophotochemical heteroarylation proceeds at room temperature, requires no external oxidants, and features short reaction times, yielding higher productivity than existing protocols. To enhance the applicability of this approach, subsequent research should concentrate on developing more efficient catalytic systems that enable electrophotocatalysis to be performed at inert C(sp³)-H bonds.

In **Chapter 3**, we described an oxidant-free electrophotocatalytic route for the direct coupling of aldehydes with *N*-nucleophiles. This C(sp²)-N bond-forming approach was achieved by simultaneously harnessing photons and electrons in a batch reactor. Product formation follows an electrochemically induced radical-polar crossover mechanism coupled to hydrogen atom transfer photocatalysis and occurs under notably mild conditions. The method supports functionalization across a wide range of substrates and is amenable to late-stage modifications relevant to drug development. Electrophotocatalytic amide formation takes place at room temperature, requires no external oxidants, and its overall productivity could be further enhanced using flow systems. To improve the relevance of this methodology, future endeavors should focus on developing more efficient catalytic systems that enable electrophotocatalysis to be performed at lower potentials. As a result, the overall conditions will be milder, paving the way for functionalization of more sensitive molecules, like free amines or other pharmaceutically relevant compounds.

In **Chapter 4**, we presented a modular flow dye-sensitized photoelectrochemical cell (*f*-DSPEC) for efficient light-to-chemical conversion to value-added products, while simultaneously generating fuels. Through deliberate engineering of mass and charge transport, using a narrow interelectrode gap, a flow-guiding path, and optimized flow conditions, the reactor overcomes limitations of batch DSPECs and achieves substantially enhanced photocurrent densities and product throughput. Benchmarking with benzyl alcohol oxidation demonstrated an increase in productivity relative to previous batch DSPECs, while maintaining high Faradaic efficiencies. Incorporation of phosphonic-acid-functionalized dyes improved photoanode stability during extended operation. Future development should prioritize new materials that deliver more efficient and durable photoanodes; with such advances the *f*-DSPEC is positioned as a scalable, versatile platform for solar-driven chemical

synthesis, with applications in both fuel production and green chemical manufacturing.

In **Chapter 5**, we described the design and construction of a modular flow photoelectrochemical cell (*f*-PEC) capable of using absorbed light to convert water into hydrogen and oxygen. Benchmarking with BiVO₄ photoanodes for water oxidation revealed a strong dependence of reactor performance on the photoanode properties and on engineered reactor components. The addition of an electrocatalyst enhanced both stability and efficiency, while the introduction of microfluidic channels was critical for efficient gas collection. The reactor operated stably over extended periods, indicating the feasibility of a future scale-up. Nonetheless, targeted redesign of the electrode and membrane components is required to raise Faradaic efficiencies and enable large-scale production of hydrogen free of O₂ contamination.

In conclusion, the contributions described in this thesis establish design principles and practical implementations for photoelectrochemical flow reactors, showing both synthetic versatility and promising routes to scalable solar fuel generation. At the same time, this work identifies key avenues for further improvement: the development of more active and selective catalytic systems to broaden electrophotocatalysis to inert substrates and to operate at lower potentials, the discovery of more efficient and durable photoanode materials, and targeted redesign of electrode and membrane components for scalable hydrogen production. By combining conceptual advances in reaction design with pragmatic reactor engineering, this thesis lays a foundation for future efforts to translate photoelectrochemistry from laboratory demonstrations into industrially relevant technologies for fine-chemical synthesis and sustainable fuel production.