PHI-Single-Atom Photocatalyst for Biomass Conversion

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Resumo/Abstract

RESUMO
Os nitretos de carbono, como PHI e PTI, apresentam propriedades ópticas e eletrônicas únicas, o que os torna materiais promissores para aplicações fotocatalíticas. Esses materiais possuem uma estrutura planar análoga ao grafeno e podem ser modificados para aprimorar suas propriedades de superfície. Sua organização estrutural excepcional e comportamento semicondutor na região da luz visível os tornam candidatos ideais para a fotocatálise em reações de oxirredução, incluindo fotólise da água, redução de CO2, captação de poluentes e processos direcionados de oxidação e redução. Os nitretos de carbono também têm o potencial de gerar catalisadores de átomo único ao se coordenarem com diferentes metais, resultando em sítios metálicos dispersos atomicamente que maximizam a atividade química. Isso permite a produção química sustentável, utilizando a energia solar como força motriz para reações oxidativas. Uma aplicação específica envolve a produção de produtos furfurálicos oxidados, como o furanoato de metila, que podem ser derivados de biomassa e apresentam características ecologicamente amigáveis. A transição para fontes renováveis de carbono assegura a retenção do equilíbrio de carbono no ecossistema, ao mesmo tempo em que gera combustíveis e produtos químicos com menores impactos ambientais.

*Palavras-chave: nitretos de carbono, biomassa, fotocatálise, catalisadores de átomo único.*

ABSTRACT -
Carbon nitrides, such as PHI and PTI, exhibit unique optical and electronic properties, making them promising materials for catalytic applications. These materials possess a planar structure similar to graphene and can be modified to enhance their surface properties. Their exceptional structural organization and semiconducting behavior in the visible light region make them ideal candidates for photocatalysis in redox reactions, including water splitting, CO2 reduction, pollutant harvesting, and targeted oxidation and reduction processes. Carbon nitrides also have the potential for generating single-atom catalysts (SACs) by coordinating with different metals, resulting in atomic dispersed metal sites that maximize chemical activity. This enables sustainable chemical production by utilizing solar energy as a driving force for oxidative reactions. Some of the potential application for these materials involves the production of oxidized furfural products, such as methyl furanate, which can be derived from biomass and offers environmentally friendly characteristics. Shifting towards renewable carbon sources ensures carbon balance retention in the ecosystem while generating fuels and chemical products with lower environmental impacts.

*Keywords: carbon nitrides, biomass, photocatalysis, single atom catalysts (SACs).*

## Introduction

Carbon nitrides are polymeric carbon-based compounds with a planar structure and an ideal general formula of C3N4. These materials possess unique optical and electronic properties that make them promising for photocatalytic applications. Graphitic carbon nitrides, in particular, have a 2D stackable crystal structure that not only enhances their optical properties, but also allows for surface modifications for different applications (1-2), such as photooxidation of biomass derivatives.

Using photocatalysis, it is possible to drive oxidative reactions using solar energy as an irradiation source. This process offers a promising alternative for producing oxidized furfural products, utilizing efficient oxidation catalysts. A highly desirable product derived from the esterification of furfural is methyl furanate. This substance can be obtained through a two-step process. In the first step, furfural undergoes oxidation, resulting in furfuric acid. Then, in the second step, furfuric acid undergoes esterification to produce methyl furanate Methyl furanate, derived from biomass, has significant market potential due to its environmentally friendly properties. As a result, biomass has been gaining attention as a potential substitute for fossil fuel resources, particularly for generating fuels and chemical products with lower environmental impacts (3-4).

## Experimental

*1 Synthesis of Na-PHI*

A highly crystalline carbon nitride material, known as Na-PHI, was synthesized by polymerizing melamine in the presence of molten salt (NaCl) at a ratio of 1:10 (wt%). The resulting mixture was then ground using a ball mill and transferred to an alumina crucible. The crucible was subjected to calcination at 600 °C with a ramp rate of 2.3 °C/min for 4 hours, under a constant flow of nitrogen gas (0.1 L/min). After calcination, the yellowish Na-PHI product was washed multiple times with deionized water to remove excess salts and then dried overnight at 60 °C.

*1.1 Metal single-atoms incorporation*

To introduce transition metals into the Na-PHI framework, a cation exchange method was employed. Specifically, 200 g of Na-PHI was suspended in a 10 mL aqueous solution containing 0.01 M metal chloride (FeCl3.6H2O or CoCl2.6H2O). The suspension was sonicated for 30 minutes and then washed several times with deionized water to remove any remaining metal ions. Finally, the sample was dried overnight at 60 °C.

*1.2 Photo-catalysis tests*

The synthesized catalysts were tested for the oxidation reaction of furfural, aiming to produce carboxylic acids and esters as reaction products. In a typical reaction, 25 mg of catalyst was added to a 50 mL quartz reactor tube containing a mixture of 0.1 mmol of substrates, and oxygen flushed to 2 bar as the oxidizing agent. The reaction mixture was then placed in a photocatalytic reactor equipped with a purple LED lamp (410 nm, 50 W). After the reaction, the products were separated from the catalyst through centrifugation and analyzed using gas chromatography-mass spectrometry (GC-MS).

## Resultados e Discussão



Figure 1. XRD diffractogram of spectra for Na-PHI, Co-PHI-1% and Fe-PHI.

X-ray diffraction analysis revealed that both Na-PHI, Fe-PHI and Co-PHI exhibit highly crystalline and well-organized structures in a hexagonal lattice, although with different space groups. The substitution of metal in the Na-PHI structure caused some distortion in the lattice, which was observed through signal attenuation.



Scheme 1. Furfural oxidative esterification reaction.

Figure 2.Photocatalytic results for the oxidation of furfural catalysed by Co-PHI 1%.

Figure 3. Photocatalytic results for the oxidation of furfural catalysed by Fe-PHI 1%.

Preliminary tests were conducted using gas chromatography coupled with mass spectrometry to evaluate the efficacy of catalysts in the furfural esterification reaction, when exposed to purple light, aiming to analyze the reaction conditions in which the catalyst can be more efficient. The results indicated that materials creating a slightly acidic environment are highly effective in this reaction. Among the examined catalysts, Fe-PHI 1% exhibited an 89% conversion in the production of methyl furanoate, while Co-PHI 1% demonstrated a 92% conversion for obtaining furoic acid.
 Conclusões
 Thus, based on the obtained data, it can be concluded that
Fe-PHI demonstrates superior performance in the synthesis of methyl furanate from furfural, while Co-PHI exhibits a higher yield in the production of furfuric acid.
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## Referências

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