PHD PROPOSAL

Advanced polymer colloids designed for continuous-flow photochemical processes

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Host laboratories **Laboratoire de Génie Chimique (LGC UMR 5503),**
http://www.lgc.cnrs.fr/

Keywords : Chemical engineering, flow photochemistry, singlet oxygen, photosensitizer, colloid, membrane science

Academic context

This PhD position is part of the research program "APOFLOW" funded by the French Research Agency (ANR-21-CE06-0038-02). Started in April 2022 for a duration of 4 years, this program involves three academic French laboratories (IPREM-Pau; IMMM-Le Mans, LGC-Toulouse), bringing together different fields of expertise (macromolecular engineering, colloid science, photochemistry and chemical engineering).

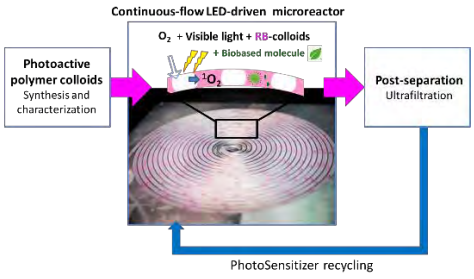
Scientific context

Organic photochemistry becomes a key synthesis pathway in sustainable chemistry[1] as :

- multi-step syntheses of complex molecules are shortened and simplified,
- a portfolio of novel compound families (e.g. strained rings) is becoming accessible,
- in many reactions, the photon acts as a "traceless reagent",
- no chemical catalysts (acid, base, metal, etc.) or activating groups are needed.

Among the large panel of photochemical transformations, photochemical reactions involving *singlet oxygen* are particularly attractive[2]. Singlet oxygen is then generated by photosensitization of molecular (triplet) oxygen, most often in the visible range with catalytic amounts of an organic sensitizer (dye). These sensitized photooxygenations find applications in the flavour and fragrant industry (rose oxide), in the pharmaceutical industry (antimalarials) or for the synthesis of building blocks (hydroxyfuranone).

Project summary



In this context, the APOFLOW project aims at designing innovative continuous-flow microstructured technologies combined with LEDs as light sources, for photooxygenation, whose benefits for organic photochemistry of biobased molecules have already been highlighted at lab scale[3-5]. The project APOFLOW will be based on colloid-supported sensitizers (when most of the literature considers a sensitizer solubilized in the reaction medium)[6].

Such solutions offer many advantages for the sustainability of the process : (i) the separation of the organic sensitizer from the other reactants and products is made easier avoiding expensive downstream separation, (ii) green solvents can be used even with poorly soluble photosensitizers, (iii) the photostability and reusability of the photosensitizers are enhanced[7,8].

Description of the PhD

The PhD student will investigate how these colloid-supported sensitizers can help to intensify the performances (conversion, selectivity and energy-saving) of the LED-driven continuous-flow photooxygenation and how the photosensitizer can be recycled. For this purpose, a continuous microstructured process will be designed and operated, that combines both photooxygenation and ultrafiltration separation steps. Such integrated process will enable to evaluate the photooxygenation efficiency and the reusability of the polymer colloids, depending on the operating conditions. Special attention will be also paid for understanding the relationship between photosensitizer-grafted colloid properties and transport phenomena. For that, specific experiments will be done, supported by the development of modelling tools.

This work will be based on the existing skills of the LGC research groups (Departments STPI and GIMD), but also on the expertise of the different partners of the project. Several missions of the PhD student in the different laboratories involved in the project will be thus realized.

[1] Hoffmann, Photochemical reactions of aromatic compounds and the concept of the photon as a traceless reactant. *Photochem. Photobiol. Sci*. **2012** *11* 1613.

[2] DeRosa and Crutchley, Photosensitized singlet oxygen and its applications, *Coord. Chem. Rev*. **2002** *233* 351.

[3] Oelgemöller and Shvydkiv, Recent Advances in Microflow Photochemistry, *Molecules* **2011** *16* 7522.

[4] Loubière et al, Continuous flow photochemistry: a need for chemical engineering, *Chem. Eng. Process.* **2016** *104* 120.

[5] Buglioni et al, *Chem. Rev.* **2022** 122, 2, 2752–2906

[6] Radjagobalou et al, *Chem. Eng. Process*. **2018** 130 214-228

[7] Petrizza et al, *Polym. Chem.* **2019** 10, 23, 3170–3179.

[8] Radjagobalou et al, *ACS Sustainable Chem. Eng.* **2020** 8, 18568−18576.

Profile

The PhD candidate should have a strong background in chemical engineering, with good knowledge in organic synthesis and membrane/colloid science. He/She should also demonstrate good skills in experimental work and modelling, and must have a strong scientific curiosity.

Administrative aspects

Location: Laboratoire de Génie Chimique, Site ENSIACET, 4 allée Emile Monso, BP 84234, 31432 Toulouse, France.

Duration: 3 years. Starting date : September or October 2022.

Gross Salary : ~2300 € per month (employer : Toulouse INP)

Ecole Doctorale **:** Ecole Doctorale Mécanique, Energétique, GEnie civil & Procédés (MEGeP ED 468), http://www.ed-megep.fr/index.php

Terms for applying to the position.

Please send CV (2 pages), letter of motivation and recommendation letters to:

- Karine LOUBIERE (karine.loubiere@cnrs.fr)
- Patrice BACCHIN (patrice.bacchin@univ-tlse3.fr)

Deadline: **May 15th 2022**