

Photocatalytic Production of Hydrogen Peroxide

KEYWORDS: Photocatalysis/ Carbon nitride/ Visible light/ 3D-structures/ Hydrogen Peroxide/ Seawater

Hydrogen peroxide (H_2O_2) can act as a highly powerful oxidant capable of decomposing organic compounds in contaminated water and can also be employed as an energy carrier. Successful strategies for modifying graphitic carbon nitride ($g-C_3N_4$) were developed for enhanced production of H_2O_2 . During its production, various operational parameters were investigated, aiming for high yields as well to optimise the synthesis process by immobilising the photocatalyst on a 3D printed structure.

Introduction

The possibility of using H_2O_2 as a chemical oxidiser or as a green liquid fuel to produce electricity has encouraged both the scientific and industrial communities to investigate green technologies aimed at the sustainability of the production process. In particular, the light-induced synthesis of H_2O_2 from water and oxygen has attracted significant attention using optical semiconductors. $g-C_3N_4$ photocatalyst has particularly revealed great potential for H_2O_2 production using aqueous solutions under visible light. Concerning the photocatalytic pathway for the H_2O_2 generation using $g-C_3N_4$, the reaction is usually described by two-electron reduction of O_2 , with the experiments being mainly performed using alcohol derivatives as sacrificial agents [1-3]. In addition, the band structure of the photocatalysts proves one of the most important features to optimize to promote the subsequential redox reactions that generate H_2O_2 from water and oxygen (Fig 1).

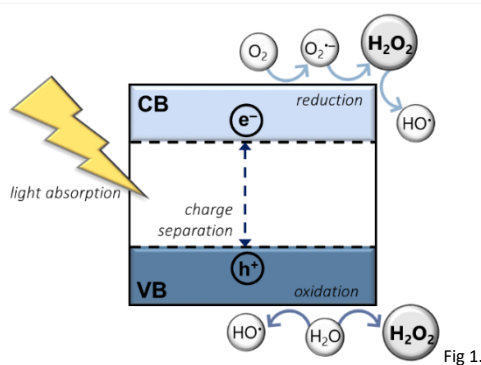


Fig 1. Photocatalytic activation and formation of reactive oxygen

Implementing techniques to modify the band gap, increase surface area, tune optical and electronic properties aiming to capture a greater fraction of visible light as well as the use of appropriate sacrificial agents for H_2O_2 production have been greatly investigated [3], aiming to overcome one of the main limitations for the applicability of $g-C_3N_4$ in photocatalysis - fast electron/hole recombination. Functionalisation methods can be applied to improve the efficiency of this material, such as via a hydrothermal route using glucose (G), perylene (P) and anthraquinone (A), yielding CN-G, CN-P and CN-A, respectively [4].

Currently, at LSRE-LCM we have been focusing on the photocatalytic oxidation of organic pollutants with simultaneous evolution of H_2O_2 by $g-C_3N_4$ based materials [1-3]. In addition, given the potential of this oxidiser as a possible chemical carrier investigations have been continually sought [5, 6].

Current Development

In-situ H_2O_2 Generation in the Degradation of Aromatic Compounds

The photocatalytic performance of neat $g-C_3N_4$ was investigated in the degradation of the various aromatic compounds with simultaneous H_2O_2 production under visible light. Overall, larger amounts of H_2O_2 were obtained for the most reactive molecules. The nature, order and position of substituent groups on the aromatic ring seem to be the main responsible for the different efficiencies in the degradation and mineralization of the pollutants. Moreover, the pKa does not affect the H_2O_2 production, which seems to be mainly influenced by the dissolved oxygen content and the presence of more $-OH$ groups in the

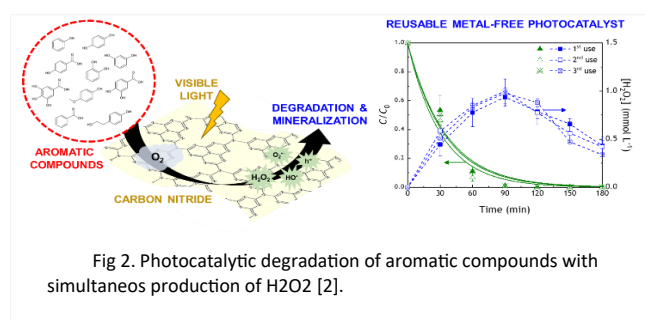


Fig 2. Photocatalytic degradation of aromatic compounds with simultaneous production of H_2O_2 [2].

aromatic ring. Additionally, according to the reutilisation tests, $g-C_3N_4$ photocatalyst can be reused without showing any loss of photocatalytic activity [1]. This work promoted a study to better investigate the mechanism involved on the H_2O_2 generation and allowed us to conclude that under the experimental conditions it is possible to produce a commodity chemical with high added-value.

Hydroperoxyl Radical Role on Photocatalytic H_2O_2 Production

A kinetic modeling (Fig 3) using the Kintecus software was developed and proved that photogenerated electrons are consumed by dissolved oxygen in the aqueous media, forming H_2O_2 by the two-electron or one-electron reduction routes [3]. With this knowledge, it was possible to tailor the band structure of $g-C_3N_4$ towards obtaining more efficient H_2O_2 production rates [5] (Fig 4).

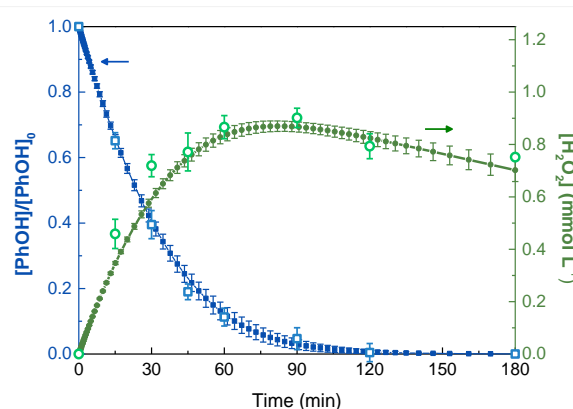


Fig 3. Experimental data (open symbols) and model outputs (full symbols) for the degradation of PhOH and the simultaneous H_2O_2 generation [3].

This work provided considerable kinetic data of radical reactions with the $g\text{-C}_3\text{N}_4$ material [3]; many of them were estimated for the first time. Multiple combinations of all different degradation pathways identified in the literature were investigated, deducing for the first time that hydroperoxy radical, as a secondary radical, is the main species involved in both the primary oxidation of PhOH and simultaneous H_2O_2 generation.

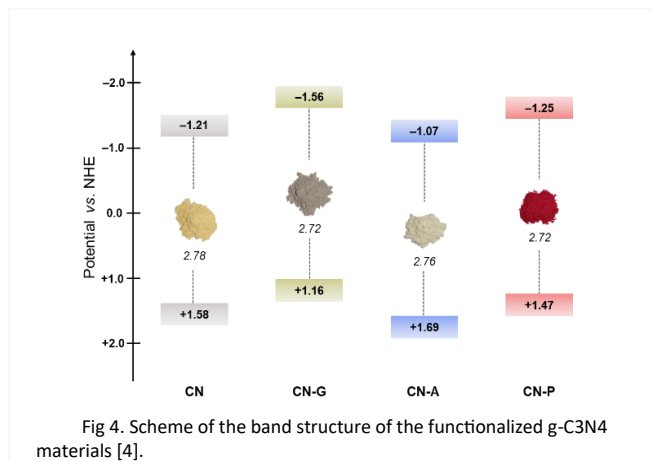


Fig 4. Scheme of the band structure of the functionalized $g\text{-C}_3\text{N}_4$ materials [4].

Boosting $g\text{-C}_3\text{N}_4$ Materials for H_2O_2 Production

The impact of precursor molecule on the synthesis of $g\text{-C}_3\text{N}_4$ was assessed (Fig. 4.) taking into account the activity of photocatalytic H_2O_2 production in the presence of isopropyl alcohol [5]. Six precursors (dicyandiamide, melamine, guanidine carbonate, guanidine hydrochloride, thiourea, or urea) were employed to obtain materials with distinct morphological, structural and optical properties. The control over the specific surface area, crystallinity, surface chemistry and photoluminescence proved to be fundamental to determine each material's behaviour as a function of the nature of each precursor. For instance, the use of urea as the sole precursor for $g\text{-C}_3\text{N}_4$ it was possible to eliminate the need for a posterior thermal exfoliation step, reducing processing costs. The urea-derived $g\text{-C}_3\text{N}_4$ demonstrated very high H_2O_2 generation rates of $3906 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$, using isopropyl alcohol and saturated air conditions.

Overall, the introduction of oxygenated groups, increased visible-light absorption, improved charge carrier separation and band structure realignment were the main reasons behind the higher production rates of H_2O_2 , along with slower H_2O_2 decomposition. Taking into account that oxygen reduction into H_2O_2 occurs at $+0.33 \text{ V vs NHE}$, it was possible to observe from the band structure of the functionalised materials (Fig. 4) that CN-A, with the most positively-shifted conduction band, yields the higher rates of $24975 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$.

Sustainable H_2O_2 Generation from Saccharide Derivatives

In a parallel study, the photocatalytic production of H_2O_2 using $g\text{-C}_3\text{N}_4$ (prepared with dicyandiamide precursor) was explored for the production of H_2O_2 , employing various mono- and disaccharides as sacrificial electron donors under visible light exposure [6]. Various parameters were investigated, including the effect of the initial concentration of the sacrificial electron donor, the presence of ionic species during the photocatalytic reaction and the possibility of using seawater as a water source. This approach aimed to avoid the use of freshwater.

The photocatalytic production of H_2O_2 was evaluated using powder and immobilized $g\text{-C}_3\text{N}_4$. The results suggested a promising route for the generation of H_2O_2 using the most abundant water source on earth instead of potable water.

Furthermore, the immobilisation of $g\text{-C}_3\text{N}_4$ on a 3D-printed structure prepared by additive manufacturing displayed high efficiency and stability for H_2O_2 production (Fig 4.).

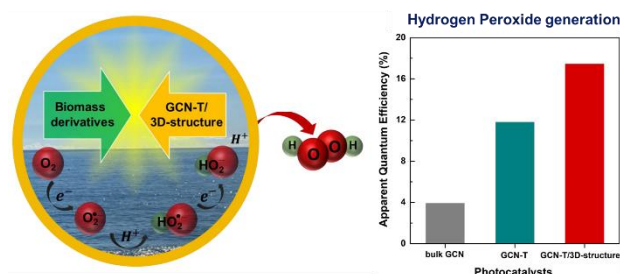


Fig 4. Photocatalytic H_2O_2 production from biomass derivatives using immobilized $g\text{-C}_3\text{N}_4$ (GCN-T/3D-structure) [5].

This strategy may represent a significant advancement in the field of photocatalysis for energy carriers by utilising an effective reaction system that can reduce operating expenses, and which has the potential for application in full-scale and continuous flow modes.

Future Work

Although challenging technological solutions have been achieved in these studies, further research is necessary to optimise various parameters. This includes improving the physical-chemical and electronic properties of the catalysts for H_2O_2 production, avoiding the addition of high concentrations of sacrificial agents, and design reaction systems aiming the intensification process.

Related Sustainable Development Goals



Outputs

Master Dissertations

André Torres-Pinto, Structured metal-free carbon materials for photocatalytic wastewater treatment, MIEQ, FEUP, 2018.
Rita Amaral Borges, Sustainable production of hydrogen peroxide using seawater and solar energy, MIEQ, FEUP, 2022.

Selected Publications

- [1] A. Torres-Pinto et al., *Catalysts* 9, 990 (2019).
- [2] A. Torres-Pinto et al., *Appl. Catal. B: Environm.* 252 128-137 (2019).
- [3] I. Vello-Gala et al., *Catalysis Science & Technology*, 11, 7712 (2021).
- [4] A. Torres-Pinto et al., *Catalysis Today* 424, 113868 (2023).
- [5] A. Torres-Pinto et al., *ACS Sustainable Chemistry & Engineering* 11, 894 (2023).
- [6] R.A. Borges, et al., *Chem. Eng. J.* 470, 144066 (2023).

Team

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Funding

LSRE-LCM Base Funding, UIDB/50020/2020, 2020-2023
LSRE-LCM Programmatic Funding, UIDP/50020/2020, 2020-2023
LA LSRE-LCM Funding, UID/EQU/50020/2019, 2019
LA LSRE-LCM Funding, POCI-01-0145-FEDER-006984, 2013-2018
MicroPhotOGen, POCI-01-0145-FEDER-030674, 2018-202
FCT Grants: CEECINST/00010/2021
FCT Scholarships: SFRH/BD/143487/2019