

Proceeding Paper

# Carbon Nitride-Based Catalysts for High Pressure CO<sub>2</sub> Photoreduction †

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**Abstract:** In this work we focus on carbon nitride materials to improve the conversion and productivity of the photoreduction of CO<sub>2</sub>, developing a coupled strategy to optimize materials and operating conditions. The metal-free polymeric catalyst, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), is a relatively novel material, characterized by a wide absorbance in the visible region and demonstrating a superior performance compared to the commercial titania P25 benchmark, the most used photocatalyst for this application. We used an innovative photoreactor operating at high pressures of up to 20 bar, which is unprecedented in photocatalytic applications where transparent windows are needed. This enabled a boost in the solubility of CO<sub>2</sub> in water when operating the reactor as a tri-phase liquid/gas/solid device and improved the surface adsorption over the catalyst. The best productivity for HCOOH so far achieved with these catalysts at 8 bar, pH = 14 and by using Na<sub>2</sub>SO<sub>3</sub> as a hole scavenger was ca. 370 g/h kg<sub>cat</sub><sup>-1</sup>. Such productivity is several orders of magnitude higher than the literature values.

**Keywords:** CO<sub>2</sub> photoreduction; high pressure photoreactor; photocatalysts; carbon nitride; titania; ultrasound exfoliation



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## 1. Introduction

Renewable energy use is a fundamental tool to reduce the emission of CO<sub>2</sub>, mitigate climate change and provide a clean environment, as well as clean energy, for the population. Despite intermittency and fluctuations in intensity, the sun is a source of practically infinite energy, which is available for free, equally distributed on Earth and free of CO<sub>2</sub> emissions. Natural photosynthesis is a process that converts atmospheric CO<sub>2</sub> into sugar-based biomass. It is viewed as model to try to store solar energy in chemical form [1]. It is possible to exploit solar light through the production of solar fuels using photocatalysis. Heterogeneous photosynthetic processes use solid semiconductors activated through the absorption of a photon with an energy larger than the band gap [2]. Upon light absorption, an electron-hole couple is formed, and the two separated charges can be used to promote reduction or oxidation reactions with redox couples present in the reaction environment. Through this principle, solar light can be used to achieve the reduction of water to H<sub>2</sub>, or of CO<sub>2</sub> to various solar fuels. The main challenges are related to the limited lifetime of the photo-promoted charges that recombine through faster processes than the reactions of interest. Furthermore, wide band gap materials are unable to harvest solar light.

In this paper, we consider the photoreduction of CO<sub>2</sub> conducted in an innovative photoreactor able to operate at up to 20 bar of pressure to favor CO<sub>2</sub> absorption in an aqueous medium and its surface adsorption on the semiconductor catalyst. The operation at high pressure allows the exploration of an unconventionally high temperature of reaction (80–120 °C) to increase the reactivity. CO<sub>2</sub> can be converted consecutively to HCOOH, HCHO, CH<sub>3</sub>OH and CH<sub>4</sub> with increasing difficulty due to the simultaneous need for

progressively more and more electrons. In preliminary studies, we have concluded that the reaction is favored at pH = 14 (starting from the carbonate ion) which leads to the highest overall productivity and energy stored in the form of HCOOH [3–5]. Finally, CO<sub>2</sub> is reduced by a photo-promoted electron, and to complete the cycle, the holes must be filled due to the action of an electron donor. Water oxidation is too slow and to improve the activity we selected Na<sub>2</sub>SO<sub>3</sub> as hole scavenger.

Titanium dioxide is a widely employed material for this application [6,7], with favorable qualities of high abundance, low-cost [8], resistance to photo-corrosion in water [9] and recyclability [10]. However, it is characterized by a relatively large band gap and a high recombination rate of the promoted photocharges, which limits the efficiency of the process. The metal-free polymeric catalyst, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), is a relatively novel catalyst compared to TiO<sub>2</sub>. g-C<sub>3</sub>N<sub>4</sub> is characterized by a graphitic 2D-type structure and a narrow band gap (on average 2.7 eV), so in principle it is suitable for activation by visible light. g-C<sub>3</sub>N<sub>4</sub> has been prepared here via direct thermal condensation of an organic precursor containing carbon and nitrogen, i.e., melamine. Tuning of the surface area was accomplished by exfoliation with an ultrasound probe operating at variable power.

## 2. Experimental

Bulk graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) was prepared by thermal condensation of melamine, which was placed in a covered ceramic crucible and heated at 2 °C min<sup>-1</sup> up to 550–600 °C. The resulting yellow powder underwent successive treatment at different ultrasound, US, intensities, in order to obtain an exfoliated material with an increased specific surface area.

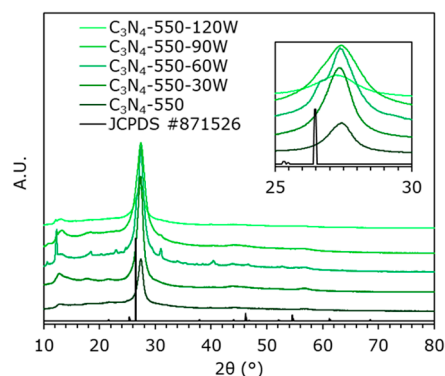
All the tests for the photoreduction of CO<sub>2</sub> were performed using an innovative pressurized batch photo-reactor, designed to work under pressures of up to 20 bar and temperatures no higher than 90 °C. Irradiation was accomplished by means of a 125 W medium pressure Hg vapour lamp made of two bulbs which emit in the range of 254–364 nm (average irradiance 153 W/m<sup>2</sup>). The optimal catalyst and hole scavenger (Na<sub>2</sub>SO<sub>3</sub>) concentrations were 31 mg·L<sup>-1</sup> for the photocatalyst and 1.67 g·L<sup>-1</sup> for the HS. Each test lasted for 24 h. The products in liquid-phase were analyzed via HPLC (LC-4000 series, Jasco, Easton, MD, USA) and the gas-phase products by GC (Agilent 7890, Santa Clara, CA, USA).

## 3. Results and Discussion

The prepared g-C<sub>3</sub>N<sub>4</sub> catalysts were analyzed by XRD and the results are reported in Figure 1. The samples were only partially crystalline and showed two main reflections at  $2\theta = 13^\circ$  and  $2\theta = 27.4^\circ$ , which were related to interplane packing of linear heptazines chains and interlayer staking of aromatic rings, respectively, in a way similar to graphite [11,12]. It is worth highlighting that there was a shift toward higher diffraction angles of the main peak with respect to the theoretical value reported in the JCPDS card. This shift is linked to the interplane distance and, in the case of the sample prepared at 550 °C, it is partially visible from the diffractogram that the exfoliation process led to a delamination of the staked sheets, though we are still far from a complete detachment [11]. C<sub>3</sub>N<sub>4</sub>-600 was more crystalline but had also a more compact structure according to the shift of the main peak.

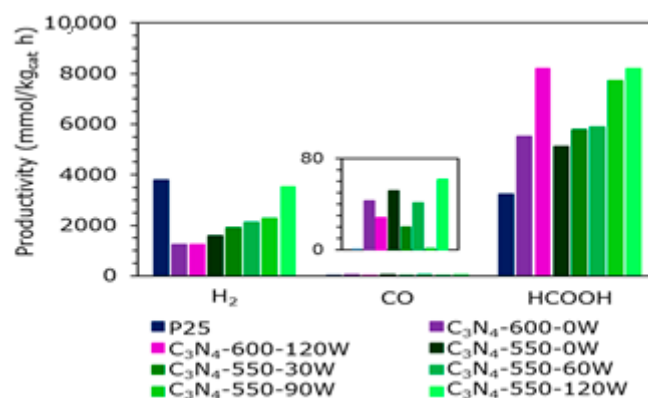
The bulk material was progressively exfoliated by using an ultrasound (US) probe at variable power of 30 to 120 W. Increasing US power led to an increase in surface area and to a decrease in crystallinity of the material, as visible by the flattening and broadening of the XRD reflections. Similar conclusions were drawn when the melamine condensation was carried out at 600 °C. Both bulk C<sub>3</sub>N<sub>4</sub> samples obtained at 550 °C and 600 °C showed low surface area, 9 and 6 m<sup>2</sup>/g, respectively, which increased to 28 and 20 m<sup>2</sup>/g when 120 W US power was applied.

The samples showed a band gap within the range 2.7–2.9 eV, as determined by diffuse reflectance UV-Vis Spectroscopy. With such a band gap the material was responsive to visible light.



**Figure 1.** XRD patterns of the g-C<sub>3</sub>N<sub>4</sub> materials prepared from melamine, calcined at 550 °C and exfoliated with variable US power (up to 120 W).

The photocatalytic activity for the photoreduction of CO<sub>2</sub> returned the following results (Figure 2) compared with commercial titania P25 nanopowder. The productivity of formic acid ranged between 4 and 8 mol/h kg<sub>cat</sub> for every sample, which is a very high value when compared with the literature. g-C<sub>3</sub>N<sub>4</sub> overperformed the commercial titania catalyst, increasing the productivity of HCOOH by at least by 30% even in the case of the bulk material, irrespective of the calcination temperature. The exfoliation procedure was effective not only in increasing the surface area, but most of all the productivity, which indeed doubled when applying the highest US power (120 W).



**Figure 2.** Productivity of HCOOH, CO and H<sub>2</sub> obtained with the prepared catalysts. Conditions: pH = 14, 31 mg/L photocatalyst, 1.67 g/L Na<sub>2</sub>SO<sub>3</sub>, 24 h reaction time, 80 °C, 8 bar.

H<sub>2</sub> productivity was in general lower than for P25, but again increased with the US power, while very small amounts of CO were observed. The gas-phase products are formed due to consecutive photo-reforming of formic acid which acts itself as a hole scavenger when the sulfite is fully consumed.

#### 4. Conclusions

A high pressure photoreactor was used for CO<sub>2</sub> photoreduction aimed at maximizing the productivity of formic acid and to develop stable materials for solar light harvesting. Graphitic carbon nitride was prepared by thermal condensation of melamine. Due to the low surface area achieved through this synthesis route, exfoliation was accomplished by US at variable power (30–120 W). Delamination was proven by XRD, and an increase in surface area from <10 to ca. 30 m<sup>2</sup>/g was indeed demonstrated. The prepared materials were more active than commercial P25, achieving 8 mol/h kg<sub>cat</sub> (i.e., ca. 370 g/h kg<sub>cat</sub>) of HCOOH at 8 bar and 80 °C, which is one of the highest productivities reported in the literature.

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