

Photocatalytic Organic Synthesis

KEYWORDS: Photocatalysis / Organic Synthesis / Aromatic Aldehydes / Imines/Carbon Nitride / Perovskites/Green Chemistry

The development of novel photocatalysts tailored for the selective synthesis of aromatic aldehydes and imines using supported materials in batch and continuous mode systems are the most relevant results for this topic.

Introduction

The discovery and implementation of energy-efficient and sustainable technologies for organic synthesis to reduce the ecological impact of important industrial routes has been a hot topic in worldwide research. Conventional chemical processes require the use of hazardous oxidants/reductants and harsh operation conditions. In this scenario, photocatalysis appears as a novel alternative for synthesising a wide range of organic compounds since it is environmentally friendly and straightforward as a reaction strategy.

Partial oxidation of aromatic alcohols to the corresponding aldehydes or the oxidative self-coupling of amines to imines are important reactions at the industrial scale. Specifically, benzaldehyde (BAD), anisaldehyde (AAD), and vanillin (VAD) are important industrial chemicals used as raw materials for a wide range of applications. Imines, as N-benzylidenebenzylamine (BZI), play a pivotal role in pharmacophores, fragrances, and in numerous biologically active compounds. Due to their wide application in many fields, the synthesis of aldehydes and imines has gained attention in recent years.

The integration of sustainable processes and highly active materials, such as metal-free graphitic carbon nitride-based photocatalysts, represents a crucial step towards industrial implementation. Furthermore, bismuth halide perovskites are characterized by their unique electronic properties and tunable bandgaps, exhibiting remarkable photocatalytic activity, making them promising candidates for sustainable synthesis processes. Immobilized materials offer several benefits, including easy scalability, making them proper for large-scale applications, which enables efficient production and reduces the amount of catalyst required. Furthermore, the use of micro-mesostuctured photoreactors provides larger surface areas per reaction volume, ensuring a higher spatial illumination homogeneity and better light penetration through the entire reactor.

Current Development

Optical semiconductors based on carbon nitride were prepared by thermal condensation of dicyandiamide followed by a thermal post-treatment (GCN-T) and further sonication (GCN-TS). The efficiency of these materials was evaluated on the selective conversion of various aromatic alcohols to the corresponding aldehydes, namely AAD, BAD, tolualdehyde (TAD), piperonal (PAD) and VAD. Among the evaluated scenarios, GCN-T (1 g L^{-1}) demonstrated better performance in the conversion of anisyl alcohol to anisaldehyde, achieving >99% conversion and selectivity after 45 min of UV-LED irradiation (Fig. 1). The alcohol conversion and yield for aldehyde formation was related with the number, electronic nature and position of the functional groups in the aromatic ring. This underscores the significance of tailoring the photocatalytic process to the specific molecular features of the alcohol substrates, providing valuable insights for optimizing future organic synthesis methodologies. When GCN-TS was employed, it also achieved >99% conversion and selectivity towards AAD while reducing the reaction time to 30 min and the catalyst load to 0.2 g L^{-1} [1].

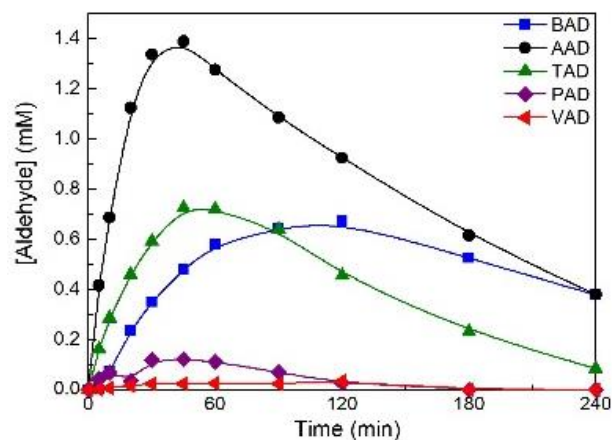


Fig 1. Concentration profiles of the aldehydes BAD, AAD, TAD, PAD, and VAD after 4 hours of reaction using GCN-T catalyst.

Composites of GCN and small amounts of reduced graphene oxide (rGO) (up to 1 wt.%) were used as photocatalysts for the BAD production. Results show that small amounts of the rGO phase can lead to a maximum of 16 % improvement in the yield of the process [2].

A more technological approach was employed in the preparation of a magnetically recoverable $\text{Fe}_3\text{O}_4/\text{g-C}_3\text{N}_4$ composite for photocatalytic production of BAD under UV-LED radiation [3], and by immobilising GCN-T over glass Raschig rings for the continuous production of AAD.

Hybrid materials were developed by combining zinc oxide (ZnO) prepared through chemical vapor deposition with different amounts of carbon nanofibers (CNF). These hybrid materials were used for the synthesis of several aromatic aldehydes. Notably, in the particular case of vanillin synthesis, the selectivity was significantly enhanced by a factor of 2.5 compared to previous studies, with the additional advantage of carrying the reaction in aqueous medium [4]. Graphite-like carbon nitride-based photocatalysts with morphological and textural modifications were obtained using SiO_2 through the hard-templating technique, showing its high potential in heterogeneous photocatalysis, as an alternative to the conventional synthesis of value-added products, as *p*-anisaldehyde [5]. The modification of $\text{g-C}_3\text{N}_4$ with citric acid has also been studied for simultaneous production of the anisaldehyde and H_2 . The best-performing photocatalyst (GCN-20CA) achieved 63 % yield after a 240 min reaction. The modified material practically duplicated the hydrogen production when compared to unmodified $\text{g-C}_3\text{N}_4$ (75 and 44 $\mu\text{mol H}_2$ evolved in three hours, respectively), by using platinum nanoparticles as co-catalyst and EDTA as sacrificial electron donor [6].

Due to the several practical problems arising from the use of powder materials (e.g., separation of the catalyst), different techniques were used to immobilise the photocatalyst. Firstly, a coating technique using polyester fibre was employed to GCN-TS. The PES surface was treated with different concentrations of HNO_3 aqueous solutions, enhancing the adhesion of GCN-TS on PES fibres. Notably, treating the coated PES surface with a 1% v/v HNO_3 solution resulted in a uniformly deposited photocatalyst layer and increased hydrophilicity. The photocatalytic synthesis of AAD in an aqueous solution assisted by visible LED, resulted in 95% yield operating in batch mode [7]. Aiming at industrial processing, a microcapillary system (Fig 2a) and a micro-meso

structured photoreactor implemented with light-emitting diodes (LED-NETmix) (Fig. 2b) were employed using immobilised graphitic carbon nitride catalysts to enhance the aldehydes production. So, operating in a microfluidic reactor, the BAD yield was increased by a remarkable 9-fold after 2.4 minutes when using suspended GCN-T compared to a batch reactor [8-9]. This work was conducted in collaboration with the Department of Chemical Engineering at the University of Bath.

A biodegradable matrix composed of sodium alginate was also used as support for both GCN and GCN-TS, with their catalytic performance evaluated in the synthesis of aromatic aldehydes through selective photocatalytic oxidation of alcohols using the LED-NETmix as photoreactor. The assessment of photocatalytic performance involved systematic adjustments to various operational parameters, including the flow rate, the amount of photocatalyst impregnated in the polymer, the irradiation source, position, and initial alcohol concentration. Under visible light, employing a continuous flow of 230 mL min⁻¹ of 1 mM anisyl alcohol, the maximum production of anisaldehyde (0.23 mM) was reached after 2 hours. Notably, using GCN-TS supported, it was possible to reduce 4 times the amount of photocatalyst impregnated when compared to GCN, reaching the same AAD production. Moreover, this novel green approach for organic synthesis presents easy scalability for large-scale production, using several reactors in series or parallel, with great potential from the industrial point of view.

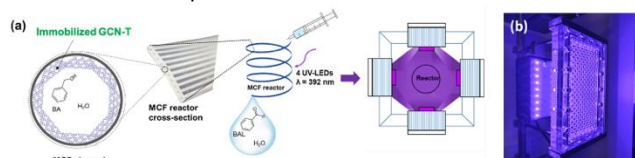


Fig 2. Schematic view of LED irradiation microfluidic reactor setup using (a) immobilized catalyst and LED-NETmix photoreactor (b).

Sodium alginate hydrogel was also used as supporting matrix for carbon nitride materials thermally modified under a nitrogen atmosphere (GCN-T-N), intended for the photocatalytic synthesis of vitamin B3 through the oxidation of 3-pyridinemethanol. GCN-T-N demonstrated to be highly efficient, achieving a 100% 3PM conversion and selectivity towards VB3 production after 7 hours of irradiation. The immobilization of GCN-T-N in sodium alginate hydrogel emerged as a highly promising strategy for the production of vitamin B3 [10].

Concerning the selective synthesis of fine chemicals, the photocatalytic synthesis of imines was evaluated using different photocatalysts. GCN-T was applied for the photocatalytic oxidative coupling of amines into the corresponding imines, under visible LED as the irradiation source. Results showed that the GCN-T material presented a high photocatalytic activity toward BZI production, providing a low environmental impact and straightforward as a reaction strategy, owing to the possibility of operating under mild conditions and generating low amounts of undesirable by-products. Under visible LED, the reaction achieved remarkable 99% selectivity toward BZI after just 45 minutes. Investigating the catalytic mechanism, EPR spectroscopy was employed in collaboration with the Faculty of Sciences of the University of Porto. EPR revealed the critical involvement of superoxide radicals, singlet oxygen, and delocalized electrons in the photocatalytic process. The synergy between superoxide and singlet oxygen radicals was confirmed through EPR measurements, highlighting their role in GCN-T excellent catalytic performance for amine-to-imine conversion reactions [11].

New perovskites-based materials, specifically bismuth halide perovskites (Cs₃Bi₂X₉, where X = Cl, Br and I) were synthesised and employed for the photocatalytic oxidative coupling of benzilamine to produce BZI. This collaborative research was conducted in partnership with the Instituto de Tecnología Química (ITQ) - Universitat Politècnica de València (UPV). Under visible light irradiation, a maximum BZI concentration of 5.7 mM was attained after 1.5 hours for 77% conversion of BZA using Cs₃Bi₂Br₉ as photocatalysts. However, a high level of instability was observed. To improve the stability, mixed Cs₃Bi₂(Cl_xBr_{1-x})₉ materials were synthesised with different amounts of chloride and bromide ions. The mixed Cl/Br content reduced the bandgap energy and electron-hole recombination of the synthesised materials. The reduced optical bandgap of the photocatalysts moves the light absorption to higher wavelengths, such as visible light, widening the portfolio of possibilities for industrial organic synthesis at a practical level and cost-effective for real-world applications.

Future Work

Development of an efficient photoreactor system using LEDs as irradiation sources for the continuous production of imines. The combination of perovskite and carbon nitride materials as hybrid semiconductors will be attempted.

Related Sustainable Development Goals



Outputs

PhD Theses

Maria José Bastos Pires de Lima, Selective Photocatalytic Conversions

Integrated on a Continuous-flow Microfluidic Process, PDEQB, FEUP, 2019

Ana Raquel Almeida Fernandes, Design of optical semiconductors optimized for photocatalytic organic synthesis, PDEQB, FEUP, 2020

Master Dissertations

Joana C. Lopes, Produção de compostos aromatizantes através de tecnologias verdes, MIEQ, FEUP, 2018

Selected Publications

- [1] J.C. Lopes et al., *Catalysis Today* 357, 32 (2020).
- [2] M.J. Lima et al., *ChemistrySelect* 3, 28 (2018).
- [3] M.J. Lima et al., *Catalysis Today* 328 (2019).
- [4] R.A. Fernandes et al., *Catalysis Today* 328 (2019).
- [5] R.A. Fernandes et al., *RSC Advances* 10, 33 (2020).
- [6] R.A. Fernandes et al., *Applied Catalysis A: General* 609 (2021).
- [7] J.C. Lopes et al., *Surfaces and Interfaces* 30 (2022).
- [8] M.J. Lima et al., *Applied Catalysis A: General* 608 (2020).
- [9] M.J. Lima et al., *Chemical Engineering Journal* 430 (2022).
- [10] R.A. Fernandes et al., *Molecules* 27, 4 (2022).
- [11] J.C. Lopes et al., *Catalysis Today* 418 (2023).

Team

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