# Visible light-driven selective C-C cleavage of glycerol into formic acid using Ni-poly(heptazine) imide

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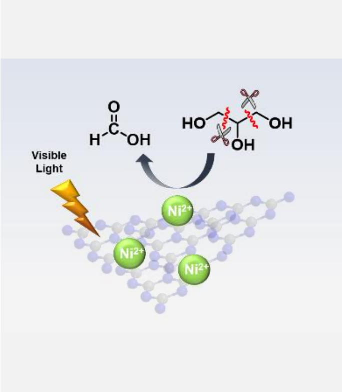

Glycerol is a byproduct massively produced in the biodiesel industry that can be used as a substrate for the production of several value-added chemicals, such as formic acid. Heterogeneous photocatalysis is a promising technique to promote this type of transformation, since it is possible to use solar energy (mostly visible radiation) to trigger the mechanism. However, this process is challenging due to the radical nature of photocatalytic processes. In this work it was observed that the insertion of nickel (Ni) into the structure of crystalline carbon nitrides synthesized via NaCl salt polymerization (called Na-poly(heptazine) imides, or simply Na-PHI) improved selectivity from 41.0% to 73.7% in 22h of radiation of blue-violet LED (415 nm). The modification was performed by the efficient cation exchange step, replacing Na with Ni in the material lattice.

## Introduction

Glycerol has already been listed among the 12 most important platform molecules for the production of energy and chemicals [1]. It is estimated that in the production of 10 tons of biodiesel, 1 ton of this compound is generated as a byproduct [2]. The inherent physicochemical properties of glycerol, such as viscosity and polymerization susceptibility, make its direct use difficult. One strategy to overcome this application obstacle is to transform it into other chemicals that can be used in other downstream processes ref. Heterogeneous photocatalysis has already proven to be a green and versatile technique for the production of organic compounds, including the conversion of glycerol [3,4].

A new class of semiconductors based on carbon nitride (g-$C_3N_4$) that is being studied intensively are Poly(heptazine) imides (PHI). Such materials are structurally ordered, absorb in the visible (largest fraction of the solar spectrum) and have a photocatalytic activity superior to conventionally synthesized g-$C_3N_4$. Another advantage is that PHI has cations that act as counter ions of the negative groups of imides that can be exchanged for transition metals, for example, and adjust their redox properties [5]. The literature on glycerol valorization through oxidation typically focuses on the formation of mildly oxidized products such as glyceraldehyde and dihydroxyacetone that are even more difficult to work with than glycerol itself.

The present work, on the other hand, aims at the production of formic acid (FA) from glycerol via photocatalysis. Formic acid, which is a stable, versatile chemical that can even be used as a source of green hydrogen if obtained from sustainable routes such this one. For this, Na-PHI was synthesized, also modified with Nickel (resulting in Ni-PHI), and both materials were evaluated in the proposed reaction.

## Material and Methods

### *Photocatalysts Synthesis*

A 1:10 solid mixture of melamine and NaCl was ground and added to a crucible which was inserted into an $N_2$-flow tube furnace, which was programmed as follows: heats at a rate of 2.3°C/min to 600°C and remain at this temperature for 4 hours. Right after reaching room temperature, the yellow solid obtained was washed abundantly with distilled water to remove excess salt and dried in an oven at 100 °C for 24 hours. This material was called Na-PHI. The insertion of nickel (2% w/w) into the structure was carried out using the cation exchange methodology [6].

### *Photocatalytic tests*

Photocatalysis tests were carried out using 20 mg of material in 2 mL of a 10 mM glycerol solution. This suspension was bubbled with oxygen for 1 min, sealed with a rubber septum, magnetically stirred and illuminated by a 415nm LED for 22h at a temperature of 25°C. An aliquot was extracted at the end of the reaction and analyzed on a Bruker 600 MHz spectrometer, adding an internal standard for product quantification.

### *Characterization*

The synthesized materials were characterized by X-ray diffractometry (XRD), diffuse reflectance spectoscopy (DRS) and Sacnning Transmission Electron Microscopy (STEM). The % Ni in the Ni-PHI structure was quantified by ICP-OES.

## Results and Discussion

The ICP-OES analysis confirmed the 2% (w/w) of nickel in Ni-PHI material. The UV-Vis spectra acquired by DRS, Fig.1 (a), indicate that both materials can absorb in the visible region. They have a similar band-gap of ~ 2.7 eV consistent with the excitation source used for the reactions. The XRD patterns, Fig.1 (b), of the two materials are identical and show sharp peaks, demonstrating the crystallinity of the material. The main reflections are (100), (110) and (002), (100) and (110) refers to trigonal lattice while (002) to stacked heptazine units [7]. The absence of additional peaks in Ni-PHI indicates that there is no formation of any type of nickel-related crystalline phase, suggesting that the transition metal is highly dispersed in the carbon nitride structure. This assumption is corroborated when TEM images are analyzed (Figure 1 d and e). The first of them, Fig. 1(c), shows the network fringes and the layers of the PHI structure. On the other hand, Fig.1 (d), obtained by the high angle annular dark field detector (HAADF) shows the contrast of Nickel in relation to the carbon/nitrogen matrix, the bright spots highlight that in fact this nickel is well dispersed in the case of Ni- PHI.

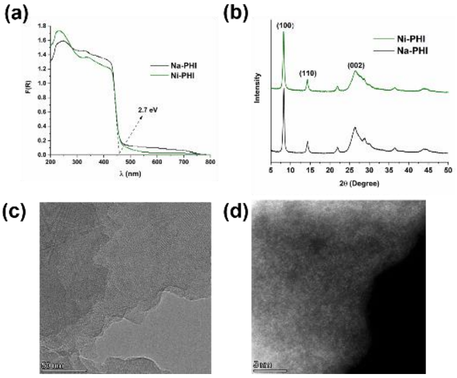

**Figure 1.** (a) Kubelka-Munk Function and (b) XRD patterns of Na-PHI and Ni-PHI, (c) HR-TEM image and (d) HAADF of Ni-PHI.

In the photocatalytic results (Fig. 2) it is possible to observe the comparison of glycerol conversion and the selectivity of the two main products: formic acid (FA) and glyceric acid (GA). It is noted that although Na-PHI shows a conversion of approximately 6% above that of Ni-PHI, the latter is capable of cleaving C-C of glycerol efficiently, 73.7% vs 41.0% of Na-PHI. The selectivity for glyceric acid does not differ in the proportion of formic acid, being 15.6% and 12.4% for Na-PHI and Ni-PHI, respectively. The increase in the oxidative character of PHI by the addition of transition metals has already been reported due to the change in the oxidation state of the metal and the formation of hydroxyl radicals [6,7].

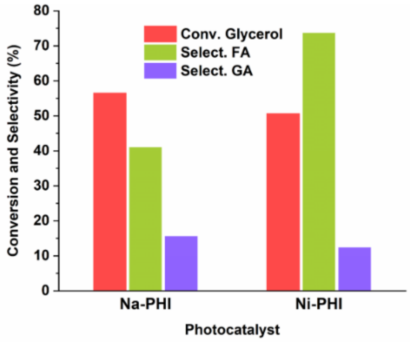

**Figure 2.** Photocatalytic conversion of glycerol comparing Na-PHI and Ni-PHI. The initials FA and GA means formic and glycolic acid, respectively.

## Conclusions

The Na-PHI photocatalyst was synthesized and modified via cation exchange using nickel to obtain Ni-PHI. These two materials showed similar crystallinity and optical absorption, but their catalytic activity differs significantly for formic acid selectivity. Na-PHI and Ni-PHI showed a conversion of 56.5 and 50.6%, respectively. However, Ni-PHI showed a selectivity of 32.7% over that obtained by the nickel-free photocatalyst, indicating that the presence of this transition metal is essential to promote the C-C cleavage of glycerol and generate formic acid.

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