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EFFICIENT PHOTOOXYGENATION PROCESS OF BIO-SOURCED ALPHA-TERPINENE BY COMBINING CONTROLLED LED-DRIVEN FLOW PHOTOCHEMISTRY AND ROSE BENGAL-ANCHORED POLYMER COLLOIDS

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PURPOSE OF THE ABSTRACT

Organic photochemistry is a key synthetic pathway for sustainable chemistry (Hoffmann 2008). In particular, photooxygenation reactions are very attractive as they involve only singlet oxygen, a powerful selective oxidant, which is produced by safe photosensitization of oxygen in the visible range and at ambient temperature (Ghogare and Greer, 2016). They have proved to be very efficient for the preparation of endoperoxides from biosourced molecules such as terpene and furanone derivatives (Iesce et al 2012). Only a limited number of these transformations can be carried out thermally, as they require the use of complex oxidants containing either hazardous peroxides or hypervalent iodine compounds or metal catalysts. Until now, their industrial implementation is limited to a few examples in the flavour, fragrance or pharmaceutical industries (Braun et al, 2014). Batch reactors equipped with energy-demanding mercury light sources are the main systems currently used. Non-eco-friendly solvents are generally used to maximize the singlet oxygen lifetime, and the photosensitizer (as solid powder) should be regularly fed to counterbalance its degradation.

Continuous-flow microstructured technologies, combined with LEDs as light sources, are promising alternatives to batch photochemical processing. Their benefits for organic photochemistry have been highlighted at lab scale (Cambié et al, 2016). Most of the literature considers a sensitizer solubilized in the reaction medium, even if the concept of solid-supported sensitizers offers many advantages. The separation of the organic sensitizer from the other reactants and products is then made easier, avoiding expensive downstream separation. It is also a strategy for transposing poorly soluble photosensitizers into green solvents, while simultaneously enhancing their photostability and reusability.

In this context, the present work studies the reactivity of poly(N-vinylcaprolactam-co-vinyl acetate-co-vinylbenzyl Rose Bengal) microgels as heterogeneous photosensitizers in a continuous-flow process for sustainable singlet oxygen sensitized photooxygenation of a bio-based molecule.

Photoactive colloids were synthetized by miniemulsion copolymerization of vinyl acetate, N-vinyl caprolactam,

divinyl adipate crosslinker and vinyl benzyl Rose Bengal monomer (Petrizza et al, 2019). The hydrodynamic diameters were ranged between 200250 nm. The related singlet oxygen quantum yield was measured equal to 0.27- 0.35 and the sensitizer loading onto the polymer microgels to 215 µmoles of Rose Bengal (RB) per gram of dried microgel.

Experiments were carried out in a LED-driven spiral-shaped microreactor used in Radjagobalou et al (2021), in which slurry Taylor flows were generated. This process allowed accurate control of irradiation (emission spectrum and intensity), light absorption (tunable absorbance) and gas-liquid flow conditions (volumetric and stoichiometric ratio). The benchmark photooxygenation of alpha-terpinene was implemented in ethanol to provide a green solvent using air as a safe supply of oxygen.

The present work demonstrated that the swollen RB-grafted colloids in ethanol phase were efficient in converting alpha-terpinene into ascaridole with high conversion and high selectivity, and in short residence times (few minutes). The supported RB exhibited a reactivity similar to that of the free RB. The photo-reactivity of RB-supported microgels was stable over 8 months of storage with good reproducibility. The photoactive colloids also proved to be reusable during several cycles. Finally, with a stoichiometric excess of alpha-terpinene compared to oxygen, in presence of high photon flux and for the highest concentration of Rose Bengal photosensitizer, the colloids allowed the RB photobleaching levels to be decreased compared to free RB. This important result suggests that the covalent anchoring of RB molecules inside submicronic polymer colloids can prevent their photodegradation.

FIGURES

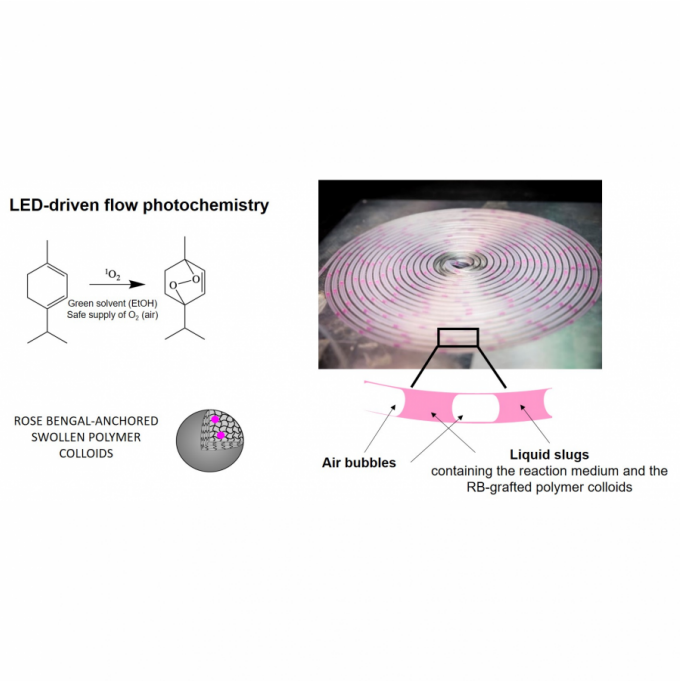

FIGURE 1

LED-DRIVEN FLOW PHOTOOXYGENATION WITH ROSE BENGAL-ANCHORED POLYMER COLLOIDS

Photooxygenation of alpha-terpinene in LED-driven spiral shaped microreactor in which slurry Taylor flows are generated

FIGURE 2

KEYWORDS

Flow photochemistry | Photooxygenation | Rose Bengal-grafted colloids | LED -driven microreactor

BIBLIOGRAPHY