Phenanthroline-based COFs for Solar-Driven Hydrogen Peroxide Production from Water and Air

Gustavo Felix Bitencourt,[1,2] Gobinda Das,[3] Fayrouz Abou Ibrahim,[3] Jihan Dhainy,[1] Abdel Aziz Wayzani,[1] Dalmo Mandelli,[2] Ali Trabolsi,[3] Mohamad El-Roz[1]

[1]University of Caen, UNICAEN, ENSICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, France; [2]Universidade Federal do ABC – UFABC, Centro de Ciências Naturais e Humanas; Brazil; [3] New York University Abu Dhabi – NYUAD, Chemistry Program, United Arab Emirates.

Resumo/Abstract

RESUMO - O peróxido de hidrogênio (H_2O_2) é um composto químico essencial, porém os métodos atuais de produção são energeticamente intensivos e ambientalmente não sustentáveis, baseando-se geralmente no processo de oxidação da antraquinona. As *covalent-organic frameworks* (COFs) surgem como fotocatalisadores não metálicos promissores devido à sua estrutura facilmente modificável (diversos tipos de ligantes orgânicos) e excelente estabilidade. Neste estudo, três novas COFs, PTA-TTT, PTA-TAB e PTA-THB, foram sintetizadas pela reação entre a 1,10-fenantrolina-2,9-dicarbaldeído (PTA) e diferentes ligantes à base de aminas. A atividade fotocatalítica para produção de H_2O_2 foi avaliada sob luz solar simulada. Todas as COFs apresentaram-se ativas na produção de H_2O_2, com destaque para a PTA-TAB, que alcançou 1921 µmol g_{cat}^{-1} em 23 h e demonstrou excelente estabilidade ao longo de três ciclos. PTA-THB apresentou alta taxa de produtividade, mas sofreu desativação parcial ao longo do tempo. Os resultados demonstram o potencial das COFs como fotocatalisadores eficientes para a geração de H_2O_2 utilizando apenas água, ar e luz visível, oferecendo uma alternativa sustentável para aplicações industriais.
Palavras-chave: fotocatálise, fotossíntese artificial, covalent-organic frameworks

ABSTRACT - Hydrogen peroxide (H_2O_2) is an essential chemical, but current production methods are energy-intensive and environmentally unsustainable based on anthraquinone oxidation process. Covalent organic frameworks (COFs) have emerged as promising metal-free photocatalysts due to their tunable structures and excellent stability. In this study, three novel COFs, PTA-TTT, PTA-TAB, and PTA-THB, were synthesized by coupling 1,10-phenanthroline-2,9-dicarbaldehyde (PTA) with different amine-based linkers. Their photocatalytic performance was evaluated under solar-simulated light using a custom-built glass reactor. All COFs exhibited H_2O_2 production activity, with PTA-TAB reaching 1921 µmol g_{cat}^{-1} over 23 h and showing excellent stability over three cycles. PTA-THB showed a high initial rate but partial deactivation. The results demonstrate the potential of COFs as efficient, sustainable photocatalysts for H_2O_2 generation using only water, air, and visible light, offering a green alternative for industrial applications.
Keywords: photocatalysis, artificial photosynthesis, covalent-organic frameworks

Introduction

Hydrogen peroxide is a vital chemical used in disinfection, chemical synthesis, and environmental remediation. However, conventional production methods, such as the anthraquinone process, rely on fossil-derived organics and noble-metal catalysts, generating chemical waste and also being energy-intensive. Alternative routes, including electrochemical synthesis and direct $H_2 + O_2$ reactions, face challenges like high costs, catalyst degradation, and safety risks. Thus, developing a sustainable and efficient approach for H_2O_2 production is crucial nowadays (1). In this sense, covalent-organic frameworks (COFs) have emerged as promising free-metal photocatalysts due to their tunable porosity, high surface area, and excellent stability. Their conjugated structures enable efficient light absorption and charge separation, making them ideal for photocatalysis applications (2). Thus, in this study, we synthesized three novel COFs by coupling 1,10-phenanthroline-2,9-dicarbaldehyde (PTA) with three amine-based linkers: 4,4',4''-(1,3,5-triazine-1,3,5-triyl)trianiline (TTT), 5'-(4-aminophenyl)-[1,1':3',1''-terphenyl]-4,4''-diamine (TAB), and benzene-1,3,5-tricarbohydrazide (THB), forming PTA-TTT, PTA-TAB, and PTA-THB, as depicted in **Figure 1**. All of them were evaluated for H_2O_2 photosynthesis using only water and air (no sacrificial agents).

Experimental

Synthesis of Covalent-Organic Frameworks

The organic linkers (30 mg each) were dispersed in DMF (15 mL) with malononitrile (30 mg) and triethylamine (20 mg). The mixture was sonicated for 10 min. After, it was kept stirring for 24 h at 70 ºC. The resulting solid was isolated by filtration and washed with DMF. The products were evacuated at 120 ◦C under vacuum overnight to obtain the dried materials.

Photocatalytic tests for H_2O_2 production

In a typical experiment, 1.5 mg of COF was dispersed in 30 mL of deionized water inside a quartz reactor. The suspension was homogenized by ultrasonication for 30 min, and no sacrificial agent was added. Prior to illumination, the suspension was stirred in the dark for 30 min to establish equilibrium. The photocatalytic reaction was initiated using a 150 W xenon lamp equipped with a visible light filter (λ = 390–720 nm). The concentration of H_2O_2 formed during the reaction was quantified using the potassium titanium oxalate colorimetric method. At designated time intervals, 1.5 mL of the reaction solution was withdrawn using a syringe with a 0.2 µm filter, and mixed with 2.5 mL of 0.02 M potassium titanium oxalate (3). The formation of titanium oxalate complexes with the H_2O_2 produced resulted in a color change from transparent to yellow, which was measured by UV-Vis at 379 nm.

Results and Discussion

The synthesized COFs passed through a series of physico-chemical, optical and electrochemical characterization techniques, aiding for fully elucidate the structural differences and understanding the impact of the different THB, TTT and TAB ligands in the COFs activity.

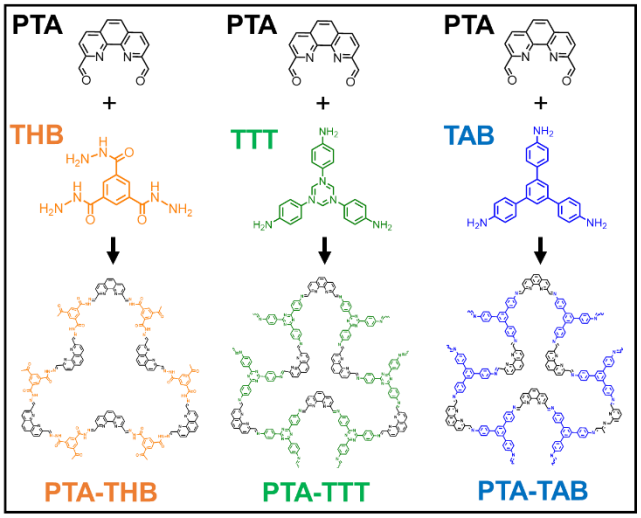

Figure 1. Chemical structure of the new COFs studied in this work.

The results indicate that all COFs exhibit catalytic activity, with PTA-TAB, PTA-THB, and PTA-TTT achieving productivities of 729, 827, and 260 µmol H_2O_2 $gcat^{-1}$ over 7 h, respectively. Despite PTA-THB having the highest initial rate, slight deactivation was observed over time, whereas PTA-TAB maintained stability over 23 h, making it the most promising candidate (**Figure 2**).

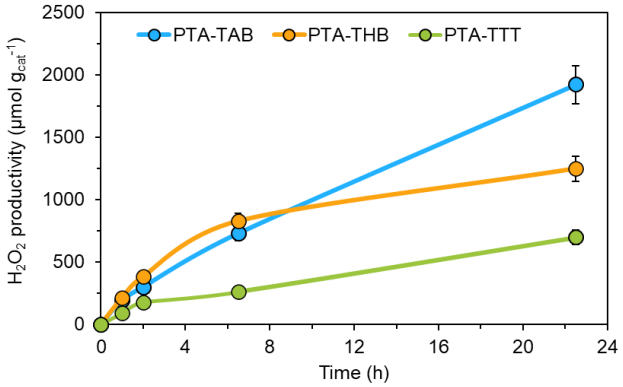

Figure 2. Evaluation of H_2O_2 production under water and air atmosphere (no purge) among the synthesized COFs.

Recyclability tests confirmed PTA-TAB robustness, with minimal productivity loss over three cycles (1921 → 1789 → 1687 µmol H_2O_2 $gcat^{-1}$). Thus, at long-term performance, PTA-TAB demonstrates stability and efficiency, making it a promising material for green chemical applications and industrial processes.

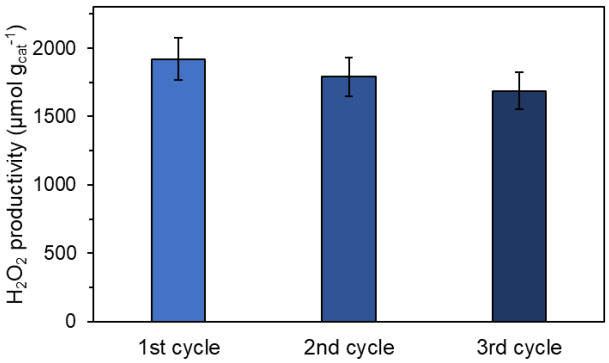

Figure 3. Stability of PTA-TAB over consecutive cycles (t = 23 h) for H_2O_2 production under water and air atmosphere (no purge).

Conclusions

These findings highlight the potential of COFs as efficient, metal-free, and sustainable photocatalysts for H_2O_2 production, utilizing only water, air, and visible light. More information regarding reaction mechanisms and optimization of the reaction conditions will be investigated.

Acknowledgements

FAPESP (Nº. 2024/01609-3 and 2023/08875-8), CAPES, CNPq, CNRS and Normandy Region (SunToChem project).

References

1. Yong, Z.; Ma, T. *Angew. Chem*. **2023**, *4*.
2. Kou, M.; et. al. *Angew. Chem*. **2023**, *61, 19*.
3. Liu, Y.; et. al. *Appl. Catal. B.* **2023**, *331*.