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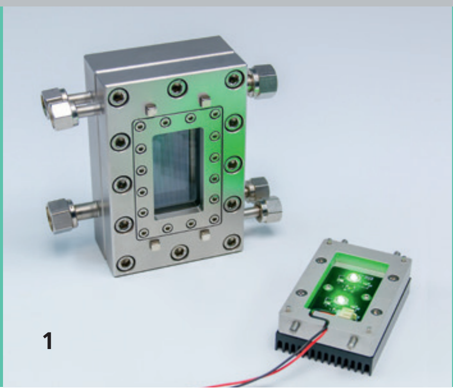

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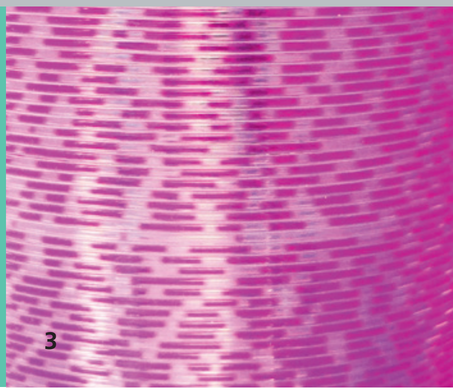

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1 *Falling Film Microreactor with a high power LED array*

2 *Capillary Photoreactor*

3 *Slug-flow of Rose Bengal solution and synthetic air for singlet oxygen generation*

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CONTINUOUS FLOW PHOTO-CHEMISTRY IN MICROREACTORS

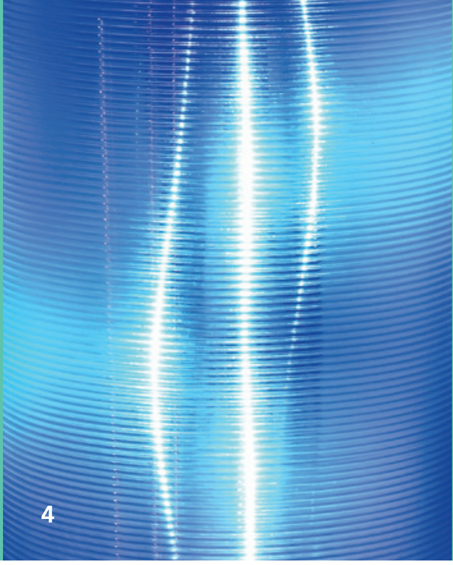
Why photochemistry?

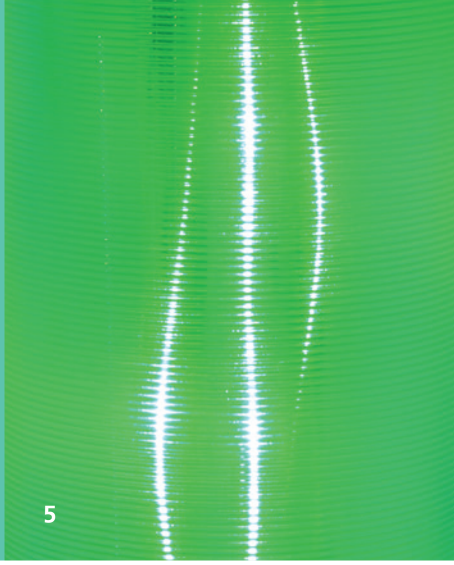
Photochemistry in general describes the physical and chemical processes of material conversion initiated by the absorption of photons, often performed at or close to room temperature and under normal pressure. Under such sustainable and environmentally friendly conditions reagents and follow-up products 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.

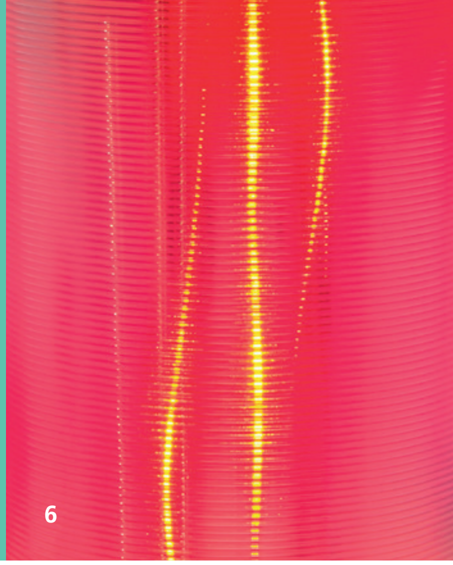
Advancing photochemistry with microreactors and LEDs

With the advent of photochemically catalyzed reactions, every experimenter has to face up to the special challenges of applied photochemistry. For example, standard lab equipment like a 10 mL quartz glass flask is only suitable to a certain degree as its complete reaction volume is irradiated over the whole reaction time. Prolonged irradiation for achieving full conversion can also lead to product degradation. Commonly used high power mercury lamps can deliver a considerable amount of light of wavelengths, which cannot be used for the desired reaction or which is even detrimental for the reaction. Expensive filter equipment might become necessary and an efficient heat management has to be installed for avoiding any thermal reaction pathways.

Both technological challenges can be solved by applying microstructured reactor equipment for continuous flow synthesis in conjunction with LED technology as an energy efficient light source. Microreactors combine several advantages in a single architecture. The generation of very thin liquid streams enables the full illumination of a defined volume of the reaction solution inside a microchannel or a capillary of defined length within a defined time frame determined by the flow rate. This accurate







spatial and time control is clearly superior to any photochemical batch synthesis. Due to the small reaction volumes any heat stemming from light absorption can be more easily withdrawn compared to any batch vessel. In the case of the light source used for photochemical conversions the energy efficient LED technology shows also several advantages. The emission wavelength of high power LEDs meanwhile covers the complete spectral range from UV light over the visible part to the near-IR region. Due to their nearly monochromatic emission, LEDs can be directly adapted to the necessary absorption wavelength of the chemical reaction without any filter equipment. Finally, the very small dimension of LED emitters can be perfectly adapted to many microreactor architectures allowing not only plane but also curved LED arrays of defined size.

Reactor types for photochemical conversions

In 2013 the Falling Film Microreactor (FFMR) has been introduced for photochemical reactions performed with visible light. The reaction plate of the FFMR is the key component of this reactor class as it can produce very thin liquid streams with a thickness of some 10 micrometers inside the microchannels. Beside the full illumination of the liquid thin film (photonic contacting), a highly efficient diffusion of reactant gas, e.g. oxygen, into the thin liquid film is possible as well (gas-liquid contacting). In addition, several methodologies are available that allow the incorporation of solid photocatalyst material like TiO_2, ZnO or Bi_2O_3 onto the microchannel walls. This combination of photonic and solid contacting together with liquid or gas-liquid streams allows heterogeneous photocatalysis applied in a continuous flow microreactor. The FFMR can be equipped with several LED arrays of different emission wavelength, e.g. 365 nm, 410 nm, 455 nm, 525 nm, or cold-white (6500 K). They can be easily exchanged due to a customer-friendly magnetic holder system.

The FFMR-LARGE has been adapted as well for photochemical applications. With a tenfold increase in flow rate to 10 mL/min this reactor can be used as scale-up approach to the standard FFMR.

As a second reactor type, the Capillary Photoreactor has been introduced for photochemical reactions. Its design is based on literature known reactors with a capillary wrapped around a central light source. But instead of mercury lamps exchangeable arrays with 36 water-cooled high power LEDs are available allowing an illumination with actinic blue (410 nm), royal blue (455 nm), green (530 nm) or cold-white (6500 K) light. 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 inside the capillary. The Capillary Photoreactor can be used for liquid and gas-liquid reactions, making this design also a scale-up alternative to the FFMR-LARGE.

Current applications

The *in-situ* generation of singlet oxygen is a very important method in preparative organic chemistry, e.g. for the synthesis of active pharmaceutical ingredients like artemisinin. Both FFMR as well as the Capillary Photoreactor are perfectly suited for the photochemical generation of singlet oxygen under very mild conditions. Efficient illumination of the liquid stream and excellent oxygen gas-contacting are the necessary advantages of these continuous flow reactor designs, which have been successfully used for photooxygenation and photooxidation reactions [1].

Just recently, the FFMR was used for the first time with TiO_2 as immobilized photocatalyst for the blue-light mediated C-H arylation of heterocycles like furan, thiophene and pyridine with a broad substrate scope of diazonium salts [2].

The Capillary Photoreactor has also been used for the dye-sensitized preparation of silver nanoparticles in continuous flow. Depending on the dye and the flow rate of the liquid stream Ag nanoparticles can be generated with different size ranging from 4 to 20 nm.

References

[1] Thomas H. Rehm,* Sylvain Gros, Patrick Löb and Albert Renken, *React. Chem. Eng.*, **2016**, *1*, 636-648.

[2] David C. Fabry, Yee Ann Ho, Ralf Zapf, Wolfgang Tremel, Martin Panthöfer, Magnus Rueping* and Thomas H. Rehm*, *Green Chem.*, **2017**, *19*, 1911-1918.

4 – 6 *Cutout of the Capillary Photoreactor with blue, green and red LED illumination*