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Enlightening chemical processes

Photochemistry in flow as tool for sustainable syntheses

Quick Facts

- sustainable alternative to thermal chemistry
- customized reactor types with high-power LEDs
- inorganic solids and high-performance dyes as photocatalysts
- sustainable by light

Photochemistry in general describes the physical and chemical processes of material conversion initiated by the absorption of photons, often performed at or close to room temperature and under normal pressure. Under such sustainable and environmentally friendly conditions, reagents and follow-up products can be obtained which are rarely available via thermal treatment. This alternative draft for doing chemistry with light power of appropriate wavelength as the only activation energy is another step forward to understand and implement *Green Chemistry* principles.[1]

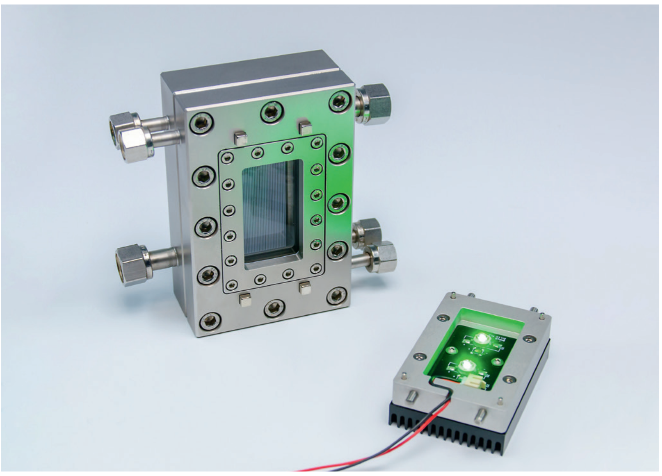
Why photochemistry in flow?

With the advent of photochemically catalyzed reactions, every experimenter has to face up to the special challenges of applied photochemistry. Prolonged irradiation of the reaction volume in a standard 10 ml quartz glass flask can also lead to product degradation while achieving full conversion. Commonly used high power mercury lamps often need expensive filter equipment and an efficient heat management to avoid undesired thermal reaction pathways.

Advancing photochemistry with flow and LED technology
Both technological challenges can be solved by applying microstructured reactor equipment in conjunction with LED technology. Such microreactor systems combine several advantages in a single architecture [2]:

- accurate spatial and time control with full illumination of thin liquid streams inside a microchannel or a capillary of defined length
- improved heat management of small reaction volumes
- energy efficient LED technology allows reaction specific and nearly monochromatic emission of defined wavelengths from UV over visible light to near-IR
- improved assembly of small LED emitters to LED arrays for many microreactor architectures

Reactor types for photochemical conversions
The Falling Film Microreactor (FFMR) has been introduced for photochemical reactions. The reaction plate as FFMR key component can produce very thin liquid streams with a thickness of some 10 micrometers. Full illumination of the liquid thin film is possible as well as a highly efficient diffusion of reactant gas, e.g. oxygen, into the thin liquid film. Several methodologies also allow the fixation of heterogeneous photocatalysts onto the microchannel walls, e.g.:



- TiO_2
- ZnO
- Bi_2O_3
- $BiVO_4$
- boron-doped diamond

In addition, homogeneously dissolved organic sensitizers and organometallic complexes can be applied as well:

- organic high performance dyes like Rose Bengal, Eosin Y, riboflavins, porphyrins, perylene diimides, …
- organometallic complexes with Ir, Ru, Cu, …

The FFMR can be equipped with several LED arrays of different emission wavelengths, which can be easily exchanged due to a customer-friendly magnetic holder system:

- UV-A: 365–395 nm
- visible light: 405–630 nm
- white light: 2700–6500 K

For scale-up approaches, the FFMR-LARGE has been adapted as well for photochemical applications with a ten-fold increase in flow rate up to 10 ml/min.

As a second reactor type, the Capillary Photoreactor has been introduced for photochemical reactions with a capillary wrapped around a central light source. Here, exchangeable arrays of water-cooled high power LEDs are available. Two capillary layers are installed, which can be used either separately or in series for a prolonged residence time in the Capillary Photoreactor. Capillary cooling was implemented as well, which allows an exact temperature control of the photoreaction. The Capillary Photoreactor can be used for liquid and gas-liquid reactions, making this design also a scale-up alternative to the FFMR-LARGE. Just recently, the Capillary Photoreactor has been also extended to the use of solid photocatalysts suspended in a gas-liquid stream inside the capillary.

Our portfolio of applications for flow photochemistry

- *in situ* generation of singlet oxygen [3]
- photooxidation
- *cis-trans* isomerization
- fluorination
- cyanation
- carbon-carbon bond formation via diazonium chemistry [4]

Services and benefits

Our services in the field of photocatalysis

- feasibility studies to understand your needs
- transfer of your batch process to continuous flow mode
- development of your unique flow reactor for your needs
- dedicated plant development as blue print for your future process

Your benefit

We offer you a one-stop service including the entire development chain from batch to flow process testing with reactor and plant development for your dedicated flow photochemistry equipment.

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1 Thomas H. Rehm, Chem. Eur. J. 2020, 26, 16952-16974. | **2** Thomas H. Rehm, ChemPhotoChem, 2020, 4, 235-254. | **3** Thomas H. Rehm, Sylvain Gros, Patrick Löb and Albert Renken, React. Chem. Eng., 2016, 1, 636-648. | **4** David C. Fabry, Yee Ann Ho, Ralf Zapf, Wolfgang Tremel, Martin Panthöfer, Magnus Rueping and Thomas H. Rehm, Green Chem., 2017, 19, 1911-1918.