This article can be cited before page numbers have been issued, to do this please use: U. Caudillo, D. Rodriguez-Padron, M. J. Muñoz-Batista, A. Kubacka, R. Luque and M. Fernández-García, Green Chem., 2020, DOI: 10.1039/D0GC01326A.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Facile Synthesis of B/g-C$_3$N$_4$ Composite Materials for the Continuous-Flow Selective Photo-production of Acetone

Uriel Caudillo-Flores, a Daily Rodríguez-Padrón, b Mario J. Muñoz-Batista, a,c Anna Kubacka, a Rafael Luque, a,d Marcos Fernández-García a,*

In this work versatile boron–carbon nitride composite materials were synthesized and utilized in a sustainable process using sunlight as the energy source for the continuous-flow selective photocatalytic production of acetone from 2-propanol. It is worth to highlight that the samples preparation were carried out by environmentally friendly strategy, in absence of solvent or additional reagents. Samples contained boron in a 1 to 10 wt. % were subjected to physico-chemical characterization using XRD, porosimetry, UV-visible, TEM, energy-dispersion x-ray spectroscopy and XPS. Analysis of the reaction output was carried out on the basis of the reaction rate, selectivity and quantum efficiency of the process. A correlation analysis between catalytic properties with two observables, the boron phase distribution in the materials and charge handling efficiency (measured using photoluminescence), rationalizes photoactivity. Such analysis indicates that the presence of an amorphous boron metallic phase and its contact with the carbon nitride component are key to set-up a renewable and easy scalable chemical process to obtain acetone.

The most desired renewable energy source for any catalytic process corresponds to sunlight irradiation, a cost-free and endless (at least at human scale) source. Catalytic materials able to use sunlight need to efficiently use the UV and visible electromagnetic ranges of the solar spectrum. 3 In addition, photocatalysts based in cheap and high available materials such as carbon nitride are required. 4 Graphitic carbon nitride (g-C$_3$N$_4$) consists on a graphite-like structure of tris-z-triazine layers connected through amino groups. As discussed in the literature, carbon nitride owns good electronic and chemical properties and thermal stability. These properties have triggered the use of the g-C$_3$N$_4$ material as a free metal catalysis for many photochemical reactions such as organic photodegradation, water splitting or alcohol reforming. 7–11 Moreover, its use as main component in composite catalysts for attaining sunlight operated materials is a recent and hot topic nowadays explored in the current literature. 11–18

Herein, we propose the use of composite materials containing boron and carbon nitride as a sunlight-operating catalytic system, utilized in a continuous flow process for selective photo-oxidation of alcohols to ketones. Metallic Boron and doped Boron have been used previously in titania-based materials for photocatalytic applications. 10–26 In these processes, the use of boron improved the performance of the titania reference materials. In spite of the mentioned successful examples for the use of metallic boron as modifier or co-catalyst of most-frequent photocatalytic semiconductors, its combination with carbon nitride, to the best of our knowledge, has not been explored in the literature. Therefore, herein we present the synthesis of such boron – carbon nitride composite materials in a series of samples.

Introduction

The exponential growth of human population and industrial activities urges chemistry to diversify the sourcing of raw materials and to decrease its impact on environment by reducing or eliminating waste. Catalysis plays a key role for the chemical industry, being present in at least one step of ca. 80 % of the industrial chemical processes. 1 Catalytic processes are well-established and continuously but slowly being optimized to decrease energy demand and increase activity, selectivity, stability and lifetime. 2 However, to accomplish the above goals, a deep revolution in catalysis, focusing on sustainability and circular use of materials in industrial processes, is required. 3 In this context, a particularly important effort in catalysis combines the use of renewable energy sources together with catalysts obtained by facile and environmentally viable synthetic methods as well as driving the desired reaction from both activity and selectivity points of view, rendering this way high efficient and sustainable chemical processes.

---

a Instituto de Catálisis y Petroleoquímica, CSIC, C/Marie Curie 2, 28049-Madrid, Spain. E-mail: M.F-G. mfg@icp.csic.es
b Departamento de Química Orgánica, Universidad de Córdoba, Edificio Marie-Curie (C-3), Ctra Nal IV-A, Km 396, Córdoba, Spain.
c Department of Chemical Engineering, University of Granada, Av. de la Fuente Nueva S/N, 18071-Granada, Spain. E-mail: M.J. M-B. marioyunoz@ugr.es
d Peoples Friendship University of Russia (RUDN University), 6 Mikluho-Maklaya str. Moscow, 117198, Russia.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/E0xxxx00000x
containing boron in quantities going from 1 to 10 wt. %. These materials have been tested in the gas-phase continuous flow selective transformation of 2-propanol to acetone. The use of sunlight and the detailed analysis of UV and visible contributions have been also considered. In this way, outstanding yields can be achieved under all illumination (but particularly sunlight) conditions in the 2-propanol to acetone transformation using an easily synthesized combination of boron and carbon nitride components, rendering thus a truly renewable process.

**Experimental**

**Materials**

![Scheme 1. Illustrative representation of the synthetic protocol.](image)

Following a previously described procedure, graphitic carbon nitride (g-C₃N₄), employed here as a support, was prepared by calcination of melamine, during 4 h, at 580 °C in a semi-closed system. The thermal treatment was carried out employing a heating rate of 5 °C min⁻¹.¹⁴,¹⁸ Subsequently, catalyst preparation was performed following a mechanochemical approach (Scheme 1), using a Retsch PM100 planetary ball mill, with a 125 ml reaction chamber and eighteen 10 mm stainless steel balls. Proper amounts of the previously synthesized g-C₃N₄ and commercial boron (Sigma-Aldrich) were milled at 350 rpm for 15 min, in order to obtain a series of 4 samples with different boron content, ranging from 1 wt.% to 10 wt. %.

**Characterization**

XRD patterns were acquired in the Bruker D8 Advance Diffractometer with the LynxEye detector. The experiments were recorded in a 2θ scan range from 10° to 70°. Phase identification was carried out employing the Bruker Diffrac-plus Eva software, supported by Power Diffraction File database. Specific Surface area, average pore volume and size were obtained with the help of a Micromeritics equipment (model, ASAP 2010) following nitrogen adsorption at 77 K and using the Brunauer-Emmett-Teller (BET) method. Samples were degassed under argon flowing at 473 K for 2 h before nitrogen adsorption. Photoluminescence spectra were measured at room temperature on a Photoluminescence Spectrophotometer (Perkin Elmer LS50B). The optical properties of the materials (transmission or diffuse reflectance) were measured on a Shimadzu apparatus (model, UV2100) using BaSO₄ or Teflon as a reference for diffuse experiments. SEM-EDX micrographs were acquired in the JEOL-SEM JSM-7800 LV scanning microscope. Transmission electron microscopy images were taken in a JEOL 2100F TEM/STEM microscope. XPS measurements were accomplished in an ultrahigh vacuum multipurpose surface analysis instrument: SpectrUM. The samples were evacuated overnight under vacuum (10⁻⁶ Torr) and subsequently, measurements were performed at room temperature using a conventional X-ray source with a Phoibos 150-MCD energy detector. XPS CASA software was employed for the analysis of XPS results.

**Catalytic experiments and Quantum Efficiency calculation**

Photocatalytic activity and selectivity of the different solid g-C₃N₄ powders were evaluated by the photo-degradation of 2-Propanol (Aldrich, 99 %) in gas phase. The photo-degradation reactions were carried out in a continuous flow annular photo-reactor using a setup described elsewhere.²⁷ The catalyst amount employed for photo-degradation was 40 mg. The powder was suspended in 1 ml of ethanol, which was deposited on a Pyrex tube (cut-off at ca. 290 nm), and dried at room temperature to form a thin film. The gaseous mixture (prepared before entering the reaction system) in the reactor (100 ml min⁻¹) was obtained by mixing 2-propanol (Aldrich, 99.00 %) with N₂ flow, humidified at 90%. After flowing the mixture for 4-6 h in the dark (control test), the photocatalytic experiments were carried out under UV-A (Philips TL 6 W/08-F6T5 BLB, 6 W) or Sunlight type (Philips TL54-765; 6W) irradiation. For visible light experiments, we used sunlight-type lamps and a flexible polyester filter made from a deeply dyed PET material to absorb ultraviolet rays. In all cases, four fluorescent lamps symmetrically positioned outside the photo-reactor were used (see configuration at supporting information section, Fig. S1). Reaction rates were evaluated under steady-state conditions, typically achieved after ca. 2 h from the irradiation starting. Stability of the catalytic properties was tested for 24 h. The concentration of reactants and products was analyzed using an on-line gas chromatograph (Agilent GC 6890) equipped with HP-Plot-Q/HP-Innowax columns (0.5/0.32mm I.D. x 30 m) and TCD/FID detectors. Carbon balance was calculated in all reaction experiments and values above 98 %
were obtained. Selectivity data are presented as percentages on molar carbon basis.

According to the IUPAC recommendation, the quantum efficiency was calculated as the ratio of the number of molecules reacting by the number of photons interacting with the sample (Equation 1).28

$$Q.E. (\%) = 100 \times \left( \frac{n}{(\epsilon \cdot \lambda)} \right) \left( \text{mol m}^{-2} \text{s}^{-1} \right)$$

(1)

Where: $\epsilon$ is the reaction rate normalized by catalytic area and $<A>_{\text{US}}$ is the averaged local superficial rate of photon absorption (also described in the literature as LSRPA).29,30 The first observable is defined in Equation 2, and the $<A>_{\text{US}}$ one is defined by Equation 3.30,31

$$\langle \gamma \rangle = \frac{Q(C_O) - Q(C_i)}{m \cdot S}$$

(2)

$$e_{\lambda}^{A} = q_{\text{US}}(\lambda) \cdot F_{\text{As}}$$

(3)

In Equation 2, $C_o$ and $C_i$ are the concentration of the target organic molecule at times $t$ and $t=0$, $Q$ is the total flow, $S$ is the BET area ($m^2 g^{-1}$) and the mass used (m) in the reaction. In Equation 3, $F_{\text{As}}$ is the fraction of light absorbed by the sample and $q_{\text{US}}$ the radiation flux at each position ($\lambda = \chi x, y$) of the catalytic film. The surface average of the $e_{\lambda}^{A}$ observable is used in Equation 1. The $q_{\text{US}}$ term and calculation are described in the ref.27

**Results and discussion**

**Catalysts characterization**

Through this work, a simple solvent-free mechanochemical procedure was developed for the preparation of boron-modified g-C$_3$N$_4$. It is worth to remark that use of mechanochemistry possesses a strong sustainable character since it allows the preparation of outstanding materials in short reaction times (in this case 15 min) and, additionally, it avoids the use of solvents and/or other reagents, which are otherwise required by conventional methods.

The prepared materials have been fully characterized utilizing a multi-technique strategy. In particular, crystal structure and arrangement of the samples were investigated by XRD analysis (Figure 1). XRD patterns of the five studied samples displayed the presence of two main crystallographic peaks located at 13.1º and 27.4º, which are attributed to (100) and (002) planes of typical g-C$_3$N$_4$ based materials.7,14 Even if certain decrease of intensity was observed for the obtained diffractograms after the incorporation of boron, not considerable changes on the main structure of the carbon nitride phase was found. Hence, these results validated the suitability of mechanochemical procedures for the modification of g-C$_3$N$_4$ without affecting its structure by controlling the milling conditions. Moreover, not clear evidences of boron incorporation were found by XRD analysis, although the mild decrease in crystallinity may be associated with it.32,33 Such result is further discussed in the paragraphs below.

---

**Table 1. Textural and optical features of the synthesized samples.**

| Catalyst          | BET Surface area (m$^2$ g$^{-1}$) | Pore volume (m$^3$ g$^{-1}$) | Pore size (nm) | Band gap (eV) |
|-------------------|----------------------------------|------------------------------|----------------|---------------|
| g-C$_3$N$_4$      | 17.8                             | 0.101                        | 16.1           | 2.7           |
| g-C$_3$N$_4$ (M)* | 13.0                             | 0.046                        | 17.6           | 2.7           |
| 1B/g-C$_3$N$_4$   | 11.6                             | 0.047                        | 19.7           | 2.68          |
| 2.5B/g-C$_3$N$_4$ | 10.5                             | 0.047                        | 21.6           | 2.67          |

---

Textural properties of the studied materials were analyzed by N$_2$-physisorption analysis (Table 1). g-C$_3$N$_4$ sample showed surface area, pore volume and pore size, within the range of the expected and reported values for this kind of material, in accordance with other reports in the literature.14,34,35 Additionally, boron incorporation represented a loss of 50% of the initial surface area, which was not further affected by the different boron concentrations. Such results suggested that the observed changes in the textural properties were associated not exclusively (or at least not completely) to the direct functionalization with boron, but in turn with the disruption of g-C$_3$N$_4$ structure, induced by the employed mechanochemical strategy. Accordingly, pore volume values exhibited a similar tendency, while pore sizes remain stable between 16.0 and 22.0 nm. In any case, it is important to highlight that neither the process of mechanochemistry nor the increment of the boron content affect considerably the textural properties of the samples. This behavior could be beneficial for the catalytic behavior, allowing the incorporation of more active species without affecting the surface area of the final structures.
The laminar structure of the carbon nitride component is observed in the TEM micrographs presented in Figure 2 (panels A and B). As it is well-known, this laminar structure is the main responsible for the morphological properties already presented in Table 1. Presence of boron in the composite materials is easily identified as part of the darkest zones in the low magnification images included in Figure 2 (panels C and E). More detailed views obtained at higher magnifications (Figure 2D and 2F) show isolated particles of boron in the ca. 5-20 nm range for all the studied samples. In addition, it was observed certain modification of the support around the boron particles for the 10B/g-C$_3$N$_4$ sample. Amorphization of the boron-neighboring zones of carbon nitride apparently takes place, in correspondence with the change of textural properties presented in Table 1.

The amorphization corresponds to dark zones which are visible in the high resolution micrographs presented in Figure 2. A potential inclusion of B in the carbon nitride structure may concomitantly occur for samples with B content above 2.5 wt. %.

To clarify the chemical composition of the carbon nitride zones adjacent to B nanoparticles and how these zones evolved with the total B content of the materials, a TEM-EDX analysis of selected samples is presented in Figure S2.

The quantitative analysis in terms of B/C+N ratio shows that the darkest zones in sample 10B/g-C$_3$N$_4$ displays two distinctive zones of B content, likely corresponding to B nanoparticles (A3-A5) and zones where B presence is significantly lower (A2,A6,A7). Both zones display higher B content than other, more “clear” zones, separated from the boron nanoparticles. We note that the zone of intermediate B content is not detected in the case of the 2.5B/g-C$_3$N$_4$ sample. The microscopy analysis (Figures 2 and S2) strongly suggest the existence of two B rich zones. The first is associated with the presence of B nanoparticles, a fact shared by all samples. For such zones the nanoparticles are present as separate nanoparticles as well as coalescing in agglomerates, presenting in a few cases relatively high secondary particle size of dozens of nanometers (Figure 2). The second may content smaller B nanoparticles but the high resolution micrographs and EDS analyses (Figures 2 and S2), as well as the two distinctive B 1s XPS signals for loadings above 2.5 wt. % (see below) strongly suggest that doping of the carbon nitride structure by B takes place and is the dominant chemical species containing B in such zones.”

| 5B/g-C$_3$N$_4$ | 10.3 | 0.042 | 17.5 | 2.62 |
| 10B/g-C$_3$N$_4$ | 10.4 | 0.038 | 16.5 | 2.53 |

* pristine g-C$_3$N$_4$ sample mechanochemically treated.
The chemical properties of the designed materials were thus analyzed by XPS measurements. XPS spectra revealed the presence of carbon, nitrogen and boron in the catalysts. Figure 3 provides an overview of the N 1s, C 1s and B 1s regions. As can be seen in Figure 3, the spectra for both N 1s and C 1 of the g-C3N4 reference present the typical shapes as well as the peak positions (398.6 and 288.1 eV for N1s and C1s, respectively) of previous reports.\textsuperscript{13} N 1s and C 1s regions show that B incorporation to the composite materials has limited influence in the respective XPS spectra for the 1 and 2.5 wt. % loadings. At the 5 wt. % there is visible changes but only in the C 1s XPS spectra, while at the highest loadings (10 wt.%) both C 1s and N 1s XPS profiles display significant changes. Concomitant changes are observed in the B 1s region. At low loadings we can observe a dominant contribution at 186.7 eV, characteristic of metallic boron.\textsuperscript{20} For the 10 wt. % loadings (and a rather weak shoulder for the 5 wt. %), an additional contribution at ca.
191.7 eV is observed. This contribution is between the boron oxides and hydroxides (above 193.0 eV) and the hexagonal boron nitride (190.0 eV), and can be assigned to the interaction of B and N atoms (B in threefold coordination with N atoms), indicating that some of the boron atoms are introduced into the g-C\textsubscript{3}N\textsubscript{4} structure. B is replacing C atoms at the carbon nitride network.

![Graph](image_url)

**Fig. 3.** XPS spectra of the prepared samples in the N 1s (A), C 1s (B) and B 1s (C) regions.

A detailed analysis of the boron effect in the C 1s and N 1s XPS peaks was carried out. A summary of the fitting results is presented in Figure 4 for representative samples. As previously mentioned, the pure g-C\textsubscript{3}N\textsubscript{4} reference and the composite samples with loadings from 1 to 5 wt. %, present similar N 1s XPS spectra with three main contributions, related to C-N (N\textsubscript{3c}), N-C-N (N\textsubscript{2c}), N-H\textsubscript{x} contributions. This result is illustrated in Figure 4A for the 1B/g-C\textsubscript{3}N\textsubscript{4} sample. Peaks at the C 1s XPS region (Figure 4C) showed three contributions assigned to C-C, N-C=N and C-NH\textsubscript{x} (connected with the N-H\textsubscript{x} contribution above mentioned at the N 1s peak) bonds of the carbon nitride component. As it is well-known, the carbon-carbon contribution has intensity coming also from spurious carbonaceous entities (C-C/C=C). For the samples having 5 and 10 wt. % B loadings, additional contributions directly associated with the boron species present at the carbon nitride network are detected, as illustrated for the 10B/g-C\textsubscript{3}N\textsubscript{4} sample in Figure 4. In this cases, N 1s and C 1s XPS regions displayed two (corresponding to B=N-C and N-(C\textsubscript{2})B bonds) and one (C-B bond) contributions, respectively.\textsuperscript{37,38–40}

The presence of these B-related signals justified the strong shape changes observed in the N 1s and C 1s XPS regions for the tested higher loadings (Figure 3).

From the detailed analysis of the XPS spectra (Figures 3 and 4) we can thus provide evidence for the presence of a dominant metallic boron species, which according to XRD is essentially amorphous. In addition, from a 5 wt. % of boron, XPS detected the presence of a minor boron doping species at the carbon nitride network. According to the discussion of Figures 3 and 4, this doping process takes place by substitution of carbon atoms by boron and leads to the appearance of C-B and C-N bonds in the carbon nitride structure. The analysis of the corresponding intensities at the B 1s XPS region indicates that this last (doping) specie has a negligible presence for loadings below 2.5 wt. %, while is less than 10 % of the total B content of the 5B/g-C\textsubscript{3}N\textsubscript{4} sample and ca. 28 % in the 10B/g-C\textsubscript{3}N\textsubscript{4} case.
The characterization of the samples is completed with the spectroscopic examination of their optical properties. UV-visible spectra of the samples are displayed in Figure 5. The spectra are dominated by the carbon nitride component (the component dominating the molar content of the materials) and show a decay at the band gap region of the semiconductor around 400-450 nm. Considering that graphitic carbon nitride is an indirect gap semiconductor, the calculated band gap energies are included in Table 1.\textsuperscript{7,9,41}

The band gap values are constant within experimental error for the two lower loadings (1, 2.5 wt. %) and then decreases by a maximum of ca. 0.2 eV for the rest of the samples. This behavior is clearly connected with the presence of the doped boron species at the carbon nitride component for loadings equal or above 5 wt. %. In addition, the spectra showed a broad bump absorption below the region of the carbon nitride band gap. The intensity bump evolves gradually with the boron content as is thus ascribable to the amorphous boron component. This is in accordance with the existence of a semiconductor with a band gap of ca. 1.4 eV, as described in previous reports.\textsuperscript{42}

Fig. 4. Detail of XPS fitting in the N 1s (A,B), C 1s (C,D) for the 1B/g-C\textsubscript{3}N\textsubscript{4} (A,C) and 10B/g-C3N4 (B,D) samples.
Fig. 5. UV-visible spectra of the samples

Summarizing, the mechanochemical synthesis generates a composite material consisting of amorphous metallic boron and carbon nitride components for boron loadings below or equal to 2.5 wt. %. This leads to the contact between two semiconductors with very different band gap energy, potentially allowing a large profit of the UV and visible components of sunlight light ranges. Their contact can be analyzed considering the conduction and valence band positions of the semiconductors, which provides evidence that an efficient charge separation will take place under illumination.45 For around 2.5 wt. % boron loading, we observe several physico-chemical phenomena, the insertion of boron into the carbon nitride component and a significant loss of crystallinity in the local environment of this doping process.

Catalytic performance and interpretation

The catalytic results corresponding to the photo-oxidation of 2-propanol are summarized in Figure 6. This figure displays measurements of the catalytic performance of the samples using the reaction rate and the quantum efficiency observables obtained under UV and sunlight illumination conditions. All composite samples increase the activity of the reference systems (the boron reference has negligible activity, an order of magnitude below the carbon nitride). Using the most accurate analysis of activity and thus the quantum efficiency values, we can see that boron increases the activity increase is maximized under sunlight illumination. An obvious analysis of the measured enhancement factors allows concluding that the 2.5B/g-C3N4 composite profits from both, UV and sunlight components in composite samples, a fact that Figure 6 shows, does not occur with a simple physical mixture (2.5B/g-C3N4-PM).

It is worth to highlight that the activity increase is maximized under sunlight illumination. An obvious analysis of the measured enhancement factors allows concluding that the 2.5B/g-C3N4 composite profits from both, UV and visible illumination ranges but particularly from the latest (See Figure S3).

Thus, it could be clearly stated that our system is an optimum choice for the efficient use of sunlight.

Fig. 6. Reaction rate and quantum efficiency of the 2-propanol photo-oxidation for the samples under UV and sunlight-type illumination.

As depicted in Figure 7, the carbon nitride provides a reasonably high selectivity to the partial oxidation compound, acetone, with a limited quantity (ca. 15 %) of the second product, CO2, corresponding to the total oxidation of the reactant. This selectivity to partial oxidation increases significantly for the composite sample displaying maximum activity, i.e. for the 2.5B/g-C3N4 catalyst. This sample has a selectivity to acetone approaching 98.5 %, which is higher than all the previously reported materials, including titania-based materials.15,44-52 Together with the outstanding activity presented by the composite samples, these results indicated that the B/g-C3N4 composite is a highly active and selective material.

Fig. 7. Selectivity of the of the 2-propanol photo-oxidation for the samples under UV and sunlight-type illumination.

To interpret catalytic activity we first analyzed the photoluminescence of the samples under UV (320 nm) and visible (425 nm) illumination conditions. Figure 8 presents the results for the two excitation conditions. In both cases, the photoluminescence spectra of the composite samples are dominated by the major carbon nitride component with relatively minor changes among
the composite samples in terms of spectral shape. The main differences are related to the intensity of the signal, which is known to be a measure of the charge recombination.\textsuperscript{4,7} All B/g-C3N4 composite samples display decreasing intensity with respect to the carbon nitride reference for all the tested illumination conditions and concerning UV and visible illumination conditions. The largest intensity decrease between two samples occurs between the carbon nitride reference and the 1B/g-C\textsubscript{3}N\textsubscript{4} material. This clearly demonstrates that the above-mentioned contact between the amorphous metallic boron and carbon nitride semiconductors makes a profound effect in charge separation after illumination, irrespective of the wavelength, (and thus concerning the excitation of one of both semiconductors). This positive effect in charge separation takes place for all samples in correspondence with the increasing contact between the two semiconductors. However, as shown in the correlation plots included in Figure 8, the existence of a second boron species, namely the species doping of the carbon nitride structure, triggers a negative impact in catalytic activity. The shadow area in panels of Figure 8 indicates that the negative impact on activity is directly proportional to the amount of boron doping the carbon nitride for all illumination conditions (see the trend occurring from the 2.5B/g-C\textsubscript{3}N\textsubscript{4} sample, having maximum activity, and samples having higher loadings). Only the samples free of this doping boron species (and then displaying 100 % of metal B in Figure 8) are free of negative effects in catalytic properties. Maximum activity is thus not only connected with a larger contact between the amorphous boron and carbon nitride components but also with the negative effects related to the doping process of the carbon nitride. The negative effect is likely related to the decrease of crystallinity in the neighbouring of the boron doping (as suggested by TEM-EDX and XRD) and thus, likely a consequence of the preparation procedure. Disturbing the carbon nitride crystallinity (in our case as a collateral effect of the B doping process detected by XPS and TEM-EDX) affects charge separation and effective mean free path,\textsuperscript{4,5} decreasing the ability of charge carrier species to interact with chemical molecules. The 2.5B/g-C\textsubscript{3}N\textsubscript{4} catalyst activity and selectivity outstanding properties are thus the optimum achieved through a balance between positive and negative effects taking place as the boron quantity increases in the composite samples.

![Photoluminescence of the samples under UV (320 nm) and visible (425 nm) light excitation.](image)

**Fig. 8.** Photoluminescence of the samples under UV (320 nm) and visible (425 nm) light excitation. Correlation plot between quantum efficiency and photoluminescence activity or boron metal percentage. Shadow zones highlight the region with the presence of boron in the carbon nitride network.

**Conclusions**

B/g-C\textsubscript{3}N\textsubscript{4} materials were synthesized using a facile and green mechanochemical protocol. Remarkably, the aforementioned methodology could trigger the sustainable development of cost-effective protocols for...
nanomaterials synthesis, avoiding excess of reagents or the use of solvents, as well as decreasing reaction times, and hence energy consumption. Moreover, increasing boron content in the system generates different types of materials. Up to a 2.5 wt.% loading, it was obtained a binary system consisting on amorphous metallic boron nanoparticles supported on a carbon nitride compound. Above this point, the carbon nitride component is doped with boron. In such case, a minor part of boron (a maximum of ca. 30% in the 10B/g-C3N4 sample) occupies carbon positions of the carbon nitride component network.

The composite system provides high activity and selectivity in the photo-oxidation of 2-propanol to acetone. The optimum activity is achieved with a 2.5B/g-C3N4 sample which renders outstanding activity and near complete selectivity to the conversion of the alcohol moiety to the corresponding ketone. The above discovery unveils the potential of the B/g-C3N4 composite system (consisting on amorphous metallic nanoparticles supported on carbon nitride) for partial oxidation reactions under continuous flow and sunlight illumination conditions. This leads to a candidate to scale up such type of partial oxidation reaction within a truly renewable process.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support from MINECO (Spain; ENE2016-77798-C4-1-R grant), CSIC and the Secretaría de Ciencia Tecnología e Innovacion de CDMX (SECTEI, Mexico) gratefully acknowledged. M. Fernández-García acknowledges fruitful general discussions with Prof. F. Fernández-Martín. M.J. Muñoz-Batista thanks the “Plan Propio de Investigación-Proyectos de investigación precompetitivos para Jóvenes Investigadores” from UGR. Rafael Luque gratefully acknowledges MINECO for funding project CTQ2016-78289-P, co-financed with FEDER funds. Daily Rodríguez-Padrón also gratefully acknowledge MINECO for providing research contract under the same project. The publication has been prepared with support from RUDN University Program 5-100.

Notes and references

1. D. Rodríguez-Padrón, A. R. Puente-Santiago, A. M. Balu, M. J. Muñoz-Batista and R. Luque, ChemCatChem, 2019, 11, 18–38.
2. M. J. A., M. Michiel and van D. A. E., Chemical Process Technology, John Wiley & Sons, Second Ed., 2013.
3. P. Lanzafame, S. Perathoner, G. Centi, S. Gross and E. J. M. Hensen, Catal. Sci. Technol., 2017, 7, 5182–5194.
4. A. Kubacka, M. Fernández-Garcia and G. Colón, Chem. Rev., 2012, 112, 1555–1614.
5. J. C. Colmenares and R. Luque, Chem. Soc. Rev., 2014, 43, 765–778.
6. D. Rodríguez-Padrón, R. Luque and M. J. Muñoz-Batista, Top. Curr. Chem., 2020, 378, 1–28.
7. W.-J. Ong, L.-L. Tan, Y. H. Ng, S.-T. Yong and S.-P. Chai, Chem. Rev., 2016, 116, 7159–7329.
8. Cui Yanjuan, Wang Yuxiong, Wang Hao and Chen Fangyan, Prog. Chem., 2016, 28, 428–437.
9. I. F. Teixeira, E. C. M. Barbosa, S. C. E. Tsang and P. H. C. Camargo, Chem. Soc. Rev., 2018, 47, 7783–7817.
10. K. H. Leong, P. F. Lim, L. C. Sim, V. Punia and S. Pichiah, Appl. Surf. Sci., 2018, 430, 355–361.
11. A. Akhundi, A. Badiei, G. M. Ziarani, A. Habibi-Yangjeh, M. J. Muñoz-Batista and R. Luque, Mol. Catal., 2020, 488, 110902.
12. B. Lin, H. An, X. Yan, T. Zhang, J. Wei and G. Yang, Appl. Catal. B Environ., 2017, 210, 173–183.
13. N. F. F. Moreira, M. J. Sampaio, A. R. Ribeiro, C. G. Silva, J. L. Faria and A. M. T. Silva, Appl. Catal. B Environ., 2019, 248, 184–192.
14. M. J. Muñoz-Batista, D. Rodríguez-Padrón, A. R. Puente-Santiago, A. Kubacka, R. Luque and M. Fernández-García, ChemPhotoChem, 2018, 2, 870–877.
15. L. Chen, X. Zhou, B. Jin, J. Luo, X. Xu, L. Zhang and Y. Hong, Int. J. Hydrogen Energy, 2016, 41, 7292–7300.
16. M. L. Yola, T. Eren and N. Atar, Chem. Eng. J., 2014, 250, 288–294.
17. W. Zhang, T. Hu, B. Yang, P. Sun and H. He, J. Adv. Oxid. Technol., 2013, 16, 261–267.
18. A. Zaleska, J. W. Sobczak, E. Grabowska and J. Hupka, Appl. Catal. B Environ., 2008, 78, 92–100.
19. A. Zaleska, E. Grabowska, J. W. Sobczak, M. Gasza and J. Hupka, Appl. Catal. B Environ., 2009, 89, 469–475.
20. E. Grabowska, A. Zaleska, J. W. Sobczak, M. Gasza and J. Hupka, in Procedia Chemistry, Elsevier, 2009, vol. 1, pp. 1553–1559.
21. E. Bilgin Simsek, Appl. Catal. B Environ., 2017, 200, 309–322.
22. R. Khan, S. W. Kim, T. J. Kim and C. M. Nam, Mater. Chem. Phys., 2008, 112, 167–172.
23. M. J. Muñoz-Batista, A. Kubacka, A. B. Hungria and M. Fernández-García, J. Catal., 2015, 330, 154–166.
24. S. E. Braslavsky, A. M. Braun, A. E. Cassano, A. V. Emeline, M. I. Litter, L. Palmisano, V. N. Parmmon and N. Serpone, Pure Appl. Chem., 2011, 83, 931–1014.
25. G. E. Imoberdorf, A. E. Cassano, O. M. Alfano and H. A. Irazoqui, AIChE J., 2006, 52, 1814–1823.
26. M. J. Muñoz-Batista, M. M. Ballari, A. Kubacka, O. M. Alfano and M. Fernández-García, Chem. Soc. Rev., 2019, 48, 637–682.
27. G. E. Imoberdorf, A. E. Cassano, H. A. Irazoqui and O. M. Alfano, Chem. Eng. Sci., 2007, 62, 1138–1154.
32 J. Zou, Y. Yu, W. Yan, J. Meng, S. Zhang and J. Wang, J. Mater. Sci., 2019, 54, 6867–6881.
33 J. Li, M. Ran, P. Chen, W. Cui, J. Li, Y. Sun, G. Jiang, Y. Zhou and F. Dong, Catal. Sci. Technol., 2019, 9, 4531–4537.
34 M. J. Muñoz-Batista, L. Andrini, F. G. Requejo, M. N. Gómez-Cerezo, M. Fernández-Garcia and A. Kubacka, Mol. Catal., 2020, 484, 110725.
35 C. Leal-Rodriguez, D. Rodriguez-Padron, Z. A. ALothman, M. Cano, J. J. Giner-Casares, M. J. Muñoz-Batista, S. M. Osman and R. Luque, Nanoscale, , DOI:10.1039/d0nr00818d.
36 C. D. Wanger, W. M. Riggs, L. E. Davis, J. F. Moulder and G. E. Muilenberg, Handbook of X-ray photoelectron spectroscopy: a reference book of standard data for use in X-ray photoelectron spectroscopy, Physical Electronics Division, Perkin-Elmer Corp., 1979.
37 J. Wei, W. Shen, C. Zhang, Y. Zhou and H. Liu, Catal. Today, 2018, 316, 199–205.
38 V. Thirumal, A. Pandurangan, R. Jayavel and R. Ilangoovan, Synth. Met., 2016, 220, 524–532.
39 H. J. Muhr, R. Nesper, B. Schnyder and R. Kötz, Chem. Phys. Lett., 1996, 249, 399–405.
40 U. Caudillo-Flores, M. J. Muñoz-Batista, R. Luque, M. Fernández-Garcia and A. Kubacka, Chem. Eng. J., 2019, 378, 122228.
41 G. Mamba and A. K. Mishra, Appl. Catal. B Environ., 2016, 198, 347–377.
42 P. L. Jones, L. J. Dimmey, H. Park, F. H. Cocks and H. Hacker, J. Non. Cryst. Solids, 1983, 55, 335–341.
43 X. Yong and M. A. A. Schoonen, Am. Mineral., 2000, 85, 543–556.
44 A. Mylonas, A. Hiskia, E. Androulaki, D. Dimotikali and E. Papaconstantinou, Phys. Chem. Chem. Phys., 1999, 1, 437–440.
45 F. Arsac, D. Bianchi, J. M. Chovelon, C. Ferronato and J. M. Herrmann, J. Phys. Chem. A, 2006, 110, 4202–4212.
46 G. Marci, E. García-López, L. Palmisano, D. Carriazo, C. Martin and V. Rives, Appl. Catal. B Environ., 2009, 90, 497–506.
47 G. Marci, E. I. García-López, F. R. Pomilla, L. F. Liotta and L. Palmisano, Appl. Catal. A Gen., 2016, 528, 113–122.
48 U. Caudillo-Flores, M. J. Muñoz-Batista, F. Ung-Medina, G. Alonso-Núñez, A. Kubacka, J. A. Cortés and M. Fernández-García, Chem. Eng. J., 2016, 299, 393–402.
49 M. J. Muñoz-Batista, U. Caudillo-Flores, F. Ung-Medina, M. del Carmen Chávez-Parga, J. A. Cortés, A. Kubacka and M. Fernández-García, Appl. Catal. B Environ., 2017, 201, 400–410.
50 M. J. Muñoz-Batista, A. Kubacka, O. Fontelles-Carceller, D. Tudela and M. Fernández-García, ACS Appl. Mater. Interfaces, 2016, 8, 13934–13945.
51 M. J. Muñoz-Batista, A. Kubacka and M. Fernández-García, Catal. Sci. Technol., 2014, 4, 2006.
52 M. J. Muñoz-Batista, A. Kubacka, M. N. Gómez-Cerezo, D. Tudela and M. Fernández-García, Appl. Catal. B Environ., 2013, 140–141, 626–635.
53 W.-J. Ong, L.-L. Tan, S.-P. Chai and S.-T. Yong, Dalt. Trans.,
Metal boron-g-C₃N₄ composite samples synthesized by mechanochemistry with remarkable selectivity to acetone during the photo-oxidation of 2-propanol.