Solar Fuels and Chemicals

Photocatalytic Reactors

KEYWORDS: Photoreactors / Optical semiconductors / Artifical Light/ Prototypes / Chemicals / Oxygen Evolution

Innovative photoreactors using artificial light were developed and applied in different fields, such as water/wastewater decontamination, synthesis of fine chemicals, hydrogen production and oxygen evolution.

Introduction

The design of photocatalytic reactors is crucial to improve the efficiency and applicability of heterogeneous photocatalysis in different fields, including environmental remediation and energy conversion. The main aspects of ideal designs include optimising reaction kinetics through appropriate irradiation, enhancing mass transfer for effective contact between organic/inorganic molecules and the photocatalyst surface, and ensuring scalability for industrial applications. The choice of the photocatalyst, control of reaction conditions, and considerations for long-term stability and durability are also essential for reactor design. Additionally, well-designed reactors can reduce energy consumption, be integrated with other technologies, and contribute to the success of photocatalytic processes in realistic scenarios.

In the reported period, we have been exhaustively pursuing the development of photocatalytic reactors operating on both batch and continuous modes (Fig 1) using suspended and immobilized photocatalysts [1-4]. Different photoreactor prototypes were designed, constructed and tested for the photocatalytic degradation of pollutants in wastewaters [1], for the production of several aromatic aldehydes from the respective alcohols [2], hydrogen production (H_2), and oxygen evolution (O_2) [3].

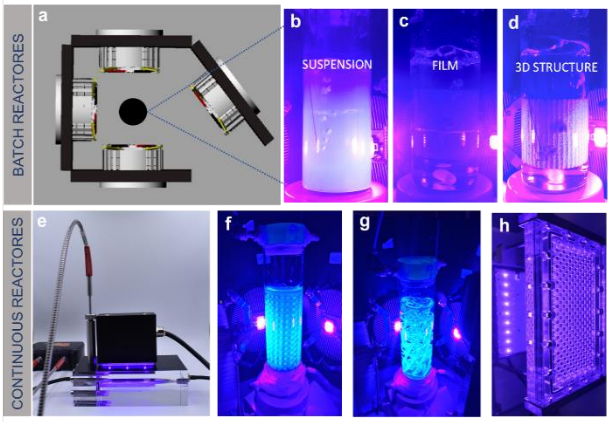

Fig 1. Examples of photocatalytic systems constructed at LSRE-

Current Development

Developing a Device for Oxygen Evolution

Oxygen is used in numerous industrial processes, for example, synthesis of chemicals, petroleum processing, glass, ceramic, pulp and paper manufacture. It is mainly used to enhance the reaction rates and to ensure the complete oxidation of possible undesired by-products occurring during some processes. Unfortunately, the transport and delivery of gaseous molecular O_2 pose several treads to its industrial application. Production in situ is undoubtedly an alternative forwarded by many technological strategies.

Thus, due to the crucial importance of O_2 in various processes, during the reported period, we explored *in situ* O_2 production by water oxidation based on semiconductor photocatalysis technology [4]. The influence of oxygen defects, optical and crystalline properties of TiO_2 samples calcined at different temperatures was investigated for O_2 evolution using a low concentration of Fe^{3+} aqueous solution (Fig 1b) rather than the typical electron acceptor (Ag^+). The lower price, high abundance and broad availability of iron compared to silver, the use of Fe^{3+}/Fe^{2+} in low concentrations, makes this a cost-effective and sustainable process. In addition, considering the advantages of using continuous mode systems, a selected TiO_2 sample was deposited in a glass support, and the rate of O_2 production was assessed (Fig 1e). To the best of our knowledge, this was the first study on photocatalytic water oxidation using immobilised TiO_2 towards *in situ* O_2 production under continuous mode, which avoided the need of recovery the catalyst as an additional step. Concerning the results obtained with the TiO_2 samples using the Fe^{3+} ion solutions it seems reasonable to propose that the overall process is governed by the mechanism illustrated in Fig 2.

The remarkable efficiency of the TiO_2-700 (calcined at 700 ºC under air atmosphere) for O_2 evolution was correlated with the highest ratio between anatase and rutile phases (88%), which seems to indicate an efficient separation of the photogenerated

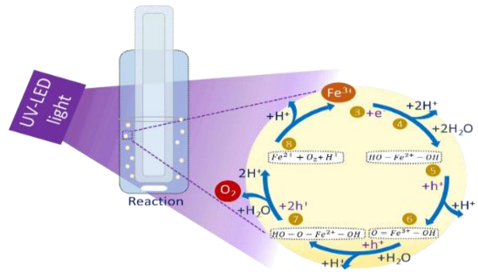

Fig 2. Schematic representation of a proposed mechanism for O_2 evolution from $Fe(NO_3)_3{\cdot}9H_2O$ water solution under UV-LED light irradiation using TiO_2 photocatalysts [3].

electron/hole carriers. In addition, the superior reactivity of the TiO_2-700 sample was ascribed to the enhancement of the oxygen vacancies at the photocatalyst surface, which act as active sites for water oxidation. The continuous-flow reaction system demonstrated promising results for water oxidation, revealing a superior apparent quantum efficiency at 384 nm compared with the results obtained in the batch system, 0.60 and 0.53, respectively. This study involved the cooperation between the LSRE-LCM and the International Iberian Nanotechnology Laboratory.

Innovative Photoreactor for Chemical Synthesis

The LED-NETmix prototype was designed using 3D CAD software (Solidworks® and MayCAD®). The irradiation setup, based on LED technology, was designed to homogeneously distribute the light on the flat surface of the NETmix® reactor (Fig 1h, Fig 4). The LED-NETmix prototype was assembled with connecting tubes and 3-way valves, allowing it to operate either in batch or continuous mode and use one or two reactants simultaneously. It was also equipped with a compact LED system, which can be replaced very easily in order to use different wavelengths (from UV to Visible). The photoreactor structure presents an effective network area of 98.6 cm² and a volume of 31.5 mL. The conversion of anisyl alcohol to anisaldehyde was used as a model reaction for finding the optimal operating conditions [4]. For that, several operating parameters were studied, including the flow rate, irradiation position (frontside and backside), irradiation source (UV and visible), initial alcohol concentration (0.5 and 1.5 mM), and the photocatalyst to polymer weight ratio. Novel photocatalytic thin films were developed using a biopolymer, sodium alginate (SA), combined with graphitic carbon nitride (g-C_3N_4). The photocatalytic activity of the film was tested under Vis-light irradiation (420 nm) for the synthesis of anisaldehyde, benzaldehyde , piperonal, tolualdehyde, and vanillin.

A photochemical reactor design using CFD requires simulations of hydrodynamics, radiation distribution, and reaction process, which integrates the chemical reaction of the system (Fig 3).

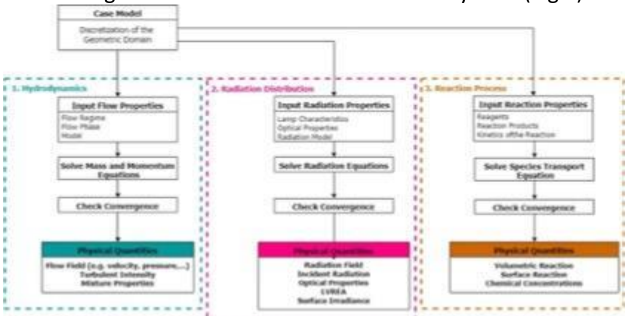

Fig 3. The sequential steps to model a photocatalytic reactor.

The LED-NETmix photoreactor was studied using the NETmix Unit Block (NUB) model, which is a simplified model of an infinitely wide NETmix, that only considers a section of the full geometry (Fig 4). This structure is constituted by a central column of chambers and two columns of half chambers, where is applied translational periodic boundary conditions. Based on the NUB, a new model was adopted – LOOP NUB, with periodic conditions between inlets and outlets, creating a recirculation model. Thus, the project of the photoreactor was facilitated, allowing the studies of its parameters in a reasonable computing time.The mass transport phenomena in the different sy stems were evaluated using the species model transport. The laminar finite-rate model was considered to simulate the chemical reaction. Reactional continuous systems were compared with the experimental data obtained in a conventional batch reactor, specifically for the photocatalytic synthesis of AAD and the same yield was achieved. Regarding the LED-NETmix reactor, the validation of the LOOP NUB was successful, therefore it was used for the 3D heterogeneous catalysis simulation. Moreover, the simplification of the NETmix CFD model for catalysis will make possible the study of the design and performance of industrial reactors.

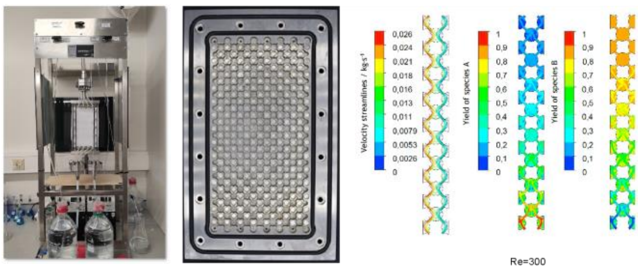

Fig 4. The LED-NETmix photoreaction system, the NETmix system and CFD simulation usinf the LOOP NUB model

This study involves the cooperation between the Product Engineering and the Catalysis and Carbon Materials groups.

3D-printed photoreactors

The interest in additive manufacturing (AM) technologies as a tool to develop and build highly adapted reactors increases with the available 3D printer models and materials at lower costs. In the last few years, there has been a rapid development of 3D printing technology, improving the materials and processes to build 3D printed structures. The design of photocatalytic systems requires some additional parameters, such as the radiation field, the interaction of the composition of the reactor with the photocatalyst, and the optimisation of photochemical reactions. This plethora of physical phenomena raises a considerable number of hurdles when moving forward to industrial processes, raising the need for rapid prototyping technologies that require research of many technical solutions for process intensification in photoreactors. Both Strereoliothography (SLA) and Fused Deposition Modeling (FDM) printing techniques were applied to the development of 3D photoreactors and structures for catalyst immobilization. In the first one, the photocatalytic structure is printed using the catalyst incorporated in a resin that is then cured by light. In the later case, the structure is first printed using an adequate filament and then covered by a film of the catalyst. These systems have already been applied by our group for the development of photocatalytic systems for the production of H_2, H_2O_2, and NH_3 and for water and wastewater treatment.

Future Work

To improve the efficiency of the photoreactors key parameters need to be continuously investigated, such as the nature of the photocatalytic material, light source characteristics, catalyst surface area, flow rate and immobilisation of the catalyst. This study is imperative for continuous flow regimes and aims to apply photocatalytic technology at an industrial scale.

Related Sustainable Development Goals

Outputs

Master Dissertations

Beatriz Filipa Leal de Oliveira, Development and optimization of a photocatalytic device for oxygen production, MIEQ, FEUP, 2019.

Catarina Costa Pereira, Photochemical Synthesis in a NETmix reactor, MIEQ, FEUP, 2019.

Selected Publications

[1] N.F.F. Moreira et al., Appl. Catal. B: Environm. 248, 184-192 (2019).
[2] J.C. Lopes et al., Catal. Today, 357 32-38 (2020).
[3] M.J. Sampaio et al. Sci. Rep., 11(1) 21306 (2021).
[4] D.S.M. Constantino et al., J. Clean. Prod., 340 130800 (2022).

Team

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