

IMPERIAL

**Investigating the effect of nonmetal functionalisation on the
chemical, sorptive, optoelectronic and photocatalytic
properties of semiconducting boron and carbon nitride
materials**

By Ioanna Itskou

A thesis submitted in fulfilment of the requirements for the degree of Doctor of

Philosophy and the Diploma of Imperial College London

Department of Chemical Engineering

Imperial College London, UK

February 2025

ABSTRACT

Solar-driven catalytic CO₂ conversion to carbon-containing fuels and value-added chemicals represents an interesting pathway towards achieving the United Nations' climate targets. Bifunctional photocatalysts can be employed for this process, which can capture and convert CO₂ using absorbed photon energy from sunlight. Given that a large percentage of the incident solar energy belongs to the visible range, it is important to design visible light-active photocatalysts. In addition, in prospect of any practical applicability, the CO₂ photoreduction efficiency needs to be enhanced by orders of magnitude compared to current performances, while maintaining a robust, sustainable, and scalable nature of the photocatalysts. Boron and carbon nitride materials have attracted attention as part of photocatalytic systems for CO₂ reduction. While these materials show promise, the effects of their nonmetal functionalisation on their photoactivity remain largely unknown. A greater understanding of how these functional groups incorporate within the nitride structures and impact their properties would open the route for the targeted design of better-performing photocatalysts. This thesis focuses on understanding the chemistry – functionality – photoactivity relationship of nonmetal-functionalised semiconducting nitride materials, to help design advanced photocatalysts for the CO₂ reduction reaction. Specifically, I functionalised porous boron nitride using phosphorus, and graphitic carbon nitride using boron. I used a combination of advanced characterisation techniques to explore the effects of functionalisation, including the choice of nonmetal precursor and nonmetal content, on the i) physicochemical, ii) sorptive, iii) optoelectronic and iv) photocatalytic properties of the original materials. Herein, I report

results which add to/disprove existing literature, and explore the use of some of these materials for CO₂ photo(thermal)reduction for the first time.

Overall, the findings show that the functionalised materials cannot be used as standalone photocatalysts, however the engineering of their structure can be exploited to embed them into heterojunctions and/or decorate them with cocatalysts.

STATEMENT OF ORIGINALITY

I hereby declare that this thesis is my own original work, and that any work performed by others has been properly acknowledged and referenced.

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PUBLICATIONS

As first author

1. **I. Itskou**, S. C. Sageer, D. M. Dawson, A. Kafizas, I. Nevjestic, C. M. McGilvery, M. Daboczi, G. Kerherve, S. Eslava, S. Heutz, S. E. Ashbrook, C. Petit. “Boron-functionalised graphitic carbon nitride materials for photocatalytic applications: effects on chemical, sorptive, optoelectronic and photocatalytic properties”, *under review*.
2. **I. Itskou**, A. Kafizas, I. Nevjestic, S. Gonzalez Carrero, D. C. Grinter, H. Azzan, G. Kerherve, S. Kumar, T. Tian, P. Ferrer, G. Held, S. Heutz, C. Petit. “Effects of Phosphorus Doping on Amorphous Boron Nitride’s Chemical, Sorptive, Optoelectronic and Photocatalytic Properties”, *J. Phys. Chem. C* (2024), 128, 31, 13249–13263.
3. **I. Itskou**[‡], A. L’Hermitte[‡], S. Marchesini[‡], T. Tian[‡], C. Petit. “How to Tailor Porous Boron Nitride Properties for Applications in Interfacial Processes” *Acc. Mater. Res.* (2023), 4, 2, 143–155. [‡]Equal contribution

As co-author

1. O. Olaifa, P. Alimard, **I. Itskou**, C. Petit, S. Díez-González, A. Kafizas. "Purifying the air with photocatalysis: Developing bismuth oxybromide/ copper phthalocyanine composite photocatalyst filters with enhanced activity for NO_x removal", *submitted*.
2. P. Alimard, C. Gong, **I. Itskou**, C. Petit, A. Kafizas. "Achieving High Photocatalytic NO_x Removal Activity Using a Bi/BiOBr/TiO₂ Composite Photocatalyst", *Chemosphere* (2024), 368, 143728.
3. M. Nedoma, H. Azzan, M. Yio, D. Danaci, **I. Itskou**, R. Pini, C. Petit. "The effect of adsorbent shaping on the equilibrium and kinetic CO₂ adsorption properties of ZIF-8", *Microporous Mesoporous Mater.* (2024), 380, 113303.
4. M.-Y. Low, D. Danaci, H. Azzan, A. L. Jiayi, G. W. Shun Yong, **I. Itskou**, C. Petit. "Physicochemical Properties, Equilibrium Adsorption Performance, Manufacturability, and Stability of TIFSIX-3-Ni for Direct Air Capture of CO₂", *Ener. Fuel.* (2024), 38, 13, 11947-11965.
5. B. F. Lewis, C. Huang, **I. Itskou**, G. Mallia, N. M. Harrison, J. Southouse, S. Eslava. "Ca-Doped PrFeO₃ Photocathodes with Enhanced Photoelectrochemical Activity" *Sol. RRL* (2024), 8, 14, 2400308.
6. Y. Baghdadi, F. Temerov, J. Cui, M. Daboczi, E. Rattner, M. Segundo Sena, **I. Itskou**, S. Eslava. "Cs₃Bi₂Br₉/g-C₃N₄ Direct Z-Scheme Heterojunction for Enhanced Photocatalytic Reduction of CO₂ to CO" *Chem. Mater.* (2023), 35, 20, 8607-8620.
7. G. E. M. Schukraft, **I. Itskou**, R. T. Woodward, B. Van Der Linden, C. Petit, A. Urakawa. "Evaluation of CO₂ and H₂O Adsorption on a Porous Polymer Using DFT and In Situ DRIFT Spectroscopy" *J. Phys. Chem. B* (2022), 126, 40, 8048-8057.

PRESENTATIONS AND INVITED TALKS

Invited talks/seminars

1. Imperial College Chemical Engineering Spotlight Talk, “Materials for a brighter future: designing photocatalysts for solar fuels production”, London, 24 Apr 2024.
2. Energy Futures Lab Lunchtime Seminars, “Solar fuels for combating climate change”, London, 15 Feb 2024.
3. Imperial College Towards Net-Zero Seminars, “Phosphorus-Doped Boron Nitride Materials for CO₂ Adsorption and Photoreduction”, London, 13 Oct 2023.

Poster presentations

1. Imperial College PhD Summer Showcase, “Multifunctional nanomaterials for solar fuels production”, London, UK, 13 Jul 2023.
2. 6th Annual UK Porous Materials Conference, “Investigation of P doping on porous BN properties”, Sheffield, UK, 19-20 Jun 2023.
3. STEM for Britain, “Investigation of P doping on porous BN properties”, London, UK, 6 March 2023.
4. Catalysis Fundamentals and Practice Summer School, “Investigation of phosphorus doping on porous boron nitride optoelectronic and photocatalytic properties”, Liverpool, UK, 18-22 Jul 2022.
5. Imperial College Chemical Engineering PhD Symposium, “Investigation of phosphorus doping on porous boron nitride optoelectronic and photocatalytic properties”, London, UK, 28 Jun 2022.

Oral presentations

1. 2024 MRS Fall Meeting & Exhibit, “Boron (B)-doped carbon nitride (gC_3N_4) materials for photocatalytic applications”, Boston, MA, USA, 1-6 Dec 2024.
2. Imperial College Chemical Engineering PhD Symposium, “Materials for a brighter future: designing photocatalysts for solar fuels production”, London, UK, 27 Jun 2024.
3. MATSUS Spring 2024 conference. “Boron (B)-doped carbon nitride (gC_3N_4) materials for photocatalytic applications”, Barcelona, Spain, 2-8 March 2024.
4. FEMS EUROMAT Congress, “Porous Phosphorus-Doped Boron Nitride Materials for CO_2 Adsorption and Photoreduction”, Frankfurt am Main, Germany, 3-7 Sep 2023.
5. AIChE Annual Meeting, “Investigation of phosphorus doping on porous boron nitride properties”, Phoenix, AZ, USA, 13-18 Nov 2022.
6. 10th UK Solar Fuels Symposium an ECR Event, “Investigation of phosphorus doping on porous boron nitride optoelectronic and photocatalytic properties”, Newcastle, 14-15 Jul 2022.

ACKNOWLEDGEMENTS

I am lucky to be surrounded by so many supportive people; people who have contributed in their own way to my PhD journey, and who helped me make it to this point, and I would be remiss if I did not acknowledge them.

Thank you to ...

... my PhD supervisor, Professor Camille Petit. Thank you for taking a chance on me and welcoming me in (y)our group, for your trust and your continuous support in more-than-one ways, for helping me grow personally and professionally, for being someone I aspire to be like.

... my assessor, Dr Salvador Eslava, and my collaborators from all different research groups, departments, institutes. Thank you for your advice and expertise, for your technical support, for broadening my knowledge, and for making our research stronger.

... my fellow past and current Petit Group members. Thank you for making the group an enjoyable and accepting place to be, for your technical help/advice, for our fun activities.

... my friends, Valia, Sofia, Anna, Anastasia, Lila, Katerina, May, Kleio, Hassan, Reza, Elena, Thanos, Chris. Thank you for your patience, for our happy moments, for lifting me up and making me laugh, for always being there for me.

... my family. Thank you for encouraging me to be myself, for your support and guidance, for giving me everything I needed, for helping me follow my ambitions, for being my safe place.

... Killian. Thank you for being by my side, for supporting me, for reminding me to take a step back when I felt overwhelmed, for the many happy memories.

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LIST OF ABBREVIATIONS

aBN	Amorphous boron nitride
ATR	Attenuated total reflectance
B	Boron
BA	Boric acid
BCN	Boron carbonitride
B-CN	Boron-functionalised graphitic carbon nitride
BET	Brunauer-Emmett-Teller
BN	Boron nitride
C ₃ N ₄	Carbon nitride
CB	Conduction band
cBN	Cubic boron nitride
CP	Cross polarisation
DFT	Density functional theory
DRS UV/Vis	Diffuse reflectance spectroscopy in the UV-visible
DSL	Dual site Langmuir
EDS or EDX	Energy dispersive X-ray spectroscopy
EELS	Electron energy loss spectroscopy
EPR	Electron paramagnetic resonance spectroscopy
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
gC ₃ N ₄ or CN	Graphitic carbon nitride
GCMS	Gas chromatographer – mass spectrometer

GHGs	Greenhouse gases
GIPAW	Gauge-including projector augmented wave
hBN	Hexagonal boron nitride
ICP	Inductively coupled plasma spectroscopy
IL	Ionic liquid
IR	Infrared
IRF	Instrument response factor
MAS	Magic-angle spinning
MQ	Multiple quantum
n.a.	Not applicable
n.d.	Not detected
NHE	Normal hydrogen electrode
NMR	Nuclear magnetic resonance
PA	Phosphoric acid
P-BN	Phosphorus-functionalised boron nitride
PCA	Principal component analysis
PL	Photoluminescence
PMT	Photomultiplier tube
QE	Quantum efficiency
rBN	Rhombohedral boron nitride
S(T)EM	Scanning (transmission) electron microscopy
S-BN	Sulfur-functionalised boron nitride
SCE	Saturated calomel electrode

TAS	Transient absorption spectroscopy
tBN	Turbostratic boron nitride
TCSPC	Time-correlated single photon counting
TEM	Transmission electron microscopy
TEY	Total electron yield
TOF	Turnover frequency
TON	Turnover numbers
UV	Ultraviolet
VB	Valence band
XANES/NEXAFS	Near edge X-ray absorption fine structure spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZORA	Zeroth order relativistic approximation

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1. INTRODUCTION

Today's society is faced by a state of emergency to address the environmental crisis the world is currently facing due to ever increased greenhouse gases (GHGs) emissions. In fact, the European Energy Roadmap's 2050 ambition includes the reduction of GHGs emissions up to 80-95% below 1990 levels, with the simultaneous exploitation of renewable energy (a share of at least 55% in annual energy consumption)¹. This situation presents a great opportunity to reshape our energy portfolio, replace fossil fuels and implement alternative routes to the production of fuels and chemicals.

One of the pathways towards achieving these goals is the use of solar fuels, where a starting molecule like carbon dioxide (CO_2) or water (H_2O) gets converted into fuels (*e.g.* H_2 , CH_4 , CH_3OH) or value-added chemicals (*e.g.* CO) with the use of solar energy. This light-assisted conversion can be performed through state-of-the-art technologies such as photoelectrocatalysis², photovoltaic/electrocatalysis³, photocatalysis⁴ and photothermal⁵ catalysis. Photocatalysis only requires the solar energy input to reach the necessary activation energy for product (solar fuels) formation, as opposed to the other methods which require applied electric field, thermal energy or tandem devices. Out of the examined photocatalytic reactions, *i.e.* H_2O splitting for H_2 production and CO_2 photoreduction to C-based chemicals and fuels, the latter is the least extensively studied due to inherent thermodynamic barriers and kinetic requirements⁶. However, it remains highly interesting as it provides a unique route to build a new chemicals and fuels production platform based on CO_2 as feedstock as opposed to fossil fuels.

Emerging photocatalysts for CO_2 reduction include materials based on boron nitride⁷ and carbon nitride⁸ (BN and gC_3N_4) due to their interesting properties; however, these materials

need to be functionalised to overcome applicability limitations. A promising nanoengineering strategy is the integration of nonmetal heteroatoms into the materials' structure⁹. This strategy has been explored in literature, but the chemistry – structure – photoactivity relationship of the modified materials is yet to be elucidated. The goal of this thesis is to investigate the effects of phosphorus (P) and boron (B) functionalisation of BN and gC₃N₄, respectively, on the chemical, sorptive and optoelectronic properties influencing the CO₂ photo(thermal) reduction.

This thesis comprises eight chapters in total, including the present introductory **Chapter 1**. **Chapter 2** presents the fundamentals of photocatalysis and CO₂ reduction reaction, and offers a comprehensive review of the reported effects of nonmetal functionalisation on BN and gC₃N₄'s chemical, sorptive, optoelectronic and photocatalytic properties. In **Chapter 3**, the literature gaps in the field of nonmetal-functionalised BN and gC₃N₄ for CO₂ photo(thermal) reduction are identified, leading to the objectives of my research. **Chapter 4** involves an experimental section with the most frequently used techniques throughout my PhD. The motivation and experimental details behind the projects I led, along with results, discussion and supporting information thereof, are analysed in **Chapters 5** through **7**. Finally, the conclusions of my study and the suggested next steps for future research are summarised in **Chapter 8**.

2. LITERATURE REVIEW

2.1. Fundamentals of photocatalysis and CO₂ reduction

As mentioned in **Chapter 1**, photocatalysis is one of the pathways towards the production of sustainable solar fuels and value-added chemicals. The specific reaction of interest in this thesis is CO₂ conversion using functionalised boron and carbon nitride materials. In this Section, we look into the fundamentals of the photocatalytic process, delve into light- and/or heat-assisted catalytic CO₂ reduction, and explore boron and carbon nitride-based materials that have been studied for this reaction.

2.1.1. Photocatalysis step-by-step

The photocatalytic process can be divided into four distinct stages¹⁰. First comes the light absorption. Certain materials, when irradiated with light of energy $h\nu$, can absorb part of the incident photons, and convert light (ideally solar energy) into chemical energy. Secondly, due to the newly absorbed energy, valence electrons get excited to the conduction band (CB), leaving positively charged species (holes) in the valence band (VB). Therefore, we have formation of photoexcited electron-hole pairs, also known as excitons, charge carriers, or charged species. The next step is charge carrier migration and diffusion. These charged species, while formed in the bulk, need to transfer to the surface of the material to take part in reactions. Lastly, the final stage is the completion of redox reactions. Reduction takes place in the CB, where the adsorbed reactant (acceptor molecule such as CO₂) accepts photoexcited electrons and gets reduced; in parallel, oxidation takes place in the VB, where the adsorbed reactant (donor molecule such as H₂O or H₂) donates electrons to the photoexcited holes and

gets oxidised. Materials able to conduct a photocatalytic process are called photocatalysts. A scheme describing photocatalysis is presented in **Figure 2.1.1** below.

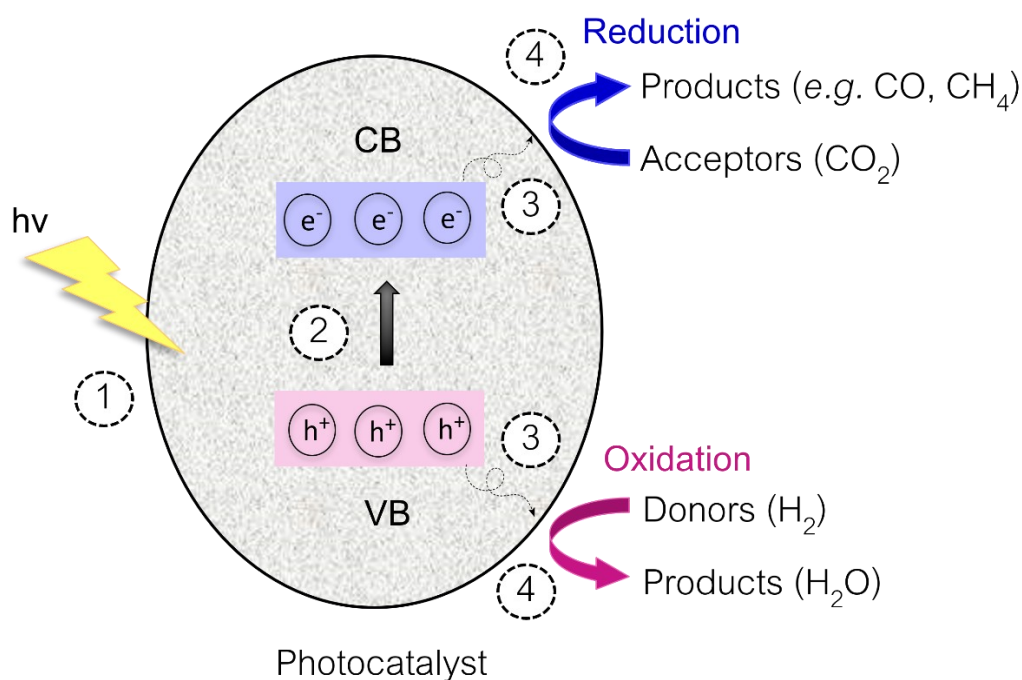


Figure 2.1. 1. Schematic describing the four steps of a photocatalytic process: 1-light absorption, 2-exciton formation, 3-charge carrier migration, 4-redox reactions. e^- and h^+ represent the photogenerated electrons and holes, respectively.

Photocatalysis, like natural photosynthesis, is a complex procedure, as there are numerous requirements and limitations involved in the different steps¹¹. A material can only absorb photons with energy equal to or greater than its bandgap energy (difference between the CB and VB). This limits the light absorption and the amount of energy that can be harvested from the illumination source (ideally the sun). For example, almost 45 % of the incident solar energy on the earth's surface belongs to the visible range (380-780 nm, *i.e.* 1.6-3.3 eV), and only 3 %

belongs to UV light (100-400 nm, *i.e.* 3.1-12.4 eV). Common photocatalysts have moderate to wide bandgap (2.3-4.0 eV)⁶, mostly absorb in the UV range with limited, if any, visible light absorption, and thus, their practical applicability remains limited. Upon irradiation, the photoinduced electron-hole pairs are formed ultrafast within fs-ps, but their recombination rates can be as fast as 10s of ps and range all the way up until some ms (in rare cases)⁶. Usually, the exciton lifetimes are only a few ns. Within these few ns, they need to migrate to the surface and take part in reactions. The charge carrier fast recombination rate is one of the limiting steps of photocatalysis, and a lot of effort is being made to probe and prolong the excitons' lifetimes¹². It needs to be pointed out that, even though a narrow bandgap favours extended light absorption, it also favours fast exciton recombination due to the small energetic difference. While the charge carriers diffuse in the bulk and transfer to the material's surface, they can be shallowly or deeply trapped in midgap states (energetic excited states in between the bandgap). Although these midgap states prolong their lifetimes, charge carriers lose part of their kinetic energy, and if they are deeply trapped, this can result in major losses in their thermodynamic (or potential) energy to take part in reactions¹². Reactant adsorption and activation is also an important factor in photocatalysis, as if these two criteria are not fulfilled, no reaction will take place¹³. In the case that all these challenges are overcome, there still exist certain requirements for the desired reaction to take place. The CB of the material needs to be lower (more negative) than the desired reaction's reduction potential; respectively, the VB needs to be higher (more positive) than the desired reaction's oxidation potential. This is the reason why most studied photocatalysts have a wide bandgap, as it can more easily encompass reactant activation and product formation potentials.

In conclusion, the ideal photocatalyst – other than being stable, non-toxic, recyclable, sustainable, easy/cheap to make – needs to display qualities that regulate the discussed limiting steps. **Table 2.1.1** below summarizes limiting steps in photocatalysis, requirements of an ideal photocatalyst, and relevant material property. It is clear that a standalone, non-engineered photocatalyst would hardly fulfil all the different requirements (as well as the mentioned standard requirements of a catalyst); there has to be a trade-off.

Table 2.1. 1. Summary of the limiting steps in photocatalysis, requirements of an ideal photocatalyst, and relevant material property.

Limiting step	Photocatalyst requirement	Material property
Limited light absorption (bandgap energy $\leq h\nu$)	Narrow enough bandgap to allow visible light absorption (min 1.6 eV)	Optoelectronic
Fast charge carrier recombination	- Wide enough bandgap to hinder fast exciton recombination - Long-lived photoexcited species	- Chemical - Structural - Optoelectronic
Charge carrier migration	Porous	Sorptive
Reactant adsorption and activation	- Porous/high surface area - Appropriate CB or photoexcited electron energy	- Chemical - Structural - Sorptive
- CB < desired reduction potential (-) - VB > desired oxidation potential (+)	- Appropriate CB and VB potentials - Appropriate bandgap	- Chemical - Optoelectronic

So far, research has focused on photocatalytic reactions of industrial and environmental interest. These involve environmental remediation (e.g. organics/dyes degradation, NO_x

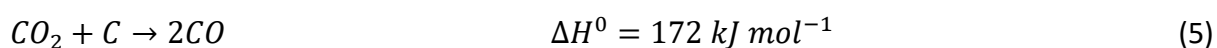
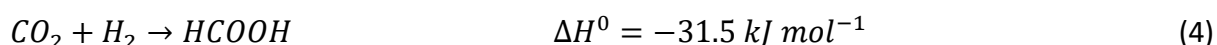
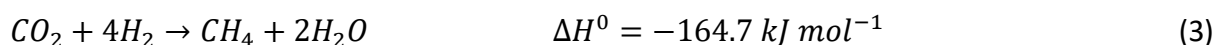
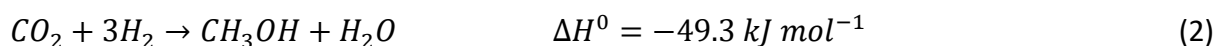
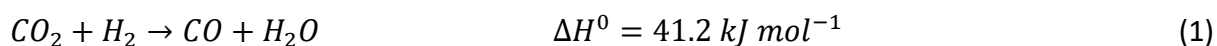
removal, metal trace removal) and production of fuels (mainly for heating and transportation) and large-scale, high-in-demand chemicals/feedstock molecules (solar fuels/chemicals). The solar fuels/chemicals production has focused on H_2O splitting (for parallel H_2 and O_2 production), CO_2 reduction (to C_1 and C_1+ products and H_2O or H_2), and N_2 fixation/reduction (to NH_3)¹⁴. Production of such fuels/chemicals is currently operated under energy-intensive conditions, and photocatalysis provides a possible alternative, greener path. More specifically, the focus of this thesis is CO_2 photo(thermal) reduction.

2.1.2. CO_2 reduction reaction

A major challenge inherent to the CO_2 conversion is the molecule's activation. CO_2 is a linear, nonpolar, thermodynamically inert and stable molecule that requires a large energy input for its $\text{C}=\text{O}$ bond dissociation (750 kJ mol^{-1}). To overcome such thermodynamic barriers, high pressure and temperature conditions are traditionally employed in thermal catalysis^{6,15}. In photocatalysis, the required energy input stems from solar energy, and the photocatalyst's ability to convert solar to chemical energy. Admittedly, although greener, it is a more challenging and complex route than traditional catalysis. In photothermal catalysis of CO_2 , the energy input is a combination of solar energy and increased temperature (and occasionally, pressure too).

Traditionally, thermal CO_2 reduction takes place in gas phase using mostly transition metal oxide-based catalysts (*i.e.* TiO_2 , CeO_2 , Al_2O_3 , ZrO_3 , MgO , NiO , BiVO_4), often decorated with metals, under 1-30 bar and $300\text{-}1000^\circ\text{C}$ ¹⁶. Depending on the reaction conditions, such as the choice of reactants, reactant ratio, temperature and pressure, different final products will be obtained. Product yield can be boosted by catalyst engineering and reaction duration, while

product selectivity can be greatly affected by choice of catalyst. CO₂ can also be used as soft oxidant for alkane dehydrogenation (alkene production), alkane cracking (CH₄ production) and reforming (CO production) reactions^{17–19}. The main CO₂ conversion reactions, along with enthalpy of the reaction at 25 °C (ΔH^0), are^{20,21}:



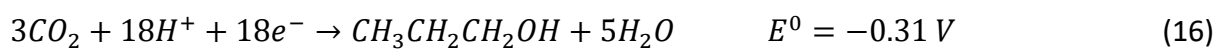
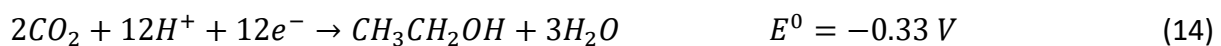
CO₂ photoreduction

Research is being conducted to form the previously mentioned desired fuels/products (CO, C₁ and C₁+ hydrocarbons) from CO₂ under milder conditions (*i.e.* ambient temperature and pressure) using renewable energy (*e.g.* solar energy). One of the pathways towards achieving this – other than photoelectrocatalysis² and photovoltaic/electrocatalysis³ – is photocatalytic CO₂ reduction^{4,6,22}. This reaction was originally performed in liquid phase, inspired by (photo)electrocatalysis and H₂O splitting, but nowadays is mostly performed in gas phase, similar to traditional thermal catalysis and taking better advantage of gas adsorption and active sites. Xe arc lamps (220-1200 nm), Hg or HgXe arc lamps (higher intensity in the UV range than Xe, 250-700 nm) or solar simulators (solar spectrum and intensity, 250-2500 nm) can be used as light sources for the reaction; solar simulators are generally preferred due to their resemblance to natural sunlight and realistic testing.

CO₂ photoconversion is a multi-step process which involves¹³:

- i) Adsorption of CO₂ onto the photocatalyst surface.
- ii) Activation of CO₂, usually through single photogenerated electron transfer for the formation of active CO₂^{δ-} species^{23–26}. It needs to be noted here that CO₂^{δ-} are not the sole possible activated species, and there can be alternative activation routes.
- iii) Reduction of CO₂ to products through complex, proton-coupled multielectron pathways involving photogenerated electrons and protons. Respectively, parallel oxidation of a proton donor (usually H₂O or H₂) to products²⁷.
- iv) Desorption and release of formed products from the photocatalyst surface.

The possible CO₂ conversion proton-coupled multielectron reactions, along with formed products and their relevant potentials vs Normal Hydrogen Electrode (vs NHE) at pH=7, are as follows (also including CO₂ activation potential)^{6,9,23,28}:



It is noted that the above refer to CO₂ reactions' electrochemical potentials at specific conditions (aqueous solution with pH=7) but are experimental conditions-dependent. For example, a photocatalyst with CB higher (more positive) than -1.90 V vs NHE (CO₂ activation potential) may prove successful for CO₂ photoreduction, and vice versa. This would be due to either: i) a different CO₂ activation pathway which does not involve the suggested CO₂^{δ-} species (different activation potential), and/or ii) different experimental conditions (*e.g.* non-aqueous solution, different pH) than the ones specified for the potential calculation (shifted potential values). Therefore, in this thesis, the potential values are used only as a general baseline for comparison to the electronic structure of photocatalysts, but not as strict criteria.

The field of CO₂ photoreduction faces numerous challenges. For instance, although it is clear that various products can be formed through CO₂ photoreduction, the intermediate products, final products and photocatalytic mechanism of any route are highly dependent on the experimental conditions and employed photocatalyst's properties^{6,25,29}. In addition, the complexity and ultrafast kinetics of the photocatalytic process make it even more challenging to elucidate the reaction mechanism. As a result, it is hard to establish a general agreement on the way forward (*i.e.* photocatalyst design, set experimental procedure and apparatus). Due to the duality of photocatalysis – it being light-driven and at the same time being a catalytic reaction – many different metrics are used for evaluating its efficiency, as listed in **Table 2.1.2**. There is a lack of consensus on the metrics that should be reported, even on their calculation, making it difficult to compare photocatalysts' activity and efficiency over studies of different research groups³⁰. Nevertheless, there are a few reports that have proposed ways forward for the better benchmarking of results^{31–34}. Another major challenge in CO₂ photoreduction are the very low product evolution rates (usually not surpassing hundreds of μmol g⁻¹ h⁻¹ when 1 sun irradiation and ambient conditions are used). These yields need to be

increased by many orders of magnitude for CO₂ photoreduction to be incorporated in any viable practical application²². Finally, as with any catalytic application, catalyst stability is of major importance. In CO₂ photoreduction, photocatalyst degradation is a bottleneck, and can take up a large portion of the “activity”. Due to the lack of an established experimental protocol, the majority of studies do not report product evolution under inert conditions or isotope labelling, and claim minimal photocatalyst degradation with no solid proof^{30,35}. Overall, CO₂ photoreduction is on the forefront of research owing to its great potential as an alternative (renewable) route to fuels and chemicals production. However, the complexity of its process and the thermodynamic barriers present a significant challenge.

Table 2.1. 2. List of different metrics used in photocatalysis and traditional (thermal) catalysis.

Metric	Photocatalysis	Traditional catalysis
Reactant conversion (%)	$\frac{[r]_i - [r]_f}{[r]_i}$	$\frac{[r]_i - [r]_f}{[r]_i}$
Product yield (normalised mol for photocatalysis, % for traditional catalysis)	[n] can be normalised by catalyst loading (g ⁻¹), reaction time (h ⁻¹), reactor volume (cm ⁻³), illuminated area (m ⁻²), or combination thereof	$\frac{[n]}{[r]_i}$
Product selectivity (%)	$\frac{[n]}{[n]_{tot}}$	$\frac{[n]}{[r]_i - [r]_f}$
Efficiency (%)	Photonic yield: $\frac{d[n]/dt}{q_{n,p,\lambda}}$	$\frac{[n]}{[r]_i}$
	Photonic efficiency: $\frac{d[n]/dt}{\int_{\lambda_1}^{\lambda_2} q_{n,p,\lambda} d\lambda}$	
	Quantum yield: $\frac{d[n]/dt}{q_{n,p,\lambda}[1-10^{-A}]}$	
	Quantum efficiency: $\frac{N_A \cdot hc \cdot \sum_{n=1}^{n_x} [n]_x}{\int_{\lambda_1}^{\lambda_2} I_{l,\lambda} [1-10^{-A}] d\lambda}$	
Turnover frequency (s ⁻¹) /numbers (-)	$TON = TOF \cdot \tau$	$TOF = \frac{[n]}{t \cdot [c]}$

In **Table 2.1.2**, $[r]_i$ and $[r]_f$ indicate the initial and final amount (mol) of a specific reactant, respectively, $[n]$ is the amount (mol) of a specific product, $[n]_{\text{tot}}$ is the total amount (mol) of all products, photonic yield is the production rate of specific product ($d[n]/dt$) over the number of incident photons (q) under a monochromatic irradiation (λ), photonic efficiency is the production rate of specific product over the number of incident photons in a wavelength range (λ_1 - λ_2), quantum yield is the production rate of specific product over the number of absorbed photons in monochromatic irradiation, quantum efficiency is the production rate of specific product over the number of absorbed photons in a wavelength range, TON are turnover numbers, TOF is turnover frequency, τ is the photocatalyst lifetime (s), t is the reaction duration (s), and $[c]$ is the amount (mol) of catalytic active sites. In the case of TOF, and of TON by extension, $[n]$ and $[c]$ are normalised by the same quantity (*e.g.* mass of catalyst).

CO₂ photothermal reduction

Leveraging the advantages of both photocatalysis (*i.e.* simple, sustainable, safe, cost-effective) and traditional thermal catalysis (*i.e.* reliable, consistent, scalable), photothermal reduction of CO₂ has gained a lot of scientific interest recently⁵. Photothermal CO₂ reduction reactions are usually operated within 1-20 bar and up to 300 °C^{36–38}. While not carried out at ambient conditions (like in photocatalysis), it does offer the ability to catalyse the reaction at milder conditions than traditional thermal catalysis. This makes the process safer than thermal catalysis, potentially more cost-effective, and decreases the chance of catalyst deactivation (*e.g.* from thermal degradation or sintering)^{5,39}. It also enhances (usually hundreds/thousands of $\mu\text{mol g}^{-1} \text{h}^{-1}$, with 2 mol $\text{g}_{\text{active site}}^{-1} \text{h}^{-1}$ being the highest⁴⁰) the low product yields inherent in the pure photocatalytic process. Photothermal CO₂ reduction is usually performed using H₂ or

H₂O as proton donors, a light source (arc lamp or solar simulator) and a heat-controlled photoreactor. A wide range of nanomaterials have been deployed for this reaction, including but not limited to metal oxides, nitrides, chlorides, metal-organic frameworks, usually as metal supports, decorated with cocatalysts or part of heterojunctions. Research studies report a synergy between thermal and solar energy effect, as both energy sources contribute to achieving the necessary activation energy for product formation^{36,37}. Usually, the main products from CO₂ photothermal conversion are CO, CH₄ or CH₃OH, and on certain occasions production of C₂+ hydrocarbons has also been reported. Photothermal catalysis shares the same challenge as photocatalysis in the absence of an established protocol for experimental testing and results reporting. The most used metrics are product yield and selectivity (as defined for photocatalysis in **Table 2.1.2**), however the results often lack comparability as experimental conditions and set-up differ between studies.

Photothermal catalysis can be divided into four separate categories, depending on the role of light (solar) and thermal energy³⁶:

- i) Light-assisted thermal catalysis: In principle a thermocatalytic process, where the material acts as a thermal catalyst and the heat provides the activation energy for product formation. The heat could be provided by an external field or released by the catalyst upon light absorption. Light increases the local temperature of the catalyst, reduces the activation energy, facilitates reactant conversion and limits catalyst poisoning^{41–43}.
- ii) Heat-assisted photocatalysis: In principle a photocatalytic process, where the photocatalyst absorbs light and photogenerates charge carriers which take part in the reaction. The heat could be provided by an external field or released by the catalyst

upon light absorption. The photocatalyst cannot act as thermal catalyst, but the heat has a positive effect on photocatalytic activity by promoting the charge carrier mobility and reactant mass transfer^{44,45}.

- iii) Heat- and light-assisted (co)catalysis: Simultaneously a photo- and thermo-catalytic process, where both external light and heat directly contribute to the activation energy. The photothermal activity exceeds the sum of the individual photocatalytic and thermal activities⁴⁶.
- iv) Light-driven thermal catalysis: In principle a thermocatalytic process, where the catalyst converts concentrated solar energy into thermal energy through good light-to-heat conversion, and then drives the thermal reaction. This process involves mild heat input and good solar energy harvesting^{47,48}.

As mentioned, these different photothermal categories exist depending on the light and thermal energy roles and mechanistic pathways. In reality, the uncoupling of individual light and heat effects is challenging and the total/individual reaction mechanism is rarely thoroughly examined.

2.1.3. Boron and carbon nitride-based materials for CO₂ photo(thermal) reduction

Various photocatalytic systems (*i.e.* semiconductor, biological, biohybrid, and metal-organic systems) have been deployed for photo(thermal) catalytic CO₂ reduction⁴⁹. The main advantages and disadvantages of each system are listed in **Table 2.1.3** below. Aforementioned metal oxides, nitrides and chlorides belong to semiconductor systems as their bandgaps are narrower than in insulators and wider than in conductors. Semiconductor systems are the

most prominently used photocatalytic systems due to their promising and tunable optoelectronic properties, and versatility⁴⁹.

Table 2.1. 3. Comparison of advantages and disadvantages of photocatalytic CO₂ reduction systems.

System	Advantages	Disadvantages
Semiconductor	▪ Tunable ▪ Versatile	▪ Low efficiencies ▪ Often need for sacrificial agents
Biological	▪ Sustainable ▪ High CO₂ conversion rates ▪ Range in products	▪ Large space needed ▪ High operating costs ▪ Limited lifetime ▪ Short margins for operation
Biohybrid	▪ Nature-inspired ▪ Product-selective	▪ Challenging synthesis ▪ Short margins for operation
Metal-organic complex	▪ Non-rare, available metals ▪ Tunable	▪ Photodegradation

Out of all semiconductors, nitrides such as boron nitride (BN) and carbon nitride (C₃N₄) are of particular interest due to their tunable properties, stability and also their chemistry; both materials consist of nontoxic, earth-abundant elements, graphene-like structure of alternating heteroatoms in six-member rings, and are easy to synthesise. Their versatility may render them appropriate for use in multiple applications through targeted functionalisation.

In the case of CO₂ photoreduction, porous amorphous BN exhibits competitive activity in CO formation with benchmark material TiO₂ and better visible light absorption⁷. This could be potentially linked to BN's high porosity and CO₂ adsorption, and longer charge carrier

lifetimes. However, this activity is still very low for any practical applications, and the visible light photoactivity should be extended. C_3N_4 is a benchmark material for photo(thermal) CO_2 reduction due to its thermal and chemical stability and interesting optoelectronic properties, however it exhibits low activity and low porosity/ CO_2 adsorption⁸.

As mentioned in **Chapter 2.1.1**, it is more than challenging for a standalone, nonengineered material to fulfil all criteria for the ideal photocatalyst. To overcome this challenge, there are various strategies to engineer and functionalise photocatalysts' properties for targeted CO_2 photo(thermal) reduction to fuels and chemicals. These strategies include^{9,50}:

- i) Band structure engineering: Tuning the photocatalyst's optoelectronic properties which include CB, VB, Fermi level (E_F , hypothetical energy level with 50 % possibility of being occupied by an electron), midgap states and bandgap. This affects the light absorption, thermodynamic and kinetic energy of excitons and exciton lifetimes. It can be achieved through heteroatom (metal and nonmetal) doping and solid solution (*i.e.* homogeneous alloy between at least two different elements/semiconductors with similar crystal structures, electronegativity, valency and atomic radii).
- ii) Morphology engineering: Tuning the morphology, dimensions and particle size of the catalyst, which affects porosity, surface area, adsorption capacity and charge carrier migration/recombination. Different shaped nano- and microstructures include 0D (*i.e.* quantum dots, nanoparticles), 1D (*i.e.* nanorods, nanowires, nanotubes, nanofibers, nanoribbons, nanobelts), 2D (*i.e.* nanosheets), 3D (*i.e.* hierarchical or hollow structures), nano- or microporous structures.
- iii) Surface structure engineering: Manipulating either the surface structure or the crystal facets of a photocatalyst, which affects porosity, adsorption capacity, active site

accessibility and charge carrier migration. It can be achieved by exposing reactive facets, creating facet junctions, adding surface acidic/basic sites and creating vacancies.

- iv) Heterostructure engineering: Creating an interface between photocatalyst and another material with specific functionality, which affects physicochemistry, porosity, adsorption capacity, creation, separation, migration and recombination of charge carriers. It can be achieved through adding cocatalyst(s) and surface plasmon resonance materials, creating heterojunctions and composites.

Overall, the focus of this thesis is the investigation of BN- and C_3N_4 -based materials for CO_2 photo(thermal) reduction. As already mentioned, these materials come with their own limitations. To overcome said limitations, the thesis aimed to functionalise BN and C_3N_4 and uncover the effects of such functionalisation on the materials' physicochemical, sorptive, optoelectronic and photocatalytic properties. Heteroatom functionalisation has proved to effectively tune BN⁵¹ and C_3N_4 's^{8,52} properties towards an improved photocatalytic activity for various reactions (*e.g.* H_2O splitting, CO_2 reduction, H_2O /air purification, heavy metal's removal). Especially nonmetal heteroatom functionalisation is very promising as it combines i) the advantages of functionalisation, with the use of ii) earth-abundant, inexpensive elements with similar chemistry to the original consisting elements of BN and C_3N_4 . Similar chemistry (*cf.* position in the Periodic Table) is an important aspect of functionalisation, as elements with similar properties (amount of valence electrons, amount of orbitals) can be easily integrated in the existing structure, either by atoms replacements or by forming interstitial bonds. In the next Sections, I will discuss the effects of nonmetal functionalisation on BN and C_3N_4 's chemical, sorptive, optoelectronic and photocatalytic properties.

2.2. Porous boron nitride

Some parts discussed in this Section have been used or adapted from the author's publication in Accounts of Materials Research⁵³.

Boron nitride (BN) is a material consisting of alternating B and N atoms connected with single/double bonds (sp^2 or sp^3). BN can exist in crystalline – hexagonal (hBN), rhombohedral (rBN), cubic (cBN) – and non-crystalline forms – turbostratic (tBN), amorphous (aBN)⁵⁴, and in different micro- (*i.e.* bulk, nanosheets, nanotubes, nanoribbons, fullerenes)^{55–58} and macro-shapes (*e.g.* foams, aerosols, pellets)^{59–63}.

Specifically, hBN has been commonly known and widely used in the ceramics (as coating/dye) and cosmetics (as formulating/blending agent) industries, owing to its high thermal and chemical stability and commercial availability. hBN has a structure similar to graphene, where the alternating B and N atoms are arranged in six-member rings, as shown in **Figure 2.2.1a**. The terms hBN and BN are often used interchangeably – even though the former is a subcategory of the latter – and there is a confusion in the literature nomenclature with regards to the type of BN (*e.g.* tBN referred to as hBN) and its form (*e.g.* bulk can be misinterpreted as nanosheets). It needs to be emphasised here that i) this confusion often stems from misinterpreted or inappropriate characterisation results, and hence ii) proper material characterisation is a significant aspect of research, especially in the solar fuels field.

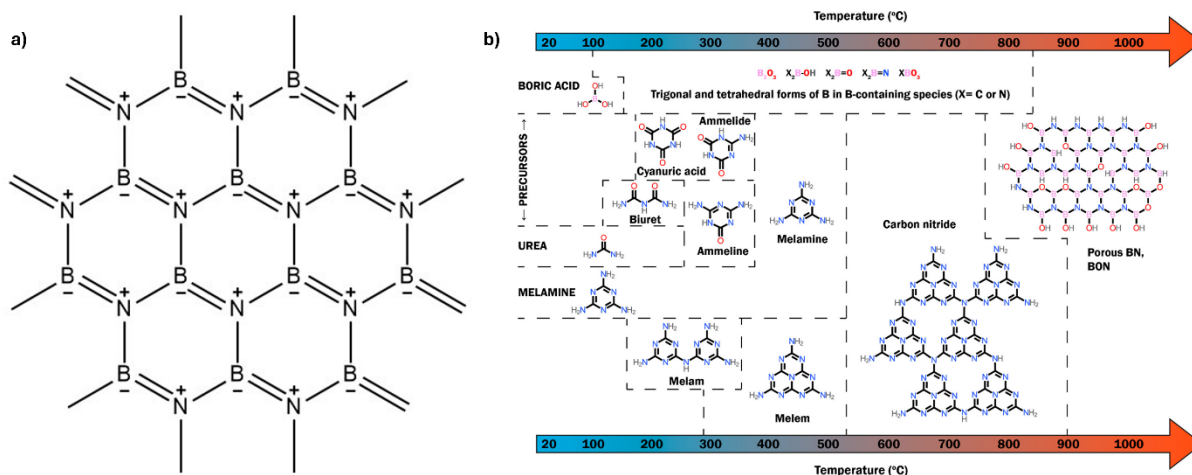


Figure 2.2. 1. a) Chemical structure of BN, and b) formation mechanism of porous BN during heating of precursor mixture (boric acid, melamine, urea) under N_2 ⁶⁴. b) is reproduced with permission from reference ⁶⁴. Copyright 2021 American Chemical Society.

Even though crystalline hBN is commercially used, it lacks porosity. High surface area BN (with surface areas $> 100 \text{ m}^2 \text{ g}^{-1}$) can be synthesised top-down (*e.g.* by hBN exfoliation) or bottom-up (*e.g.* by introduction of micro/mesoporosity through thermal treatment), and has gained a lot of attention by the scientific community for its applicability, and is the focus of this Section from here on^{53,65}. Following the latter method, porous BN (with BET areas normally in the range $1000\text{-}1500 \text{ m}^2 \text{ g}^{-1}$) is obtained usually in the form of aBN or tBN. Typically, a mixture of B-containing (*e.g.* boric acid, boron trioxide, ammonia borane, hexamethylenetetramine) and N-containing (*e.g.* urea, melamine, biuret) precursors is heated under high temperature ($800\text{-}1800 \text{ }^\circ\text{C}$) and controlled gas flow (*e.g.* N_2 , NH_3 , Ar, H_2)^{53,63}. During this synthetic route, under N_2 , the precursors degrade into subproducts up to $\sim 550 \text{ }^\circ\text{C}$, then carbon nitride is being formed between $\sim 550\text{-}900 \text{ }^\circ\text{C}$, leading to the formation of porous BN from $\sim 700 \text{ }^\circ\text{C}$ onward (**Figure 2.2.1b**)⁶⁴. Other bottom-up synthetic routes for porous BN include chemical blowing,

chemical vapor deposition, solvothermal and template-assisted. With porosity and disturbance/discontinuation of crystallinity comes a defective and tunable nature, which provides BN with rich chemistry that can be tailored to different applications (*i.e.* gas separations, gas storage, photo-/electro-/normal catalysis)⁵³.

Heteroatom introduction into the BN structure (functionalisation) has been studied before for tailoring the BN properties relevant to the application. For this purpose, a great number of alkali/alkaline earth metals (*i.e.* Li, Na, K, Be, Mg, Ca, Se, Ba)^{66,67}, transition metals (*i.e.* Ti, Cu, Zn, Fe, Co, Mo, Rh, Ni, V, Cr, Mn, Pd, Pt, Au)^{68,69,78–81,70–77}, metals (*i.e.* Al, Ga, In)^{82,83}, and lanthanides (*i.e.* Ce, Gd, Eu)^{84,85} have been explored, both experimentally and theoretically. However, the focus of the next Sections will be the reported effects of nonmetal (*i.e.* B, C, N, O, F, Si, P, S, Cl, As, Se, Br, Te, I) functionalisation on BN's chemical, sorptive, optoelectronic and photocatalytic properties. It is noted here that, in the interests of this thesis, cases where nonmetal-doped BN are part of a composite/heterojunction, or decorated with cocatalysts, or referred to as boron carbonitride (BCN), are excluded.

2.2.1. Chemical properties

Pristine porous BN is inherently defective and, other than B (48-52 at%) and N (39-41 at%) atoms, contains chemical impurities originating from the B-containing and N-containing precursors used during synthesis⁵³. Such impurities take the form of C (up to 2 at%) and O (up to 5 at%) atoms (mostly through C_B and C_N replacements⁸⁶, and O_N replacements and creation of -OH groups at the planar edges⁸⁷, respectively) and structure discontinuation (*i.e.* V_N vacancies). Therefore, C-C, C-N, C-B, O-B, and O-H bonding can be present in the BN structure,

as illustrated in **Figure 2.2.2**. In the case of both C and O atoms present, C-O or C=O bonds can also exist.

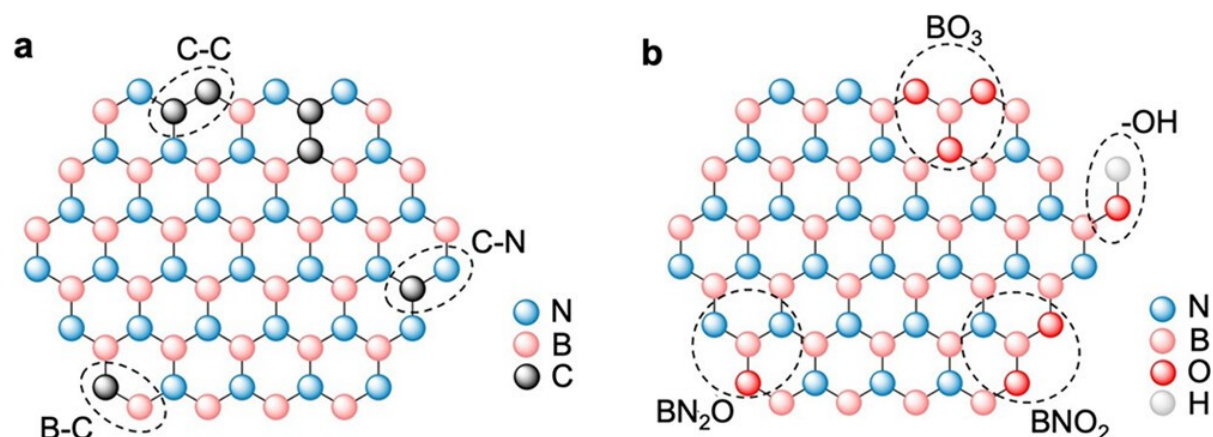


Figure 2.2. 2. Schematic representation of a) carbon sites in C-doped BN and b) oxygen sites in O-doped BN⁵³. Reproduced from reference ⁵³ under CC-BY 4.0 Licence. Copyright 2023 American Chemical Society.

It needs to be noted here that, since B, N, C and O atoms pre-exist in the pristine BN structure, the use of the term “doping” is incorrect – although frequently used in literature – and it is suggested to replace it by “functionalisation”, especially given the concentration of such elements in the material. Functionalisation of BN with these elements results in a B-, N-, C- or O-richer content compared to the original material. Out of the nonmetals that have been used for the functionalisation of BN, C is the most extensively studied. Some examples of nonmetal functionalisation of BN and their integration into the molecule’s chemical structure are presented in **Table 2.2.1** below. In most cases, it is suggested that the nonmetal (X) replaces B and/or N atoms in the BN basal planes, creating X-N and/or X-B bonds, respectively.

Sometimes nonmetal islands are created within the structure (domain of X-X bonds), or the nonmetal is integrated on the planar edges by B and/or N replacement. Some reports also propose the attachment of the nonmetal onto B or N atoms, creating X-N or X-B bonds in between basal planes or at the edges. In all cases, the presence of nonmetal elements causes some structural deformation, and their integration (*i.e.* chemical bonding and environment) is dictated by the most thermodynamically favourable formation energy.

Table 2.2. 1. Examples of nonmetal (B, C, N, O, F, Si, P, S, Cl, As) functionalisation of BN and their integration into BN's chemical structure.

Nonmetal studied	*BN structure	Nonmetal content	Nonmetal chemical environment	Nature of the study	Ref
C	hBN nanorice	Not reported	C-C C-B C-N C-O/C=O	Experimental	88
C, O	hBN monolayer	Not reported	C-N O-B	Computational	89
C	hBN nanoribbon monolayer	0.3-2 at% C	C-B	Computational	90
C (as graphene domain)	hBN nanosheets	6 at% C	C-C C-B C-N C-O	Experimental	91
C	hBN monolayer	1-3 at% C	C-C C-B C-N	Computational	92
C	porous hBN	Not reported	C-C C-B C-N	Experimental	93
C	BN nanotubes	Not reported	C-B C-N	Computational	94
C	hBN monolayer	Not reported	C-B C-N	Computational	95
C	porous BN monolayer	17 at% C	C-C C-B C-N	Computational	96

Nonmetal studied	*BN structure	Nonmetal content	Nonmetal chemical environment	Nature of the study	Ref
C	BN nanosheets	4-11 at% C	C-C C-B C-N	Experimental	97
C	porous BN	2 at% C	C-C C-B C-O	Experimental	98
C	hBN monolayer	2 at% C	C-B C-N	Computational	99
C, O	BN nanosheets	5-20 wt% C 9-13 wt% O	C-C C-B C-N	Experimental	100
C	BN nanosheets	2 at% C	C-C C-B C-N	Experimental	101
C	BN nanoribbon monolayer	12-13 at% C	C-C C-N C-O C-H	Computational	102
C	BN nanosheets	23 at% C	C-C C-B C-N C-O	Experimental	103
C	BN monolayer	2 at% C	C-B C-N	Computational	104
C, O	porous BN microsponges	0-2 at% C 2-10 at% O	C-C C=N C-O O-B	Experimental	105
C	BN nanotubes	Not reported	C-B C-N	Computational	106
C	BN nanofilms	6-8 at% C 3 at% O	C-C C-B C-N	Experimental	107
C	BN nanoplate	19 at% C	C-C C-B C-N C-O	Experimental	108
C	BN fullerene	4-8 at% C	C-N	Computational	109
C, O	hBN monolayer hBN fullerene	4-8 at% C 4 at% O	C-N O-B	Computational	110
C	BN nanotube	8 at% C	C-B C-N	Computational	111

Nonmetal studied	*BN structure	Nonmetal content	Nonmetal chemical environment	Nature of the study	Ref
C, B, N, O	BN monolayer	2 at% C 50-52 at% B 50-52 at% N 2 at% O	C-B C-N B-B B-N N-N O-B O-N	Computational	112
B, N	BN monolayer	47-53 at% B 47-53 at% N	B-B B-N N-N	Computational	113
B	BN monolayer	Not reported	B-B B-N B-H	Computational	114
O	mesoporous BN nanowires	Not reported	O-B	Experimental	115
O	BN BN monolayer	2-10 at% O	O-C O-B O-H	Experimental + Computational	116
O	porous BN	2-14 at% O	O-B	Experimental	117
O	BN nanotubes	Not reported	O-B O-N	Computational	118
O	porous BN	10-33 at% O	O-B O-H	Experimental	119
O	BN nanosheets	5-25 at% O	O-B O-H	Experimental + Computational	120
Si	BN nanosheets BN nanotubes	2.5 at% Si	Si-N	Computational	121
Si	BN monolayer	Not reported	Si-B Si-N	Computational	122
Si	hBN nanosheet	2 at% Si	Si-N	Computational	123
Si	BN nanotubes	3 at% Si	Si-C Si-N	Experimental	124
Si	cBN	Not reported	Si-B Si-N	Computational	125
P	BN fullerene	4 at% P	P-B	Computational	70
P, As	BN nanotube	3 at% P 3 at% As	P-B As-B	Computational	126
P	BN monolayer	2 at% P	P-N	Computational	127
P	BN nanosheets	0.3-1 at% P	P-B P-N	Experimental	128
P	hBN nanosheet	4-11 at% P	P-OH P=O	Experimental	129
P	Porous BN	10-15 at% P	P-OH P=O	Experimental	130

Nonmetal studied	*BN structure	Nonmetal content	Nonmetal chemical environment	Nature of the study	Ref
S	hBN nanosheets	3-9 at% S	S-B	Experimental + Computational	131
S	hBN films	Not reported	Not reported	Experimental	132
S	hBN nanosheets	5 at% S	S-B S-N	Experimental	133
S	BN nanotube	10-21 at% S	S-B S-N	Computational	134
S	hBN monolayer hBN nanotube	Not reported	S-B S-N	Computational	135
S	BN nanosheet BN nanotube	1 at% S	S-B S-N	Computational	136
C, O, Si, P, S, F, Cl	multilayer hBN	3 at% C 3 at% O 3 at% Si 3 at% P 3 at% S 3 at% F 3 at% Cl	C-N O-N Si-N P-N S-N F-N Cl-N	Computational	137

* The terminology used refers to that employed in the reference and may loosely agree with the nomenclature used in this thesis.

In general, the chemical environment around integrated nonmetal atoms can be experimentally deciphered using Fourier Transform Infrared Spectroscopy (FTIR), Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS), X-ray Absorption Spectroscopy (XANES/NEXAFS), solid-state Nuclear Magnetic Resonance (NMR), Energy Dispersive X-ray Spectroscopy through Scanning Electron Microscopy (SEM-EDS) or through Scanning Transmission Electron Microscopy (STEM-EDX), and Electron Energy Loss Spectroscopy (EELS). On occasion, the introduction of nonmetals can cause paramagnetic chemical impurities containing unpaired electrons which can be probed using Electron Paramagnetic Resonance spectroscopy (EPR)^{7,120}. The material's chemical composition can be determined

experimentally via XPS, SEM-EDS, STEM-EDX, EELS, elemental analysis, and Inductively Coupled Plasma spectroscopy (ICP).

2.2.2. Sorptive properties

As previously mentioned in the beginning of **Section 2.2**, BN materials are promising candidates for gas separation, gas storage and catalysis applications, owing to their tunable porous structure and chemistry. For context, porous BN can exhibit $>1 \text{ cm}^3 \text{ g}^{-1}$ total pore volume, mostly occupied by mesopores (2-50 nm) or micropores and BET areas in the order of $2000 \text{ m}^2 \text{ g}^{-1}$ (theoretical maximum is $4800 \text{ m}^2 \text{ g}^{-1}$ for monolayer hBN)^{53,63,65}. The adsorption of many organic and inorganic compounds has been investigated on nonmetal functionalised BN materials⁵³; however, this Section will focus on adsorption of gases relevant to the solar fuels/chemicals field (*i.e.* involving CO_2 , H_2O , H_2 , O_2 , N_2 , NO_x , NH_3). Some examples of nonmetal functionalisation of BN materials and its effects on BN's porosity and adsorption are presented in **Table 2.2.2** below. As can be observed from the Table, limited studies provide information on (and thus, combine) both porosity and gas adsorption of functionalised BN, despite the two being interconnected. In most experimental works, the integration of nonmetals (usually C and O) alters the pore size distribution and structure of the original material, resulting in lower or unchanged BET areas, but increased micropore/ultramicro pore volume. The outcome is an enhanced CO_2 adsorption capacity compared to non-functionalised BN. In addition, theoretical studies support that the creation of defects such as X_B , X_N , V_B , V_N (where X=nonmetal) by nonmetal functionalisation can add adsorption sites and/or change the gas adsorption energy, thereby tuning gas adsorption for various gases (*e.g.* CO_2 , H_2 , O_2 , NO_2). Overall, in the case of CO_2 uptake, it has been shown that the presence of

micropores (<2 nm) and ultramicropores (<0.7 nm) and H-containing groups (Lewis bases, such as -NH₂ or -OH) favour CO₂ (Lewis acid) adsorption capacity^{138–140}. Nonmetal functionalisation can also reduce or enhance hydrolytic stability. Indeed, when BN contains -OH edge groups and exhibits a high surface area, this favours H₂O adsorption and limits hydrolytic stability. This situation represents an important bottleneck for the utilisation of BN as adsorbent or catalyst for processes requiring presence of H₂O. To counteract this, it has been suggested to “cap” the -OH groups on the planar edges (therefore reducing O content) and/or reduce the specific surface area^{141,142}. In some experimental studies, O, P and S functionalisation results in an enhanced BET area compared to the original material; nevertheless, the effect of this change in BN’s porosity (especially in the cases of P and S) on gas adsorption is unknown.

Table 2.2. 2. Summary of nonmetal (B, C, N, O, Si, P, S) functionalisation of BN and their effects on porosity and gas adsorption. S_{BET} , V_{tot} , R and ΔH_{ads} refer to the BET surface area, total pore volume, reduction reaction and isosteric enthalpy of adsorption, respectively.

Nonmetal studied	*BN structure	Porosity	Gas adsorbed	Effect on adsorption	Ref
C	BN nanotube	Not reported	O ₂	Chemisorption of O ₂ onto C _B and C _N sites. Non-functionalised BN is inert	106
C	BN nanotube	Not reported	NO CO	Chemisorption of CO and NO onto CN and CB sites. Non-functionalised BN shows physisorption	94
C	BN nanoribbon	Not reported	CO ₂ R intermediates	Edge and near-vacancy C _N sites and neighbouring B atoms provide adsorption sites for intermediates	143
C	BN nanosheet	Not reported	NO	(NO) ₂ dimer is most favourably bound to C _N -B adsorption sites	104

Nonmetal studied	*BN structure	Porosity	Gas adsorbed	Effect on adsorption	Ref
C	BN nanosheets	Not reported	N ₂	C functionalisation results in defects creation (such dangling unsaturated B atoms). N ₂ can get adsorbed onto such defect sites	101
C	BN nanosheets	S _{BET} 488-680 m ² g ⁻¹ V _{tot} 0.24-0.34 cm ³ g ⁻¹	Not reported	Not reported	100
C	BN monolayer	Not reported	O ₂ O ₂ R intermediates	C _N and neighbouring B atoms around C _B offer adsorption sites for O ₂ and O ₂ reduction intermediates	99
C	porous BN	S _{BET} 2-91 m ² g ⁻¹	Not reported	Not reported	98
C	BN nanotube	Not reported	H ₂	C _N and C _B offer adsorption sites for atomic H (chemisorption) and molecular H ₂ (physisorption). H ₂ binding energy is enhanced for functionalised BN nanotube compared to non-functionalised	95
C	BN nanoribbon	Not reported	N ₂ N ₂ R intermediates	C functionalisation causes charge redistribution to edge B atoms (adsorption sites) in B-C _N bonds, favouring adsorption of N ₂ reduction intermediates. N ₂ is chemisorbed on C-functionalised BN, as opposed to its physisorption on non-functionalised	90
C	BN nanoplates	S _{BET} 793 m ² g ⁻¹ V _{tot} 0.26 cm ³ g ⁻¹	Not reported	Not reported	108
C	BN monolayer	Not reported	N ₂ O CO SO ₂	C _B offers adsorption site for N ₂ O, CO and SO ₂ molecules	144
C	BN fullerene	Not reported	H ₂	C-functionalised and non-functionalised BN fullerene show similar H ₂ storage capacity (7 wt%) at 25 °C and 10 bar through chemisorption. C functionalisation facilitates subsequent dehydrogenation (desorption) at 100 °C and 1 bar	109

Nonmetal studied	*BN structure	Porosity	Gas adsorbed	Effect on adsorption	Ref
C	BN monolayer	Not reported	O ₂	In the case of C _N , C _N provide the sole adsorption sites for O ₂ . In the case of C _B , C _B as well as neighbouring B atoms provide adsorption sites for O ₂	145
C	BN nanosheets	S _{BET} 45-114 m ² g ⁻¹	Not reported	Not reported	146
C	Porous BN	S _{BET} 512 m ² g ⁻¹	H ₂ CO ₂ CO ₂ R intermediates	C _B provide adsorption sites for H ₂ , CO ₂ and CO ₂ reduction intermediates	147
C	hBN monolayer	Not reported	CO ₂ H ₂ S NO ₂	C _N defects are the most favourable configuration for CO ₂ , H ₂ S and NO ₂ adsorption. Physisorption occurs for CO ₂ and H ₂ S, while chemisorption occurs for NO ₂ . Non-functionalised hBN has lower affinity to these gases	148
C	porous BN	S _{BET} 11-767 m ² g ⁻¹ V _{tot} 0.09-0.33 cm ³ g ⁻¹	CO ₂ N ₂	C-functionalised BN with highest S _{BET} exhibits 2 mmol g ⁻¹ CO ₂ uptake at 25 °C and 1 bar (increased ultramicroporosity), and ΔH _{ads} = -30 kJ mol ⁻¹ at 0 loading (physisorption of CO ₂). The material has <0.2 mmol g ⁻¹ N ₂ uptake at the same conditions (good CO ₂ /N ₂ selectivity)	149
C, N	BN monolayer	Not reported	CO ₂ H ₂ O	C-functionalised BN favours CO ₂ adsorption more than N-functionalised and non-functionalised. In all cases, presence of H ₂ O facilitates CO ₂ adsorption by reducing adsorption energy barrier	150
C	porous BN	S _{BET} 727-877 m ² g ⁻¹ V _{tot} 0.35-0.51 cm ³ g ⁻¹	CO ₂ N ₂	C-functionalised BN exhibits ~4 mmol g ⁻¹ CO ₂ uptake at 25 °C and 1 bar (increased ultramicroporosity), and ΔH _{ads} = -32-35 kJ mol ⁻¹ at 0 loading (physisorption of CO ₂). The material has ~0.2 mmol g ⁻¹ N ₂ uptake at the same conditions (good CO ₂ /N ₂ selectivity)	139
C	porous BN	S _{BET} 120-1167 m ² g ⁻¹	CO ₂	C-functionalised BN materials exhibit 0.5-0.8 mmol g ⁻¹ CO ₂ uptake at 25 °C and 1 bar (increased ultramicroporosity), and ΔH _{ads} = -70-120 kJ mol ⁻¹ at 0 loading (chemisorption of CO ₂)	151

Nonmetal studied	*BN structure	Porosity	Gas adsorbed	Effect on adsorption	Ref
C	BN monolayer	Not reported	O ₂ H ₂ N ₂ CO NO H ₂ O CO ₂ NO ₂ SO ₂ NH ₃	C functionalisation enables chemisorption of O ₂ , NO, NO ₂ , CO ₂ and SO ₂ , and physisorption of N ₂ , H ₂ , CO, H ₂ O and NH ₃ onto BN structure. Non-functionalised BN exhibits physisorption for all gases	152
C, O	BN microsponges	S_{BET} 397-1290 m ² g ⁻¹ V_{tot} 0.45-1.04 cm ³ g ⁻¹	H ₂	C-, O- co-functionalised BN microsponges adsorb ~1 wt% H ₂ at -196 °C and 1 bar	105
C, O	BN monolayer BN fullerene	Not reported	H ₂	Neighbouring B atoms near C _B , and B atoms from B-O _N bonds act as H ₂ adsorption sites. C- and O- co-functionalised BN can adsorb up to ~7 wt% H ₂	110
C, O	BN nanocrystals	S_{BET} 286 m ² g ⁻¹ V_{tot} 0.16 cm ³ g ⁻¹	CO ₂	C-, O- co-functionalised BN exhibits ~1 mmol g ⁻¹ CO ₂ uptake at 0 °C and 1 bar (mostly microporous nature)	153
C, Si, F	porous BN BN pellet	S_{BET} 600-800 m ² g ⁻¹ V_{tot} 0.50-0.75 cm ³ g ⁻¹	CO ₂ N ₂ H ₂ O	C-, Si- and F- co-functionalised BN pellets show enhanced hydrolytic stability compared to pristine BN. Continuous CO ₂ /N ₂ separation in presence of H ₂ O was improved	141
B	BN monolayer	Not reported	N ₂ N ₂ R intermediates	B atoms in B-B bonds provide adsorption sites for N ₂ and intermediates for N ₂ reduction	114
B, N	BN monolayer	Not reported	O ₂ O ₂ R intermediates	B _N , N _B , V _B and V _N defects can be adsorption sites for O ₂ . N _B defects are the most favourable for O ₂ adsorption and O ₂ R	113
O	mesoporous BN nanowires	S_{BET} 295 m ² g ⁻¹ V_{tot} 0.37 cm ³ g ⁻¹	Not reported	Not reported	115
O	porous BN	S_{BET} 247-474 m ² g ⁻¹	Not reported	Not reported	119
O	BN nanosheets	S_{BET} 561 m ² g ⁻¹ V_{tot} 0.33 cm ³ g ⁻¹	Not reported	Not reported	120

Nonmetal studied	*BN structure	Porosity	Gas adsorbed	Effect on adsorption	Ref
O	hierarchical BN	S_{BET} $75 \text{ m}^2 \text{ g}^{-1}$	CO_2	O-functionalised hierarchical BN exhibits $\sim 2 \text{ mmol g}^{-1} \text{ CO}_2$ uptake at 1 bar (mostly mesoporous nature)	154
O	hBN nanosheets	S_{BET} $541 \text{ m}^2 \text{ g}^{-1}$	CO_2 CO_2R intermediates	O-functionalised BN nanosheets exhibit $\sim 0.2 \text{ mmol g}^{-1} \text{ CO}_2$ uptake at 1 bar (mostly microporous nature). B atoms from B- O_N bond provide adsorption sites for CO_2R intermediates	155
Si	BN nanosheets BN nanotubes	Not reported	O_2 CO	Si_B offers adsorption sites for CO and O_2	121
P	BN monolayer	Not reported	NO NOR intermediates	P_B offers adsorption sites for NO, but the adsorption energy is minimal	127
P	porous BN	S_{BET} $530\text{-}837 \text{ m}^2 \text{ g}^{-1}$	Not reported	Not reported	156
P	BN monolayer	Not reported	CO_2 CO O_2 O	P_B offers adsorption sites for CO and O_2 , and for oxidation intermediates such as atomic O and CO_2	157
P	porous BN	S_{BET} $101\text{-}498 \text{ m}^2 \text{ g}^{-1}$ V_{tot} $0.29\text{-}0.84 \text{ cm}^3 \text{ g}^{-1}$	Not reported	Not reported	130
S	hBN nanosheets	S_{BET} $262 \text{ m}^2 \text{ g}^{-1}$	Not reported	Not reported	131
S	hBN nanosheets	S_{BET} $44 \text{ m}^2 \text{ g}^{-1}$	Not reported	Not reported	133

* The terminology used refers to that employed in the reference and may loosely agree with the nomenclature used in this thesis.

2.2.3. Optoelectronic properties

While hBN is a wide bandgap insulator (5.5-7.1 eV experimentally^{158,159}, 4.5-8.4 eV theoretically^{160,161}), porous BN shows a reduced bandgap (4.2 eV experimentally⁷) and is an interesting option for applications in optoelectronic and magnetic devices and

photo(electro)catalytic reactions. As mentioned in **Section 2.1**, there is a need for the deployment of narrow bandgap semiconductors to absorb visible light and increase the efficiency of light harvesting from the sun. Other than the bandgap and light absorption range, interesting properties for optoelectronic and photocatalytic materials include: (conduction and valence) band edges and Fermi level positions, charge carrier behaviour and lifetimes, existence and amount of excited species. The meaning and importance of such properties has been previously discussed in **Section 2.1.1**. Nonmetal functionalisation has been explored to tailor BN's optoelectronic properties, and some examples of its effect on light absorption, bandgap, charge carrier lifetimes and photoexcited electron concentration are presented in **Table 2.2.3**. Overall, the introduction of nonmetals to the BN structure results in reduction of the bandgap, hence an extended light absorption (red shift). This bandgap reduction can be due to either introduction of intraband states, lowered CB and/or elevated VB, or both. The position of the Fermi level is also influenced depending on the added nonmetal, forming an n-type semiconductor if closer to the CB (n = negative, abundance of electrons), or p-type if closer to the VB (p = positive, excess of holes). On occasion, charge carrier lifetimes can be prolonged due to their shallow or deep trapping in intermediate midgap states caused by defects (*i.e.* vacancies, atom replacements or nonmetal atom chemical orbitals). Finally, nonmetal functionalisation can also increase the amount of photoexcited species formed upon irradiation, as evidenced by TAS measurements (in fs- μ s timescales) or, on occasion, by EPR (in s-min timescales).

Table 2.2. 3. Summary of nonmetal (B, C, N, O, F, Si, P, S, Cl, As) functionalisation of BN and their effects on light absorption, bandgap, charge carrier lifetimes and photoexcited electron concentration.

Nonmetal studied	*BN structure	Light absorption	Bandgap	Charge carrier lifetime	Unpaired electron concentration	Ref
C	BN nanotube	UV-visible	2.5-3.0 eV	Not reported	Not reported	106
C	BN nanotube	UV	4.0 eV midgap states n-type (C_B) p-type (C_N)	Not reported	Not reported	94
C	BN nanosheet	UV-visible red shift	2.7—3.5 eV (experimental) 1.9-7.8 eV (theoretical)	Not reported	Not reported	103
C	BN monolayer BN nanosheets	UV-visible red shift	2.1-2.7 eV (experimental) 2.9 eV (theoretical)	0.5-4.5 ns	Increased upon irradiation	100
C	BN monolayer BN nanosheets	UV	4.9 eV n-type (C_B) p-type (C_N)	Not reported	Not reported	97
C	BN monolayer	UV	4.8 eV n-type (C_B) p-type (C_N)	Not reported	Not reported	99
C	porous BN	UV-visible red shift	-	Not reported	Not reported	98
C	porous BN	UV-visible	2.8 eV or 4.0 eV (different theoretical calculations)	Not reported	Not reported	96
C	BN nanotube	UV	4.0 eV midgap states n-type (C_B) p-type (C_N)	Not reported	Not reported	95
C	BN monolayer	UV	5.5-5.9 eV	Not reported	Not reported	92
C	hBN	UV	3.8-4.0 eV	Not reported	Not reported	91
C	hBN nanoribbon	UV	4.1-5.0 eV midgap states p-type (C_N)	Not reported	Not reported	90

Nonmetal studied	*BN structure	Light absorption	Bandgap	Charge carrier lifetime	Unpaired electron concentration	Ref
C	BN nanofilms BN monolayer	UV-visible	2.7-2.9 eV (experimental) 2.3-3.5 eV (theoretical) p-type ($C_N + C_B$)	12.9-54.6 ns	Not reported	107
C	hBN crystals	UV	shallow (5.0-5.7 eV) and deep (4.1-4.2 eV) midgap states from C_N defect	Not reported	Not reported	162
C	hBN monolayer	UV	~4.0 eV midgap states n-type (C_B, C_{BN}) p-type (C_N)	Not reported	Not reported	145
C	BN nanosheets	UV-visible	2.3-2.7 eV (experimental) 1.6-3.3 eV (theoretical)	0.9-1.5 ns	Increased upon irradiation	146
C	multiple BN forms	UV-visible red shift	-	Not reported	Increased upon irradiation	163
C	hBN epilayers	UV	6.5 eV midgap states created ~0.5 eV below the CB due to C_B , and ~2.3 eV above the VB due to C_N	Not reported	Not reported	164
C	porous BN	UV	2.6 eV (experimental) 4.5 eV (theoretical) midgap states	Not reported	Not reported	147
C, P	bulk BN BN nanosheets	UV-visible red shift	1.0-2.0 eV	2.8-4.0 ns	Not reported	165
C, O	porous BN	UV	3.3 eV	Not reported	Not reported	153
C, B, N, O	BN monolayer	UV-visible	~4.5 eV, n-type (O_N) ~0.7 eV, p-type (O_B) ~0.7 eV, n-type (C_B) ~0.8 eV, p-type (C_N) ~1.4 eV, p-type (B_N) ~2.3 eV, n-type (N_B) midgap states	Not reported	Not reported	112
B, N	hBN monolayer	UV-visible	3.3 eV (N_B) 1.5 eV (B_N)	Not reported	Not reported	113

Nonmetal studied	*BN structure	Light absorption	Bandgap	Charge carrier lifetime	Unpaired electron concentration	Ref
O	mesoporous BN nanowires	UV-visible red shift	Not reported	Not reported	Not reported	115
O	BN nanoparticles	UV-visible red shift	2.7 eV (experimental) ~3.0-3.5 eV (theoretical) midgap states	Not reported	Not reported	116
O	BN nanotube	UV	~3.7-4.0 eV p-type (O_B) n-type (O_N) p- or n-type (O_{BN})	Not reported	Not reported	118
O	BN nanoflakes	UV-visible red shift	2.1 eV (experimental) 1.7-5.2 eV (theoretical) midgap states	Not reported	Not reported	120
O	hierarchical BN	UV-visible red shift	2.3 eV	1.8 ns	Not reported	154
O	BN nanosheets	UV-visible red shift	5.4 eV (experimental) 5.7 eV (theoretical)	Not reported	Not reported	155
O	porous BN	UV-visible	1.5-2.9 eV	Not reported	Increased upon irradiation	166,167
Si	BN monolayer BN nanotube	UV	4.6 eV	Not reported	Not reported	121
Si	hBN monolayer	UV-visible	1.2 eV (Si_B) 0.8 eV (Si_N) p-type midgap states	Not reported	Not reported	122
Si	BN monolayer	UV	3.0-4.5 eV p-type midgap states	Not reported	Not reported	168
B, N, P, As	BN nanotube	UV-visible	~3.2 eV, p-type (B_N) ~3.0-4.1 eV, n-type (N_B) ~2.5-3.5 eV, n-type (P_N) ~2.0-4.1 eV, n-type (As_N) midgap states	Not reported	Not reported	169
P	porous BN	UV-visible	2.0-3.4 eV (experimental) 3.9-4.4 eV (theoretical)	Not reported	Not reported	130
P	BN monolayer	UV	5.8 eV	Not reported	Not reported	170

Nonmetal studied	*BN structure	Light absorption	Bandgap	Charge carrier lifetime	Unpaired electron concentration	Ref
S	hBN nanosheet	UV-visible red shift	2.9-3.2 eV (experimental) 2.9-3.7 eV (theoretical)	18.8 ns	Increased upon irradiation	131
S	hBN nanosheets	UV-visible red shift	3.9 eV (experimental) 4.1 eV (theoretical)	Not reported	Not reported	133
S	BN nanotube	UV-visible	1.9-2.4 eV	Not reported	Not reported	134
F	hBN monolayer hBN nanotube	UV	~3.7-4.1 eV	Not reported	Not reported	135
F	BN nanotube	UV	~3.6-4.0 eV p-type	Not reported	Not reported	136
C, O, Si, P, S, F, Cl	multilayer hBN	UV-visible	4.5 eV, n-type (Si _B) 3.5 eV, n-type (P _B) 3.7 eV, n-type (C _B) 4.7 eV, n-type (S _B) 2.0 eV, p-type (Cl _B) 2.5 eV, p-type (O _B) 2.2 eV, p-type (F _B)	Not reported	Not reported	137

* The terminology used refers to that employed in the reference and may loosely agree with the nomenclature used in this thesis.

2.2.4. Photocatalytic properties

Albeit the use of BN materials for photo(thermal)catalytic applications has recently gained interest in the research community (*i.e.* in the solar fuels/chemicals production, water purification, organics degradation), it remains limited. In the interests of this thesis, this Section will focus on the reported use of nonmetal-functionalised BN materials for photocatalytic solar fuels/chemicals production, which is presented in **Table 2.2.4** below. Two main reactions have been investigated so far: i) H₂O splitting for the evolution of H₂ (reduction) or O₂ (oxidation), and ii) CO₂ reduction. As expected, given the thermodynamic barriers of

each reaction, H₂O splitting generates higher product (especially H₂) yields than CO₂ reduction (CO as main product, H₂ can exist as byproduct). Nonmetal-functionalised BN outperforms benchmark materials (*e.g.* gC₃N₄ and TiO₂ P25) in both reactions, however the product yield remains too low for practical applications, and the visible light needs to be more efficiently harvested, which limit the quantum efficiency of the system. In general, C functionalisation seems to achieve higher yields for the CO₂ photoreduction reaction than simply O functionalisation, although it is noted that a fair comparison is challenging due to different experimental set-ups/conditions. The investigation of S and P introduction to the BN structure is certainly promising for the photocatalytic field, given their sole reported use has been for H₂O reduction, while coated with Pt.

Table 2.2. 4. Summary of nonmetal (C, O, P, S) functionalisation of BN and their effects on solar fuels/chemicals production.

Nonmetal studied	*BN structure	Light source	Reaction	Proton donor/ Sacrificial agent	Product formed	Ref
C	BN nanosheets	300 W Xe arc lamp	H ₂ O reduction	TEOA	900 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 300 \text{ nm}$) 60 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 420 \text{ nm}$)	100
C	BN nanosheets	300 W Xe arc lamp	H ₂ O oxidation	AgNO ₃ /La ₂ O ₃	20 $\mu\text{mol g}^{-1} \text{h}^{-1}$ O ₂ ($\lambda > 300 \text{ nm}$)	100
C	BN nanosheets	300 W Xe arc lamp	CO ₂ reduction	H ₂ O/CH ₃ CN/ TEOA/CoCl ₂ / 2,2-(C ₅ H ₄ N) ₂	80 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO ($\lambda > 420 \text{ nm}$) 40 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 420 \text{ nm}$)	100

Nonmetal studied	*BN structure	Light source	Reaction	Proton donor/ Sacrificial agent	Product formed	Ref
C	porous BN	300 W Xe arc lamp	CO ₂ reduction	H ₂ O	61 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO ($\lambda > 320 \text{ nm}$) 8 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ ($\lambda > 320 \text{ nm}$) 19 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 320 \text{ nm}$)	147
C	bulk BN	300 W Xe arc lamp	H ₂ O reduction	TEOA	**8-14 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 420 \text{ nm}$)	171
C, P	BN nanosheets	300 W Xe arc lamp	H ₂ O reduction	TEOA	**82 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 420 \text{ nm}$)	171
C, O	BN nanocrystals	300 W Xe arc lamp	CO ₂ reduction	H ₂ O	0.2 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO ($\lambda > 320 \text{ nm}$) 0.5 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ ($\lambda > 320 \text{ nm}$)	153
O	hierarchical BN	300 W Xe arc lamp	CO ₂ reduction	H ₂ O/TEOA	10 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO ($\lambda > 320 \text{ nm}$) 1 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ ($\lambda > 320 \text{ nm}$) 1.5 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 320 \text{ nm}$)	154
O	bulk BN	300 W Xe arc lamp	CO ₂ reduction	H ₂ O/TEOA	1.5 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO ($\lambda > 320 \text{ nm}$) 1 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 320 \text{ nm}$)	154
O	BN nanosheets	300 W Xe arc lamp	CO ₂ reduction	H ₂ O	13 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO ($\lambda > 320 \text{ nm}$) 3 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 320 \text{ nm}$)	155
O	porous BN	300 W Xe arc lamp	CO ₂ reduction	H ₂	1 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO ($\lambda > 325 \text{ nm}$) 0.2 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO ($\lambda > 400 \text{ nm}$)	7
O	porous BN	300 W Xe arc lamp	CO ₂ reduction	H ₂ O	0.8 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO ($\lambda > 325 \text{ nm}$)	7
S	BN nanosheets	300 W Xe arc lamp	H ₂ O reduction	TEOA	**1349 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 420 \text{ nm}$)	133

*The terminology used refers to that employed in the reference and may loosely agree with the nomenclature used in this thesis.

**1 wt% Pt was photodeposited for the reaction.

2.3. Graphitic carbon nitride as photocatalyst for CO₂

photoreduction

Graphitic carbon nitride (gC₃N₄) is a metal-free material with similar chemical structure to previously discussed BN. gC₃N₄ consists of six-member rings with alternating C and N atoms, connected with each other with single/double bonds, as shown in **Figure 2.3.1a** below¹⁷². It can be easily synthesised via thermal polymerisation of C- and N-containing precursors (*e.g.* urea, melamine, dicyandiamide, cyanuric acid) at relatively low temperatures (~450-650 °C)¹⁷³. During thermal polymerisation, the formation of the final structure can take place through repetitive connection of melem (C₆H₆N₁₀) units while NH₃ groups are being removed from the structure (**Figure 2.3.1b**). There are other synthetic pathways as well, including solvothermal, hydrothermal, self-assembly, polycondensation and microwave heating¹⁷⁴. The tri-s-triazine structure depicted in **Figure 2.3.1a**, which involves heptazine rings bridged to each other through N-(C)₃ bonds, is considered to be the most stable gC₃N₄ structure¹⁷⁵.

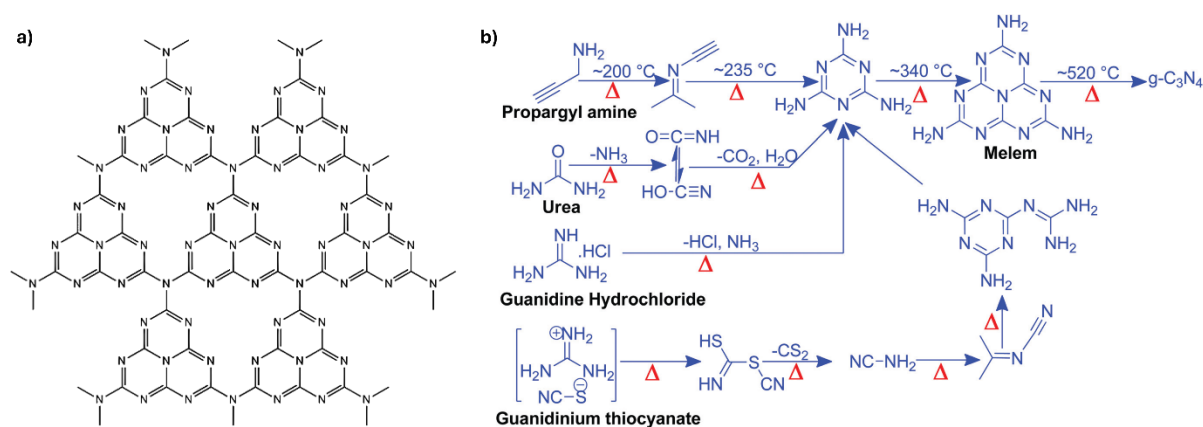


Figure 2.3. 1. a) tri-s-triazine structure of gC₃N₄, and b) formation mechanism of gC₃N₄ from various precursors¹⁷³. b) is reproduced from reference ¹⁷³ under a CC-BY 4.0 Licence. Copyright 2020 Royal Society of Chemistry.

gC₃N₄, owing to its excellent thermal and chemical stability, and interesting optoelectronic properties, has been studied as a catalyst for thermal and electro- catalytic reactions, but more extensively for photocatalytic reactions^{173,176}. The majority of the reported photocatalytic applications for gC₃N₄-based materials involve H₂O splitting – followed by organics/dyes degradation, CO₂ reduction, reduction of toxic metals, NO_x removal and Fenton reaction¹⁷⁷. More often than not, gC₃N₄ is not employed as a standalone photocatalyst; rather, it is used as part of heterojunctions, decorated with cocatalysts, (surface-)modified with defects/heteroatoms, or a combination of the above. In the interest of this thesis, we will focus on heteroatom functionalisation and its effects, excluding the influence of heterojunctions and cocatalysts. While several metals (*i.e.* Li, Na, K, Rb, Fe, Ni, Co, Cu, Mo, Ru, Mg, Mn, Au, Pt, Pd, Eu) have been investigated for the functionalisation of gC₃N₄¹⁷⁴, my interests lie in the use of nonmetals (described in **Section 2.2**). As gC₃N₄ has been sufficiently explored for CO₂ photoreduction – in contrast to porous BN –, the aim of this Section will be a comprehensive review of the reported effects of nonmetal-functionalised gC₃N₄ on the chemical, sorptive, optoelectronic, and photocatalytic properties of the original material, when employed for the CO₂ reduction reaction.

2.3.1. Chemical properties

Pristine gC₃N₄ structure, other than C and N atoms (in a C/N atomic ratio ranging from 0.55 to 0.75), contains chemical moieties in the form of H (up to 2 at%) within -N(H)C and -NH₂ bonds, mostly at the edges, and O (up to 5 at%) atoms in -OH groups at the edges, and sometimes vacancies (*i.e.* V_N) causing structural discontinuation, as shown in **Figure 2.3.2** below¹⁷⁶.

Therefore, C-C, N-C=N, N-H, N-(C)₃, C-O/C=O and O-H chemical bonds can be found in the pristine gC₃N₄ structure.

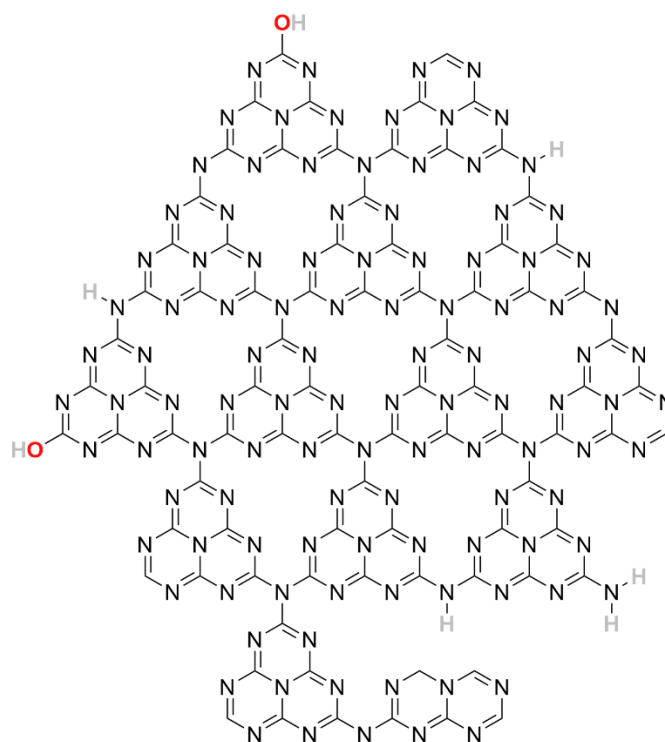


Figure 2.3. 2. gC₃N₄ structure including defects and chemical moieties.

Some examples of nonmetal-functionalised gC₃N₄ materials, including the nonmetal integration into the structure, are presented in **Table 2.3.1**. In this case – analogous to the case of porous BN – when referring to C and N functionalisation, we mean C-rich and N-rich gC₃N₄, respectively. Most studies suggest that nonmetals (heteroatoms or excess of already existing elements) are integrated in the gC₃N₄ structure by C (*e.g.* B_C, P_C, S_C) or N (*e.g.* C_N, O_N, S_N) substitution, causing a slight structural deformation and charge redistribution. Other research work reports that the integration of heteroatoms such as B or P interstitially between

coordinated N atoms in the “gaps” of gC₃N₄ structure is more thermodynamically favourable.

Surface amine functionalisation at the planar edges creates N- and H- richer chemical environment, often at the expense of C atoms (V_C) and N-(C)₃ bond scission.

Table 2.3. 1. Summary of nonmetal (B, C, N, O, F, P, S, Cl, Br, I) functionalisation of gC₃N₄ and their integration into gC₃N₄’s chemical structure.

Nonmetal studied	gC ₃ N ₄ structure	Nonmetal content	Nonmetal chemical environment	Ref
C	gC ₃ N ₄ nanorods	58 at% C (experimental) 51-52 at% C (theoretical)	C-C N-C=N N-(C) ₃	178
C, O	bulk gC ₃ N ₄	45 at% C (XPS) 2 at% O (XPS) 34 at% C (elemental analysis) 2 at% O (elemental analysis)	C-C C=C N-C=N N-(C) ₃ C-O C=O	179
C, O	gC ₃ N ₄ nanosheets	38 wt% C 2 mol% O	C-C N-C=N N-(C) ₃ C-O	180
N, H	gC ₃ N ₄ nanotubes	55-60 at% N 2 at% H	C-N=C N-(C) ₃ C-N-H N-O	181
N, H	gC ₃ N ₄ nanosheets	Not reported	C-N=C N-(C) ₃ N-H N-NH ₂	182
N	gC ₃ N ₄ nanosheets	Not reported	C-N=C N-(C) ₃ C-N-H	183
O	gC ₃ N ₄ nanotubes	3 at% O	O-H O-C O-N	184
B	bulk gC ₃ N ₄	Not reported	N-B=N	185
B	gC ₃ N ₄ nanosheets	Not reported	N-B=N	186

Nonmetal studied	gC ₃ N ₄ structure	Nonmetal content	Nonmetal chemical environment	Ref
B	gC ₃ N ₄ nanosheets	0.6 at% B	B-N	187
B	gC ₃ N ₄ nanosheets	5 at% B	B-N	188
B, N, H	bulk gC ₃ N ₄ gC ₃ N ₄ nanosheets	Not reported	B-N B-O B-C C-N=C N-(C) ₃ N-H N-O	189
B, P, N, H	bulk gC ₃ N ₄ ultrathin gC ₃ N ₄ nanosheets	Not reported	B-N B-O B-C C-N=C N-(C) ₃ N-H P-N P=N B-N-P	190
P, N, H	gC ₃ N ₄ nanotubes	Not reported	C-N=C N-(C) ₃ C-N-H P-O P=O O-H	191
P	bulk gC ₃ N ₄	Not reported	P-N	192
P, C, N	gC ₃ N ₄ nanosheets	39 at% C 61 at% N 0.1 at% P	C-C N-C=N C-NH ₂ N-(C) ₃ C≡N P-N	193
P, F	bulk gC ₃ N ₄	1-5 at% P (XPS) 1 at % F (XPS, elemental analysis) 7 at% P (elemental analysis)	P=O P-OH N=P-N F-C	194
S	bulk gC ₃ N ₄	1 at% S	S-N	195
S	bulk gC ₃ N ₄	0.05 at% 1 at% S (theoretical)	S-C S-N S-O S=O	196
S	gC ₃ N ₄ ribbons	1 wt% S	S-C	197
S	gC ₃ N ₄ monolayer	2 at% S	S-C	198
F, Cl, Br, I	gC ₃ N ₄ nanotubes	0.3 wt% F (SEM-EDS) 0.6 wt% F (XPS)	Not reported	199

2.3.2. Sorptive properties

A major bottleneck of bulk gC_3N_4 towards CO_2 photoreduction is its limited CO_2 adsorption capacity ($\sim 0.05 \text{ mmol g}^{-1}$ at 25°C and 1 bar)¹⁸⁹. As mentioned in **Section 2.2**, CO_2 uptake can be mostly affected by increase in (ultra)micropore volume and/or introduction of chemical bonds (chemisorption) through Lewis bases (*e.g.* $-\text{NH}_2$ groups). Although pristine gC_3N_4 does contain some $-\text{NH}_2$ groups, its main CO_2 adsorption mechanism is physisorption (weak interactions). As a predominantly mesoporous (pore size between 2-50 nm) material, it lacks the micropore volume essential for an enhanced CO_2 capacity. The challenges gC_3N_4 is facing with regards to its sorptive properties can be, to a certain extent, overcome by nonmetal functionalisation. Some examples of nonmetal-functionalised gC_3N_4 and their effects on porosity and CO_2 adsorption are listed in **Table 2.3.2**. The reported results vary, even for the same nonelement studied. In some cases, the introduction of nonmetals (*e.g.* B, P, S) enhances the BET area and pore volume of the original gC_3N_4 structure and researchers connect this to increased CO_2 adsorption capacity – depending on the study, this is usually a speculation, and only on occasion is combined with experimental CO_2 adsorption measurements. In other cases, there is no change in BET area, and the reported increased CO_2 adsorption is attributed to larger amount of $-\text{NH}_2$ groups present in the structure. Admittedly, this attribution is often questionable, as the alleged increase in N and H content is not always supported by experimental data, or is overstated. With nonmetal functionalisation, gC_3N_4 remains mainly mesoporous and more mesopores (*i.e.* 2-5 nm) are introduced, with no evidence of micropore formation. CO_2 adsorption can be, indeed, improved by nonmetal functionalisation (up to 0.4 mmol g^{-1} at 25°C , with the use of P), however the uptake value remains quite low. Nonmetal

functionalisation enhances pristine gC₃N₄'s porosity (usual $S_{\text{BET}}=10 \text{ m}^2 \text{ g}^{-1}$, $V_{\text{tot}}=0.07 \text{ cm}^3 \text{ g}^{-1}$ for bulk pristine material)^{200,201}. However, it is noted that a significant contribution can come from engineered morphology (*e.g.* by creating 2D nanostructures or 3D hierarchical porous structures), as the pristine material can reach $S_{\text{BET}}=130 \text{ m}^2 \text{ g}^{-1}$, and $V_{\text{tot}}=0.30 \text{ cm}^3 \text{ g}^{-1}$ ^{200,202}. The enhanced BET area, while not always influencing CO₂ adsorption, can promote charge carrier diffusion and separation, and access to reactants, thereby potentially boosting the photocatalytic activity.

Table 2.3. 2. Summary of nonmetal (B, C, N, O, F, P, S) functionalisation of gC₃N₄ and their effects on porosity and CO₂ adsorption.

Nonmetal studied	gC ₃ N ₄ structure	Porosity	Effect on adsorption	Ref
C	gC ₃ N ₄ nanorods	S_{BET} : $154 \text{ m}^2 \text{ g}^{-1}$	It is suggested that larger surface area compared to non-functionalised nanorods ($S_{\text{BET}}=113 \text{ m}^2 \text{ g}^{-1}$) promotes CO ₂ adsorption capacity, but with no direct proof. Mesoporosity is maintained, with introduction of more mesopores	178
C, O	bulk gC ₃ N ₄	S_{BET} : $12\text{-}18 \text{ m}^2 \text{ g}^{-1}$ V_{tot} : $0.07\text{-}0.13 \text{ cm}^3 \text{ g}^{-1}$	It is suggested that O-containing functional groups enhance hydrophilicity, and therefore CO ₂ and H ₂ O adsorption on the photocatalytic surface, but with no direct proof	179
C, O	gC ₃ N ₄ nanosheets	S_{BET} : $8\text{-}14 \text{ m}^2 \text{ g}^{-1}$	Not reported	180
N, H	gC ₃ N ₄ nanotubes	S_{BET} : $57\text{-}136 \text{ m}^2 \text{ g}^{-1}$	It is suggested that the 1D tubular structure, increased surface area and presence of more -NH ₂ functional groups (Lewis bases, hydrophiles) resulting from functionalisation, enhance CO ₂ adsorption, but with no direct proof	181
N	gC ₃ N ₄ nanosheets	S_{BET} : $33\text{-}35 \text{ m}^2 \text{ g}^{-1}$ V_{tot} : $0.14\text{-}0.15 \text{ cm}^3 \text{ g}^{-1}$	N-functionalised gC ₃ N ₄ exhibits enhanced CO ₂ uptake of 0.2 mmol g^{-1} at 25 °C and 1 bar due to existence of -NH ₂ groups. CO ₂ adsorption is a combination of physi- and chemisorption	183

Nonmetal studied	gC ₃ N ₄ structure	Porosity	Effect on adsorption	Ref
O	gC ₃ N ₄ nanotubes	S _{BET} : 36 m ² g ⁻¹ V _{tot} : 0.13 cm ³ g ⁻¹	*O-functionalised gC ₃ N ₄ nanotubes exhibit higher CO ₂ uptake (0.05 mmol g ⁻¹) than bulk gC ₃ N ₄ (0.02 mmol g ⁻¹) at 1 bar, due to the higher surface area and larger pore volume	184
B	bulk gC ₃ N ₄	S _{BET} : 41 m ² g ⁻¹	Not reported	185
B	gC ₃ N ₄ nanosheets	S _{BET} : 91 m ² g ⁻¹	Not reported	187
B	gC ₃ N ₄ nanosheets	S _{BET} : 62-80 m ² g ⁻¹ V _{tot} : 0.17-0.33 cm ³ g ⁻¹	B atoms in interstitial B-N bonds provide adsorption and activation sites for CO ₂ (physisorption), with higher adsorption free energy than non-functionalised gC ₃ N ₄	188
B	bulk gC ₃ N ₄	S _{BET} : 9 m ² g ⁻¹	B-functionalisation slightly enhances the CO ₂ uptake, based on temperature-programmed CO ₂ desorption profiles, due to its electron donor ability to increase the electron abundance in adjacent N atoms	203
B, N, H	bulk gC ₃ N ₄ gC ₃ N ₄ nanosheets	S _{BET} : 10 m ² g ⁻¹ (bulk) 42-143 m ² g ⁻¹ (nanosheets) V _{tot} : 0.02 cm ³ g ⁻¹ (bulk) 0.09-0.24 cm ³ g ⁻¹ (nanosheets)	B-functionalisation of bulk gC ₃ N ₄ results in reduced CO ₂ uptake (~0.02 mmol g ⁻¹), while B-functionalised nanosheets show higher CO ₂ uptakes (~0.08-0.2 mmol g ⁻¹) at 25 °C and ~1 bar. CO ₂ adsorption is a physisorption process, promoted by enhanced surface area and pore network, with some chemical interactions with -NH ₂ groups	189
B, P, N, H	bulk gC ₃ N ₄ ultrathin gC ₃ N ₄ nanosheets	S _{BET} : 4-13 m ² g ⁻¹ (bulk) 63-82 m ² g ⁻¹ (ultrathin nanosheets) V _{tot} : 0.02-0.09 cm ³ g ⁻¹ (bulk) 0.36-1.08 cm ³ g ⁻¹ (ultrathin nanosheets)	Bulk B-, P- and B/P-functionalised gC ₃ N ₄ show lower CO ₂ uptake (0.02-0.05 mmol g ⁻¹), than their ultrathin, NH ₂ -functionalised counterparts (~0.10-0.14 mmol g ⁻¹) at 25 °C and 1 bar, due to a combination of pore network, surface area and basic sites. CO ₂ adsorption is a physisorption process with some chemical bonding to -NH ₂ groups. B/P-functionalised ultrathin gC ₃ N ₄ nanosheets show ΔH _{ads} =17 kJ mol ⁻¹ at 0 CO ₂ loading	190
P, N, H	gC ₃ N ₄ nanotubes	S _{BET} : 13 m ² g ⁻¹	*P-functionalisation increases the CO ₂ uptake to 0.4 mmol g ⁻¹ at 25 °C and 1 bar due to the presence of NH ₂ groups	191
P, C, N	gC ₃ N ₄ nanosheets	S _{BET} : 30 m ² g ⁻¹	Not reported	193
P, F	bulk gC ₃ N ₄	S _{BET} : 31-261 m ² g ⁻¹ V _{tot} : 0.07-0.61 cm ³ g ⁻¹	Not reported	194

Nonmetal studied	gC ₃ N ₄ structure	Porosity	Effect on adsorption	Ref
S	bulk gC ₃ N ₄	S _{BET} : 4 m ² g ⁻¹ V _{tot} : 0.01 cm ³ g ⁻¹	Not reported	196
S	gC ₃ N ₄ ribbons	S _{BET} : 27-44 m ² g ⁻¹	Not reported	197
S	gC ₃ N ₄ monolayer	Not reported	C atoms in S _N -C bonds provide adsorption sites for CO ₂ , and the CO ₂ adsorption (physisorption) free energy is higher in S-functionalised gC ₃ N ₄ , showing a stronger interaction	198
F	gC ₃ N ₄ nanotubes	S _{BET} : 20-29 m ² g ⁻¹ V _{tot} : 0.10-0.19 cm ³ g ⁻¹	Not reported	199

* These studies do not report absolute CO₂ pressure, but relative pressure P/P₀ for the CO₂ adsorption measurements. In these cases, it is assumed by the thesis author that P₀ is equal to atmospheric pressure, therefore absolute pressure is calculated and listed.

2.3.3. Optoelectronic properties

Pristine gC₃N₄ is a moderate-bandgap semiconductor (~2.7 eV) with light absorption in the UV-visible range, and electronic band structure relevant for the CO₂ photoreduction reaction (and parallel H₂O or H₂ oxidation). Its photoexcited electrons' radiative relaxation (charge carrier lifetimes) are usually ~4 ns^{180,184,185,193}, and the fast exciton recombination in this material is considered a major limiting step towards CO₂ photoreduction¹⁷⁶. Some examples of nonmetal-functionalised gC₃N₄ and their effects on light absorption, bandgap, charge carrier lifetimes and photoexcited electron concentration are presented in **Table 2.3.3** below. In most cases, nonmetal functionalisation seems to slightly extend light absorption (red shift) and reduce the bandgap by ~0.1-0.3 eV (max 1.0 eV). The bandgap reduction can occur

through either lowering the CB, or elevating the VB. In cases where the bandgap is not altered, CB and VB levels can still shift (usually deeper), keeping the appropriate band positions for CO₂ reduction to products, however not reaching the CO₂^{δ-} activation potential. In most cases, the exciton lifetimes of functionalised gC₃N₄ are shorter than the original material (as probed through time-resolved photoluminescence), and this is attributed to an increase in non-radiative photoexcited electron relaxation, although not proved experimentally. The unpaired electron concentration under dark conditions (no irradiation) is higher in functionalised materials which can be later helpful for the photocatalytic reaction. On some occasions, these unpaired electrons appear non-localised, which could facilitate the exciton separation and reduce recombination rates. Overall, nonmetal functionalisation introduces functional groups and defect sites which reportedly redistribute electrons and create midgap (trapping) states. As a result, functionalisation is speculated to promote charge carrier separation and migration, thus limiting the exciton recombination rate.

Table 2.3. 3. Summary of nonmetal (B, C, N, O, F, P, S, Cl, Br, I) functionalisation of gC₃N₄ and their effects on light absorption, bandgap, charge carrier lifetimes and photoexcited electron concentration.

Nonmetal studied	gC ₃ N ₄ structure	Light absorption	Bandgap	Charge carrier lifetime	Unpaired electron concentration	Ref
C	gC ₃ N ₄ nanorods	UV-visible red shift	2.4 eV (experimental) 2.5-3.3 eV (theoretical) midgap states	Not reported	Not reported	178
C, O	bulk gC ₃ N ₄	UV-visible red shift	2.0-2.5 eV	Not reported	Higher than non-functionalised gC ₃ N ₄ under dark	179

Nonmetal studied	gC ₃ N ₄ structure	Light absorption	Bandgap	Charge carrier lifetime	Unpaired electron concentration	Ref
C, O	gC ₃ N ₄ nanosheets	UV-visible red shift	2.5-2.7 eV	3.46 ns	Not reported	180
N	gC ₃ N ₄ nanotubes	UV-visible blue shift	Not reported	Not reported	Not reported	181
N, H	gC ₃ N ₄ nanosheets	UV-visible no shift	2.8 eV	Not reported	Not reported	182
N	bulk gC ₃ N ₄	UV-visible no shift	Not reported	Not reported	Not reported	183
O	gC ₃ N ₄ nanotubes	UV-visible red shift	2.6 eV (experimental) 1.0 eV (theoretical)	3.71 ns	Not reported	184
B	bulk gC ₃ N ₄	UV-visible no shift	2.6 eV	3.25 ns	Not reported	185
B	gC ₃ N ₄ nanosheets	UV-visible no shift	2.5 eV	Not reported	Higher than non-functionalised gC ₃ N ₄ under dark	186
B	gC ₃ N ₄ nanosheets	UV-visible red shift	2.4 eV	Not reported	Not reported	187
B	bulk gC ₃ N ₄	UV-visible red shift (low B content) blue shift (higher B content)	2.5 eV (theoretical)	Longer for lower B content Shorter for higher B content	Higher than non-functionalised gC ₃ N ₄ under dark	188
B	bulk gC ₃ N ₄	UV-visible no shift	2.7 eV	Not reported	Not reported	203
B, N, H	gC ₃ N ₄ nanosheets	UV-visible red shift blue shift	2.6-3.0 eV (experimental) 2.8-2.9 eV (theoretical)	2.79-4.32 ns	Not reported	189
B, P	bulk gC ₃ N ₄	UV-visible no shift	2.7 eV (B) 2.7 eV (P)	Not reported	Not reported	190
B, P, N, H	ultrathin gC ₃ N ₄ nanosheets	UV-visible red shift	2.6 eV (P) 2.7 eV (B) 2.8 eV (B/P, experimental) 2.7 eV (B/P, theoretical) midgap states	2.06 ns (B/P)	Not reported	190
P, N, H	gC ₃ N ₄ nanotubes	UV-visible red shift	2.6 eV	Not reported	Not reported	191
P	bulk gC ₃ N ₄	UV-visible red shift	2.4 eV	Not reported	Not reported	192

Nonmetal studied	gC ₃ N ₄ structure	Light absorption	Bandgap	Charge carrier lifetime	Unpaired electron concentration	Ref
P, C, N	bulk gC ₃ N ₄	UV-visible red shift	2.2-2.5 eV	3.96 ns	Not reported	193
P, F	bulk gC ₃ N ₄	UV-visible red shift	1.8 eV	Not reported	Not reported	194
S	bulk gC ₃ N ₄	UV-visible red shift	2.2-2.8 eV	Not reported	Not reported	195
S	gC ₃ N ₄ nanosheets	UV-visible red shift	2.6 eV (experimental) 1.2 eV (theoretical) n-type midgap states	Not reported	Not reported	196
S	gC ₃ N ₄ ribbons	UV-visible red shift	2.2 eV n-type	Not reported	Not reported	197
S	gC ₃ N ₄ monolayer	UV-visible red shift	2.4 eV	Not reported	Not reported	198
F	gC ₃ N ₄ nanotubes	UV-visible blue shift	2.8-2.9 eV	3.01 ns	Higher than non-functionalised gC ₃ N ₄ under dark	199
Cl	gC ₃ N ₄ nanotubes	UV-visible blue shift	2.8-2.9 eV	Not reported	Not reported	199
Br	gC ₃ N ₄ nanotubes	UV-visible blue shift	2.8-2.9 eV	Not reported	Not reported	199
I	gC ₃ N ₄ nanotubes	UV-visible blue shift	2.7-2.9 eV	Not reported	Not reported	199

2.3.4. Photocatalytic properties

Pristine gC₃N₄ has been explored for CO₂ photoreduction owing to all the interesting properties that were discussed throughout **Section 2.3**. It usually i) reduces CO₂ into C₁ products (*i.e.* CO, CH₄, CH₃OH), ii) oxidises H₂O into O₂ or H₂O₂, or H₂ into H₂O (depending on which is used as electron donor), and iii) produces H₂ from the competing H₂O reduction. The product yield and selectivity greatly vary depending on the experimental conditions (as

discussed in **Section 2.1**). Although variable, gC₃N₄'s CO₂ photoreduction efficiency remains low (usually 0.1-10 $\mu\text{mol g}^{-1} \text{h}^{-1}$ product evolution), hence its use in junctions and cocatalyst interfaces. A review of studied nonmetal-functionalised gC₃N₄ and their effects on CO₂ photoreduction activity is presented in **Table 2.3.4**. Overall, all nonmetals employed have enhanced the activity of their pristine counterparts, and this is attributed to a number of reasons connected to the chemical, sorptive and optoelectronic properties that were previously discussed: i) presence of functional groups which act as CO₂ adsorption/activation sites, ii) introduction of defects/moieties resulting in redistribution and delocalisation of electrons, iii) enhanced surface area and pore network, iv) better charge separation and migration, so limited recombination, v) extended light absorption and bandgap reduction, vi) more even/deeper light diffusion, and vii) creation of more excitons. This attribution, depending on the study, is proven experimentally or speculated; the latter situation being most frequent. In many cases, nonmetal functionalisation introduces defects which are beneficial for the CO₂ reduction reaction; however one needs to regulate the amount of functionalisation as exceeding a certain defect concentration can result in the opposite effect. The reported enhanced photoactivity for CO₂ reduction via nonmetal functionalisation, and the recently developed reaction mechanism investigation certainly pave the way for further exploration of the field, and for the design of optimised gC₃N₄-based photocatalysts.

Table 2.3. 4. Summary of nonmetal (B, C, N, O, F, P, S, Cl, Br, I) functionalisation of gC₃N₄ and their effects on CO₂ photoreduction.

Nonmetal studied	gC ₃ N ₄ structure	Light source	Conditions	Proton donor/ Sacrificial agent	Product formed	Ref
C	gC ₃ N ₄ nanorods	500 W Xe arc lamp	Not reported	H ₂ O/NaOH	346-651 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₃ OH ($\lambda > 300 \text{ nm}$)	178
C, O	bulk gC ₃ N ₄	4 W lamp	20 °C	H ₂ O	4-9 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO ($\lambda = 254 \text{ nm}$)	179
C, O	gC ₃ N ₄ nanosheets	300 W Xe arc lamp	25 °C	H ₂ O/MeCN/TEOA	1-5 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO 0.1-0.2 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ 0.2-0.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 420 \text{ nm}$)	180
N	gC ₃ N ₄ nanotubes	300 W Xe arc lamp	10 °C 0.7 bar	H ₂ O/MeCN/TEOA/CoCl ₂ /(C ₅ H ₄ N) ₂	37-104 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO 8-55 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 420 \text{ nm}$)	181
N, H	gC ₃ N ₄ nanosheets	300 W Xe arc lamp	Not reported	H ₂ O	3 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO 0.2 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ ($\lambda > 200 \text{ nm}$)	182
N	bulk gC ₃ N ₄	300 W Xe arc lamp	Not reported	H ₂ O/H ₂ SO ₄ /NaHCO ₃	0.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₃ OH 0.1-0.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ ($\lambda > 200 \text{ nm}$)	183
O	gC ₃ N ₄ nanotubes	350 W Xe arc lamp	Not reported	H ₂ O/H ₂ SO ₄ /NaHCO ₃	1 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₃ OH ($\lambda = 420 \text{ nm}$)	184
B	bulk gC ₃ N ₄	300 W Xe arc lamp	30 °C	H ₂ O	1 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO 0.03 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ 0.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 420 \text{ nm}$)	185
B	gC ₃ N ₄ nanosheets	300 W Xe arc lamp	Not reported	H ₂ O/H ₂ SO ₄ /NaHCO ₃	5 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO 0.5 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ 0.1 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ 3.8 $\mu\text{mol g}^{-1} \text{h}^{-1}$ O ₂ ($\lambda = 400 \text{ nm}$)	186
B	gC ₃ N ₄ nanosheets	300 W Xe arc lamp	Not reported	H ₂ O	71 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ ($\lambda > 320 \text{ nm}$) 15-43 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ ($\lambda > 420 \text{ nm}$)	187
B	bulk gC ₃ N ₄	300 W Xe arc lamp	Not reported	H ₂ O/H ₂ SO ₄ /NaHCO ₃	0.3-0.5 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO 0.03-0.16 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ ($\lambda > 320 \text{ nm}$)	188
B, N, H	gC ₃ N ₄ nanosheets	solar simulator	20-30 °C	H ₂ O	2-5 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO ($\lambda > 400 \text{ nm}$)	189

Nonmetal studied	gC ₃ N ₄ structure	Light source	Conditions	Proton donor/ Sacrificial agent	Product formed	Ref
B	bulk gC ₃ N ₄	solar simulator	25 °C	H ₂ O	5 μmol g ⁻¹ h ⁻¹ CO (λ>400 nm)	190
B	ultrathin gC ₃ N ₄ nanosheets	solar simulator	25 °C	H ₂ O	9 μmol g ⁻¹ h ⁻¹ CO (λ>400 nm)	190
P	bulk gC ₃ N ₄	solar simulator	25 °C	H ₂ O	3 μmol g ⁻¹ h ⁻¹ CO (λ>400 nm)	190
P	ultrathin gC ₃ N ₄ nanosheets	solar simulator	25 °C	H ₂ O	7 μmol g ⁻¹ h ⁻¹ CO (λ>400 nm)	190
B, P	bulk gC ₃ N ₄	solar simulator	25 °C	H ₂ O	11 μmol g ⁻¹ h ⁻¹ CO (λ>400 nm)	190
B, P, N, H	ultrathin gC ₃ N ₄ nanosheets	solar simulator	25 °C	H ₂ O	15-22 μmol g ⁻¹ h ⁻¹ CO (λ>400 nm)	190
P, N, H	gC ₃ N ₄ nanotubes	300 W Xe arc lamp	20 °C	H ₂ O/H ₂ SO ₄ /NaHCO ₃	2 μmol g ⁻¹ h ⁻¹ CO 2 μmol g ⁻¹ h ⁻¹ CH ₄ (λ>400 nm)	191
P	bulk gC ₃ N ₄	300 W Xe arc lamp	1 bar	H ₂ O	35 μmol g ⁻¹ CH ₄ (λ>400 nm) 0.3-2 μmol g ⁻¹ CH ₄ (365≤λ≤520 nm)	192
P, F	bulk gC ₃ N ₄	34 W blue LED	Not reported	H ₂ O	120 μmol g ⁻¹ h ⁻¹ CH ₃ OH (450≤λ≤495 nm)	194
S	bulk gC ₃ N ₄	300 W Xe arc lamp	1 bar	H ₂ O	60-145 μmol g ⁻¹ h ⁻¹ CH ₄ (λ>420 nm) 1-11 μmol g ⁻¹ CH ₄ (365≤λ≤550 nm)	195
S	gC ₃ N ₄ nanosheets	solar simulator 300 W Xe arc lamp	25 °C 1 bar	H ₂ O/HCl/ NaHCO ₃	0.4 μmol g ⁻¹ h ⁻¹ CH ₃ OH (λ>300 nm)	196
S	gC ₃ N ₄ ribbons	300 W Xe arc lamp	Not reported	H ₂ O	20-30 μmol g ⁻¹ h ⁻¹ CO (λ>420 nm)	197
F	gC ₃ N ₄ nanotubes	300 W Xe arc lamp	0.8 bar	H ₂ O/MeCN/ TEOA	0.5-3 μmol g ⁻¹ h ⁻¹ CO 0.1-0.2 μmol g ⁻¹ h ⁻¹ CH ₄ 0.8-0.9 μmol g ⁻¹ h ⁻¹ H ₂ (λ>420 nm)	199
Cl	gC ₃ N ₄ nanotubes	300 W Xe arc lamp	0.8 bar	H ₂ O/MeCN/ TEOA	2-3 μmol g ⁻¹ h ⁻¹ CO 0.2 μmol g ⁻¹ h ⁻¹ CH ₄ 0.8-0.9 μmol g ⁻¹ h ⁻¹ H ₂ (λ>420 nm)	199

Nonmetal studied	gC ₃ N ₄ structure	Light source	Conditions	Proton donor/ Sacrificial agent	Product formed	Ref
Br	gC ₃ N ₄ nanotubes	300 W Xe arc lamp	0.8 bar	H ₂ O/MeCN/ TEOA	2-3 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO 0.2 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ 0.6-0.7 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 420 \text{ nm}$)	199
I	gC ₃ N ₄ nanotubes	300 W Xe arc lamp	0.8 bar	H ₂ O/MeCN/ TEOA	2 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CO 0.2 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ 0.6-0.8 $\mu\text{mol g}^{-1} \text{h}^{-1}$ H ₂ ($\lambda > 420 \text{ nm}$)	199

3. RESEARCH GAPS & OBJECTIVES

3.1. Research gaps

Research involving BN- and gC₃N₄-based materials for the photo(thermal) CO₂ reduction usually revolves around optimisation. This can be optimisation of the material structure/chemistry (*e.g.* through morphology engineering, creation of heterojunctions, use of cocatalysts), reaction optimisation (*e.g.* by adding sacrificial agents, applying external fields, increasing light intensity) or a combination thereof. Certainly, optimisation is necessary for advancing the field and for shortening the distance from practical applications. Another research interest, attracting comparatively less attention from the scientific community, is the investigation of fundamentals. The understanding of the role of the material (and hence the material's properties) in the reaction, and of the reaction mechanism, is equally important and essential for the design of enhanced, functional photocatalysts. Due to the apparent disconnect in the literature between optimisation and understanding of reaction mechanisms, there are many knowledge gaps on the functionality and pure effect of BN and gC₃N₄ materials on the photo(thermal) CO₂ reduction reaction.

Based on the literature review on porous BN, this material has only recently started being used as a photocatalyst, mainly for H₂O splitting and CO₂ reduction. There is still some confusion regarding BN nomenclature and forms. The examination of C and O as nonmetal dopants is much more common and complete (both theoretically and experimentally) than for other elements. Although there are multiple theoretical calculations on other nonmetals, such as S and P, there is a gap in their experimental reports, especially for photocatalytic applications. Therefore, several questions arise: can S and P be used for the functionalisation of porous BN for the photo(thermal) catalytic CO₂ reduction? What products would be

formed? How would S and P integrate in the structure? Which precursors could/should be used for the synthesis? How would CO₂ adsorption be affected? How would the charge carrier behaviour and recombination rates be affected? What would be the effect of the different properties on the photoactivity? Is there an optimal nonmetal concentration?

gC₃N₄, on the other hand, is more extensively studied as a photocatalyst for CO₂ reduction. Based on the literature review, B, P and S are commonly used nonmetals for functionalisation and they enhance the original material's photoactivity. Despite the number of literature reports, the effect of functionalisation on the material's properties and its connection to the enhanced photocatalytic activity are usually speculated, and in fact, remain largely unknown. The testing of functionalised materials in the presence of sacrificial agents/cocatalysts, the skewed comparisons between carbon nitride materials of different morphologies (*e.g.* comparison of photoactivities of P-gC₃N₄ nanotubes vs bulk gC₃N₄, but not with gC₃N₄ nanotubes), or the absence of sufficient control tests, all complicate pinpointing the real effect and activity of nonmetal functionalisation. Hence, one wonders: what is the rate of material degradation (if any) during reaction for functionalised materials? Is the material photoactive without using sacrificial agents and cocatalysts? How and why does functionalisation boost the activity? What is the sole effect of the functionalisation on the material properties? Can this be experimentally proven?

3.2. Research objectives

The focus of my thesis is to identify functionalisation – property – photoactivity relationships in nonmetal-functionalised porous BN and gC₃N₄ materials in the context of photocatalysis. For porous BN, S and P are selected as interesting functionalisation candidates, due to their

similar electronic structure (*i.e.* similar position in the Periodic Table) to B and N atoms allowing them to be potentially integrated in the structure of the material, and based on the promising results achieved by C and O functionalisation. It is noted here that S- or P-functionalised BN has only been experimentally tested with the use of cocatalyst (Pt) for photocatalytic H₂O splitting, and never (to the best of my knowledge) for CO₂ photoreduction. For gC₃N₄, B is selected for the functionalisation, as one of the most widely used nonmetals whose pure effects on the gC₃N₄'s properties and their link to photoactivity remain unknown. The main objectives of my PhD are:

Objective 1

To investigate the effect of i) P and S functionalisation, ii) choice of P and S precursor and iii) P and S content on porous BN's chemical, sorptive, optoelectronic and photocatalytic properties. This includes exploring how the nonmetals would be integrated into the BN structure, how the CO₂ adsorption capacity and heat of adsorption would be affected, how the light absorption and charge carrier behaviour and lifetimes would be affected, and how all these properties would influence the photocatalytic activity for CO₂ reduction. This also covers screening for an optimal nonmetal concentration and precursor (if any).

Objective 2

To elucidate the effect of i) B functionalisation, ii) choice of B precursor and iii) B content on gC₃N₄'s chemical, sorptive, optoelectronic and photocatalytic properties. This includes clarifying the chemical environment around B atoms depending on the choice of precursor, linking the CO₂ adsorption capacity and heat of adsorption to B content and precursor, probing charge carrier creation and behaviour, and testing the materials for CO₂ photoreduction

without use of sacrificial agents. This also covers experimentally supporting the photocatalytic results with characterisation techniques.

Objective 3

To test B-functionalised gC₃N₄ materials for light- and heat- assisted CO₂ reduction for the first time, compare to pristine material, and uncover potential synergy between light and heat for this class of material.

4. METHODOLOGY

As mentioned in the introductory **Chapter 1**, the present section discusses frequently used methods throughout the experimental **Chapters 5 to 7**. Information on the synthesised materials and characterisation, adsorption and testing techniques used for each experimental project, which were not repeated for more than one Chapters, is presented in detail in each respective Chapter.

4.1. FTIR

FTIR is a characterisation technique elucidating IR-active chemical bonds and functional groups present in a material, meaning molecules which vibrate in different modes after absorbing specific IR wavelengths. The attenuated total reflectance FTIR (ATR-FTIR) instrumentation involves an IR beam source, a detector, and an ATR crystal on which the sample (solid or liquid) is deposited (pressed, if the sample is solid). The IR beam produced by the source is focused on the ATR crystal, creating an evanescent wave which penetrates through the sample (in a depth usually 0.5-2 μm). This wave is attenuated and partly absorbed by the sample's IR-active molecules, and the attenuated IR beam is then refracted by the crystal into the detector²⁰⁴. The ATR-FTIR measurement process is described in **Figure 4.1.1** below.

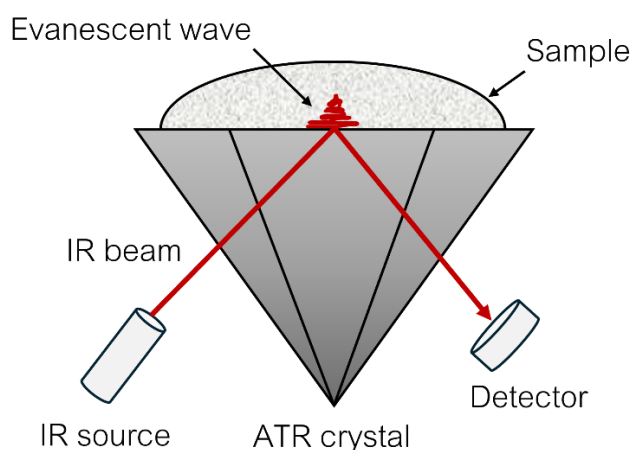


Figure 4.1. 1. Schematic representation of the ATR-FTIR principle. Adapted with permission from reference ²⁰⁵. Copyright 2021 Springer Nature Singapore Pte Ltd.

In the present thesis, ATR-FTIR was used to monitor characteristic B-N and B-O bonds in BN materials (**Chapter 5**) and C-N/C=N, heptazine and N-H/O-H bonds in gC₃N₄ materials (**Chapters 6-7**). For both BN and gC₃N₄ materials, a Cary 630 FTIR spectrometer (Agilent) equipped with an attenuated total reflectance (ATR) accessory was used. Samples were manually ground in an agate mortar, and the spectra were recorded after 32 repetitions per sample over a wavenumber range, with a 2 cm⁻¹ resolution. For BN materials, a range of 650–4000 cm⁻¹ was used for spectra collection. For gC₃N₄ materials, a range of 400–4000 cm⁻¹ was used for spectra collection.

4.2. XPS

XPS probes the surface of a solid material, and is used to identify the chemical state of and environment around its comprising elements, as well as the elemental composition of the sample. Typically operated under high ($\sim 10^{-11}$ bar) or ultra-high vacuum ($< 10^{-12}$ bar), XPS

involves flooding X-rays of energy $h\nu$ onto the sample surface, causing ejection of electrons from their molecular orbitals and from the material. This is because the incident radiation is absorbed by the electrons and converted into kinetic energy. This is known as photoelectric effect,²⁰⁶ and is visualised in **Figure 4.2.1**. The amount of ejected electrons and their respective kinetic energies are detected and measured, providing information about their binding energies – and thus about the chemical bonding of atoms – based on the equation:

$$E_b = h\nu - E_{kin} - \phi \quad (17)$$

Where E_b is the binding energy of the ejected electron (eV), $h\nu$ is the irradiated X-ray photon energy (eV), E_{kin} is the measured kinetic energy of the ejected electron (eV), and ϕ is the work function of the spectrometer (eV).

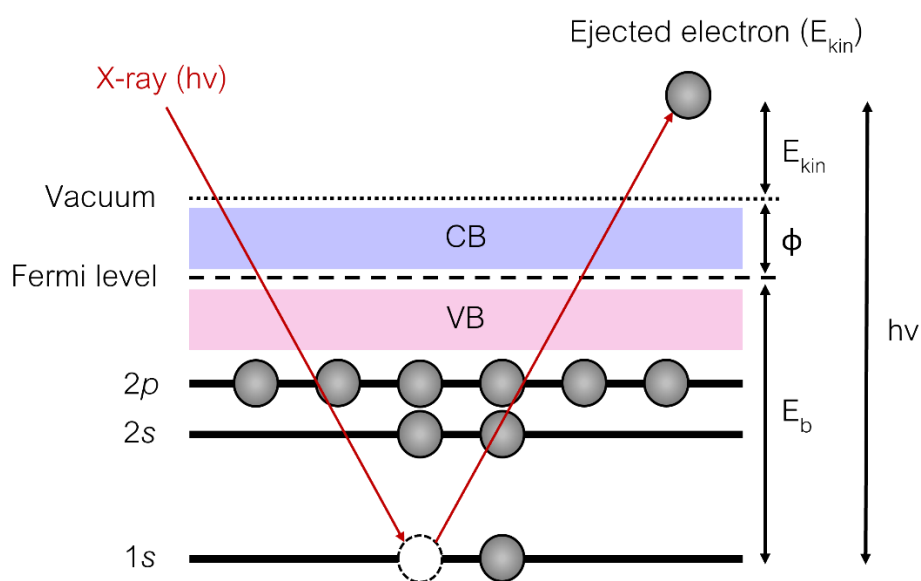


Figure 4.2. 1. Schematic representation of the XPS principle, the photoelectric effect. Adapted with permission from reference ²⁰⁷. Copyright 2015 Springer-Verlag Berlin Heidelberg.

In this thesis, in relation to photocatalysts' chemical properties, XPS was used to determine the elemental composition and chemical bonding around B, N, O, C, P and S atoms in BN materials (**Chapter 5**) and the elemental composition and chemical bonding around C, N, B and O atoms in gC₃N₄ materials (**Chapters 6-7**). For both BN and gC₃N₄ materials, a high-throughput K-Alpha X-ray Photoelectron Spectrometer (Thermo Scientific) equipped with a monochromatic Al K α source ($h\nu = 1486.6$ eV) was used. Samples were manually ground in an agate mortar and mounted on the XPS holder by using conductive carbon tape. The X-ray power gun was set to 72 W and the measurements were performed under high-vacuum conditions ($\sim 10^{-11}$ - 10^{-10} bar) with the use of a flood gun to prevent sample charging. Measurements were collected at least at three different points/areas of the mounted sample and averaged. Data analysis on the survey and core level spectra was performed using the Thermo Advantage software. The adventitious carbon (C-C) peak set at 284.8 eV was used for binding energy calibration. For BN materials, the measured core level spectra were B 1s, N 1s, C 1s, O 1s, P 2p and S 1s. For gC₃N₄ materials, the measured core level spectra were B 1s, N 1s, C 1s and O 1s.

In **Chapters 5 and 6**, Dr. Gwilherm Kerherve (Materials Department, Imperial College London) helped with the deconvolution of the core level spectra and confirmation of their validity.

4.3. XRD

Powder X-ray diffraction (XRD) is a non-destructive characterisation technique deployed for the elucidation of a solid material's crystal structure. In this technique, X-rays are irradiated from an X-ray source of wavelength λ onto the sample, at a set and varying angle θ from a

lattice plane²⁰⁸. For each angle, a constructive interference occurs between atoms from specific lattice planes and the incident beam when Bragg's law²⁰⁹ is satisfied:

$$n\lambda = 2d\sin(\theta) \quad (18)$$

Where n is an integer (no unit), λ is the wavelength of incident radiation (nm), d is the spacing distance between successive lattice planes (nm), and θ is the angle of the incident beam on the diffraction plane (°).

As a result of this constructive interference, the beam gets diffracted towards a specific direction at an angle θ from the diffraction plane, and is detected and measured by the X-ray detector. The principle of XRD is illustrated in **Figure 4.3.1** below.

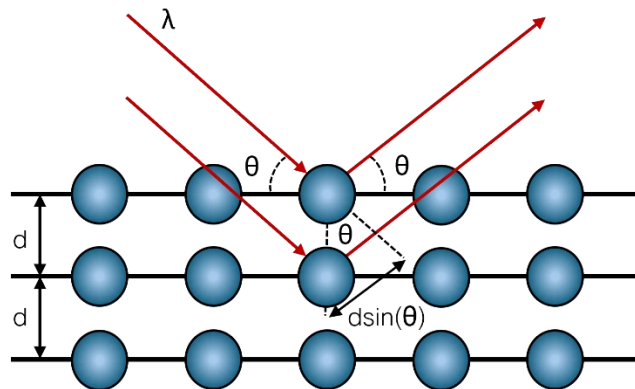


Figure 4.3. 1. Schematic representation of the XRD principle.

In this thesis, XRD was used to confirm the level of crystallinity, existence of characteristic planes and d -spacing in BN (**Chapter 5**) and gC_3N_4 (**Chapter 6-7**) materials. In **Chapters 5 and 7**, powder XRD data were collected using an X'Pert Pro X-ray diffractometer (PANalytical) in the reflection mode, using a Cu source (anode voltage=40 kV, emission current=20 mA) with Cu $K\alpha_1$ ($\lambda = 1.54060 \text{ \AA}$) and Cu $K\alpha_2$ ($\lambda = 1.54443 \text{ \AA}$) radiation, emitted with an intensity ratio of 2:1. The XRD detector used was an X'Celerator silicon strip detector. Samples were manually

ground in an agate mortar and deposited on a solid holder. For BN materials, points were recorded over a 2θ angle range of $6-60^\circ$ with a step size of 0.0340° . For gC_3N_4 materials, points were recorded over a 2θ angle range of $5-65^\circ$ with a step size of 0.0109° . In **Chapter 6**, powder XRD data were collected using an X'Pert Pro X-ray diffractometer (PANalytical) in the reflection mode, using a Cu source (anode voltage=40 kV, emission current=40 mA) with Cu $K\alpha_1$ ($\lambda = 1.54060 \text{ \AA}$) and Cu $K\alpha_2$ ($\lambda = 1.54443 \text{ \AA}$) radiation, emitted with an intensity ratio of 2:1. The XRD detector used was an X'Celerator silicon strip detector. Samples were deposited on a silicon piece on a solid holder. Points were recorded over a 2θ angle range of $5-65^\circ$ with a step size of 0.0167° .

4.4. N₂ sorption (-196 °C)

N₂ sorption at -196 °C is a technique used for the determination of a material's porosity, including its specific surface area and pore volume²¹⁰. During this process, N₂ (adsorbate) is being controllably dosed in a sample-containing tube, initiating adsorption/desorption in the pores of the sample (adsorbent). N₂ is being gradually dosed in the tube once equilibrium is reached, and the process is repeated until saturation pressure is reached. A volumetric sorption analyser is used to monitor changes in pressure within the tube, and these changes in pressure are correlated to the amount of N₂ adsorbed at any point. An inert gas (*i.e.* He) is used for the determination of dead volume (*i.e.* free space) within the tube, so that the amount of adsorbed N₂ is linked to the mass of sample used.

In this thesis, the determination of specific surface area of the tested materials is conducted using the Brunauer-Emmett-Teller (BET) method²¹¹, which is based on the following assumptions:

- Adsorbed molecules first form a monolayer, and then adopt an unrestricted multi-layer formation.
- No interactions between adsorbed molecules on the same layer.
- The energy of adsorption for the first layer is the same in all adsorption sites of the adsorbent.
- The heat of adsorption in the first layer is higher than in the subsequent layers.
- Adsorbed molecules in the second and subsequent layers act as saturated liquid.
- Adsorbed molecules between two adjacent layers are only linked through a single site.

The BET area is determined from experimental N₂ sorption isotherms at -196 °C based on the equations:

$$\frac{P}{V(P_0 - P)} = \frac{1}{CV_{mono}} + \frac{C-1}{CV_{mono}} \frac{P}{P_0} \quad (19)$$

$$S_{BET} = \frac{V_{mono} S_{ads} N_A}{V_m m} \quad (20)$$

Where P is the equilibrium pressure (bar), P₀ is the N₂ saturation pressure (bar), V is the volume of adsorbed N₂ at pressure P (cm³), C is a BET constant (no unit), V_{mono} is the volume of adsorbed N₂ in the monolayer (cm³), S_{BET} is the BET area (m² g⁻¹), S_{ads} is the cross-sectional area of N₂ (nm²), N_A is Avogadro's number (mol⁻¹), V_m is the molar volume at standard temperature and pressure (m³ mol⁻¹) and m is the mass of the sample (g).

The total pore volume can be determined from the volume of adsorbed N₂ at P/P₀≈0.97 based on the equation:

$$V_{tot} = \frac{P^0 V_m V_{0.97}}{RT^0} \quad (21)$$

Where V_{tot} is the total pore volume (cm³ g⁻¹), P⁰ is the standard pressure (bar), V_{0.97} is the

volume of adsorbed N₂ at pressure P/P₀≈0.97 (cm³), R is the universal gas constant (J K⁻¹ mol⁻¹) and T⁰ is the standard temperature (K).

The micropore volume can be determined with the Dubinin-Radushkevich method, based on the equations²¹²:

$$\log(q) = \log(q_{micro}) - D \left(\log \left(\frac{P_0}{P} \right) \right)^2 \quad (22)$$

$$V_{micro} = \frac{q_{micro} MW_{N_2}}{\rho} \quad (23)$$

Where q is the total N₂ adsorption capacity at pressure P (cm³ g⁻¹), q_{micro} is the N₂ adsorption capacity at pressure P from micropores (cm³ g⁻¹), D is an empirical constant (no unit), V_{micro} is the micropore volume (cm³ g⁻¹), MW_{N₂} is the molecular weight of N₂ (g mol⁻¹) and ρ is the N₂ density at -196 °C.

In this thesis, N₂ (-196 °C) sorption isotherms for both BN (**Chapter 5**) and gC₃N₄ (**Chapter 6-7**) materials were obtained using a 3Flex Sorption Analyser (Micromeritics) to examine the materials' porosity and BET area. N₂ (zero grade, 99.998%, BOC) was used for these measurements.

In **Chapter 5**, prior to the measurements, the BN samples were degassed *ex-situ* using a VacPrep Degasser (Micromeritics) at 140 °C overnight down to 2·10⁻⁵ bar. Then, they were *in-situ* degassed at 120 °C for 4 h down to 7·10⁻⁵ bar using the 3Flex Sorption Analyser. The BET area was derived following the BETSI approach, which expands on the Rouquerol criteria to produce a standard BET area assignment^{210,211,213}. The total pore volume was estimated from the amount of adsorbed N₂ at P/P₀ = 0.97. The micropore volume was determined using the Dubinin–Radushkevich method²¹². The ultramicropore volume was determined using the

Horvath–Kawazoe method²¹⁴. The mesopore volume was calculated by subtracting the micropore volume from the total pore volume.

In **Chapters 6-7**, prior to the measurements, the samples were degassed *ex-situ* using the same VacPrep Degasser (Micromeritics) at 120 °C overnight down to $2 \cdot 10^{-5}$ bar. Then, they were *in-situ* degassed at 120 °C for 4 h down to $7 \cdot 10^{-5}$ bar using the 3Flex Sorption Analyser. The specific surface areas were calculated using the BET method²¹¹. The total pore volume was estimated from the amount of adsorbed N₂ at $P/P_0 = 0.99$. The micropore volume was determined using the Dubinin-Radushkevich method²¹². The mesopore volume was calculated by subtracting the micropore volume from the total pore volume.

4.5. CO₂ sorption (25 °C)

In **Chapters 5 and 6**, CO₂ adsorption isotherms were measured right after finishing the N₂ sorption measurements used for porosity analyses, in order to i) quantify the CO₂ uptake at 25 °C and up to 1 bar, and ii) calculate the heat of adsorption. The samples were degassed *in-situ* at 120 °C for 4 h down to $7 \cdot 10^{-5}$ bar using the same 3Flex Sorption Analyser. CO₂ gas (research grade, 99.999%, BOC) was used, and the sorption isotherms were measured sequentially at 15, 25, and 35 °C up to 1 bar. The isotherms were fitted using dual site Langmuir model²¹⁵:

$$q_j^* = \frac{q_{sb,j} b_j p}{1 + b_j p} + \frac{q_{sd,j} d_j p}{1 + d_j p} \quad (24)$$

$$b_j = b_{0,j} \exp\left(\frac{-\Delta U_{b,j}}{RT}\right) \quad (25)$$

$$d_j = d_{0,j} \exp\left(\frac{-\Delta U_{d,j}}{RT}\right) \quad (26)$$

Where q_j^* is the adsorbed amount of gas j at pressure p and temperature T , b and d are adsorption coefficients, b_0 , d_0 , ΔU_b , and ΔU_d are constants, R is the universal gas constant, and q_{sb} and q_{sd} are saturation capacities.

In **Chapter 7**, CO₂ adsorption isotherms were measured right after finishing the N₂ sorption measurements used for porosity analyses, to quantify the CO₂ uptake at 25 °C and up to 1 bar. The samples were degassed *in-situ* at 120 °C for 4 h down to $7 \cdot 10^{-5}$ bar using the same 3Flex Sorption Analyser. CO₂ gas (research grade, 99.999%, BOC) was used, and the sorption isotherms were measured at 25 °C up to 1 bar.

In **Chapters 5 and 6**, Dr. Hassan Azzan (Chemical Engineering Department, Imperial College London) helped with the dual site Langmuir fittings on the experimental CO₂ adsorption isotherms, and with the calculation of heat of adsorption.

4.6. DRS UV-Vis

Diffuse reflectance spectroscopy in the UV-visible (DRS UV-Vis) is used for the evaluation of the light absorption range of a solid or liquid material. In this technique, a light beam falls on the sample (which is pressed on the surface of a transparent holder, if solid) and the reflected light is scattered in multiple directions, independent of the incident angle (diffuse reflectance). Part of the incident light can get absorbed, depending on the sample, modifying the amount and energy of reflectance. The reflected scattered radiation gets detected and measured by a detector, over a range of wavelengths²¹⁶. The UV-visible light spectrum in which the material absorbs (absorption coefficient) can be calculated and plotted against a wavelength range, based on the Kubelka-Munk equation^{217,218}:

$$\alpha = F(R) = \frac{(1-R)^2}{2R} \quad (27)$$

Where α is the absorption coefficient (no unit) and R is reflectance (%).

The bandgap of a material can be derived using the Tauc plot and extrapolating the onset linear region of the curve²¹⁹:

$$F(R)h\nu^{1/n} \text{ vs energy} \quad (28)$$

Where n is an integer (no unit), with $n=2$ for indirect and $n=1/2$ for direct semiconductors.

In **Chapter 5**, DRS UV-Vis measurements were carried out to identify the BN materials' light absorption range. In **Chapters 6 and 7**, DRS UV-Vis measurements were carried out to identify the gC₃N₄ materials' light absorption range and bandgaps. For both BN (**Chapter 5**) and gC₃N₄ (**Chapters 6 – 7**) materials, the DRS UV-Vis measurements were collected using a UV/Vis-IRS-2600Plus (Shimadzu) spectrophotometer, equipped with an integrated sphere attachment. The resolution was set to 2 nm, with pressed BaSO₄ powder as a reference diffuse reflectance material. The samples were loaded and pressed into the holder until they covered the entire surface. Absorbance spectra were derived using the Kubelka-Munk function. In **Chapters 6 and 7**, the Tauc plots were created for identification of the materials' bandgaps, with $n=2$ since gC₃N₄ is an indirect semiconductor²²⁰.

4.7. Steady-state PL

Steady-state photoluminescence (PL) is a technique used on light-irradiated semiconductors to probe the photon (radiative) emissions of photoexcited electrons when they relax back to ground state²²¹. The photon emissions can be the total or just part of the energy difference between excited states and lower energy states, as nonradiative emissions (*e.g.* heat) occur in

vibrational transitions or transitions from CB (range of energy levels) to CB minima (minimum energy level of the CB). The PL mechanism can differ between organic and inorganic semiconductors. In organic semiconductors, the excited electrons can relax from higher singlet energy states (*e.g.* S_2 , S_3 , S_4) to the lowest singlet excited energy state (S_1) and then i) fall back to ground state (S_0) accompanied by fluorescence, or ii) move to triplet states (*e.g.* T_1 , T_2 , T_3) before falling back to S_0 accompanied by phosphorescence. In the case of inorganic semiconductors, both intrinsic (band-to-band, *i.e.* CB to VB) and extrinsic (sub-bandgap) emissions can occur in defective materials with electron-trapping midgap states.

In **Chapters 5 and 6**, steady-state PL was used to investigate the relaxation pattern of photoexcited electrons, and by extension the existence of midgap states. PL spectra were recorded at room temperature by using a Cary Eclipse fluorescence spectrometer (Agilent). For the measurements in **Chapter 5**, the excitation wavelength was set initially to 200 nm and later to 282 nm, with 5 nm excitation/emission slits, 0.5 s dwell time, 1 nm data interval, and 800 V photomultiplier tube (PMT) voltage. For the measurements in **Chapter 6**, excitation wavelength was set to 355 nm, with 2.5 nm excitation/emission slits, 0.5 s dwell time, 1 nm data interval, and 800 V PMT voltage.

In **Chapters 5 and 6**, Dr. Andreas Kafizas (Chemistry Department, Imperial College London) helped with the collection and analysis of steady-state PL spectra.

4.8. μ s-TAS

Transient absorption spectroscopy (TAS) is an ultrafast pump-probe technique employed to determine the concentrations, behaviour and lifetimes of double-photoexcited charge carriers

in photocatalytic systems²²². During TAS measurements, a pulsed laser is used to excite photogenerated carriers to higher energy states in the (liquid or solid) sample. At the same time, differences in absorption of a probe light (after going through a monochromator) are being detected and measured as a function of wavelength and time. Singlet and triplet excited states, along with electron transfer mechanisms can be deciphered with this technique.

In **Chapters 5 and 6**, TAS was employed to explore the charge carrier behaviour and lifetimes. The spectra were recorded using a purpose-built set-up in diffuse reflection mode. A Nd:YAG laser (OPOTEK Opolette 355 II, 7 ns pulse width) was used to generate 355 nm excitation pulses of $100 \mu\text{J cm}^{-2}$. A broadband probe light was generated from a quartz halogen lamp (Bentham IL1) and long pass filters were placed before the samples to reduce short wavelength irradiation of the sample. The light was collected in diffuse reflectance mode by a 2-inch diameter, 2-inch focal length lens, and relayed to a monochromator to select the probe wavelength. A long pass filter was positioned at the entrance of the monochromator to block the scattered laser light. The collected light was focused onto a Si photodiode detector (Hamamatsu S3071). Sub-ms data were processed by an electronic amplifier (Costronics) and recorded on an oscilloscope. Data on the ms time scale were simultaneously recorded by a DAQ card (National Instruments). Acquisitions were triggered by scattering from the laser excitation measured by a photodiode (Thorlabs DET10 A). A minimum of 200 laser pulses were averaged together and processed using LabVIEW home-built software.

In **Chapter 5**, the measurements were performed on powder samples in air, pressed between two microscope glass slides.

In **Chapter 6**, the measurements were performed in air: (i) on the powder samples, (ii) on the powder samples in the presence of 10 vol% TEOA, and (iii) on the powder samples in the presence of 10 mM AgNO₃, all pressed between two microscope glass slides.

In **Chapters 5 and 6**, Dr. Andreas Kafizas (Chemistry Department, Imperial College London) helped with the collection and analysis of TAS spectra.

4.9. EPR

EPR is a spectroscopic technique which probes paramagnetic unpaired electrons existent in materials, allowing the study of their electronic and chemical structure, and of their magnetic properties²²³. In this technique, usually, electromagnetic radiation (produced by microwaves) at a constant microwave frequency ν , and an increasing magnetic field B_0 (produced by a magnet) are applied on the material, which contains unpaired electrons²²⁴. An unpaired electron interacts with the applied magnetic field like a compass, due to its magnetic moment, and occupies two allowed energy spin states, $M_s = -1/2$ (parallel to the magnetic field) and $M_s = +1/2$ (antiparallel). This interaction between unpaired electron and applied magnetic field is called Zeeman effect. The energy of these two spin states can be described as:

$$E^{+1/2} = M_s^{+1/2} g \mu_B B_0 \quad (29)$$

$$E^{-1/2} = M_s^{-1/2} g \mu_B B_0 \quad (30)$$

where $E^{-1/2}$ and $E^{+1/2}$ are the energies of the parallel and antiparallel spin state (J), respectively, $M_s^{-1/2}$ and $M_s^{+1/2}$ are the allowed spin states, g is the g-factor (no units), characteristic value for each material, μ_B is the Bohr magneton (J T⁻¹), and B_0 is the magnetic field (T).

These spin states diverge with an increasing magnetic field. At a specific magnetic field (*i.e.* field of resonance) the difference of energy between the spin states ΔE , equals the energy of applied radiation $h\nu$, and absorption of energy occurs²²⁴:

$$\Delta E = h\nu = g\mu_B B_0 \quad (31)$$

The energy absorption is detected by the detector, and the EPR signal that is usually reported is the first derivative of the absorption signal. The principle of EPR is shown in **Figure 4.9.1**.

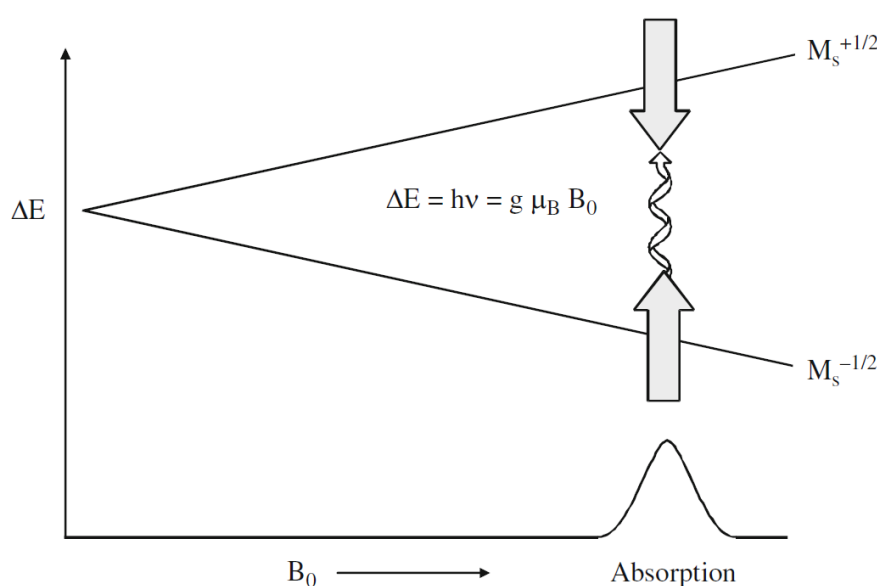


Figure 4.9. 1. Basic principle behind EPR signal. Reproduced with permission from reference ²²⁴. Copyright 2010 Springer-Verlag/Wien.

In **Chapters 5 and 6**, EPR was used to i) discover differences in chemistry between samples, caused by different concentrations of – or different environment around – unpaired electrons, and ii) verify the existence of photoexcited electrons upon material illumination. All EPR measurements were performed using an Eleksys E500T continuous-wave CW EPR spectrometer (Bruker) operating at X-band frequencies (9.5–9.9 GHz/0.35 T) and equipped

with an ER4118-X MD5 resonator (Bruker). Irradiation measurements of the samples were carried out immediately after EPR measurement under dark was obtained for each sample, under direct illumination of an LSH302 light source (LOT Quantum Design) equipped with a 300 W Xe arc lamp (UXL-302-O, Ushio) through an optical access port. The samples were placed inside 4 mm EPR quartz tubes, and each EPR tube was filled with the sample to the same height. EPR spectra got normalised for the mass of the samples. Care was taken to position the centre of each sample in the centre of the resonator.

In **Chapter 5**, the EPR spectrometer was additionally equipped with a cryogen free variable temperature cryostat for EPR (Cryogenic). The microwave frequency used was 9.61 GHz with i) a microwave power of 2 mW, 100 kHz modulation frequency with 2G modulation amplitude at room temperature, and ii) 10 kHz modulation frequency, 2G modulation amplitude, and 8 μ W power at -268°C . EPR spectra were recorded at i) room temperature in air and ii) -268°C in He. Simulations of EPR spectra were performed using the EasySpin toolbox (version 6.0.2) for MATLAB²²⁵.

In **Chapter 6**, the microwave frequency used was 9.63 GHz with a microwave power of 2 mW, 100 kHz modulation frequency with 2G modulation amplitude. EPR spectra were recorded at room temperature in air.

In **Chapters 5 and 6**, Dr. Irena Nevjestic (Materials Department, Imperial College London) helped with the collection and analysis of EPR spectra.

5. INVESTIGATING THE EFFECT OF P (AND S)

FUNCTIONALISATION ON POROUS BN CHEMICAL, SORPTIVE, OPTOELECTRONIC AND PHOTOCATALYTIC PROPERTIES

The contents of this Chapter have been used or adapted from the author's publication in Journal of Physical Chemistry C⁵¹, with permission under CC-BY 4.0 Licence. Unless otherwise stated, I have conducted all discussed experimental work and analysis thereof. Dr. Andreas Kafizas (Chemistry Department, Imperial College London) helped with steady-state PL and TAS measurements, analysis and resources. Dr. Irena Nevjestic and Prof. Sandrine Heutz (Materials Department, Imperial College London) helped with EPR measurements, analysis and resources. Dr. Soranyel Gonzalez Carrero (Chemistry Department, Imperial College London) helped with time-resolved photoluminescence measurements, analysis and resources. Dr. David C. Grinter, Dr. Santosh Kumar, Dr. Pilar Ferrer and Dr. Georg Held (VerSoX B07 beamline, Diamond Light Source) helped with measurements acquisition, analysis, experiment planning and resources for near edge X-ray absorption spectroscopy. Dr. Hassan Azzan (Chemical Engineering Department, Imperial College London) helped with code development for CO₂ adsorption isotherms fitting and for calculation of heat of adsorption. Dr. Gwilherm Kerherve (Materials Department, Imperial College London) helped with XPS results analysis and resources. Dr. Tian Tian (Department of Applied Biology and Chemical Technology, the Hong Kong Polytechnic University, former researcher at Imperial) helped with project conceptualisation.

5.1. Introduction

The literature review on nonmetal functionalisation of BN (**Section 2.2**) points to the potential of tuning the material's chemical, sorptive, optoelectronic and photocatalytic properties by introducing P or S atoms into the structure. P and S have been speculated – with limited experimental proof – to replace B or N atoms in the BN structure, creating bonds with N or B, respectively^{70,127,128,131,133–136}. For P-BN, the creation of P=O and P-OH bonds within the basal planes upon P_B replacements has also been suggested^{129,130}. In both P- and S-BN cases, theoretical studies suggest planar deformation upon the nonmetals' integration^{70,127,134–136}. To the best of my knowledge, there are no reports in literature on P-BN and S-BN materials' CO₂ adsorption property. However, some insights on their porosity have been provided. For instance, it seems S functionalisation does not impact much the surface area though the pore structure is not reported^{131,133}. On the other hand, P-BN materials' S_{BET} and porosity are not compared to pristine BN's^{130,226} – thus hindering any conclusions on effects on sorptive properties. Both P and S functionalisation are reported to reduce BN's bandgap and extend light absorption, but little if anything is known with regards to charge carrier behaviour^{131,134,227}. Finally, the sole photocatalytic solar fuels application of P- or S-BN (when not part of heterojunction) so far has been H₂ production from H₂O splitting, with *in-situ* Pt photodeposition^{133,171}.

Overall, despite some reports on P and S functionalisation of BN, a lack of fundamental understanding and direct experimental evidence of the effect of such functionalisation remains (**Section 3.1**). As already mentioned, there is no direct experimental confirmation of how P or S atoms incorporate into amorphous BN, how this is influenced by the nonmetal precursor and how the chemical environment around P or S might impact BN's properties.

Questions regarding the sorptive properties of P-BN and S-BN remain. In addition, the mechanism(s) by which P or S functionalisation changes the charge carrier behaviour are yet to be elucidated. Pure P-BN and S-BN have yet to be tested for photocatalytic CO₂ reduction when not part of heterojunctions or decorated with cocatalysts, making it difficult to isolate the effect of functionalisation. Shining light on these questions could lead to the rational design of BN-based materials with improved performance for targeted applications.

In this Chapter, I aim to tackle the above knowledge gap and address **Objective 1 (Section 3.2)**. Specifically, I will investigate: i) how P (or S) incorporates into the structure of porous amorphous BN, and ii) how this integration affects the chemical, sorptive, optoelectronic and photocatalytic properties of the material. Towards this goal, I attempted the synthesis of S- and P-functionalised porous BN using different precursors, aiming for different nonmetal contents. I carried out an in-depth advanced characterisation of the materials' chemical, sorptive, optoelectronic and photocatalytic properties, and compare them with as-prepared pristine BN. I used i) FTIR, XPS and NEXAFS to assess the chemical properties, ii) XRD and N₂ sorption (-196 °C) to probe the structural features, iii) CO₂ sorption (15, 25, 35 °C) to measure the sorptive properties, and iv) DRS UV-Vis, PL, TCSPC, TAS and EPR to measure the optoelectronic and charge carrier properties. Finally, I tested the materials for CO₂ photoreduction in gas phase using a photocatalytic set-up equipped with solar simulator, and carried out control tests.

5.2. Materials

For this Chapter, the synthesis of P- and S-functionalised BN, along with pristine BN as reference material, was attempted.

For S-BN, boric acid and urea were used as B and N precursors, respectively, and three S-containing substances have been investigated as S precursors: sublimed S, thiourea, and trithiocyanuric acid. When using sublimed S, a synthetic procedure was followed based on Feng et al.¹³¹: i) BN was first synthesised at 900 °C under N₂ atmosphere in a tubular furnace, and ii) the produced BN powders were manually mixed with S and heated at 440 °C and then at 500 °C under N₂ in the same furnace. When using the other two S-containing substances, the initial BN formation step was removed, and instead the B, N and S precursor mixture was heated at 440 °C and then at 500 °C under N₂ in the same furnace. Unfortunately, the synthesis of S-BN samples has been deemed unsuccessful as no peak was detected in S 1s XPS spectra regardless of choice of S precursor, and it is concluded that S could not be incorporated into the BN structure. It is assumed that the reason behind this is the sublimation of S at 600 °C, while 900 °C is the minimum temperature needed for BN formation – therefore, the reaction temperature cannot be lowered. My findings do not support experimental literature reports on the creation of S-functionalised BN, which used sublimed S as dopant via either the same synthetic procedure as I did¹³¹, or via (plasma-assisted) chemical vapor deposition^{132,133}. Preliminary characterisation on the attempted synthesis of S-BN samples is presented in **Figure A.1**. Since S could not be incorporated in the structure, these samples are not explored further in the thesis.

For P-BN, I employed a two-step approach as described below and two different P-containing dopants: an ionic liquid and phosphoric acid. From now on, the focus of this Chapter will be on P-functionalised porous BN materials and their comparison to pristine BN.

5.2.1. Synthesis of pristine BN

Boric acid (3.71 g, >99.5%, ACS reagent, Sigma-Aldrich) and melamine (3.78 g, 99.0%, Sigma-Aldrich) were mixed and dissolved in a beaker containing 50 mL of deionised water overnight at 80 °C using magnetic stirring. Once all the water had evaporated, the mixture was transferred to a drying oven at 65 °C for 24 h and then heated in a vacuum oven at 110 °C overnight. Approximately 2 g of the obtained powder were ground, loaded inside an alumina crucible, and placed into a horizontal tubular furnace. Initially the mixture was purged under N₂ (zero grade, 99.998%, BOC) at 250 cm³ min⁻¹ for 2 h to remove as much air and moisture as possible. Then, the furnace was heated up to 1050 °C at a heating rate of 10 °C min⁻¹ under N₂ flow (50 cm³ min⁻¹) and the temperature was held for 3.5 h. After that, the furnace was let to cool down naturally to room temperature under the same N₂ flow. The obtained porous BN powder was manually ground in an agate mortar and labelled as BN.

5.2.2. Synthesis of P-BN_{IL}

Boric acid (3.71 g, >99.5%, ACS reagent, Sigma-Aldrich), melamine (3.78 g, 99.0%, Sigma-Aldrich) and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆, 2.75 g, 2 mL, >98.0%, Acros Organics) were used as precursors and the synthesis was carried out in the same way as for pristine BN. This time, the furnace was heated up under different N₂ flows (50 or 100 cm³ min⁻¹) and once the final temperature was reached, it was let to cool down naturally under the same N₂ flow. The products were manually ground in an agate mortar and labelled P-BN_{IL-HF} for 100 cm³ min⁻¹ flow, and P-BN_{IL-LF} for 50 cm³ min⁻¹ flow.

5.2.3. Synthesis of P-BN_{PA}

The same process as aforementioned was followed, with the difference that phosphoric acid (0.95 g, >98.0%, Acros Organics) was added instead of the ionic liquid. The products were manually ground in an agate mortar and labelled P-BN_{PA-HF} for 100 cm³ min⁻¹ flow, and P-BN_{PA-LF} for 50 cm³ min⁻¹ flow.

5.3. Methods

5.3.1. Characterisation of chemical properties

FTIR and XPS measurements were performed to investigate the chemical properties of P-BN and S-BN materials, as described in **Chapter 4**.

Near edge X-ray absorption fine structure (NEXAFS) spectroscopy experiments were performed on P-BN materials and P-containing reference samples at the VerSoX B07-B beamline at Diamond Light Source, UK^{228,229}. Samples were manually ground in an agate mortar and mounted on a multisample NEXAFS holder (Omicron plate) using copper-supported conductive carbon tape. The photon energy resolutions were ~80 meV (B, N, O K-edges) and ~500 meV (P K-edge). The spectra were recorded in Total Electron Yield (TEY) mode at room temperature under 1 mbar He to compensate for sample charging.

5.3.2. Characterisation of structural properties

XRD and N₂ sorption (-196 °C) measurements were taken to characterise the structural properties of P-BN and S-BN materials, as described in **Chapter 4**.

5.3.3. Characterisation of optoelectronic properties

DRS UV-Vis, steady-state PL, TAS and EPR measurements were carried out to explore the optoelectronic properties of P-BN materials, as described in **Chapter 4**.

Time-correlated single photon counting (TCSPC) measurements were carried out on P-BN samples by using a commercial TCSPC set-up (HORIBA DeltaFlex) equipped with a pulsed LED excitation source (HORIBA NanoLED series) and a fast rise-time photomultiplier detector (HORIBA PPD-650 and PPD-900). The instrument response function (IRF) was measured at the wavelength of the excitation source (282 nm). During measurements, a suitable long pass filter was inserted between sample and detector to block off scattered excitation light.

5.3.4. CO₂ adsorption

CO₂ adsorption isotherms of P-BN materials were collected at 15, 25, 35 °C and up to 1 bar, and fitted using the DSL model, as described in **Chapter 4**.

Afterwards, the isosteric heat of adsorption was calculated for each material using the virial fit on the experimental data at the three temperatures. The virial equation is^{230–232}:

$$\ln(p) = \ln(n_i^*) + \frac{1}{T} \sum_{j=0}^{M_1} a_j n_i^{*j} + \sum_{j=0}^{M_2} b_j n_i^{*j} \quad (32)$$

where n_i^* is the amount of CO₂ adsorbed at pressure p and temperature T , and a and b are characteristic virial coefficients. In this study, we used $M_1 = 3$ and $M_2 = 1$ to provide a good fit. The Langmuir and virial isotherm fitting was carried out with MATLAB R2020a (The Mathworks Inc.) using the in-house software package isothermFittingTool²³³.

5.3.5. CO₂ photoreduction

CO₂ photoreduction experiments were performed on P-BN samples in a purpose-built set-up using a stainless steel photoreactor (17.7 cm³) equipped with a fused quartz window for irradiation. Approximately 20 mg of sample were ground and dry casted onto a stainless-steel holder (7.1 cm²) and activated at 110 °C in a vacuum oven overnight. Then, the sample holder was placed inside the photoreactor and vacuumed at approximately 0.013 bar for 15 min. CO₂ gas (80 cm³ STP min⁻¹, research grade, 99.999%, BOC) and H₂ (40 cm³ STP min⁻¹, produced in H₂ generator) were mixed and flown for 15 min. Finally, the photoreactor was filled with approximately 2 bar of the gas mixture and sealed. The sample was then irradiated for 5 h with a solar simulator equipped with a 100 W Xe arc lamp (Oriel LCS-100 solar simulator, Newport) at a distance of 15 cm from the sample, providing the intensity at the catalyst surface to be close to 1 sun power (80 mW cm⁻²). A long pass UV filter ($\lambda < 400$ nm, LOT Quantum Design) was used to conduct the test under visible light irradiation. The gaseous products were detected and analysed using a GCMS-QP2020 NX gas chromatographer (Shimadzu) equipped with Rt-Q-Bond Plot Column (30 m, 0.32 mm ID, 10 μ m, Shimadzu) and molecular sieve columns (SH-Msieve 5A plot, 30 m, 0.32 mm ID, 30 μ m, Shimadzu) in series. The tests were repeated three times on fresh samples. Control experiments were performed: a) without irradiation, b) with the stainless-steel holder and no sample, c) under N₂/H₂ atmosphere and d) under isotopic ¹³CO₂/H₂ atmosphere (99 at% ¹³CO₂, BOC).

5.4. Results & discussion

After completing the synthetic routes described previously, other than pristine BN, four P-BN samples were synthesised: P-BN_{IL-HF} and P-BN_{IL-LF} using ionic liquid as the P-containing source, and P-BN_{PA-HF} and P-BN_{PA-LF} using phosphoric acid. Optical images of the synthesised samples are shown in **Figure 5.1**. Pristine BN sample is white, while P-BN_{PA} samples show a yellowish tone, especially P-BN_{PA-HF} which was produced using high N₂ flow during synthesis. On the other hand, P-BN_{IL} samples exhibit a dark colour, with P-BN_{IL-HF} being dark brown and P-BN_{IL-LF} a lighter brown. The changes in colour originate from changes in the band structure of the materials, which I discuss in more detail in **Section 5.4.3**. In general, samples produced using a lower N₂ flow during synthesis seemed to exhibit a lighter colour, which is an aspect I comment on further below.

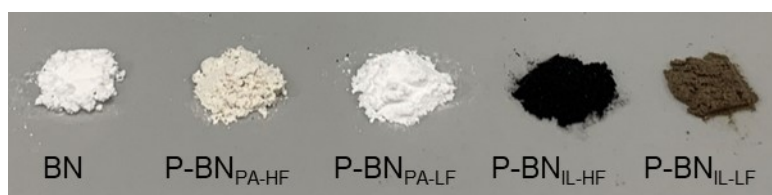


Figure 5. 1. Optical images of as-prepared pristine BN and P-BN samples. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

5.4.1. Physical & chemical properties

Following the synthesis of the materials, I analysed the functional groups in pristine BN and P-BN samples using ATR-FTIR (**Figure 5.2a**). All samples show the typical bands at $\sim 1350\text{ cm}^{-1}$ and at $\sim 800\text{ cm}^{-1}$ corresponding to B-N stretching and B-N-B bending respectively²³⁴. Less intense bands appearing in the $850\text{--}1200\text{ cm}^{-1}$ range – especially in P-BN samples – suggest

the existence of B-O and B-O-H bonds²³⁵. This agrees with previous studies on porous BN, showing the replacement of planar N atoms with O, and also the creation of -OH functional groups on the edges of BN structure^{53,120,236,237}. I then analysed the samples using XRD (**Figure 5.2b**), confirming the formation of hexagonal BN ($P 6_3/mnc$; $a = b = 2.50399(5) \text{ \AA}$, $c = 6.6612(5) \text{ \AA}$; $\alpha = \beta = 90.0^\circ$, $\gamma = 120.0^\circ$)²³⁸. The large breadth of the observed peaks shows that the materials produced contain amorphous and highly nanocrystalline regions, where I estimated using the Scherrer relation that the crystals formed are approximately 2 nm in size on average²³⁹. There is no apparent shift of the (002) or (100) plane peaks from pristine BN to P-BN samples, meaning the d-spacing and periodicity with respect to the crystalline hexagonal phase of BN did not change with functionalisation. However, the primary (002) peak is reduced in intensity and broader upon P introduction, indicating that the average crystal size decreases and that there is a greater preference for P-BN samples to grow in the (100) crystal plane. I examined the porosity and BET area of the materials using N₂ sorption at -196 °C (**Figure 5.2c**) and present the textural parameters in **Table A.1**. Pristine BN (S_{BET} : 1135 m² g⁻¹) and P-BN_{PA} samples (S_{BET} : 989-1036 m² g⁻¹) show Type I/IV sorption isotherms with H3/H4 hysteresis loops, indicative of meso- and microporosity and narrow slit-like pores respectively. I observe a clear difference when moving to P-BN_{IL} samples (S_{BET} : 1321-1351 m² g⁻¹) which show Type I isotherms with no hysteresis loop, indicative of pure microporosity. Overall, all samples are more porous than reported in the literature for functionalised P-BN. The type I isotherm of the P-BN_{IL} is quite unique for P-BN samples compared to the previous studies.

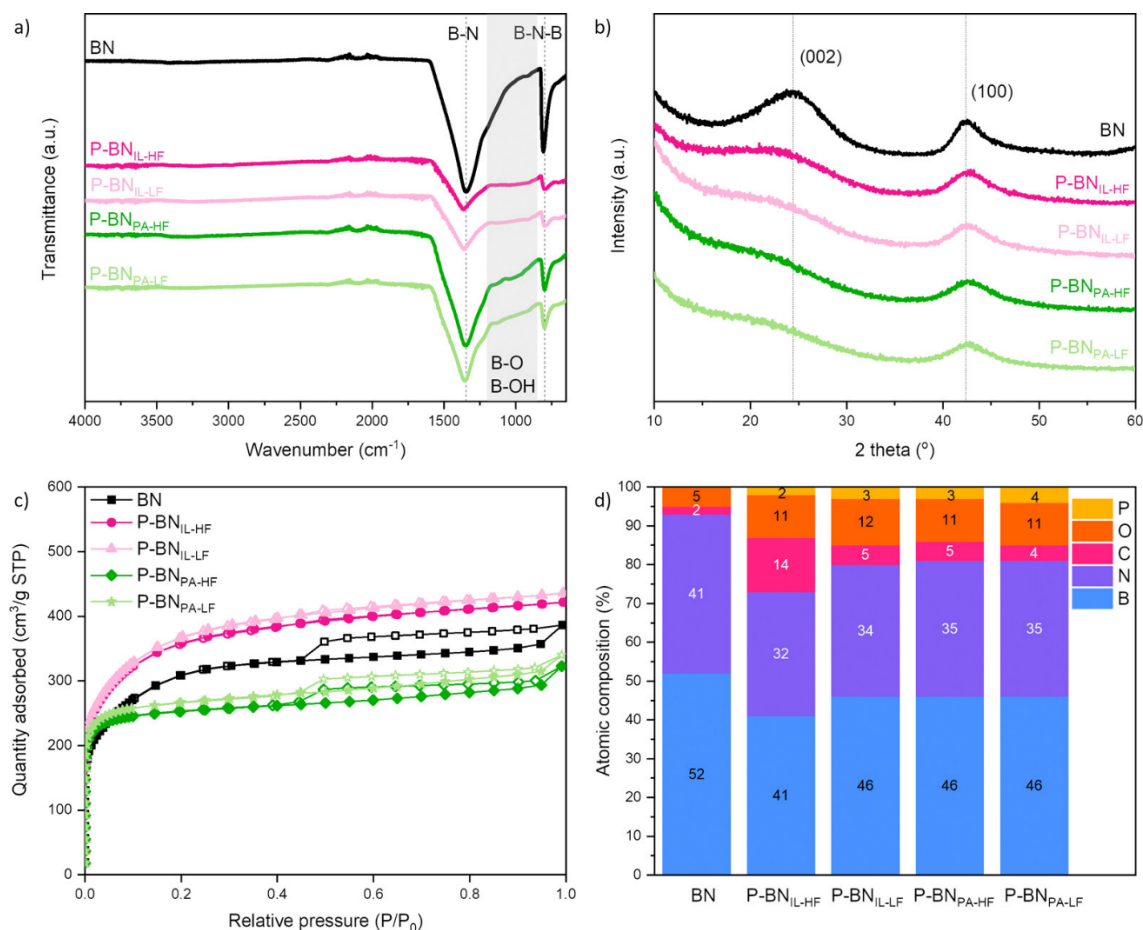


Figure 5. 2. a) ATR-FTIR spectra with highlighted IR bands, b) XRD data with highlighted plane peaks, c) N₂ sorption (-196 °C) isotherms, and d) atomic composition based on XPS analysis of pristine BN and P-BN samples. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

From a chemical analysis point of view, I assessed the atomic composition of the materials using XPS (**Figure 5.2d**). The P-functionalisation level follows the trend: P-BN_{IL-HF} (2 at%) < P-BN_{IL-LF} = P-BN_{PA-HF} (3 at%) < P-BN_{PA-LF} (4 at%). This content level is slightly higher than reported in the experimental literature for P-BN samples. Using phosphoric acid as P source generally results in higher P at% than when using ionic liquid. Lower N₂ flow rate during the synthesis (*i.e.* higher residence time) leads to higher functionalisation amount, as gaseous products

linger and react with the material for longer times than in higher flow. The difference in residence time could explain the difference in colour, mainly between P-BN_{IL-HF} and P-BN_{IL-LF}. The B:N ratio (~1.3) is similar in all samples, while O and C contents are higher in P-BN (~11 at% and 5 at% respectively) than in pristine BN (5 at% and 2 at%). The C content is significantly higher in P-BN_{IL-HF} (14 at%) – the optically darkest sample. C impurities are caused by replacement of B and N atoms (creating C-C, C-B, C-N bonds), while O usually replaces N within the structure, and also creates -OH groups on the edges (forming B-O, C-O, O-H bonds)^{53,86,87}. Although amorphous pristine BN is inherently defective (C and O impurities, N vacancies), I can conclude that P-functionalisation introduces additional defects into the BN structure compared to pristine BN.

Having confirmed the successful P-functionalisation of the materials, I further investigated for the first time their chemical structure and environment around P atoms using NEXAFS. For this purpose, I used three reference samples, all containing different P bonds (the details and structures of the reference samples are shown in **Figure A.2**): i) phosphoric acid containing P-O and P=O bonds, ii) B-phosphine complex containing P-B and P-C bonds, and iii) phosphazene containing P-N and P=N bonds. All P-BN samples show the same main P K-edge peak at ~2100 eV as the phosphazene reference sample (**Figure 5.3a**). I can conclude that, regardless of the P source, the P-BN samples share the same P-containing functionalities, and these are akin to the ones of phosphazene reference sample. Hence, these analyses suggest the creation of P-N and/or P=N bonds in the BN structure. There are no peaks corresponding to the same energy level with the other two reference samples, hence I conclude that P atoms mainly form bonds with N, rather than with C, B or O. B K-edge, N K-edge and O K-edge NEXAFS spectra of pristine BN and P-BN samples can be found in **Figure A.3**. The chemical environment around N and O

atoms appears similar between pristine and P-doped BN, yet P-BN shows more $\pi_{\text{BN}_2\text{O}}$ and π_{BO_3} bonds than π_{BNO_2} (**Table 5.1**)^{64,167}. Therefore, it is more likely that O replaces either one or three N atoms surrounding B in P-doped BN. Overall, NEXAFS provides strong, if not definite, support for the creation of P-N and/or P=N bonds. This finding is in accordance with some XPS studies reported before, though other have tentatively assigned XPS bands to P-O and P-B bonds.

Table 5. 1. π_{BN_3} : $\pi_{\text{BN}_2\text{O}}$: π_{BNO_2} : π_{BO_3} ratio in pristine and P-BN samples, as derived from B K-edge NEXAFS spectra (**Figure A.3**). Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

Sample	π_{BN_3}	$\pi_{\text{BN}_2\text{O}}$	π_{BNO_2}	π_{BO_3}
BN	0.70	0.13	0.11	0.06
P-BN _{IL} -HF	0.60	0.23	0.03	0.14
P-BN _{IL} -LF	0.59	0.23	0.04	0.14
P-BN _{PA} -HF	0.64	0.20	0.04	0.12
P-BN _{PA} -LF	0.64	0.20	0.05	0.11

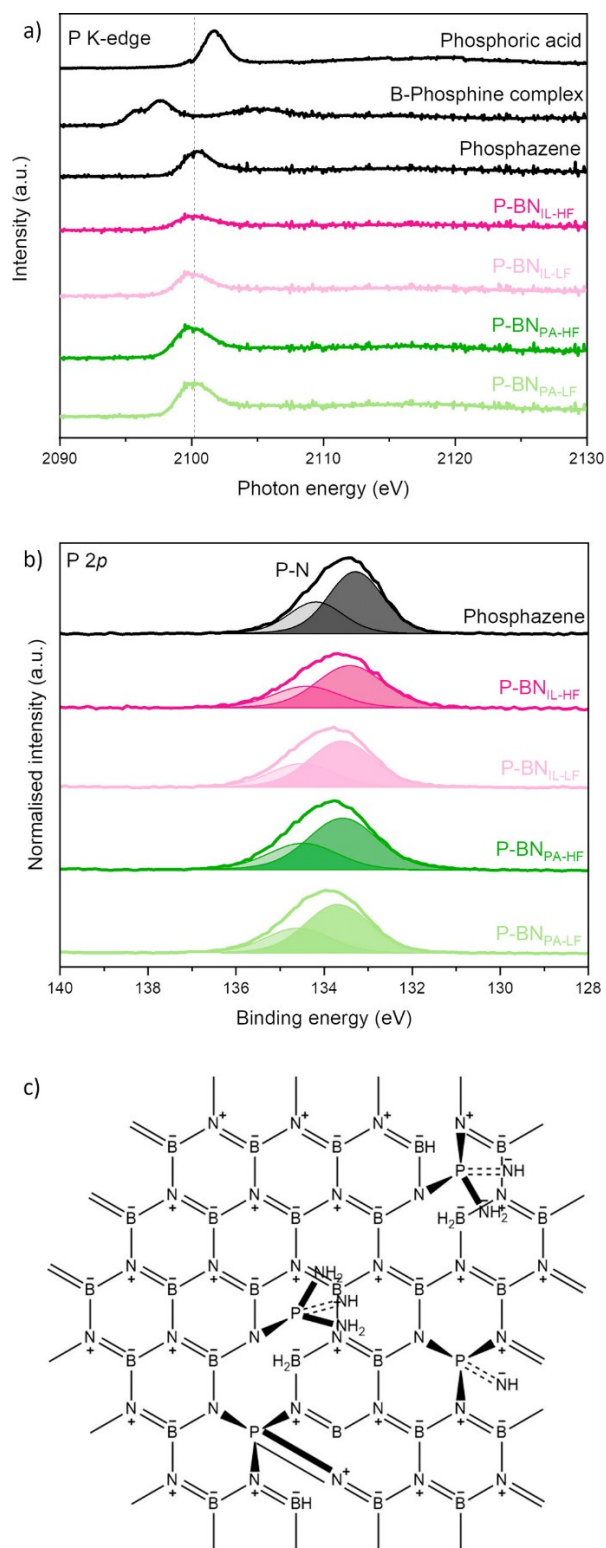


Figure 5. 3. a) P K-edge NEXAFS spectra of the three P-containing reference samples and the P-doped BN samples, b) P 2p XPS deconvolution spectra of phosphazene reference sample and P-doped BN samples, c) proposed chemical structure of the chemical environment around

P atoms in P-BN samples, as suggested by NEXAFS and XPS analyses. I note that in this proposed structure, I focus on how P atoms may be embedded, and have not included O or C presence discussed in text. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

To further examine the chemical environment in the materials, I performed XPS analysis. The B 1s, N 1s, O 1s and C 1s XPS deconvolution spectra for pristine BN and P-BN samples can be found in **Figure A.4**. By analysing the B 1s and C 1s spectra in both pristine and P-BN, I observe similar chemical states for B (B-N and B-O-N bonds) and C. The deconvolution of the N 1s spectra indicates a preference for N-B and graphitic C-N bonds in P-BN, in contrast to N-B and B-O-N bonds in pristine BN^{64,240}. Furthermore, the second chemical state of O (aside from O-B) also exhibits differences between pristine and P-BN. To determine the chemical state of P, I conducted P 2p XPS measurements on the phosphazene reference sample, and on the P-BN samples (**Figure 5.3b**). The P 2p core level of the phosphazene exhibits a doublet with the main peak positioned at 133.5 eV, which is characteristic of P-N bond^{241–245}. Again, the P-BN samples exhibit a similar chemical state for P, regardless of the P dopant source. The deconvoluted peaks, although similar, are shifted by approximately 0.1-0.7 eV compared to the phosphazene reference sample. This observation points to the creation of P-N and/or P=N bonds in the materials. The chemical environment surrounding the P atoms, as derived from XPS analysis, aligns with the previously discussed NEXAFS results. This helps suggest a plausible chemical structure for the P-BN samples (**Figure 5.3c**). Here, I propose that P atoms either “replace” B atoms and bond with three or four surrounding N atoms of the main BN structure and/or graft to the BN structure forming =NH and/or -NH₂ groups outside the plane.

The former configuration aligns with some theoretical studies that found this to be the most stable configuration. My analyses do not support the replacement of N atoms by P atoms as suggested by some former experimental work.

5.4.2. CO₂ adsorption

To examine CO₂ adsorption, I measured CO₂ uptake at 25 °C and up to 1 bar absolute pressure for pristine BN and P-BN samples (**Figure 5.4a**). I noticed the following CO₂ uptake trend at 1 bar: BN (1.13 mmol g⁻¹) < P-BN_{IL-HF} (1.86 mmol g⁻¹) < P-BN_{IL-LF} (1.98 mmol g⁻¹) < P-BN_{PA-HF} (2.77 mmol g⁻¹) < P-BN_{PA-LF} (2.93 mmol g⁻¹). I conclude that P-functionalisation, especially using phosphoric acid as the P precursor, noticeably enhances CO₂ adsorption compared with pristine BN. Given the shape of the isotherm, I do not link this to a chemisorption effect related to the presence of P. In fact, the CO₂ uptake does not correlate the amount of O-containing or P-containing functional groups in the samples. Instead, the increasing trend in CO₂ uptake seems to follow the increasing trend in the materials' ultramicropore (≤ 0.7 nm) volume (**Table A.1**). As discussed in **Section 2.2**, ultramicropores favour CO₂ adsorption. I conclude that structure/porosity plays a role in the CO₂ sorption, with the ultramicropores having the main contribution. Although the uptake values are lower compared to C-functionalised BN (**Section 2.2**), they place P-BN as potentially interesting adsorbent, and my findings provide new insights on how CO₂ adsorption is affected with P functionalisation of BN.

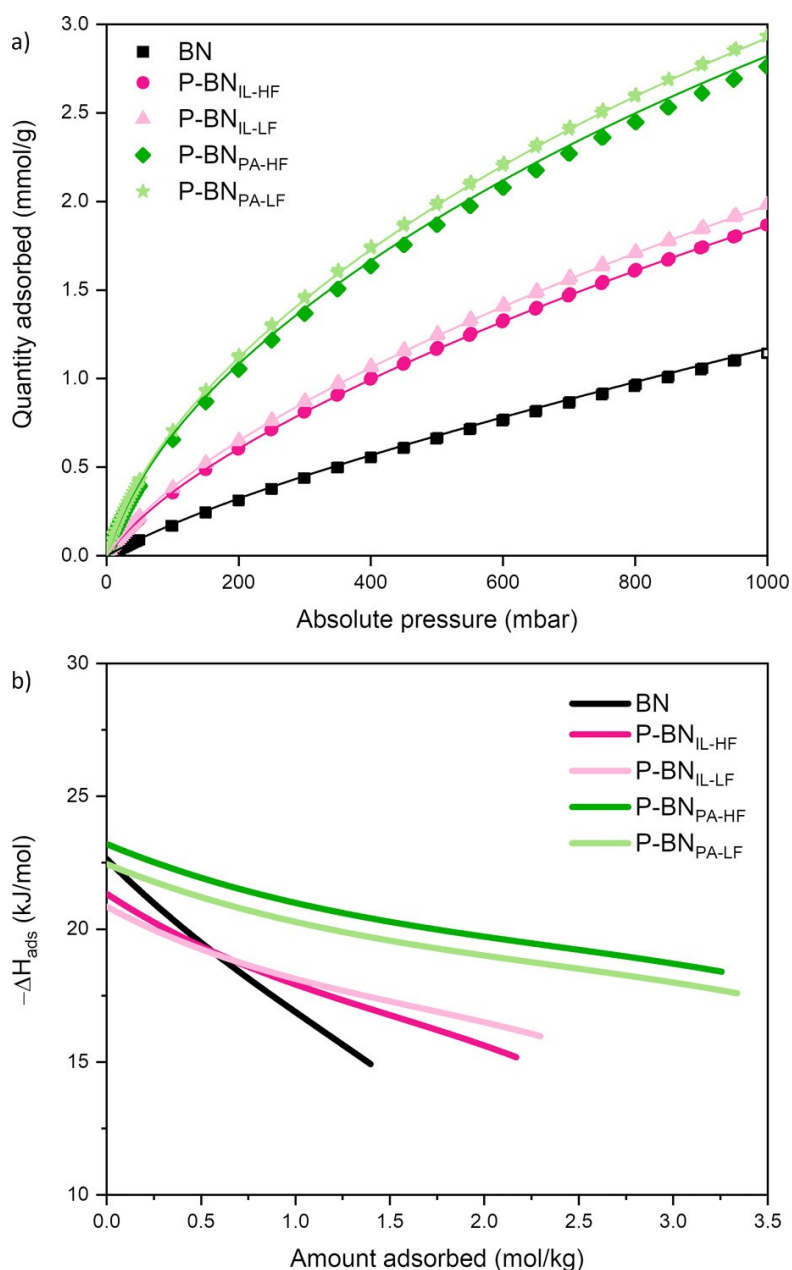


Figure 5. 4. a) Experimental CO₂ adsorption (25 °C) isotherms for pristine BN and P-BN samples fitted using a DSL fit. Symbols are used for the data points and solid line represents the isotherm fit. b) isosteric heat of adsorption for pristine BN and P-BN samples plotted vs amount of loading. Heat of adsorption was calculated by fitting experimental CO₂ adsorption data obtained at three temperatures (15, 25, 35 °C) for all materials to the virial isotherm model. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

To understand more about adsorbate-adsorbent interactions, I measured CO₂ adsorption at three different temperatures (15, 25, 35 °C), and fitted the isotherms using the DSL model. The isotherms fits and model coefficients can be found in **Figure A.5** and **Table A.2**, respectively. From the good fit of the isotherms, I conclude that this model describes the CO₂ adsorption on the materials well. Moreover, I calculated the isosteric heat of adsorption for each material by fitting the experimental CO₂ adsorption equilibrium data (at 15, 25, 35 °C) to the virial isotherm model, for which the coefficients are listed in **Table A.3**. I plotted the calculated heat of adsorption values as a function of CO₂ loading for pristine BN and P-BN samples (**Figure 5.4b**). The results confirm that CO₂ is physisorbed onto the materials, and the heat of adsorption, especially in the case of P-BN, stays relatively constant as loading increases. At zero loading, the heats of adsorption for pristine and P-BN are similar (ranging between 20 and 25 kJ mol⁻¹). My heat of adsorption values broadly agree with reported values in literature on pristine porous BN (19-28 kJ mol⁻¹), which are lower than in the case of C-BN (32-35 kJ mol⁻¹)^{63,139,246}.

5.4.3. Optoelectronic properties

To study my materials' light absorption behaviour, I used DRS UV-Vis spectroscopy (**Figure 5.5a**). P-functionalisation overall results in extended absorbance into the visible spectrum, with the choice of the P source showing differences. Using ionic liquid as the P precursor results in absorbance over the whole UV-Vis spectrum (200-850 nm), potentially because of the higher C content (scatter/reflection from C particles)²⁴⁷⁻²⁴⁹. I observed tail states near the

optical band edges pristine BN and P-BN, which can be assigned as Urbach tails, given their exponential character and the amorphous, defective nature of the materials²⁵⁰.

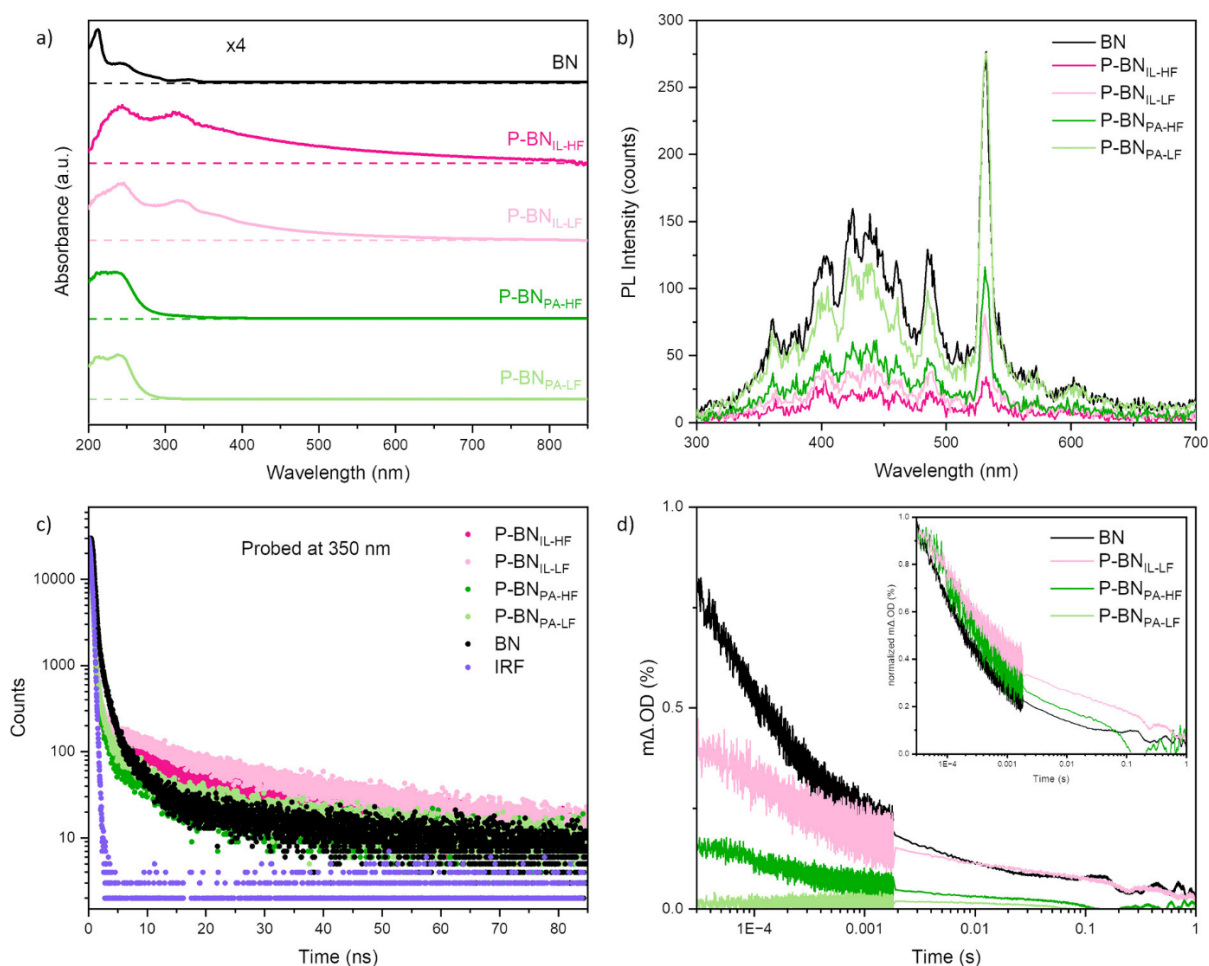


Figure 5. a) DRS UV-Vis spectra, b) steady-state PL spectra obtained upon excitation at 200 nm, c) TCSPC decay profiles probed at 350 nm upon excitation at 282 nm, and d) TAS decay profiles probed at 900 nm upon excitation at 355 nm of pristine BN and P-BN samples. Multiplication factors are shown on top of the absorption data in a) to facilitate comparison between samples. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

Steady-state PL spectra obtained upon excitation at 200 nm are shown in **Figure 5.5b**, detailing the radiative relaxation spectra for all materials. The radiative relaxation spectra are similar in pristine BN and P-BN. This indicates that electrons populate similar excited states upon irradiation, regardless of P-functionalisation. Pristine BN shows the highest signal intensity followed by P-BN_{PA-LF}, P-BN_{PA-HF}, P-BN_{IL-LF} and P-BN_{IL-HF}. This trend could be explained by either one or a combination of the following scenarios: i) pristine BN has a higher charge recombination rate than P-BN, and/or ii) photoexcited electrons in P-BN show a stronger tendency to relax non-radiatively, in a way that is not measured using PL. The lower intensity signal in P-BN samples indicates that band-to-band PL emission is lost as charges are trapped in midgap states, increasingly formed/populated with P-functionalisation. The existence and population of such midgap states could be linked to the increased colouration of P-BN_{IL} samples. The PL data indicate an unchanged bandgap with P functionalisation, which is in contrast with some literature reports of bandgap reduction in P-BN¹³⁰.

To elucidate the time-resolved behaviour of these photoexcited species, I measured for the first time the PL decay kinetics by using TCSPC. The kinetics were measured using 282 nm LED excitation source and probed at 350 nm emission wavelength (**Figure 5.5c**). I selected the probe wavelength based on steady-state PL spectra obtained after excitation at 282 nm (**Figure A.6**). The fitted decay profiles can be found in **Figure A.7**. For all samples, the PL decay kinetics exhibit two decay components as previously reported for BN⁷. In the case of P-BN, a fast exponential decay component in ps-ns timescale, which is faster than the time resolution of the instrument response (IRF~1.5 ns) limiting its analysis. The faster decay of P-BN relative to BN suggests: i) faster exciton recombination or ii) increased trapping of photoexcited charge carriers in P-BN materials, and therefore, an increased loss of the radiative decay pathway. At longer decay times (>10 ns), a second decay component dominates in the kinetics of all

samples, which might indicate shallowly trapped charges in P-BN, consistent with those kinetics reported for BN and g-C₃N₄ materials^{7,251}. These results suggest that P-functionalisation increases the number or population of midgap states in the material – and subsequently the number of trapped charges – and hence the longer lifetimes compared to pristine BN. Additionally, different P precursors have different impact on optoelectronic properties, with the IL route resulting in more long-lived decays.

To provide further insight on the charge carrier behaviour of the samples, I carried out – for the first time on P-BN materials – TAS measurements using a 355 nm laser source, with transient absorption decay profiles probed at 900 nm over time (**Figure 5.5d**). The decay profiles differ between pristine and functionalised materials, and also between P-BN_{PA} and P-BN_{IL}. Within the time resolution of the measurement (10 μ s), pristine BN shows larger transient absorption signals ($\Delta O.D$) than all other samples, which indicates that this sample possesses a larger initial population of charge carriers: BN (~ 0.8 $\Delta O.D$) > P-BN_{IL-LF} (~ 0.4 $\Delta O.D$) > P-BN_{PA-HF} (~ 0.2 $\Delta O.D$) > P-BN_{PA-LF}. However, the rate at which these charge carriers recombine differs, with P-BN samples showing longer half-times (*i.e.* the time until the initial transient absorption signal seen at 10 μ s reaches 50% of its initial value): BN (90 μ s) < P-BN_{PA-HF} (480 μ s) < P-BN_{IL-LF} (570 μ s) < P-BN_{PA-LF}. The half-times of the materials are comparable to those of pristine TiO₂ and TiO₂-MOF heterojunctions (~ 180 μ s)^{7,247,251,252}, and longer than some TiO₂ nanosheets, Bi₂WO₆-TiO₂ heterojunctions (1-1.5 ns)²⁵³, gC₃N₄ and gC₃N₄-based materials (10-100 μ s)^{247,251,254}. It should be noted that the TAS spectra notably differ between pristine BN and P-BN samples (**Figure A.8**), where bleaching processes are primarily only seen in the blue-green region of the electromagnetic spectrum in pristine BN but further into the red in P-BN. The observation of a bleach is due to the loss in ground state absorption, and the fact that this extends further into the red for P-BN is due to the red shift in bandgap due to P

functionalisation, with similar behaviour seen in N-doped TiO₂ previously²⁵⁵. Interestingly, many of these bleach states transition to a positive signal at later times (typically from ~0.1 to 1 ms), which indicates that the potential energies of the charge carriers formed in these materials change with time. As the bleach in the blue region is consistently the slowest to recover (**Figure A.9**), this indicates that the potential energy of charge carriers reduces with time as they become increasingly more deeply trapped (as the energy required to probe them increases).

Overall, TAS results support the TCSPC measurements in that they both show that BN possesses the highest populations of charge carriers (at the resolution of each measurement), yet P functionalisation causes the rate of recombination in these materials to slow. This, I propose, is likely due to the formation of midgap states in P-BN, which trap charge carriers more deeply, slowing their recombination yet likely making them less mobile.

I used EPR spectroscopy to further probe the electronic properties of the materials, and present the signal change before and after irradiation with a UV light source over continuous scanning of the magnetic field (**Figure 5.6**). Previous studies on porous BN suggest that unpaired electrons located in the paramagnetic -OB₃ bonding pattern contribute to the EPR signal^{7,120,166}. P-BN_{PA} samples show a broader signal compared to that of pristine BN and P-BN_{IL} samples. This feature suggests that, in P-BN_{PA}, the paramagnetic -OB₃ radical is less delocalised. This could lead to a partially resolved hyperfine interaction with nearby nuclei or a possible tilt with respect to the molecular frame. I simulated the EPR spectra of the samples under dark conditions, and the experimental/simulated EPR signal comparison is shown in **Figure A.10**. For pristine BN and P-BN_{IL} samples, the simulations provided a good fit to the experimental data, while for P-BN_{PA-HF} sample, the fitting error was larger (due to the broader

signal). By integrating the simulated EPR signal, I obtained the EPR absorption response for each sample, presented in **Figure A.11**. I further integrated the absorption signal and calculated the concentration of -OB_3 species in the samples, which I assume are the main contribution to the EPR signal. The calculated concentrations, with approximately 20% error, are presented in **Table 5.2** below. The -OB_3 concentration follows the trend: $\text{P-BN}_{\text{IL-HF}} > \text{P-BN}_{\text{PA-HF}} > \text{P-BN}_{\text{IL-LF}} > \text{P-BN}_{\text{PA-LF}} > \text{BN}$, suggesting that all P-BN samples have more defect sites than pristine BN, with the N_2 flow rate during synthesis being the most influencing factor on defects creation. Upon UV irradiation, pristine BN shows an increase in the signal intensity, which could be attributed to photoexcited electron–hole pairs⁷. However, I did not spot a difference in the signal in any of the P-BN samples before and after illumination, meaning there are no photoexcited electrons detected (or their concentration is too low to be detected).

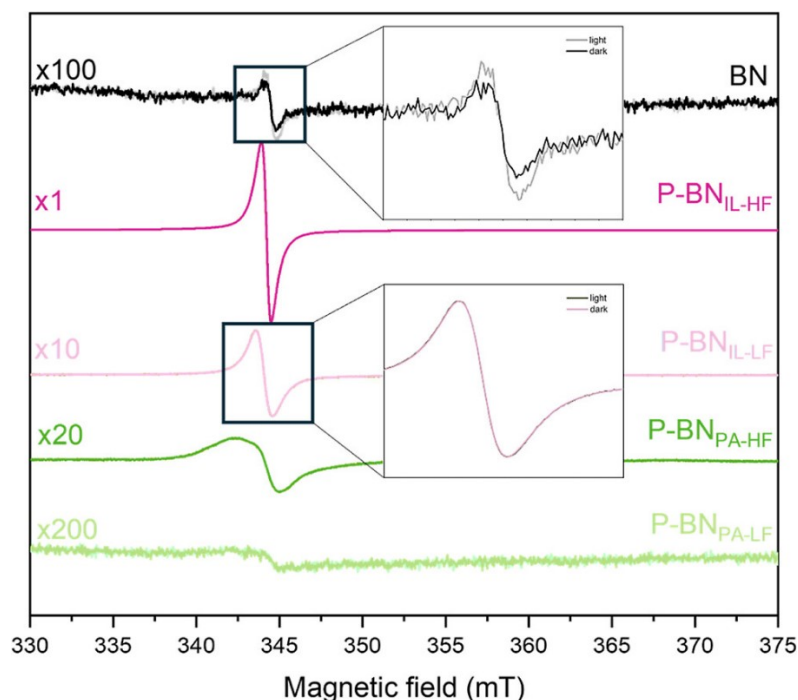


Figure 5. 6. EPR spectra of pristine BN and P-BN samples in ambient temperature and an air atmosphere. Multiplication factors are shown on the left side of the signals to facilitate

comparison between samples. Zoomed in graphs of pristine BN (up) and P-BN_{IL-LF} (below) spectra indicate change in signal before (darker colour) and after (lighter colour) irradiation with UV light source. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

Table 5. 2. –OB₃ species concentration in pristine BN and P-BN Samples, as derived from double integration of simulated EPR signal under dark conditions (**Figures A.9 and A.10**). Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

Sample	–OB ₃ concentration per g _{sample} *
BN	0.70
P-BN _{IL-HF}	0.60
P-BN _{IL-LF}	0.59
P-BN _{PA-HF}	0.64
P-BN _{PA-LF}	0.64

* Estimated error is 20%.

To provide a second level of confidence regarding the existence of photoexcited electrons in the samples, I conducted EPR measurements at –268 °C, with and without irradiation, on three selected samples: BN, P-BN_{IL-HF}, and P-BN_{PA-HF}. The results obtained through these measurements are presented individually in **Figure 5.7**, and comparatively to each other in **Figure A.12**. As shown in **Figure 5.7a**, under dark conditions and at –268 °C, pristine BN exhibits a strong central peak along with two extra smaller peaks (splitting around 700 MHz) potentially caused by a hyperfine interaction with a ¹⁴N atom. Under irradiation, the intensity of all three peaks increases significantly, confirming the existence of photoexcited electrons.

Even after switching the irradiation off, the increased signal persists, supporting these light-induced excited electrons are stable and long-lived. On the other hand, the EPR signal of P-BN samples (**Figure 5.7b-c**) before illumination shows very little difference between room temperature and $-268\text{ }^{\circ}\text{C}$ spectra. Interestingly, upon illumination, the EPR signal of both P-BN samples decreases. By performing thermal reversibility tests – heating up the sample to room temperature and then cooling it back down to $-268\text{ }^{\circ}\text{C}$ – I observe that i) the EPR signal increases back to higher than the original intensity under dark, and ii) the EPR signal decrease is photoinduced and not permanent. Therefore, I exclude the scenario of the P-BN materials degrading under light, and assign the EPR signal decrease to partial photoinduced electron transfer from paramagnetic -OB_3 species to surrounding atoms in the structure. This effect on EPR signal upon irradiation has been reported in literature, in Mo–Cu complexes, and attributed to i) spin transition on the Mo centre and ii) electron transfer from Mo to Cu atoms, changing their oxidation states²⁵⁶. From the EPR data, I can conclude that P-BN samples: i) indeed have higher concentration of defects compared to pristine BN, as suggested by XPS and NEXAFS results, and ii) do not clearly exhibit creation of photoexcited electrons upon irradiation, as opposed to pristine BN.

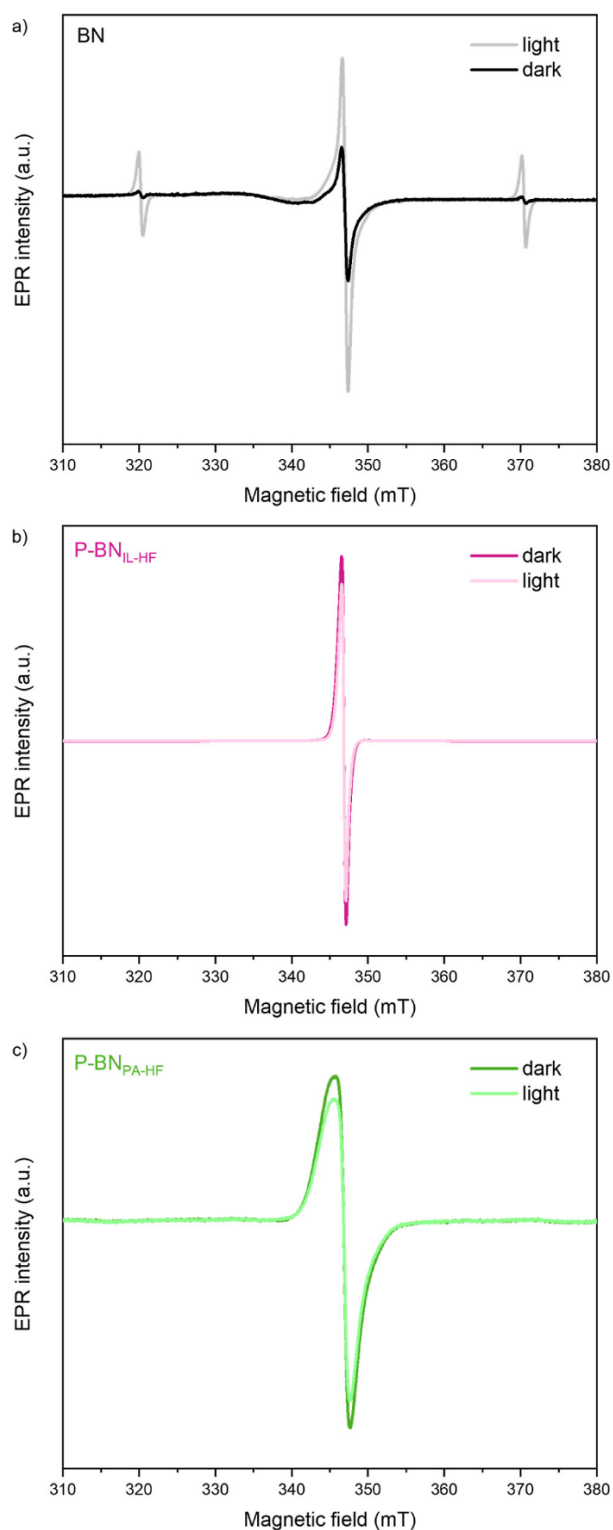


Figure 5. 7. EPR spectra of a) pristine BN, b) P-BN_{IL-HF}, and c) P-BN_{PA-HF} at -268 °C and He atmosphere, indicating change in signal before (darker colour) and after (lighter colour) irradiation with UV light source. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

5.4.4. CO₂ photoreduction

I tested the pristine BN and P-BN materials for photocatalytic CO₂ reduction using H₂ as proton donor in a gas–solid reaction. The products of this reaction are CO (main product) and CH₄ in different ratios for pristine BN and P-BN. Full details on CO and CH₄ production rates under all testing conditions including control tests can be found in **Table A.4** and **Figure A.13**. Interestingly, previous studies on CO₂ photoreduction using pristine⁷ and Cu-doped BN²⁵⁷ as well as Pd_xCu_y-BN alloys¹⁵³ point to the dominant photocatalytic activity of the materials. Yet, here, control tests point to the fact that a majority of the CO and CH₄ production of all BN samples (especially P-BN) comes from degradation of the material upon irradiation or from side-reactions with H₂, and only a small portion comes from photocatalytic reduction of CO₂. Partial degradation of the porous BN has been reported before⁷ and further work would be needed to understand its mechanism and how P functionalisation might influence it. This poor photocatalytic activity may be explained by the TCSPC, TAS, and EPR results, which indicated P functionalisation results in an increased concentration of chemical defects (such as higher O content) and, as a result, midgap states that more deeply trap charge carriers; therefore, the created midgap states hinder i) the charge carriers' ability to transport to catalytic sites and ii) the potential energy to drive CO₂ reduction. As a fact, through the EPR measurements, I show that the concentration of -OB₃ species increases from BN < P-BN_{PA-LF} < P-BN_{IL-LF}, which follows the reverse trend to the CO₂ photoreducing activity, where BN > P-BN_{PA-LF} > P-BN_{IL-LF}. The relationship between the -OB₃ concentration and photocatalytic activity is shown in **Figure 5.8**. I note that, based on literature, the presence of O (up to 10 at. %) in the pristine porous BN structure has a positive effect on the material's CO₂ photoreducing activity⁷.

Therefore, the drop in photocatalytic activity from BN to P-BN samples should be attributed to the integration of P in the structure and to the resulting increased number of defects (including, but not limited to, higher O content) and more/more populated midgap states. The connection between midgap states (acting as trapping sites) caused by structural defects and photoactivity has been previously reported for other materials in the literature, and pinpoints the importance of thermodynamics and the energetic distribution of midgap states facilitating photoactivity^{258–260}.

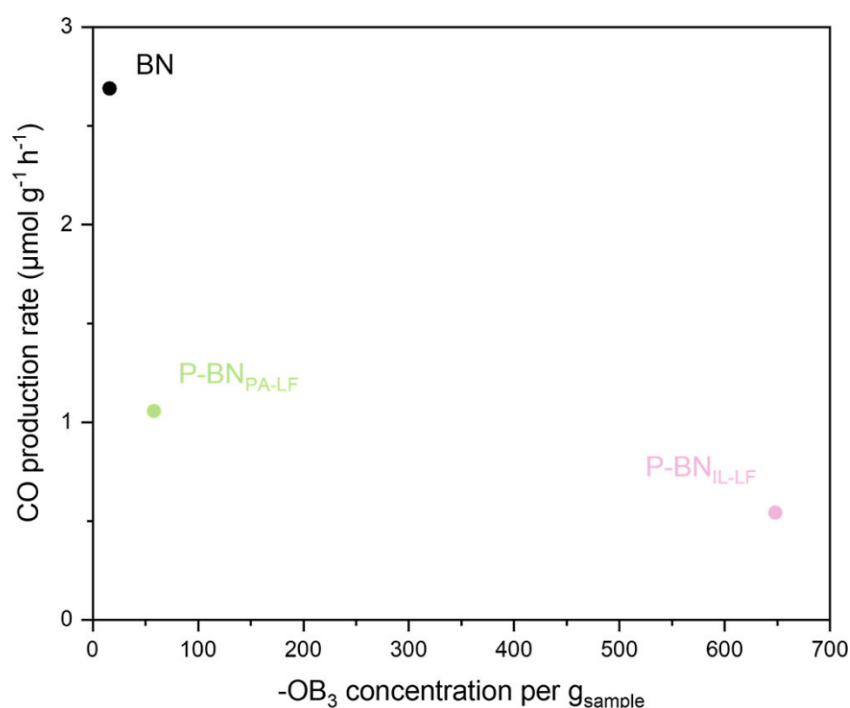


Figure 5. 8. Effect of the $-OB_3$ species concentration in pristine BN and P-BN samples (as derived from simulated EPR spectra before irradiation) on the photocatalytic production of CO (using CO_2/H_2 as feed, under ~ 1 sun irradiation, 5 h reaction). Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

5.5. Conclusions

In this Chapter, I addressed **Objective 1 (Chapter 3)**, which was to elucidate the effect of P (and S) functionalisation (including choice of precursor and nonmetal content) on the different porous BN properties. While S functionalisation was not achieved, I successfully introduced P into the structure of porous amorphous BN by using two different P-containing precursors: phosphoric acid and an ionic liquid. I reported for the first time a detailed, combined study on how P functionalisation modifies the chemistry and porosity of the material, leading to changes in sorptive, optoelectronic, and photocatalytic properties. The changes are apparent not only between pristine and functionalised samples but also between the P-BN samples from different P precursors.

From a materials chemistry point of view, in-depth XPS and NEXAFS analyses suggest that P forms bonds with surrounding N atoms, along with -NH_2 and/or =NH groups between planes in a tetrahedral configuration. This is partly in accordance with theoretical studies in the literature, which suggest that the P incorporation in the BN structure would cause distortion and that the P_B replacement would be the most thermodynamically favourable placement. While the amorphous BN structure inherently comes with defects (described in detail in **Section 2.2**), P functionalisation causes further structural defects (such as P incorporation) and increases C and O content, particularly when using ionic liquid as precursor. Resulting from these structural changes, P-BN samples have more ultramicropores than pristine BN, leading to enhanced CO_2 physisorption, especially in samples prepared using phosphoric acid. Together, the NEXAFS and EPR results indicate that the defects in P-BN samples increase the concentration of unpaired electrons. Based on EPR results, pristine BN seems to create more unpaired electrons upon irradiation than P-BN. In addition to this, PL, TCSPC, and TAS analyses

show that the creation of more defects in the structure by P functionalisation (especially when using ionic liquid precursor) results in midgap states which act as electron traps. While this leads to longer lifetimes for the charged species (slower recombination rates), their reaction with CO₂ and H₂ for photocatalytic CO₂ reduction will likely be hindered because of the loss in mobility and potential energy of charge carriers that populate these states. Nonetheless P functionalisation extends light harvesting into the visible as well as the lifetime of charge carriers, which is necessary to drive kinetically challenging catalytic conversions, such as CO₂ reduction. Therefore, I propose that future studies of this materials system focus on how the activity of these longer-lived states may be improved, through the use of co-doping strategies and/or surface cocatalysts.

5.6. Supporting information

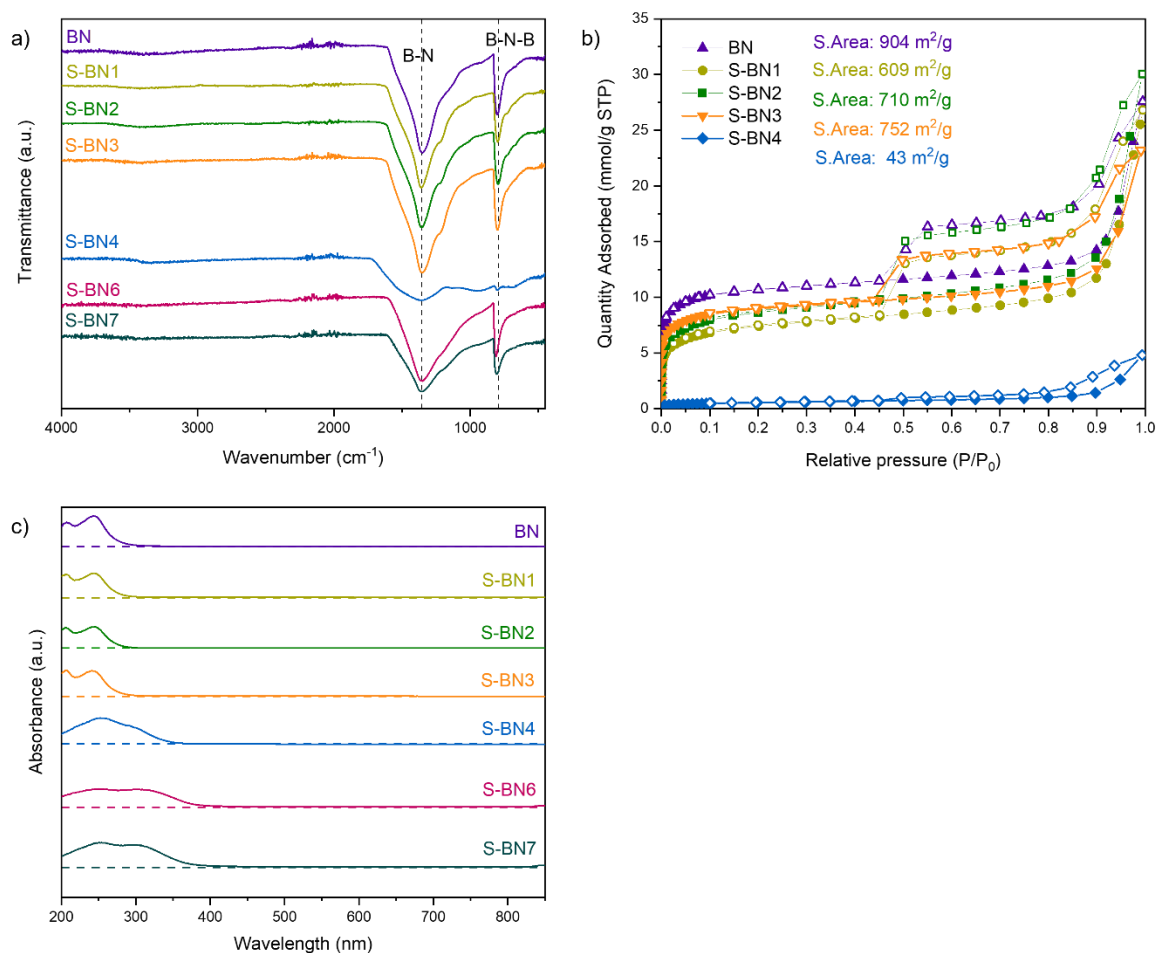


Figure A. 1. Preliminary a) FTIR, b) N₂ sorption (-196 °C), and c) DRS UV-Vis results on pristine BN and S-BN samples. The inset in b) displays S_{BET} of the materials. Sublimed S (S-BN1, S-BN2, S-BN3), thiourea (S-BN4, S-BN6), and trithiocyanuric acid (S-BN7) have been used as S precursors.

Table A. 1. Textural parameters of pristine BN and P-BN, as derived from N₂ sorption isotherms (- 196 °C). Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

Sample	S_{BET} (m² g⁻¹)	V_{tot} (cm³ g⁻¹)	V_{meso} (cm³ g⁻¹)	V_{micro} (cm³ g⁻¹)	V_{micro}/V_{tot} (%)	V_{ultra} (cm³ g⁻¹)
BN	1100	0.577	0.151	0.426	74	0.084
P-BN _{IL-HF}	1276	0.652	0.162	0.490	75	0.131
P-BN _{IL-LF}	1314	0.674	0.175	0.499	74	0.129
P-BN _{PA-HF}	991	0.479	0.082	0.397	83	0.179
P-BN _{PA-LF}	1036	0.508	0.099	0.409	81	0.184

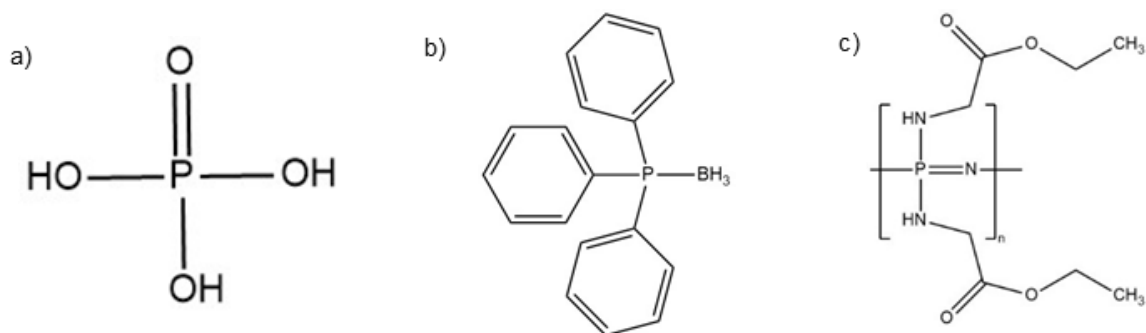


Figure A. 2. Reference samples for NEXAFS and XPS analyses. a) Phosphoric acid, b) borane triphenylphosphine complex $((\text{C}_6\text{H}_5)_3\text{P}\cdot\text{BH}_3)$, and c) poly(bis(1-(ethoxycarbonyl)methylamino)phosphazene $((\text{C}_8\text{H}_{16}\text{N}_3\text{O}_4\text{P})_n)$. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

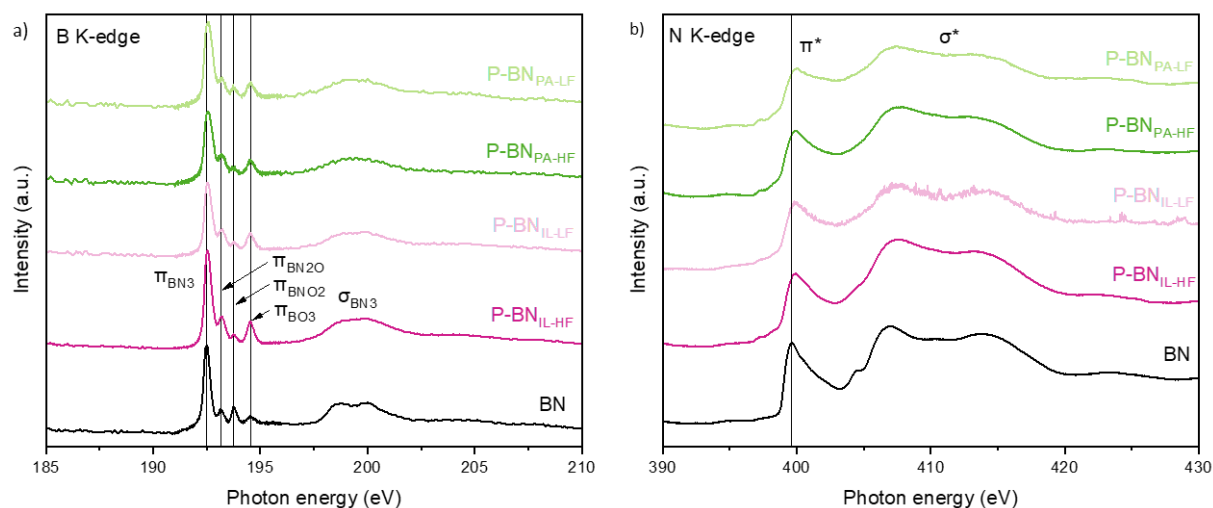


Figure A. 3. a) B K-edge and b) N K-edge NEXAFS spectra of pristine BN and P-BN samples with highlighted peaks^{64,167}. It needs to be noted that this pristine BN was prepared using different synthesis precursors (boric acid + urea) than the pristine BN described in the Chapter (boric acid + melamine). However, I have included it as a reference pristine sample since the two pristine BN samples share the same chemical bonds and environment. Reproduced from reference⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

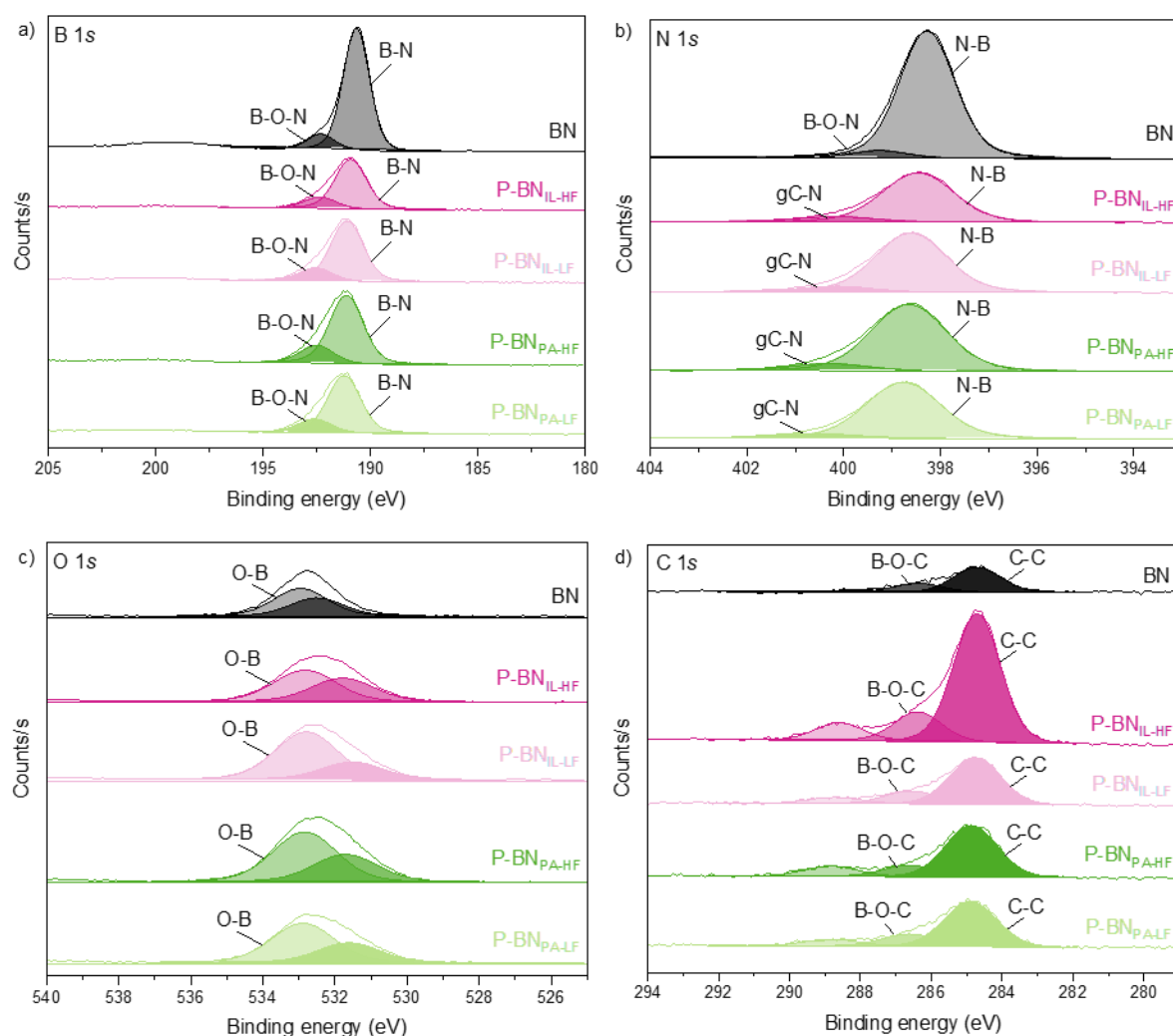


Figure A. 4. a) B 1s, b) N 1s, c) O 1s and d) C 1s XPS deconvolution spectra of pristine BN and P-BN samples. B 1s spectra indicate creation of B-N (~191 eV) and B-O-N (~192.5 eV) bonds in all samples. From N 1s spectra the peak appearing at ~398.5 eV in pristine and P-BN is assigned to N-B. The second chemical state of N in pristine BN is O-N bonding (~399 eV), while in P-BN it is gC-N (~400 eV). O 1s spectra of all samples show same O-B (~533 eV) bonding. In P-BN the second chemical state is shifted to ~531.5 eV. All samples show the same C chemical states from C 1s spectra, containing C-C (~284.8 eV) and O-C (~286.5 eV) bonds^{64,240}. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

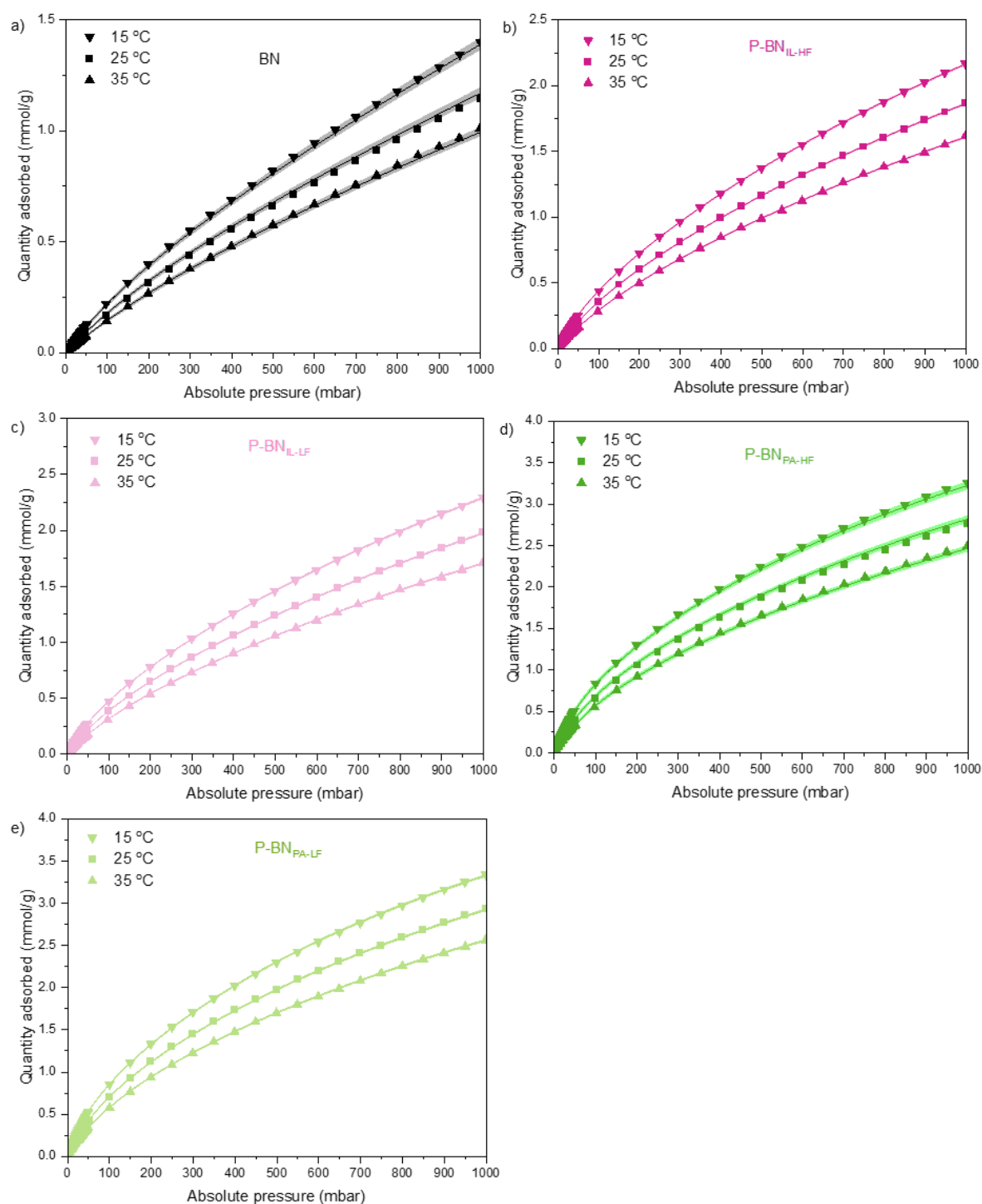


Figure A. 5. Experimental CO₂ adsorption isotherms taken at three temperatures (15, 25, 35 °C) and fitted using DSL fit for a) pristine BN, b) P-BN_{IL-HF}, c) P-BN_{IL-LF}, d) P-BN_{PA-HF}, and e) P-BN_{PA-LF}. Symbols are used for the data points, solid line represents the isotherm fit and shading indicates confidence bounds. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

Table A. 2. DSL coefficients as derived from fitting adsorption data for pristine BN and P-BN samples. The values in parentheses represent the uncertainty values. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

DSL coefficient	BN	P-BN _{IL-HF}	P-BN _{IL-LF}	P-BN _{PA-HF}	P-BN _{PA-LF}
q _{sb} (mol kg ⁻¹)	0.35 (0.01)	0.36 (0.00)	0.40 (0.00)	0.73 (0.01)	0.65 (0.00)
q _{sd} (mol kg ⁻¹)	17.98 (0.14)	6.51 (0.01)	6.83 (0.01)	6.55 (0.05)	6.41 (0.01)
b ₀ (bar ⁻¹)	9.19·10 ⁻⁴ (4.98·10 ⁻⁵)	2.97·10 ⁻⁴ (5.17·10 ⁻⁶)	3.06·10 ⁻⁴ (4.32·10 ⁻⁶)	14·10 ⁻⁴ (9.54·10 ⁻⁵)	4.17·10 ⁻⁴ (6.95·10 ⁻⁶)
d ₀ (bar ⁻¹)	1.09·10 ⁻⁴ (9.08·10 ⁻⁷)	3.87·10 ⁻⁴ (6.60·10 ⁻⁷)	3.80·10 ⁻⁴ (5.52·10 ⁻⁷)	2.70·10 ⁻⁴ (2.73·10 ⁻⁶)	3.44·10 ⁻⁴ (7.57·10 ⁻⁷)
-ΔU _b (kJ mol ⁻¹)	20.17 (0.14)	25.40 (0.04)	25.31 (0.04)	22.11 (0.16)	25.56 (0.04)
-ΔU _d (kJ mol ⁻¹)	15.32 (0.21)	16.58 (4.22)	16.63 (3.60)	18.60 (0.03)	18.36 (0.05)

Table A. 3. Virial coefficients as derived from calculations of isosteric heat of adsorption for pristine BN and P-BN samples. The values in parentheses represent the uncertainty values. The virial fit was used on experimental data from CO₂ adsorption isotherms for each material in three temperatures, which were shown in **Figure A.5**. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

Virial coefficient	BN	P-BN _{IL-HF}	P-BN _{IL-LF}	P-BN _{PA-HF}	P-BN _{PA-LF}
a ₀ (K)	-2722.5 (2.08)	-2565.8 (1.90)	-2507.7 (1.51)	-2790.7 (3.09)	-2700.2 (1.63)
a ₁ (K mol ⁻¹)	850.07 (3.17)	562.29 (2.03)	459.37 (1.43)	351.09 (1.92)	343.51 (0.99)
a ₂ (K mol ⁻²)	-219.89 (2.90)	-195.06 (1.31)	-165.99 (0.85)	-98.51 (0.76)	-94.88 (0.39)
a ₃ (K mol ⁻³)	61.90 (2.44)	42.87 (0.76)	33.61 (0.46)	13.87 (0.27)	13.31 (0.14)
b ₀ (-)	8.39 (0.01)	6.95 (0.01)	6.68 (0.01)	6.85 (0.01)	6.51 (0.01)
b ₁ (mol ⁻¹)	-1.78 (0.01)	-0.62 (0.01)	-0.35 (0.01)	-0.10 (0.01)	-0.10 (0.00)

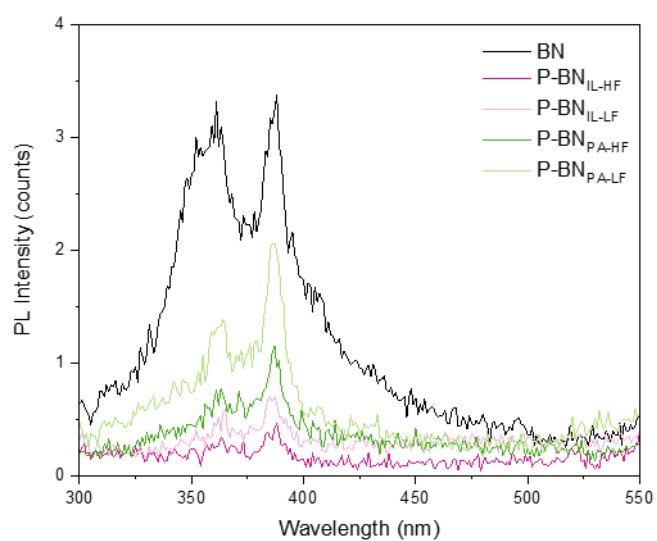


Figure A. 6. Steady-state PL spectra of pristine BN and P-BN samples obtained upon excitation at 282 nm. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

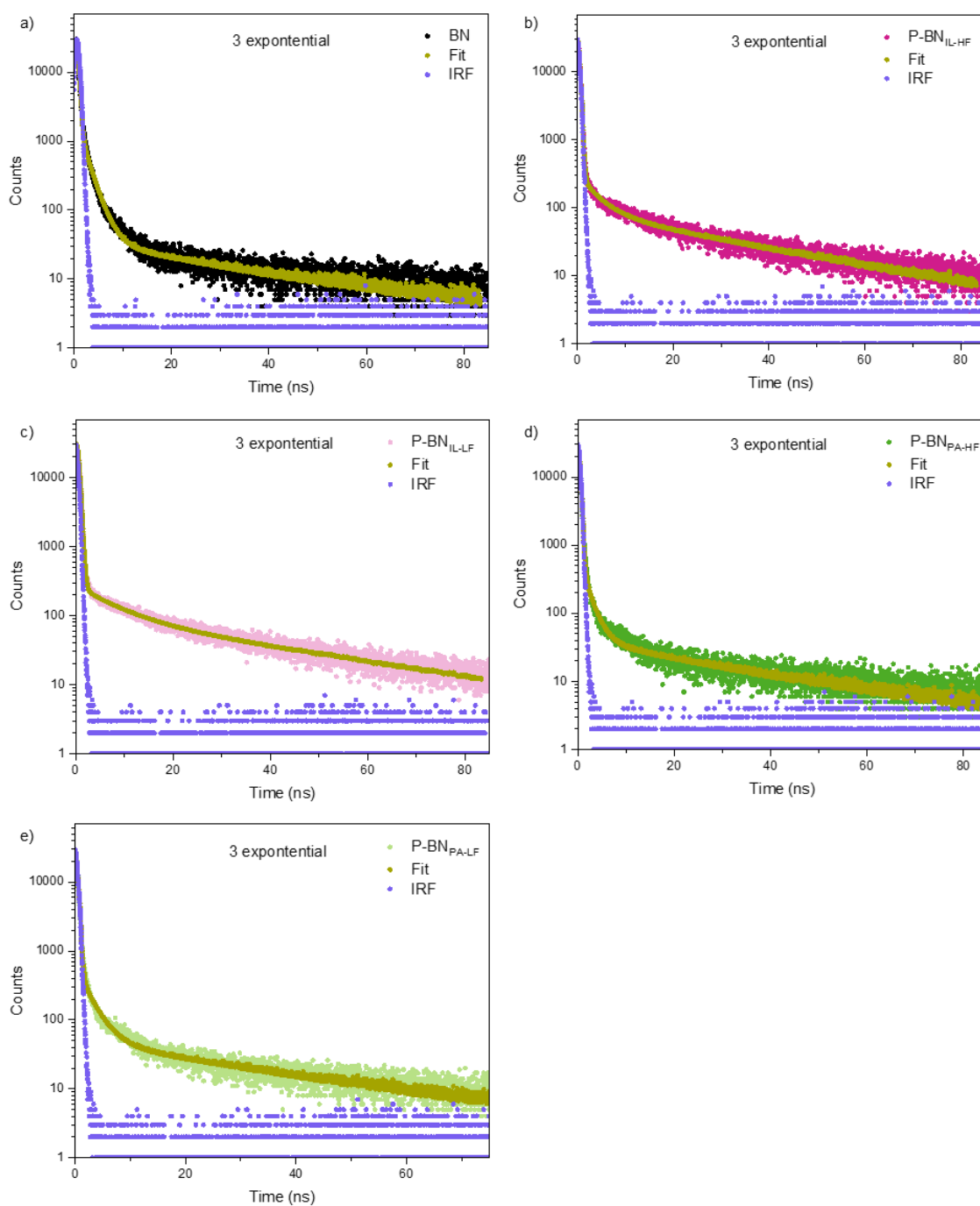


Figure A. 7. TCSPC decay profiles probed at 350 nm and fitted using triexponential function for a) pristine BN, b) P-BN_{IL-HF}, c) P-BN_{IL-LF}, d) P-BN_{PA-HF}, and e) P-BN_{PA-LF}. Shown in the plots along with the sample signal are the fit (thin line) and instrument response factor (IRF). Due to the fast decay being faster than the IRF I was unable to resolve the kinetics. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

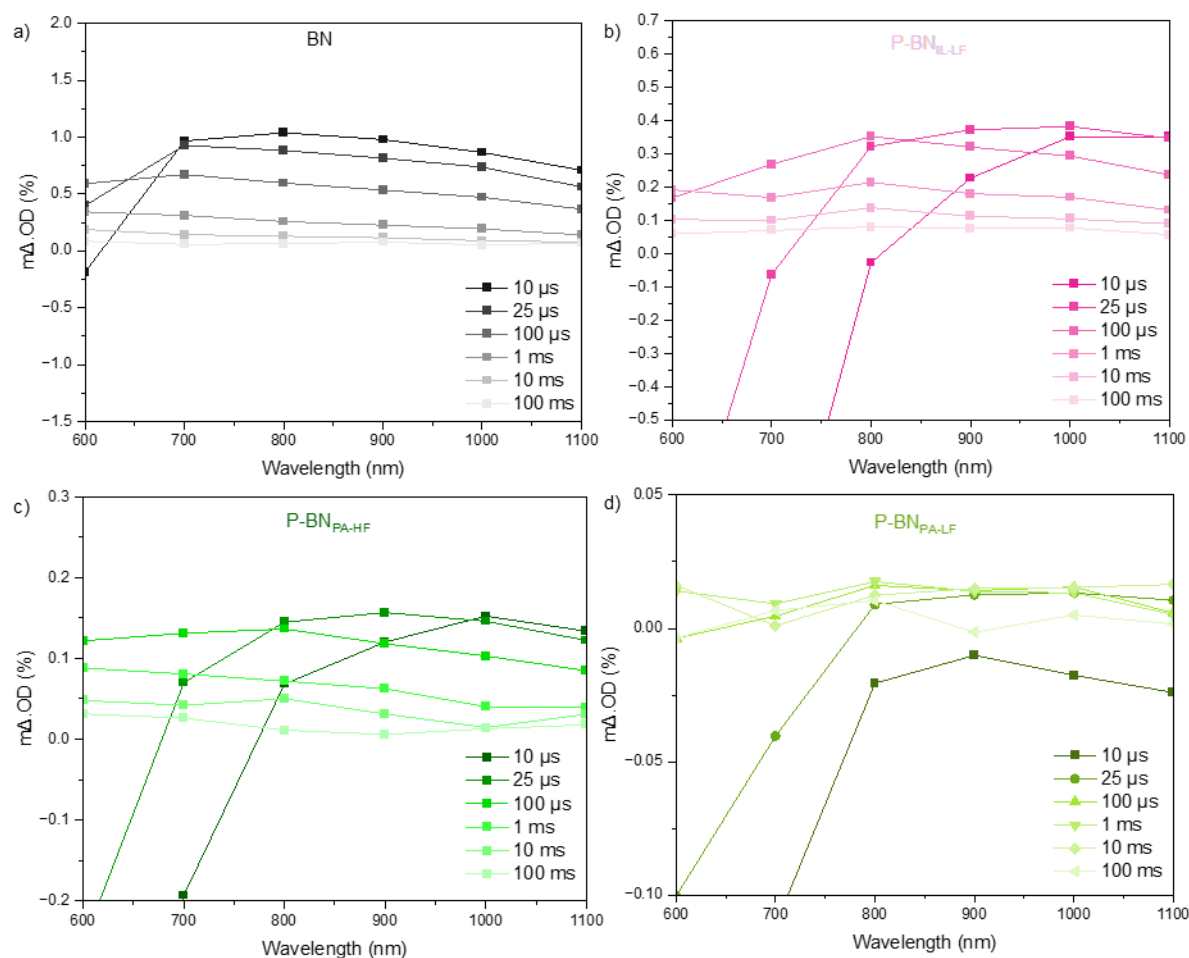


Figure A. 8. TAS data probed at a range 600 – 1100 nm of wavelengths upon excitation at 355 nm for a) pristine BN, b) P-BN_{IL-LF}, c) P-BN_{PA-HF}, and d) P-BN_{PA-LF}. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

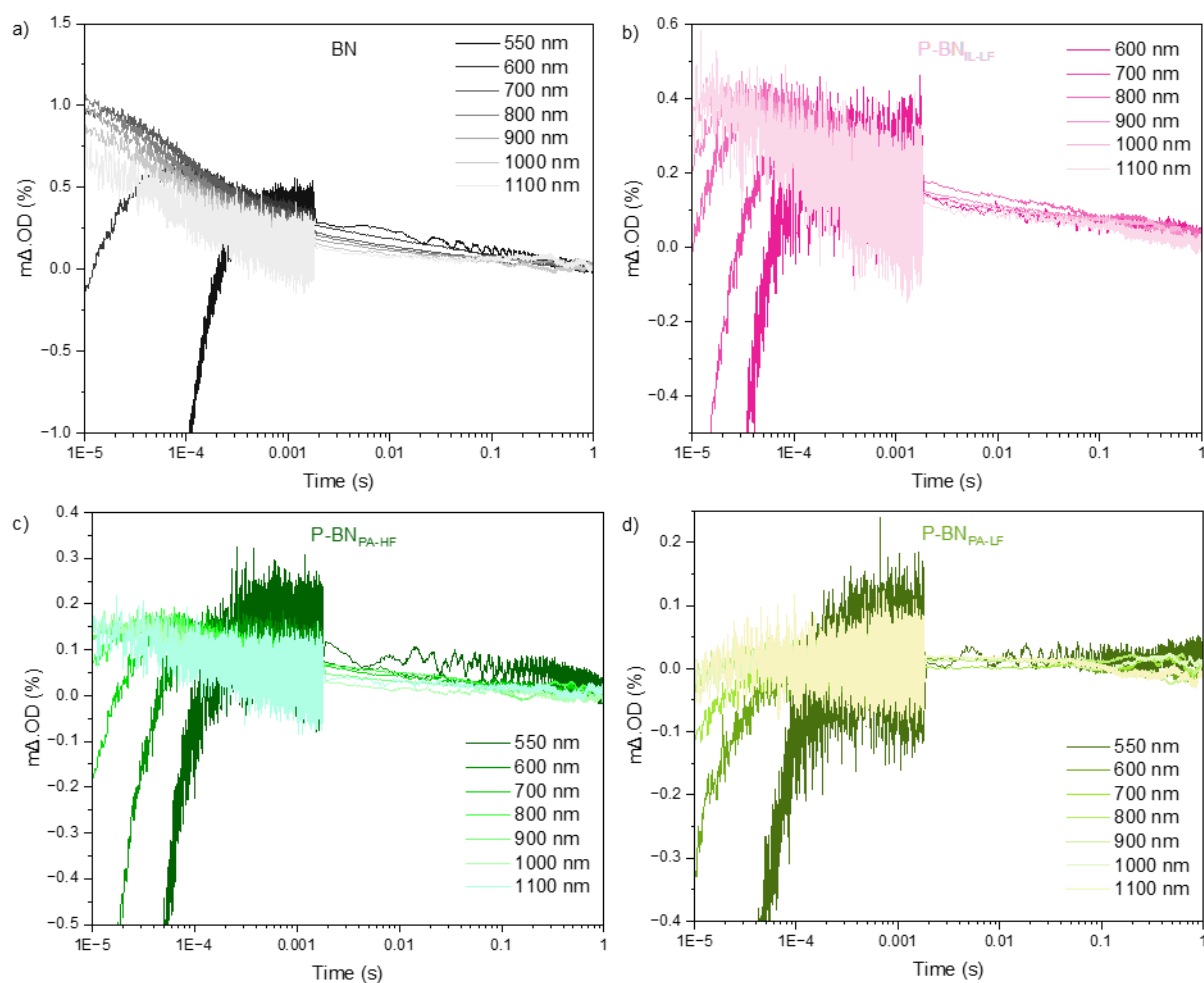


Figure A. 9. TAS decay profiles over time upon excitation at 355 nm for a) pristine BN, b) P-BN_{IL-LF}, c) P-BN_{PA-HF}, and d) P-BN_{PA-LF}. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society. I suggest that the existence of negative signals, which evolve to positive at different timescales between the samples, is due to ground state bleaching (as previously described in the text).

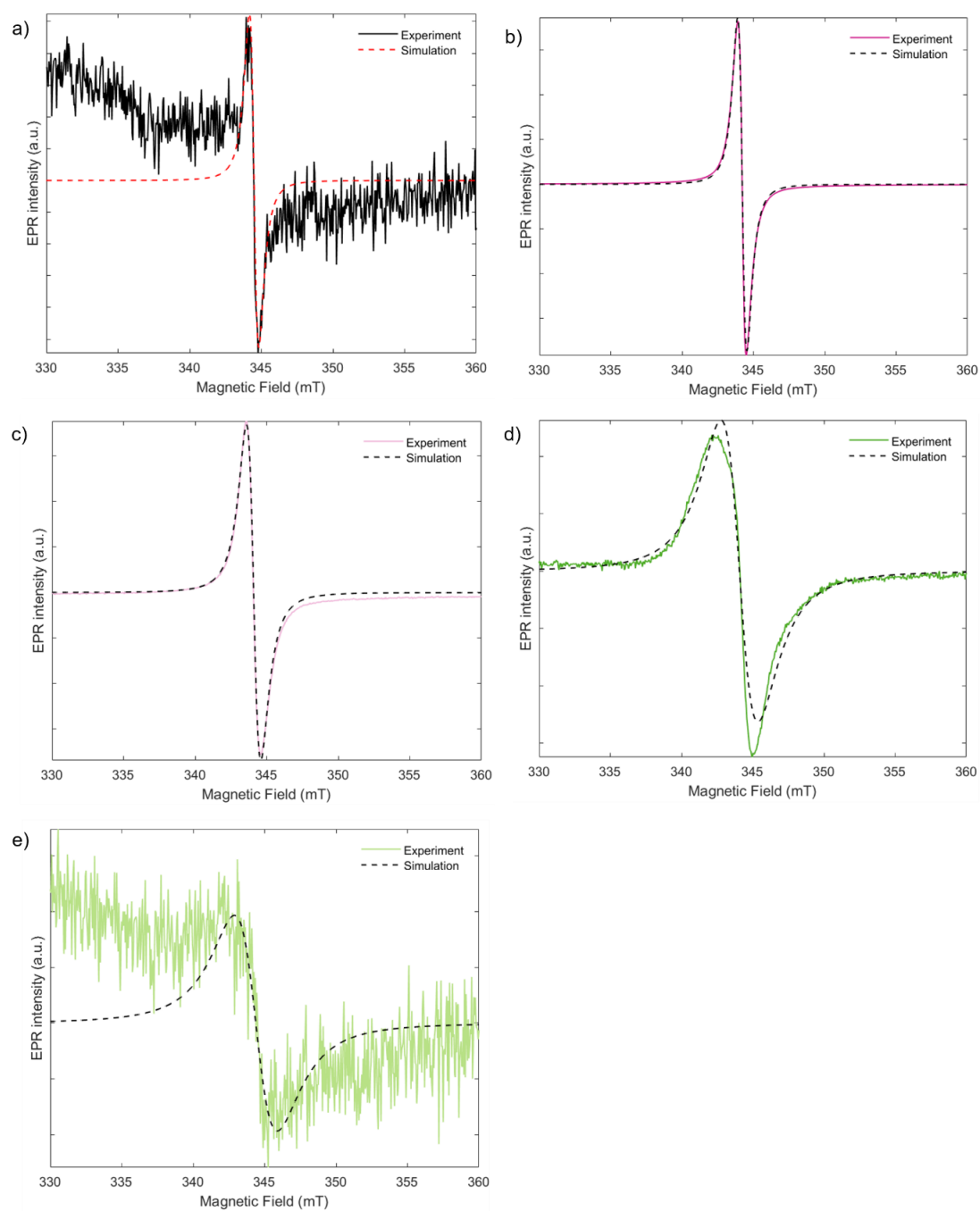


Figure A. 10. Experimental (solid line) and simulated (dashed line) EPR spectra obtained at room temperature and air atmosphere, of a) pristine BN, b) P-BN_{IL-HF}, c) P-BN_{IL-LF}, d) P-BN_{PA-HF}, and e) P-BN_{PA-LF}. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

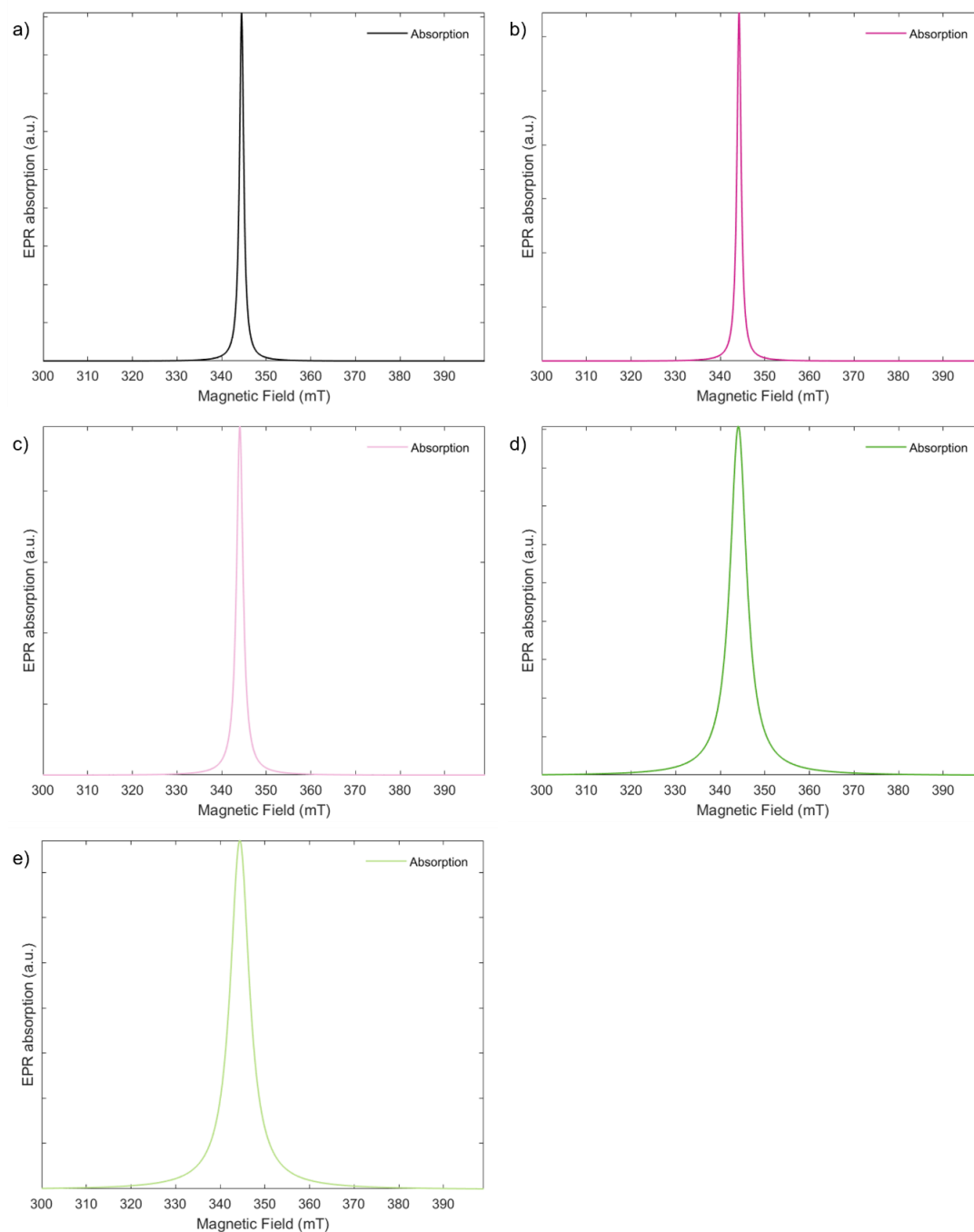


Figure A. 11. EPR absorption signal of a) pristine BN, b) P-BN_{IL-HF}, c) P-BN_{IL-LF}, d) PBN_{PA-HF}, and e) P-BN_{PA-LF}, as derived from the integration of simulated EPR signals from **Figure A.10**. By integrating the absorption signals, I obtained the concentration of -OB₃ species existing in the samples, responsible for the EPR signal. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

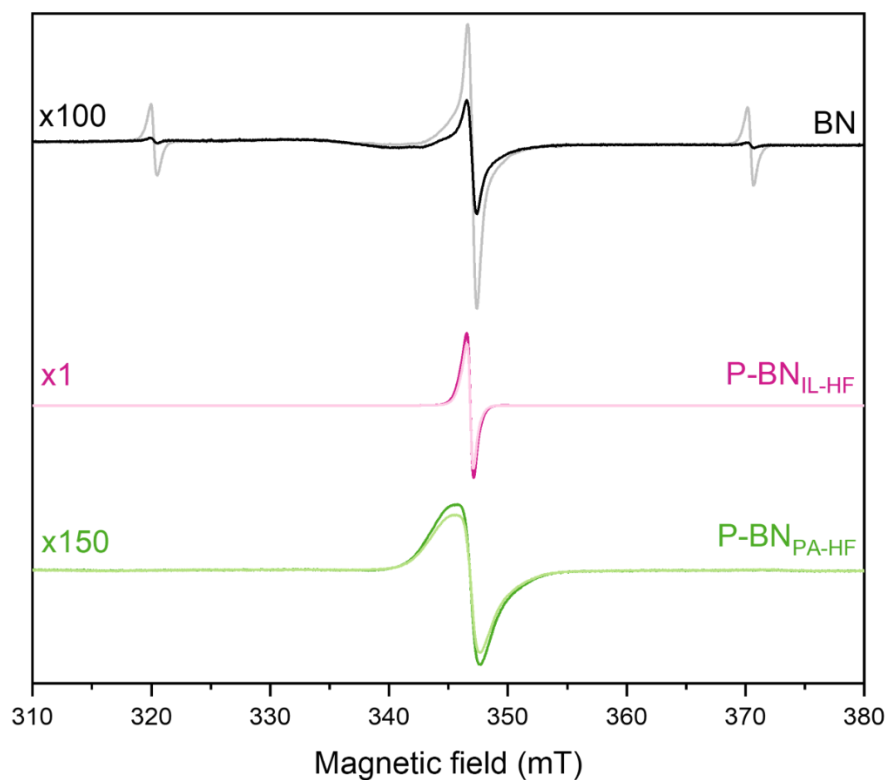


Figure A. 12. EPR spectra of pristine BN and P-BN samples at -268 °C and He atmosphere. Multiplication factors are shown on the left side of the signals to facilitate comparison between samples. The spectra indicate change in signal before (darker colour) and after (lighter colour) irradiation with UV light source. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

Table A. 4. Photocatalytic CO₂ reduction results under different conditions and control tests on pristine BN and P-BN samples. Except for the control tests, all measurements were repeated three times and the standard deviation was calculated. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

Sample	Conditions	Light	¹² CO evolution rate (μmol g ⁻¹ h ⁻¹)	¹² CH ₄ evolution rate (μmol g ⁻¹ h ⁻¹)
BN	¹² CO ₂ /H ₂	UV/Vis	2.689 ±0.245	0.244 ±0.041
BN	¹² CO ₂ /H ₂	Visible (> 400 nm)	0.101 ±0.013	n.d.*
P-BN_{PA-LF}	¹² CO ₂ /H ₂	UV/Vis	1.056 ±0.170	0.135 ±0.008
P-BN_{PA-LF}	¹² CO ₂ /H ₂	Visible (> 400 nm)	0.019 ±0.003	n.d.
P-BN_{IL-LF}	¹² CO ₂ /H ₂	UV/Vis	0.543 ±0.032	0.016 ±0.001
P-BN_{IL-LF}	¹² CO ₂ /H ₂	Visible (> 400 nm)	0.054 ±0.016	n.d.
Control tests				
No catalyst	¹² CO ₂ /H ₂	UV/Vis	n.d.	n.d.
BN	¹² CO ₂ /H ₂	No irradiation	n.d.	n.d.
P-BN_{PA-LF}	¹² CO ₂ /H ₂	No irradiation	n.d.	n.d.
BN	N ₂ /H ₂	UV/Vis	2.370	0.489
BN	¹³ CO ₂ /H ₂	UV/Vis	3.076	0.124
P-BN_{PA-LF}	¹³ CO ₂ /H ₂	UV/Vis	0.796	0.085

*n.d. = not detected

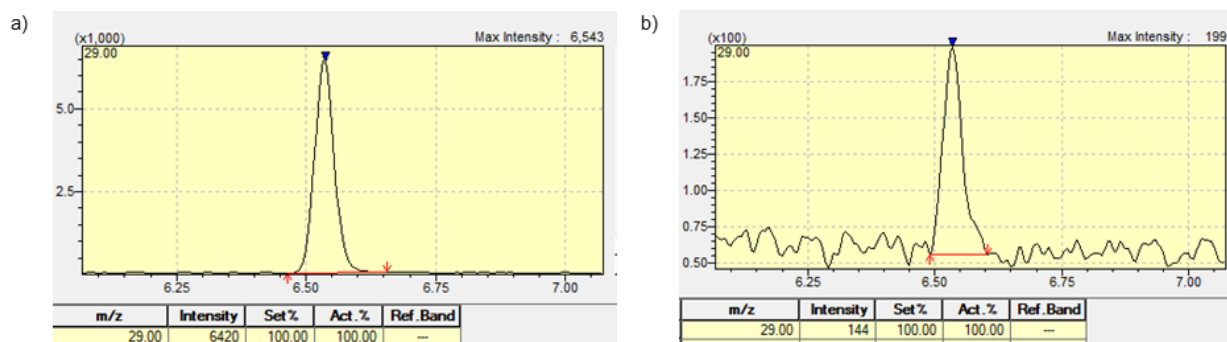


Figure A. 13. Confirmation of photocatalytic CO₂ conversion to CO. The ¹³CO (m/z = 29) peak presented at a) for BN and b) for P-BN_{PA-LF} was formed after photocatalytic tests in gas phase using ¹³CO₂/H₂ flow. It is noted that the ¹³CO₂ cylinder also contains ¹²CO₂ traces, and it is inevitable that ¹²CO₂ and ¹³CO₂ initially coexist in the system. As a result, there is production of both ¹²CO and ¹³CO during irradiation. The produced ¹³CO:¹²CO ratio is – based on their respective peak intensity ratio – 0.2 for BN and 0.02 for P-BN_{PA-LF}. Reproduced from reference ⁵¹ under CC-BY 4.0 Licence. Copyright 2024 American Chemical Society.

6. INVESTIGATING THE EFFECT OF B FUNCTIONALISATION ON gC_3N_4 CHEMICAL, SORPTIVE, OPTOELECTRONIC AND PHOTOCATALYTIC PROPERTIES

The contents of this Chapter have been submitted for publication, in the form of a manuscript. Unless otherwise stated, I have conducted all discussed experimental work and analysis thereof. Ms Sharminaz C. Sageer, Dr. Daniel M. Dawson and Prof. Sharon E. Ashbrook (Chemistry Department, University of St. Andrews) provided the resources for and performed/analysed all NMR measurements. Dr. Andreas Kafizas (Chemistry Department, Imperial College London) helped with steady-state PL and TAS measurements, analysis and resources. Dr. Irena Nevjestic and Prof. Sandrine Heutz (Materials Department, Imperial College London) helped with EPR measurements, analysis and resources. Dr. Catriona M. McGilvery (Materials Department, Imperial College London) provided the resources for and performed EELS measurements, and helped with their analysis. Dr. Matyas Daboczi (Institute of Technical Physics and Materials Science in Budapest, former researcher at Imperial College London) performed and analysed APS measurements, and with Dr. Salvador Eslava (Chemical Engineering Department, Imperial College London) they provided the resources for APS. Dr. Gwilherm Kerherve (Materials Department, Imperial College London) helped with XPS results analysis and resources.

6.1. Introduction

As shown in the gC_3N_4 (referred to as 'CN' in this Chapter) literature review (**Section 2.3**), a few research groups have tested B-functionalised CN materials (referred to as 'B-CN' in this Chapter) for CO_2 photoreduction^{185,187,189,203,261–263}. These studies report higher CO ($1.2\text{--}40.4\ \mu\text{mol g}^{-1}\text{ h}^{-1}$), CH_4 ($0.3\text{--}42.5\ \mu\text{mol g}^{-1}\text{ h}^{-1}$) and H_2 ($0.3\text{--}4.4\ \mu\text{mol g}^{-1}\text{ h}^{-1}$) production rates than pristine CN, for this reaction. The superior photocatalytic activity of B-CN is attributed – usually by speculation – to a combination of enhanced CO_2 adsorption, extended visible light absorption, better charge carrier separation, and easier access to surface redox sites. A couple of research groups have also investigated the use of B-CN for photocatalytic NO_x removal (air purification), and presented an increased NO/NO_x removal rate and selectivity to NO_3^- compared to pristine CN^{261,264}. They suggested the enhanced photoactivity was due to extended visible light absorption (smaller bandgap), a more appropriate electronic band structure (specifically, deeper conduction band) and longer-lived photoexcited electrons.

As identified in **Section 3.1**, despite the increased amount of research on B functionalisation of CN, most studies incorporate B-CN as part of composites/heterojunctions or co-doped with other metals and co-catalysts, or explore the effect of structure modification. In these studies, the testing conditions for photocatalytic CO_2 reduction often involve the use of cocatalysts and hole scavengers. While this approach focuses on boosting catalytic efficiency, it makes it difficult to elucidate the 'isolated' effect of B functionalisation on the properties of CN materials. Arguably, a lot of findings – although referring to the same material – are contradictory, especially with regards to chemistry and photoactivity. For instance, there is a lack of consensus on how B is integrated into the structure. B_C replacement is suggested by some studies, while B_N by others, and a few theoretical works also support grafting of B onto

coordinated N atoms, outside the heptazine rings. Interpretation of UV-visible spectroscopy results also varies, as B functionalisation seems to not have a significant effect, while some studies claim enhanced or extended light absorption. Finally, mainly due to different experimental set-ups and condition used, there is a wide range of CO₂ photoreducing activity reported, and it is usually assigned to different properties (as discussed above).

In this Chapter, I aim to bridge this knowledge gap and investigate the effects of i) B functionalisation, ii) B content, and iii) choice of B dopant on the different properties of bulk CN (*i.e.* **Objective 2, Section 3.2**). For this purpose, I synthesise two sets of samples with varying B content using two different B precursors (amorphous boron and boric acid), carry out advanced characterisation [FTIR, XRD, XPS, EPR, solid-state nuclear magnetic resonance (NMR), transmission energy microscopy (TEM), electron energy loss spectroscopy (EELS), N₂ and CO₂ sorption, DRS UV-Vis, PL, ambient photoemission spectroscopy (APS), TAS], theoretical calculations [density functional theory (DFT)], and test my materials for the less extensively explored photocatalytic CO₂ reduction and NO_x removal reactions. Some of the techniques I used have never been employed to characterise B-functionalised CN, namely: CO₂ sorption with related derivation of heat of adsorption, APS, and μ s-TAS. Overall, I propose i) how B is integrated into the CN structure, ii) what the isolated B functionalisation effect is on CO₂ adsorption, light absorption, electronic band structure and charge carrier behaviour, and iii) how these effects are linked to photocatalytic activity, depending on the choice of B precursor and B content. The novelty of my study lies in this multidimensional approach to clarify points of controversy in literature, and uncover the isolated effects of B functionalisation.

6.2. Materials

The same single-step process was followed to synthesise pristine and B-CN samples as described below. For the B-functionalised samples, two different precursors were used: amorphous boron, and boric acid.

6.2.1. Synthesis of pristine CN

Bulk CN was synthesised through calcination of melamine. 10 g (0.08 mol) of melamine ($\text{C}_3\text{H}_6\text{N}_6$, 99.0%, Sigma Aldrich) was placed into an alumina crucible covered with lid and heated in a muffle furnace up to 560 °C with a heating rate of 10 °C min⁻¹. The temperature was held for 4 h, and then the material was allowed to cool down naturally to room temperature. The obtained powders were ground using a mortar, and are denoted CN.

6.2.2. Synthesis of B-CN (B)

B-CN samples were synthesised using melamine ($\text{C}_3\text{H}_6\text{N}_6$, 99.0%, Sigma Aldrich) and amorphous boron (B, >95.0%, Sigma Aldrich) as precursors. 10 g (0.08 mol) of melamine and 0.02, 0.05 or 0.60 g (0.002, 0.005 or 0.06 mol) of boron were mixed using a mortar. The mixture was placed into an alumina crucible covered with lid and heated in a muffle furnace up to 560 °C with a heating rate of 10 °C min⁻¹. The temperature was held for 4 h, and then the material was allowed to cool down naturally to room temperature. The obtained powders were ground using a mortar, and denoted B-CN (0.5B), B-CN (1B) and B-CN (3B) after using gradually higher amount of B as precursor, respectively. The numbers “0.5”, “1”, and “3” in the parentheses indicate B at% content, as determined from XPS analyses.

6.2.3. Synthesis of B-CN (BA)

B-CN samples were synthesised using melamine ($\text{C}_3\text{H}_6\text{N}_6$, 99.0%, Sigma Aldrich) and boric acid (H_3BO_3 , >99.5%, Sigma Aldrich) as precursors, in the same process as described in **Section 6.2.2**. In this case, 0.17, 0.35 or 0.70 g (0.003, 0.006 or 0.01 mol) of boric acid were used instead of boron. The obtained powders were ground using a mortar, and denoted B-CN (3BA), B-CN (5BA) and B-CN (11BA) after using gradually higher amount of boric acid, respectively. The numbers “3”, “5”, and “11” in the parentheses indicate B at% content, as determined from XPS analyses.

6.3. Methods

6.3.1. Characterisation of chemical properties

FTIR, XPS and EPR measurements were collected to investigate the B-CN materials' chemical properties, as described in **Chapter 4**.

All solid-state NMR spectra were acquired using Bruker Avance III spectrometers equipped with either a 14.1 T or 9.4 T wide-bore magnets. For all NMR measurements, powder samples were packed into ZrO_2 rotors and rotated at a magic-angle spinning (MAS) rate of 14 kHz using a 4-mm HFX boron-free (14.1 T) or 4-mm HFX (9.4 T) probe. ^{11}B NMR spectra were acquired at a Larmor frequency of 192.6 MHz. Spectra were acquired using either i) a single pulse with a short flip angle ($\beta = \pi/12$, $\nu_1 = 125$ kHz) and recycle intervals of 1 s and 5 s for samples prepared using B and BA precursors, respectively, or ii) a spin echo experiment (also with short flip angle pulses) and a recycle interval of 0.5 s. Multiple quantum (MQ) MAS²⁶⁵ experiments

were carried out using a triple-quantum z-filtered pulse sequence²⁶⁶ (rotor-synchronised where possible). Spectra are shown after a shearing transformation and are referenced in the indirect dimension according to the convention of Pike et al.²⁶⁷ Chemical shifts are quoted in ppm relative to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in CDCl_3 measured using a secondary reference of BPO_4 ($\delta_{\text{iso}} = -3.3$ ppm). ^1H NMR spectra were acquired at a Larmor frequency of 400.13 MHz. Spectra were acquired using the DEPTH pulse sequence to remove probe background, a 90° pulse ($\nu_1 = 80$ – 100 kHz) and a recycle interval of 3 s. Chemical shifts are quoted in ppm relative to $\text{Si}(\text{Me})_4$ in CDCl_3 measured using a secondary reference of L-alanine ($\delta_{\text{iso}}(\text{CH}_3) = 1.3$ ppm). ^{13}C NMR spectra were acquired at a Larmor frequency of 100.6 MHz. Spectra were acquired using either i) cross polarisation (CP) with a contact pulse (ramped for ^1H) of 7.5 ms, SPINAL-64²⁶⁸ decoupling ($\nu_1 = 90$ kHz) and a recycle interval of 3 s or ii) a spin echo ($\nu_1 = 125$ kHz) with a recycle interval of 120 s. Chemical shifts are quoted in ppm relative to $\text{Si}(\text{Me})_4$ in CDCl_3 measured using a secondary reference of L-alanine ($\delta_{\text{iso}}(\text{CH}_3) = 20.5$ ppm).

For the EELS measurements, samples were prepared by suspending the powders in ethanol and drop-casting onto lacey carbon grids (300 mesh Cu, TAAB) after sonicating. To remove any residual hydrocarbon contaminants the lacey grids were heated in a clean vacuum oven at 120°C for 12 hours and then again after addition of the sample. EELS experiments were carried out at 300 kV on a Spectra 300 TEM (ThermoFisher Scientific) equipped with monochromator and Cs probe corrector. EELS spectra were acquired on a K3 direct electron detection camera mounted on a Gatan Continuum K3 HR spectrometer (Ametek). The convergence and collection semi angles were 15.7 mrad and 30.3 mrad respectively. Spectra were acquired with a probe current of around 40 pA as measured on the fluscreen, to minimise electron beam damage. Low-loss and core-loss spectra were acquired using dual EELS. Spectra were acquired

with or without sub-pixel scanning depending on the experiment. The zero-loss peak was used to align the spectra (full width at half maximum, FWHM = 1.1 eV). The core-loss spectrum image (SI) of CN was denoised using the principal component analysis (PCA) algorithm as implemented in Gatan Microscopy Suite (Ametek). Six to thirteen components were used depending on the SI, and care was taken to ensure no obvious artifacts from the PCA were present in the data in the regions being studied. Background subtraction of the B, C or N K-edges was then carried out using the power law method.

6.3.2. Characterisation of structural & morphological properties

Powder XRD data and N₂ sorption isotherms (-196 °C) were measured to identify the structural properties of B-CN materials, as described in **Chapter 4**.

For the TEM measurements, samples were prepared by suspending the powders in ethanol and drop-casting onto holey carbon grids (300 mesh Cu, TAAB) after sonicating. TEM measurements were performed using a TEM-2100Plus (JEOL) microscope with LaB₆ filament, operated at 200kV. Images were acquired in bright-field TEM mode.

6.3.3. Characterisation of optoelectronic properties

DRS UV-Vis, steady-state PL, TAS and under irradiation EPR spectra were performed to explore the optoelectronic properties of B-CN materials, as described in **Chapter 4**.

XPS valence band and work function measurements were obtained using the same X-ray Photoelectron Spectrometer and processing methodology as described in **Chapter 4**. Valence band spectra were collected using 15 eV pass energy and 0.050 eV step size, with the 'area'

mode which averages four points. The work functions for the materials, used for the determination of Fermi levels (E_F), were measured and averaged at five points. The work functions were determined by measuring the secondary electron cutoff in the low kinetic energy region, using gold as reference material. A sample bias of -29.47 V was applied using an ion gun, and the cutoff spectra were obtained using 10 eV pass energy and 0.100 eV step size.

APS measurements were conducted using an APS02 system (KP Technology). Thin, homogenous films of the powder samples were prepared on tin oxide-coated glass substrates. The measurements involved scanning the monochromatic UV light irradiation energy from 5.2 to 7.0 eV. The cube root of the photoemission as function of irradiation energy was plotted and extrapolated to zero to determine the valence band edge values (E_v) of the thin layers.

6.3.4. CO₂ adsorption

CO₂ adsorption isotherms at 15, 25 and 35 °C and up to 1 bar were carried out and fitted, as described in **Chapter 4**. The Langmuir isotherm fitting was carried out with MATLAB R2020a (The Mathworks Inc.) using the in-house software package isothermFittingTool²⁶⁹.

Subsequently, the isosteric heat of adsorption (ΔH_{ads}) was calculated by applying the Clausius–Clapeyron equation^{270–272} using the dual site Langmuir parameters²¹⁵, based on the equation²⁷³:

$$-\Delta H_{ads,j} = - \left[\frac{\frac{q_{sb,j} b_j \Delta U_{b,j}}{(1+b_j p)^2} + \frac{q_{sd,j} d_j \Delta U_{d,j}}{(1+d_j p)^2}}{\frac{q_{sb,j} b_j}{(1+b_j p)^2} + \frac{q_{sd,j} d_j}{(1+d_j p)^2}} \right] \quad (33)$$

6.3.5. Photocatalytic CO₂ reduction

Liquid phase CO₂ photoreduction experiments were performed in a home-made set-up (**Figure B.1**) using a stainless steel photoreactor (212.1 cm³) equipped with a fused quartz window for irradiation. Approximately 30 mg of sample was added to 5 mL H₂O inside a 50 mL glass beaker, with a quartz-encapsulated magnetic stirrer. Then, the beaker containing the suspension was placed inside the photoreactor under continuous stirring, and the system was placed under vacuum at approximately 0.02 bar to remove air. CO₂ gas (40 cm³ min⁻¹, research grade, 99.999%, BOC) was flown through the suspension via a quartz capillary tube for 40 min. Finally, the photoreactor was filled with approximately 1.7 bar of CO₂ gas and sealed. The sample was then irradiated for 5 h using an LSH302 light source (LOT Quantum Design) equipped with a 300 W Xe arc lamp (UXL-302-O, Ushio) at a distance of 9 cm from the surface of the suspension (area of 8 cm²), providing a 160 mW cm⁻² intensity at the surface. After 5 h reaction, the gaseous products were detected and analysed using a 7890B gas chromatographer (GC) (Agilent), equipped with a packed HayeSep Q column (Agilent J&W, 6 foot, 1/8 inch, 2 mm, 80/100 SST) and a packed MolSieve 5A column (Agilent J&W, 6 foot, 1/8 inch, 2 mm, 60/80, preconditioned) in series, a thermal conductivity detector (TCD) and a flame ionization detector (FID). The photocatalytic tests were repeated three times on fresh samples. Control experiments were performed: a) without irradiation, b) with no sample, and c) under N₂ atmosphere.

6.3.6. Photocatalytic NO_x removal

Photocatalytic NO_x removal tests were carried out in a purpose-made set-up, built in accordance with the ISO (22197-1:2016) protocol. 50 mg of sample was dispersed in ethanol

and sonicated. The dispersion was transferred to a 10 mL spray bottle and sprayed onto the surface of float glass (5 cm × 10 cm; 50 cm²) using an airbrush gun (Fengda Professional-130 with 0.3 mm nozzle). The tests were performed under continuous 1 L min⁻¹ flow of air containing 3 ppm of NO, at 50% relative humidity and room temperature. The next five steps were followed sequentially while testing each sample: i) 10 min under dark, ii) 20 min under UVA irradiation with intensity of 1.5 mW cm⁻² using two 15 W lamps (FL15T8BLB, 352 nm, Sankyo), iii) 10 min under dark, iv) 20 min under visible (white) light with intensity of 3.5 mW cm⁻² using two 15 W lamps (F15W/T8/840, Sylvania), and v) 10 min under dark. The average NO/NO₂/NO_x levels observed over 1 min intervals were measured using a Serinus 40 chemiluminescence NO_x analyser (Ecotech). The average NO/NO_x removal (%), NO deposition velocity (*v_d*, cm/s) and NO quantum efficiency (QE, %) under both UVA and white light irradiation were calculated based on the equations:

$$NO \text{ removal } (\%) = \frac{[NO]_{initial} - [NO]_{final}}{[NO]_{initial}} \cdot 100\% \quad (34)$$

$$NO_x \text{ removal } (\%) = \frac{[NO_x]_{initial} - [NO_x]_{final}}{[NO_x]_{initial}} \cdot 100\% \quad (35)$$

$$v_d \text{ (cm/s)} = \log \left(\frac{[NO]_{initial}}{[NO]_{final}} \right) \cdot F / A \quad (36)$$

$$QE (\%) = \frac{F \cdot ([NO]_{initial} - [NO]_{final}) \cdot N_{AV}}{V_m \cdot 1000000 \cdot A \cdot p_f} \cdot 100\% \quad (37)$$

where [NO]_{initial} and [NO_x]_{initial} are the average levels (ppm) of NO and NO_x under dark, respectively, [NO]_{final} and [NO_x]_{final} are the average levels (ppm) of NO and NO_x under 20 min of UVA or white light irradiation, respectively, F is the gas flow rate (cm³ s⁻¹), A is the sample area (cm²), N_{AV} is Avogadro's number (molecules mol⁻¹), V_m is the molar volume at standard temperature and pressure (cm³ mol⁻¹), and p_f is the photon flux on the sample surface under UVA or white light irradiation (photons s⁻¹ cm⁻²).

6.3.7. Computational methods

Periodic planewave DFT calculations were carried out using the CASTEP code (version 22)^{274,275}, using the PBE exchange correlation functional²⁷⁶ and the D3-BJ semi-empirical dispersion correction scheme²⁷⁷. Core-valence interactions were described by ultrasoft pseudopotentials, accounting for scalar relativistic effects using the zeroth order relativistic approximation (ZORA²⁷⁸). Planewave energy cutoffs of 60 Ry were used for geometry optimisation and NMR calculations, with the first Brillouin zone sampled using a Monkhorst-Pack grid²⁷⁹ with a reciprocal space grid spacing of $0.04 \text{ } 2\pi \text{ \AA}^{-1}$ in all cases. Initial structural models were obtained from Gracia & Kroll²⁸⁰ and Jürgens et al.²⁸¹ In the geometry optimisation all atomic coordinates and unit cell parameters were allowed to vary.

NMR parameters were calculated using the gauge-including projector augmented wave (GIPAW)²⁷⁴ approach to reconstruct the all-electron wavefunction in the presence of a magnetic field. Calculations provide the absolute shielding tensor and electric field gradient tensor ($\mathbf{V}$). Diagonalization provides their respective principal components, where $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$ and $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$. The isotropic shielding, $\sigma_{\text{iso}} = (1/3)\text{Tr}(\sigma)$, and the predicted isotropic chemical shift $\delta_{\text{iso}} = \sigma_{\text{ref}} - \sigma_{\text{iso}}$. Reference shieldings (σ_{ref}) were determined by comparing experimental shift and calculated shielding for hexagonal BN (^{11}B , 97.4 ppm)²⁸² and melem (^{13}C , 175.1 ppm)²⁸¹. The quadrupolar coupling constant, $C_Q = eQV_{zz}/h$ was obtained using a nuclear quadrupole moment of 4.059 fm^2 for ^{11}B ²⁸³. From the quadrupolar magnitude, C_Q , and asymmetry, $\eta_Q = (V_{xx} - V_{yy})/V_{zz}$ of the quadrupolar interaction, the quadrupolar product $P_Q = C_Q (1 + \eta_Q^2/3)^{1/2}$ can be determined.

6.4. Results & discussion

6.4.1. Chemistry, structure & morphology

For this study, along with a pristine CN reference sample, I synthesised two sets of B-functionalised CN samples using two B-containing precursors in different amounts: amorphous boron (B) and boric acid (BA) (**Figure 6.1**). The B-CN (BA) samples resemble pristine CN, albeit with a more intense yellow colour. However, B-CN (B) samples display an increasingly darker brown colour as the amount of the B precursor increases. This colour could be linked to the dark brown colour of the amorphous B precursor and could be a sign of (unreacted) B present in the B-CN structure.

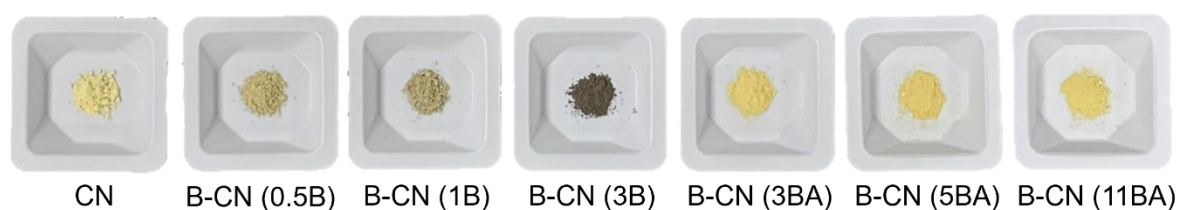


Figure 6. 1. Photographs of the as-prepared CN and B-functionalised CN samples.

To check whether the core CN structure remains unchanged with B functionalisation, I performed FTIR, XRD and N₂ sorption (77 K) measurements on the materials (**Figure 6.2**). In FTIR spectra (**Figure 6.2a**), the typical N-H/O-H (3000-3300 cm⁻¹), C=N (1500-1700 cm⁻¹), C-N (1250-1450 cm⁻¹), and triazine ring (750-900 cm⁻¹) bands of CN are present for all materials, as expected and in accordance with literature^{189,264,284,285}. These observations point to the successful synthesis of CN-based materials. Through XRD (**Figure 6.2b**), I confirm that all materials: i) exhibit the main and unshifted (100) and (002) planes, and secondary (101), (300)

and (004) planes of CN, and ii) share the stable tri-s-triazine structure of CN. I conclude that B functionalisation does not affect the planar d-spacing or π -stacking of CN. However, some B-CN samples show a decrease in (002) peak intensity, the lowest intensity corresponding to high B content (11 at%). This feature may indicate a more defective atomic structure. To examine the porosity of my materials, I performed N₂ sorption measurements at -196 °C (**Figure 6.2c** and **Figure B.2a**). All materials show Type II/III isotherms with Type H3/H4 hysteresis loops (showing a pronounced desorption at $P/P_0=0.45$ due to the tensile strength effect), typical of materials with narrow, slit-like pores²⁸⁶. The textural properties, including BET area (S_{BET}), total pore volume (V_{tot}) and micropore volume (V_{micro}) are derived from the N₂ sorption (-196 °C) isotherms (**Figure 6.2c** and **Table 6.1**). Almost all samples have similar S_{BET} (10-22 m² g⁻¹) and V_{tot} (0.045-0.076 cm³ g⁻¹), except B-CN (11BA) – the sample with the highest degree of functionalisation – which shows the highest BET area and pore volume ($S_{\text{BET}} = 40 \text{ m}^2 \text{ g}^{-1}$, $V_{\text{tot}} = 0.106 \text{ cm}^3 \text{ g}^{-1}$). These values are in accordance with literature for bulk CN (S_{BET} : 4-27 m² g⁻¹), and others have also reported negligible change in S_{BET} with B functionalisation in bulk form. The B-CN (11BA) sample is amongst the most porous B-functionalised bulk CN materials, surpassing some nanotubes^{185,189,262,264,287}. Considering V_{micro} and the ratio $V_{\text{micro}}/V_{\text{tot}}$, all samples are predominantly mesoporous with B-CN (11BA) exhibiting the largest proportion of micropores (~30%). In summary, the introduction of B and the choice of B precursor on their own do not affect the porosity of the materials; rather it is the amount of B functionalisation (*i.e.* 11 at%) that has a significant effect, enhancing the porosity and crystallinity.

Table 6. 1. Textural properties and isosteric heat of adsorption of pristine CN and B-functionalised CN samples. The textural properties were derived from N₂ sorption measurements at -196 °C, including S_{BET} , V_{tot} , V_{micro} , and $V_{\text{micro}}/V_{\text{tot}}$. The heat of adsorption (ΔH_{ads}) was calculated using the Virial fit on CO₂ adsorption data at three temperatures (15, 25, 35 °C) (**Figures B.9** and **Figure B.10**).

Sample	S_{BET} (m ² g ⁻¹)	V_{tot} (cm ³ g ⁻¹)	V_{micro} (cm ³ g ⁻¹)	$V_{\text{micro}}/V_{\text{tot}}$ (%)	Isosteric ΔH_{ads} (kJ mol ⁻¹)
CN	17	0.076	0.012	15.8	16.7
B-CN (0.5B)	13	0.066	0.010	15.2	16.1
B-CN (1B)	22	0.076	0.015	19.7	12.4
B-CN (3B)	10	0.046	0.007	15.2	11.4
B-CN (3BA)	13	0.053	0.009	17.0	12.8
B-CM (5BA)	14	0.045	0.009	20.0	11.7
B-CN (11BA)	40	0.106	0.033	31.1	17.8

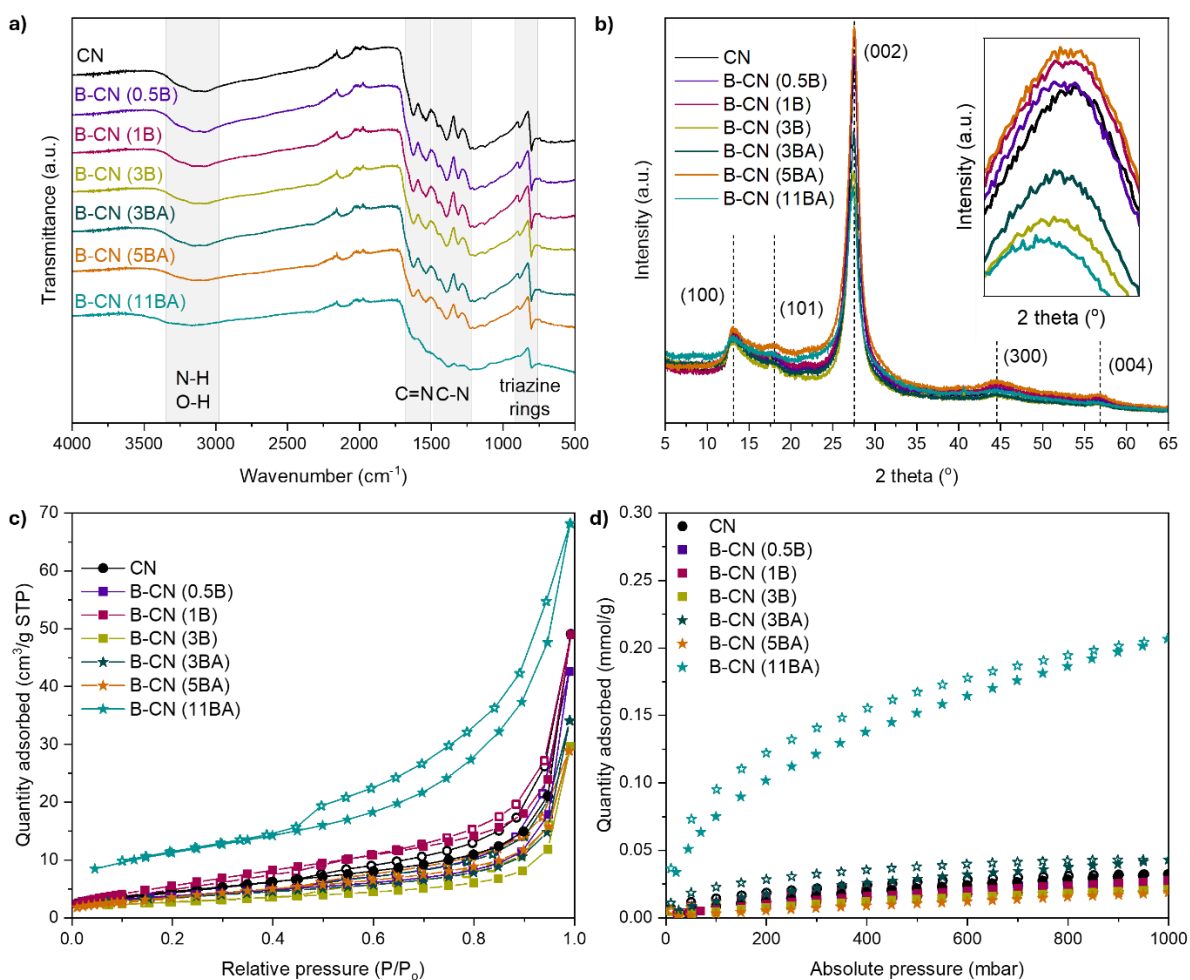


Figure 6. 2. a) FTIR spectra with highlighted IR bands, b) powder XRD patterns with zoomed-in (002) peak in the inset, c) N₂ adsorption-desorption isotherms (-196 °C), and d) CO₂ adsorption-desorption isotherms (25 °C) of pristine and B-functionalised CN samples. Filled symbols represent adsorption, and hollow symbols represent desorption in c-d). N₂ and CO₂ adsorption-desorption isotherms are also plotted in logarithmic scale (**Figure B.2**).

To explore the chemistry of the B-CN materials and identify if B is incorporated into the structure, I performed XPS, NMR and EPR analyses. Initially, to confirm the successful B functionalisation of my materials and investigate the chemical environment around B atoms, I carried out XPS measurements, focusing on B 1s, C 1s, N 1s and O 1s core level spectra.

Through XPS elemental composition analysis (**Figure 6.3a**), I verify the presence and actual composition of B in my B-CN (B) and B-CN (BA) samples: 0.5-3 at% for B-CN (B) samples, and 3-11 at% for B-CN (BA) samples. I note here that I was aiming for 3, 5 and 10 at% B content using both precursors. By comparing the nominal (*i.e.* expected) vs the actual B concentrations (based on XPS), it appears easier to functionalise and regulate B content using BA, likely due to the chemical affinity between the acid and melamine (basic). Using a higher amount of B as precursor does not result in a linearly higher amount of B content in the final sample, hence the maximum B content for B-CN (B) samples is 3 at%. Overall, the concentration of O atoms seems to follow that of B atoms, up to 5 at%, regardless of the B precursor. This observation could potentially indicate that B is bonded to O upon incorporation – although the disproportional B and O contents in B-CN (11BA) do not necessarily support this theory. I note that, based on my results, O (4 at%) is present as a defect even in pristine CN, therefore O pre-exists in the CN structure. Hence it is possible that B atoms bond to O already present in the CN structure, as well as to ‘new’ ones introduced in the synthesis. From 0.5 to 5 at% of B (and O) I see an analogous decrease in both C and N content. For 11 at% B, there is a larger decrease in the N content than in the C content, and it could indicate a high amount of B functionalisation comes mostly at the expense of N atoms (*i.e.* more N atom vacancies or replacements, than C). The relevant difference between C and N contents remains small though and can be within error. Looking at the B 1s spectra (**Figure 6.3b** and **Figure B.3**), I notice that: i) the main chemical bonding of B atoms is B-O, and ii) the choice of B precursor affects the chemistry. In general, all samples – except B-CN (11BA) – exhibit a main peak at the same binding energy (~192.5 eV) that can be deconvoluted into two peaks (~193 eV and ~192 eV), due to the asymmetry of the peak and the full width at half maximum (FWHM) values (**Table B.1**). I assign the deconvoluted peak at ~192 eV to B-O, while the secondary

deconvoluted peak at ~193 eV could be potentially assigned to B-O-H bonding after comparing to the boric acid spectrum. Both B chemical environments are equally formed in the B-CN (5BA) sample, while the ratio between the two fluctuates for the other samples. In the case of B-CN (11BA), it seems that there is only a single peak at ~192 eV, hence a single B-O coordination. On the other hand, B-CN (B) samples exhibit, other than the main B-O peak (~192.5 eV), a secondary peak at ~187.5 eV assigned to metallic B⁰. The intensity of this secondary peak increases with higher B content (3 at%) but is absent for the B-CN (3BA) sample, with the same B content (3 at%). Therefore, I am confident the secondary peak is not an artifact from B reduction due to high energy X-ray exposure, rather it is caused by agglomeration of (unreacted) B atoms in B-CN (B) samples. B functionalisation does not affect the chemical environments around C and N atoms (**Figure B.4a-b**); however, it does seem to impact the O chemical content. The single O-C (~532.5 eV) bonding in pristine CN changes to deconvoluted O-B (532-533 eV) and O=C (531-531.5 eV) bonds in B-CN samples, regardless of the B precursor (**Figure B.4c**). Combining my XPS elemental composition analysis with the XPS core level spectra, I suggest that in the B-CN materials: i) B is linked to O – and also exists in B clusters in B-CN (B) samples, ii) some O pre-exists in the CN structure by replacing N atoms (O_N) and creating -OH groups, and iii) B atoms do not replace N atoms nor C atoms (not B_C or B_N) and do not form B-N or B-C bonds. These findings are only partly in accordance with literature. The same B 1s peak at ~192 eV has also been reported multiple times in literature, but it was almost always assigned to B-N bonding (B_C substitution), and occasionally to B-C bonding (B_N substitution)^{185,187,261,284,285,288–292}. In all cases in the B-CN literature, this assignment is based on the same assumption that the B 1s peak in B-CN is more electronegative than the B-N core (190 eV) in hBN⁷ and less electronegative than the (B-(N)₃) bond (193 eV) in Kawaguchi's BCN²⁹³. This literature assignment is contradictory to the fact

that B 1s peaks in the range 191.5-193 eV are typically assigned to B-O environment^{63,64,236,294}. Therefore, my observation that B is linked to O (and can also exist in B clusters) and B atoms do not replace N atoms nor C atoms and do not form B-N or B-C bonds differs from what has previously been reported. My work on B-CN (B) materials is in agreement with a study where CN was decorated with elemental boron and the formation of B clusters was suggested²⁹¹. Albeit not many previous reports contain O 1s spectra, there are few which suggest creation of C-O and O-H bonds, thus supporting my claim that O pre-exists in the CN structure, replacing N atoms sites^{189,262,295,296}.

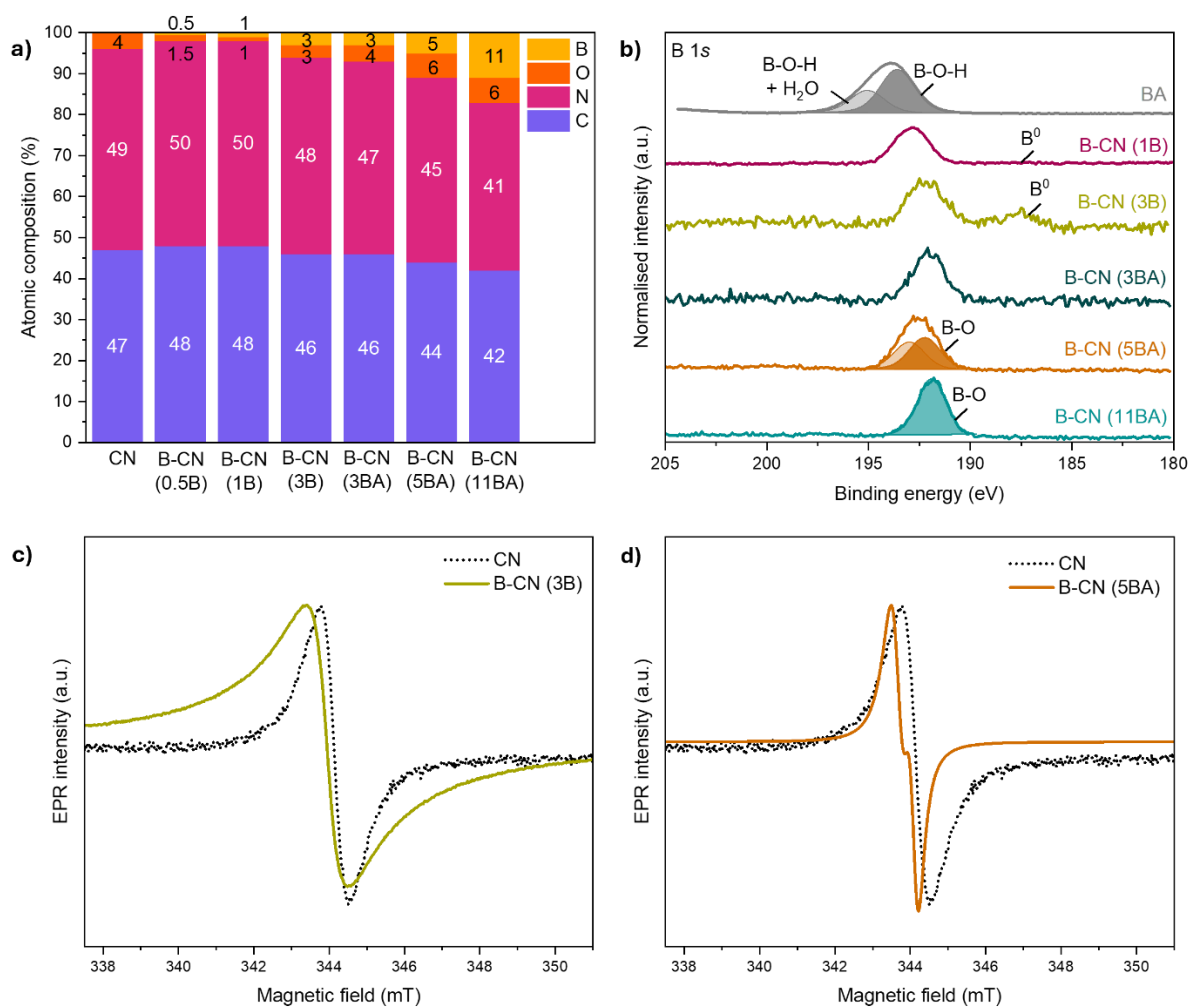


Figure 6. 3. a) Elemental composition of pristine CN and B-CN samples as derived from XPS analyses, b) XPS B 1s spectra of B-CN (1B), B-CN (3B), B-CN (3BA), B-CN (5BA) and B-CN (11BA), c-d) EPR measurements at room temperature in air for B-CN (3B) and B-CN (5BA) respectively.

To provide another level of confidence to my claims, I performed EPR measurements at room temperature in air. The EPR signal in almost all B-CN samples is similar to that of the pristine CN (**Figure B.5a-e**). According to literature²⁹⁷, the EPR signal of CN materials originates from unpaired electrons in the localised π -conjugated structure. In contrast, samples B-CN (3B) and B-CN (5BA) exhibit differences in both the intensity and shape of the EPR signal. B-CN (3B)

shows a broader EPR signal (**Figure 6.3c** and **Figure B.5f**) which could be explained by the agglomeration of B atoms in the structure, in accordance with my XPS results. The reason the rest of the B-CN (B) samples do not show this difference in signal, despite exhibiting the same chemistry, would lie in the concentration of such species: B-CN (3B) has the strongest XPS signal for B⁰, and therefore highest concentration. B-CN (5BA) is the only sample among B-CN (BA) samples to show the formation of a radical in the EPR signal (**Figure 6.3d** and **Figure B.5g**); the creation of a second deconvoluted peak (potentially secondary B-OH bonding) at 193 eV in the B 1s spectrum of B-CN (5BA) (**Figure 6.3b**) could be the cause of the radical formation in the EPR signal. The EPR signal intensity of the B-CN (3B) and B-CN (5BA) samples is also higher than the other samples (B-CN (3B): $\times 3$, B-CN (5BA): $\times 200$) (**Figure B.5h-i**). This could indicate the existence of more defects, hence increasing the concentration of unpaired electrons in the π -conjugated structure of the heptazine rings (which is the source of EPR signal).

To support my suggestions on the chemistry of B-functionalised materials, and to provide yet another level of confidence in the conclusions, my collaborators carried out solid-state NMR measurements. ¹¹B MAS NMR spectra of the B-CN samples are presented along with spectra for boric acid (**Figure 6.4a**) and boron (**Figure 6.4b**). Spectra were also recorded using a spin echo pulse sequence to ensure that no very broad lineshapes⁶⁴ were lost in the conventional MAS NMR spectra and these showed no significant differences. For the B-CN (BA) samples, two sets of signals are seen, corresponding to trigonal (12-19 ppm) and tetrahedral (2 to -4 ppm) boron environments. The relative integrated signal intensities for the two different coordination environments of B show that similar levels of tetrahedral B are seen for the two samples with lower BA content, but that this increases at the highest level of B doping (**Table 6.2**). The presence of significant amounts of tetrahedral B indicates that different types of B

species are present in addition to any substitution into the CN layers as has been suggested in previous works^{262,295}. The signal attributed to trigonal B exhibits a characteristic second-order quadrupolar broadened lineshape⁶⁴, suggesting a much larger quadrupolar coupling constant (C_Q), as would be expected from the lower site symmetry. The signal in this region is similar (although not completely identical, as discussed below) to that seen for boric acid itself, suggesting a similar local structure and the likely presence of B-O (rather than B-N) bonds. In contrast, the signals in the tetrahedral region appear much sharper, as expected given the high local site symmetry, although several overlapping resonances are present.

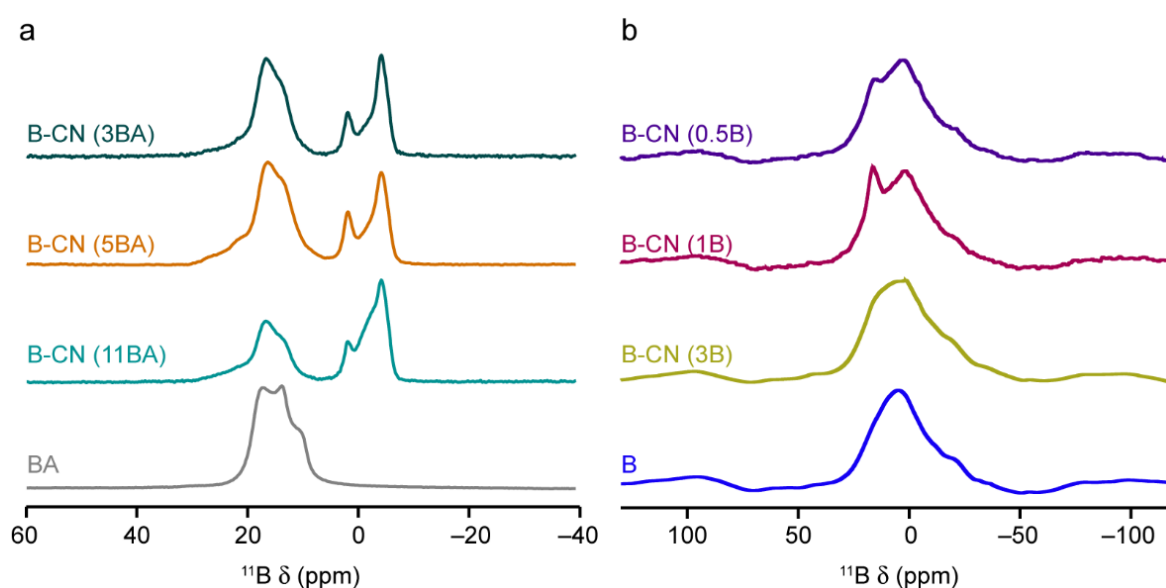


Figure 6. 4. ^{11}B (14.1 T, 14 kHz) MAS NMR spectra of a) B-CN (BA) samples and boric acid, and b) B-CN (B) samples and boron, acquired using a short flip angle.

Table 6. 2. Relative integrated signal intensities for the trigonal and tetrahedral B species in the ^{11}B MAS NMR spectra (acquired with a short flip angle) of the B-CN (BA) samples (**Figure 6.4**). The values in parentheses are the estimated uncertainties.

Sample	Trigonal B (%)	Tetrahedral B (%)
B-CN (3BA)	61 (1)	39 (1)
B-CN (5BA)	65 (1)	35 (1)
B-CN (11BA)	46 (1)	54 (1)

To remove the second-order quadrupolar broadening, ^{11}B MQMAS NMR spectra were acquired (**Figure 6.5**). These spectra confirm the presence of a single type of trigonal B species (although this is broadened by long-range disorder). The signals from tetrahedral B display very little quadrupolar broadening but at least three overlapped signals are present (confirming a range of different B environments exist in these materials). NMR parameters are extracted from the signals seen for B-CN (11BA) and presented alongside those of BN from the literature²⁸² (**Table 6.3**). It is clear that the trigonal B species present in the B-CN (BA) samples is similar to boric acid itself, but has slightly different NMR parameters, including a smaller quadrupolar interaction. However, when compared to the NMR parameters for BN in the literature, this trigonal B species has a much lower δ_{iso} (and so appears at a much lower δ_1 value in the ^{11}B MQMAS NMR spectrum). This is also in good agreement with previous work investigating the formation of porous BN⁶⁴, where BN_3 and BO_3 species were seen at $\delta_1 = 72$ and 45 ppm (14.1 T), respectively. This suggests that the trigonal B species present is more likely to be BO_3 (or perhaps BO_2N) rather than the BN_3 environment that would be expected if all B substituted directly for C in the CN layers.

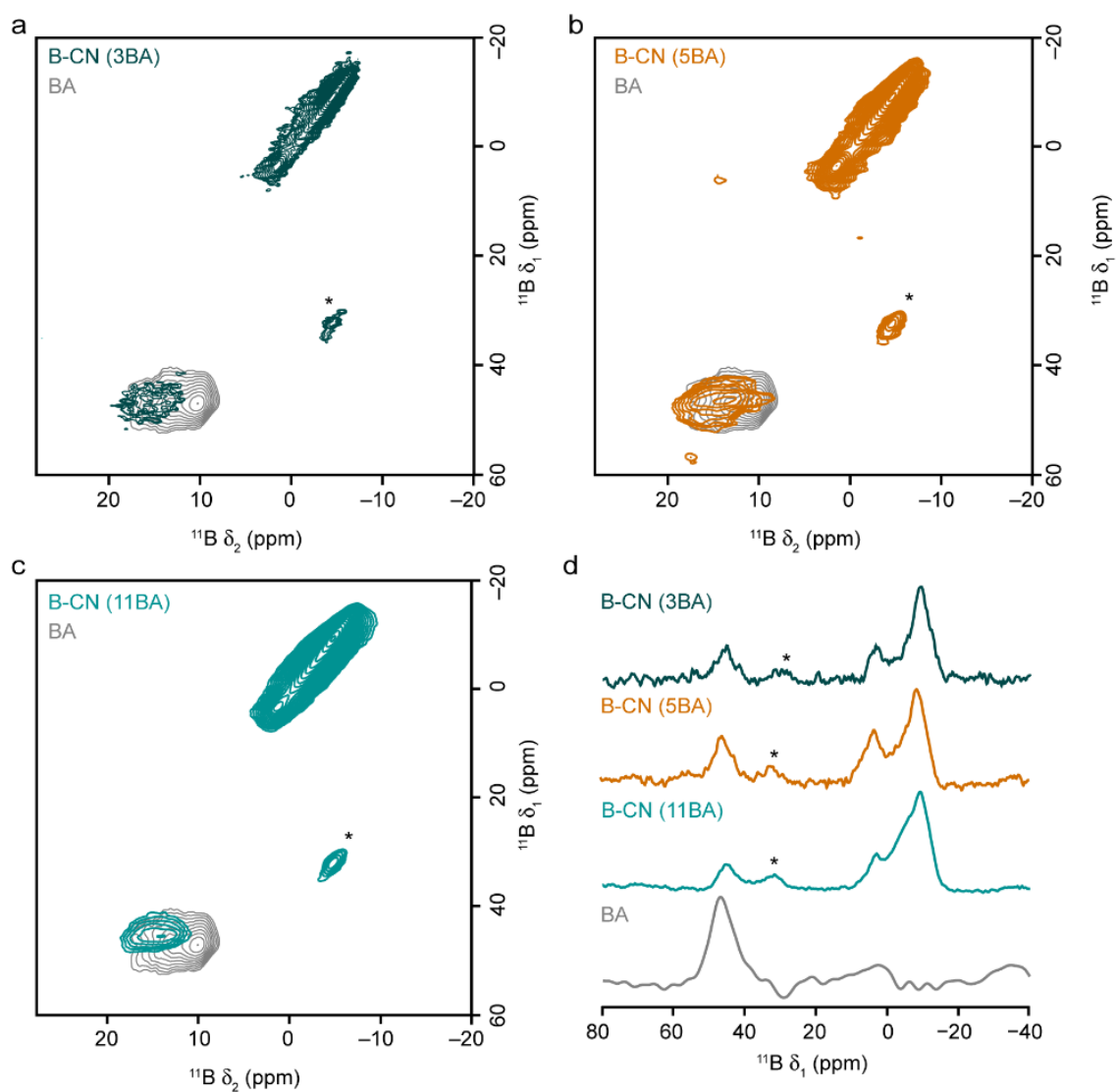


Figure 6. 5. ^{11}B (14.1 T, 14 kHz) MQMAS NMR spectra of B-CN (BA) samples for a) B-CN (3BA), b) B-CN (5BA) and c) B-CN (11BA), each overlaid with the corresponding spectrum for boric acid (BA, shown in grey), with d) corresponding isotropic projections. Spinning sidebands are marked with *.

Table 6. 3. NMR parameters extracted from the ^{11}B (14.1 T) MQMAS NMR spectra of B-CN (11BA) and boric acid (**Figure 6.5c**), along with those from the literature for hexagonal BN. Values in parentheses show the estimated uncertainties.

	δ_1 (ppm)	δ_2 (ppm)	δ_{iso} (ppm)	P_Q (MHz)
B-CN (11BA)	−9.2	−4.6	−4.4 (5)	0.5 (2)
	−5.9	−3.1	−2.9 (5)	0.5 (2)
	3.2	1.4	1.5 (5)	0.3 (2)
	45.0	14.9	18.8 (10)	2.4 (3)
Boric acid	47.0	10.4	17.8 (10)	3.3 (3)
hBN	71.6 ^a	24.7 ^a	30.4	2.9

^a These values are predicted from the NMR parameters in the literature for hexagonal BN²⁸².

The ^{11}B MAS NMR spectra of the B-CN (B) samples (**Figure 6.4b**) appear very different to those for B-CN (BA) samples, containing a broad lineshape that spans the regions where signals for both trigonal and tetrahedral B are seen (**Figure 6.4a**). The spectra shown in **Figure 6.4b** were acquired with a short flip angle to ensure results are quantitative, but only small changes in the spectral lineshapes were seen when spectra were acquired using a spin echo, and with varying recycle intervals. All spectra, however, are similar (though not identical) to that seen for elemental B itself (**Figure 6.4b**) and suggests that the B environment in this set of B-CN samples is similar to that in elemental B, and very different to that in the samples prepared with BA. To understand the origin of the spectral broadening seen (*i.e.* whether this results from a quadrupolar interaction or from a distribution of local environments, and therefore of chemical shifts), ^{11}B MQMAS spectra were acquired for B-CN (3B) and boron (**Figure 6.6**). In both cases, similar spectral lineshapes are seen, confirming the similar nature of the B environments in the two samples. The signals (overlapped even in this two-dimensional spectrum) lie not along an axis parallel to δ_2 , which would suggest the presence of

quadrupolar broadening, but along an axis that confirms a distribution of shifts is present and the intense sidebands also confirms the presence of a significant shielding anisotropy. The ^{11}B MAS NMR spectrum seen for boron agrees with that in previous literature²⁹⁸. In this earlier work, the authors suggested that the broader lineshapes seen result from the defects in the structure (*i.e.* missing B atoms that not only formally lift any equivalencies leading to disorder, but also give rise to changes in the bulk magnetic susceptibility). It is clear, however, that the similarity of the B-CN (B) spectra to that of boron suggest limited substitution of B for C in the CN layers, but the presence of B-like clusters within the material.

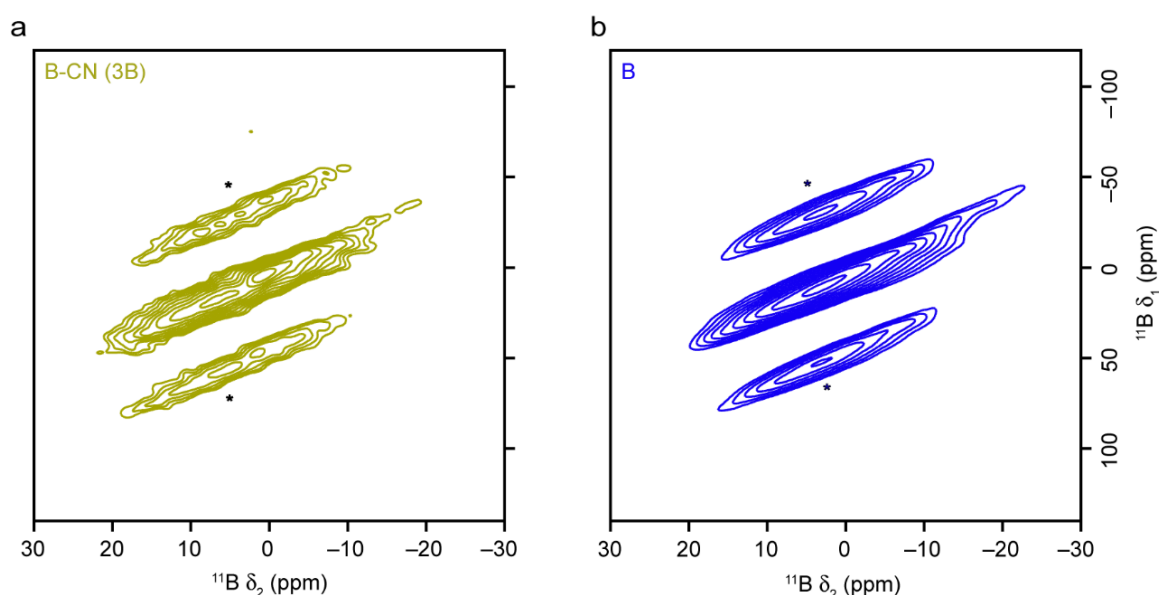


Figure 6. 6. ^{11}B (14.1 T, 14 kHz) MQMAS NMR spectra of a) B-CN (3B) and b) boron. Spinning sidebands are marked with *.

My collaborators measured ^{13}C MAS and CP MAS spectra of the B-CN (BA) and B-CN (BA) samples, along with the corresponding spectra for CN (**Figure 6.7**). The spin echo spectra have fairly poor sensitivity (largely as a result of the slow T_1 relaxation and consequently long recycle intervals that have to be used). However, these spectra, and those acquired using CP

from ^1H , contain two distinct signals (at 165 and 157 ppm). No significant differences are seen in the relative intensities of the two signals with increased B content (at least within the level of the noise for the spin echo spectra), and there are no differences between samples made using BA and B (perhaps with the exception of B-CN (11BA)), despite the very different ^{11}B spectra seen for the two sets of samples. When the similarity of these spectra to that of CN is also considered, it would appear that there is little evidence for any substitution of B into the CN layers for either set of samples, despite this being suggested in previous work where similar spectra were seen^{262,295}. For the unsubstituted CN, the integrated intensities of the two signals have different behaviour as a function of the CP contact time (**Figure B.6**), with that at 165 ppm building up more quickly, suggesting a closer proximity to ^1H (on average). The ^1H MAS NMR spectra are similar for all B-CN samples, irrespective of how they are prepared, and are dominated by a signal at 8.6 ppm, attributed previously to the NH_2 groups on the layer edges (and at defect sites)²⁹⁵ (**Figure B.7**). An additional signal is seen at 3.6 ppm (present at differing levels in each sample, including that of CN). This has been attributed in previous work to water, (or possibly OH groups on the layer edges)²⁹⁵, and varies in both intensity and width with B substitution. However, the low resolution of ^1H spectra at these slower MAS rates prevents a more detailed spectral analysis, and perhaps the most important conclusion is that no significant new environments are apparent with B functionalisation. The disordered and defective nature of CN (*i.e.* even prior to any B integration) makes unambiguous assignment of the NMR signals challenging, and it would appear that there is some confusion over the interpretation of ^{13}C and ^{11}B NMR spectra of B-CN type materials in the previous literature^{262,289,295}. For CN, the two ^{13}C signals seen have been previously assigned as those linked to amino groups (*i.e.* $\text{CN}_2(\text{NH}_x)$, where $x = 1$ or 2) at 165 ppm and those within the CN layers (*i.e.* CN_3) at 157 ppm^{262,289}. Such an assignment is consistent with the CP build-up

behaviour, which suggested that the signal at higher shift was closer to ^1H . Literature results for ^{13}C MAS NMR spectroscopy of melamine show signals at 167.5 and 169.2 ppm resulting from $\text{CN}_2(\text{NH}_2)$ groups, and similar studies of melem show signals at 164.3 and 166.4 for similar species, in addition to two signals at 155.1 and 156.0 from CN_3 groups²⁸¹. However, for the spectrum of CN the ratio of the signals at 165 and 157 ppm is $\sim 53:\sim 47$, suggesting a significant number of $\text{CN}_2(\text{NH}_2)$ groups would have to be present – many more than would be possible if any extended layer structure was present (**Figure 6.7a**).

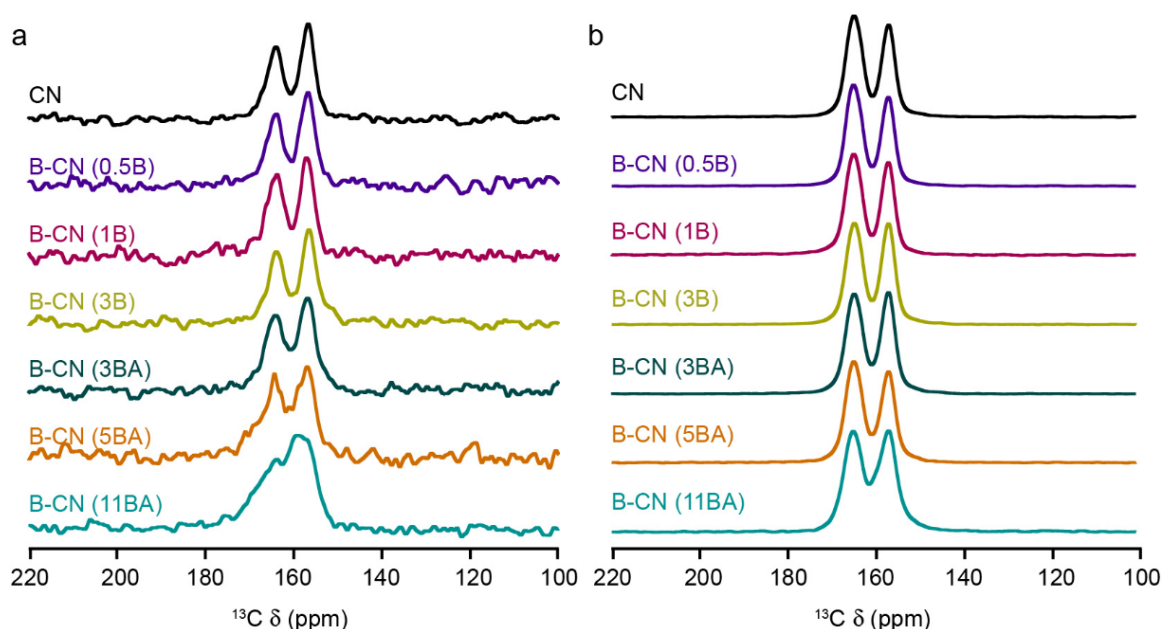


Figure 6. 7. ^{13}C (9.4 T, 14 kHz) MAS NMR spectra of pristine and B-functionalised CN samples acquired using a) a spin echo and b) CP from ^1H .

To gain further insight, my collaborators carried out preliminary DFT calculations for two models of CN: the first being an idealised structure²⁸¹ (**Figure B.8a**) and the second a more disordered material²⁸⁰ (**Figure B.8b**). It is noted that in both cases the layers are fully

connected (*i.e.* no NH₂ groups are present). The predicted ¹³C chemical shifts are given alongside those predicted for the known crystal structure of melem²⁸¹ (**Table B.2**). CN₃(i) is used to distinguish C that are bound only to N within one melem-like subunit (internal), and CN₃(e) for those C that are bound to one N in a different subunit (external). The DFT-predicted shifts for the six distinct C species in melem agree well with the four signals seen in the ¹³C MAS NMR spectrum²⁸¹, predicting overlap of signals resulting from C1/C2 and C5/C6, and confirming the preliminary signal assignment in the earlier work. The shifts calculated for the CN₂(NH₂) groups are similar to the signal at 165 ppm in the experimental spectrum of CN. However, the calculated shifts for the two models of CN also predict two sets of signals will be seen, with different shifts for CN₃(e) and CN₃(i). While the absolute predicted shifts do not exactly match experiment (which is unsurprising given the idealised nature of the models used, in particular the ordered model in **Figure B.8a**), it seems most likely that the signal at 165 ppm in the experimental spectra results from the overlap of signals from both CN₃(e) and CN₂(NH₂) groups (in fact from all CN₂(e) sites whether connected to a second melem-like subunit or an NH₂ group. This also accounts for the different CP build up behaviour seen in **Figure B.6**, but is consistent with an extended layered structure (and the decreased number of CH₂(NH₂) signals this would give).

Additional DFT calculations were carried out to predict the NMR parameters that might be observed if B were substituted within the CN layers. Six models were constructed, with B substituting for each of the 4 distinct C sites in the ordered model of CN (**Figure B.8a**), and protonation of one of the neighbouring NC₂ (*i.e.* not any neighbouring NC₃) atoms. Although this model is less realistic than that for the disordered structure, it was chosen for these preliminary calculations owing to the smaller cell size. The relative energies of the six models are compared (**Table B.3**). Substitution onto the CN₃(e) sites appears more favourable than

onto the CN₃(i) sites, although substitution onto CN₂(e) sites bonded to NH₂ (*i.e.* CN₂(NH₂) sites) is not tested by these idealised models. It should be noted that there is a significant structural change to the CN layers in this ordered model when B is substituted on any site (**Figure 6.8**) for a model where B substitutes for C4 and the neighbouring N5 is protonated. The B substitution results in a significant distortion of the melem-like rings, with distinct puckering and bending observed (and resulting in a structure that is more like that of the disordered model of CN in **Figure B.8b**). **Table B.3** also shows the resulting ¹¹B parameters for the six models of substituted ordered CN. These are similar for substitution onto each of the types of C site, with δ_{iso} values between 24 and 29 ppm and large C_Q values of ~3 MHz (as expected for trigonal B). The effect on the ¹³C δ_{iso} values for ordered CN (shown in red) of B substitution (shown in blue), as well as predicted values for disordered CN (in green) are included (**Figure B.9**). On average a decrease in shift is seen upon B substitution, suggesting peaks in B-CN materials would be broadened and shifted to lower ppm. It is noted that these calculations have been carried out using an idealised model of CN and are, as such, indicative only. Further work, involving larger and more disordered models containing CN₂NH₂ defects, would be required to obtain more than the qualitative insight afforded here. However, the present results are consistent with the suggestion that B substitution into the layers would result in more significant changes in the ¹³C NMR spectra than are seen experimentally (**Figure 6.7**).

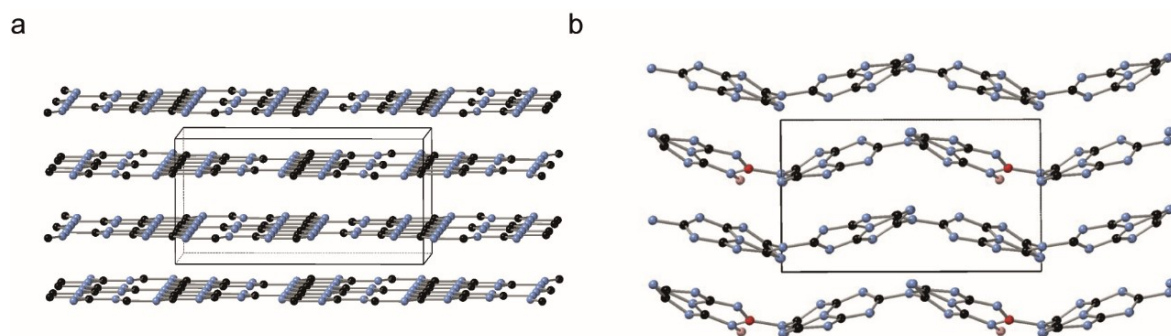


Figure 6. 8. Optimised (using DFT) structural models for a) ordered CN and b) ordered CN with B substituted on one C4 site and protonation of the neighbouring N5. (carbon = black, nitrogen = blue, boron = red, hydrogen = pink).

By combining XPS, EPR, NMR analyses and DFT calculations, I suggest a possible chemical structure for the B-CN (B) samples (**Figure 6.9a**) and B-CN (BA) samples (**Figure 6.9b**). In general, I suggest that: i) -OH groups are formed at the edges of the layers, attached to C atoms, ii) N atoms are protonated forming amine groups (=NH and -NH₂) in basal planes and at the edges, causing a discontinuation of CN structure, and iii) B atoms are integrated via B-O bonds through O_N substitution in basal planes. In addition to these: i) in the B-CN (B) samples, B clusters are present within basal planes causing further discontinuation and defects in the CN structure, and ii) in the B-CN (BA) samples, a secondary B-O environment exists within basal planes, potentially through B-OH bonds, causing further changes to the CN structure.

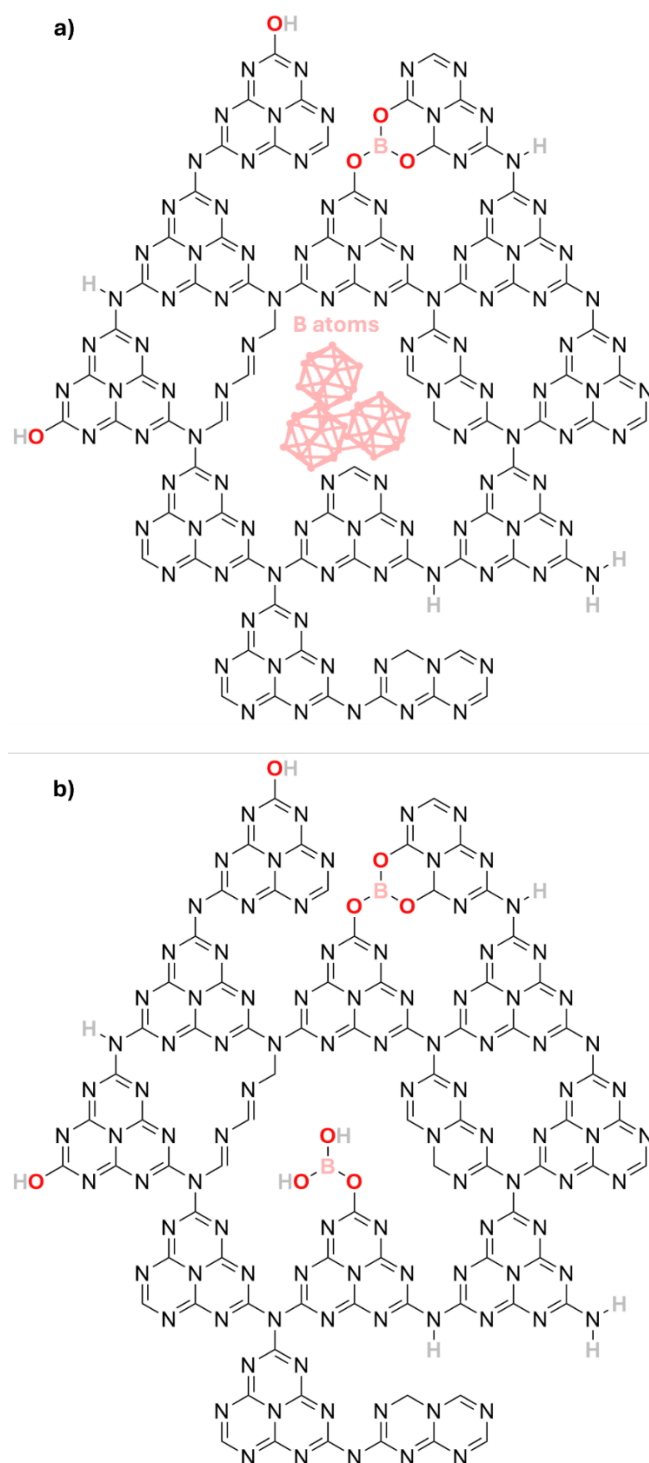


Figure 6. 9. Proposed chemical structure for a) B-CN(B) and b) B-CN(BA) samples, as suggested by XPS, EPR and NMR analyses, and DFT calculations. Included in the structures is the presence of N-H, C-/=O, O-H and V_N defects which are inherent to pristine CN structure, as well as B-O bonding and agglomerated B atoms resulting from B functionalisation.

I used TEM to examine the morphology of the pristine and B-functionalised CN materials (**Figures 6.10a-b**). Surprisingly, all materials show a wide range of morphologies present, including particle clusters, amorphous phases, nanosheets and nanotubes. Samples consist mostly of amorphous clusters, although B-CN materials seem to consist of smaller and more disperse clusters compared to pristine CN. Using EELS, I investigated the homogeneity of B functionalisation at small scale (nm- μ m), and the coordination environment around the B, C and N atoms. I selected the sample B-CN (5BA) for the EELS K-edge measurements as, based on my previous analyses, it shows a diverse B chemical bonding and has a traceable B content (5 at%). During EELS measurements, by scanning different pixels/areas in the same sample, I can see there is inhomogeneity in B functionalisation as B is not found in every particle/particle cluster. Furthermore, in the pixels/areas where B does exist, it exhibits different coordination environments – in accordance with my previous analyses. These different chemical environments appear at 192.8 eV (a), 197 eV (b) and at 199 eV (c) in the B K-edge spectra of B-CN (5BA) (**Figure 6.10c**). I note here that the spectra differ between B-CN (5BA) and boric acid (reference sample). In the B K-edge spectrum of boric acid, a main peak exists at 194 eV (shifted by 1.2 eV compared to B-CN), assigned to B-OH bonding. The appearance of B-O coordination at this energy is consistent with other reports in literature^{51,120,167,237,299}. It could be speculated that the environment around B atoms in B-CN (5BA) may consist of N-B-O coordination, such as BN₂O or BNO₂. The chemical environment around C and N atoms appears consistent between different areas/pixels of CN and B-CN (5BA), and different to the melamine reference sample, indicating that i) the precursor has mostly reacted during synthesis, and ii) the B integration has not significantly affected the core CN structure (**Figures 6.10d-e**). In C K-edge, the main bonding in CN and B-CN (5BA) is N-C=N (288.2 eV), while the B-CN sample may also contain C-O bonds (shown with * in the range

191-192 eV)^{300,301} (**Figure 6.10d**). In N K-edge, the main peaks appearing in CN and B-CN (5BA) are found at 400 eV (N-C=N) and at 403 eV (assigned to either N-(C)₃ or interlayer π - π^* interaction)^{300,301} (**Figure 6.10e**). Overall, I spot i) inhomogeneity of B functionalisation at the nm- μ m scale (B is not found in every particle), and ii) different B chemical bonds, which may point to the formation of N-B-O coordination. The EELS results confirm the existence of different B chemical environments, and consistency around C and N atoms – as observed via the other characterisation techniques. They, however, seem to not necessarily coincide with aspects of the XPS and NMR analyses where there is homogeneity in the bulk phase and a suggested B-O/B-O-H bonding pattern.

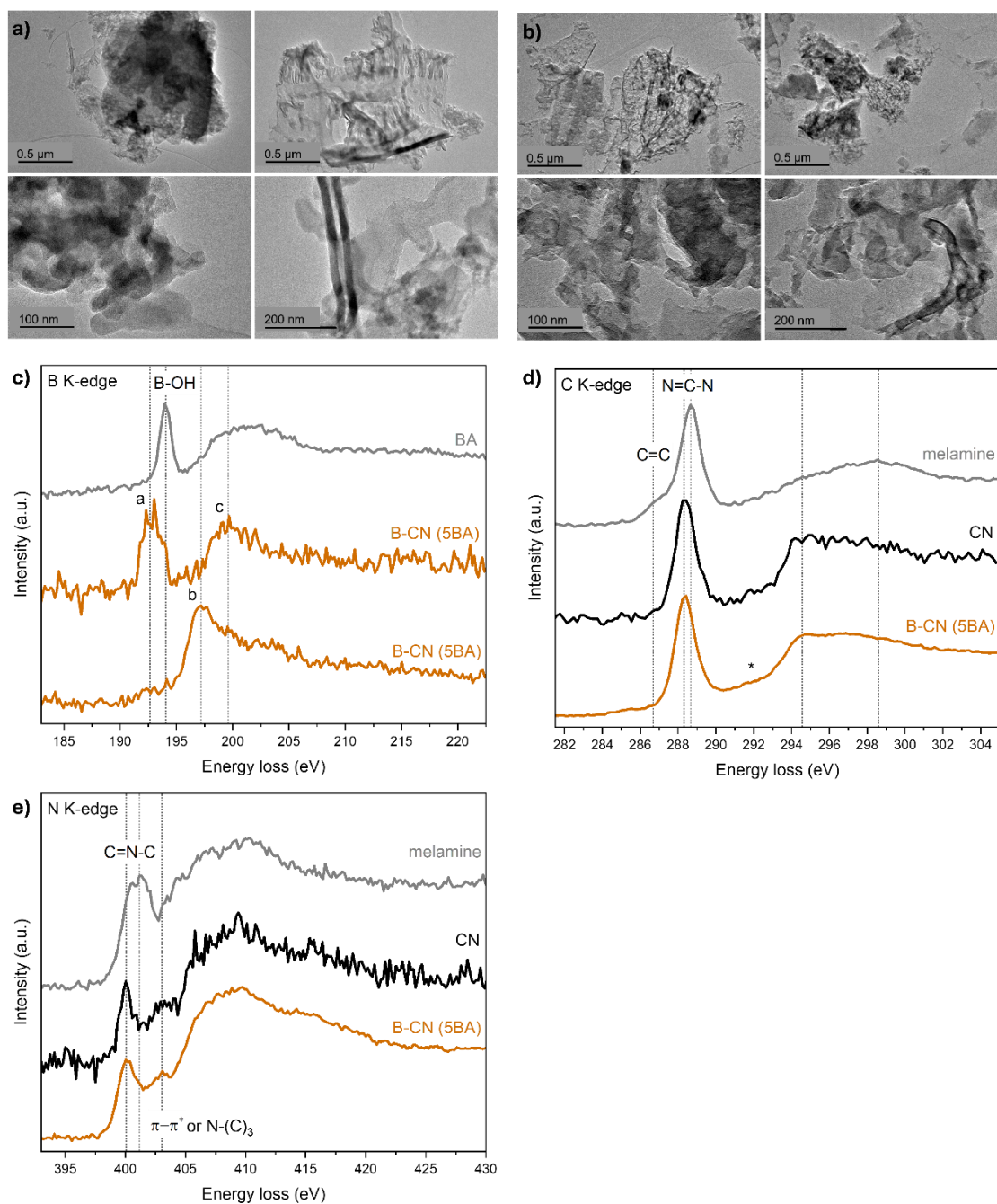


Figure 6. 10. a) TEM images of CN, b) TEM images of B-CN (3B), c) high-loss EELS B K-edge spectra taken from boric acid and from different areas of B-CN (5BA) sample, d) high-loss EELS C K-edge spectra of melamine, CN and B-CN (5BA), and e) high-loss EELS N K-edge spectra of melamine, CN and B-CN (5BA).

6.4.2. CO₂ adsorption

To determine the effect of B functionalisation on the CO₂ adsorption capacity, I measured the CO₂ sorption of the materials at 25 °C and up to 1 bar (**Figure 6.2d**). Almost all samples show minimal CO₂ uptake in these conditions (0.02-0.04 mmol g⁻¹ at 1 bar). The B-CN (11BA) sample (which has the highest B content and porosity) shows an almost tenfold increase in uptake (0.20 mmol g⁻¹ at 1 bar). I attribute the enhanced CO₂ adsorption capacity to the enhanced microporosity of the sample (**Table 6.1**). To examine the CO₂ sorption mechanism, I measured the CO₂ adsorption of my materials at three different temperatures (15, 25 and 35 °C) up to 1 bar (**Figure B.10**). The experimental isotherm data points (**Figure B.10**) are fitted using the dual-site Langmuir (DSL) model, which provides a good fit. For the first time, I calculated the isosteric heat of adsorption over varying CO₂ loading (**Table 6.1** and **Figure B.11**), using the Clausius-Clapeyron equation, by applying the DSL coefficients (**Table B.4**) derived from the experimental CO₂ adsorption data at 15, 25 and 35 °C (**Figure B.10**). The heat of adsorption of the materials (which is an indication of the affinity between the material and CO₂) remains constant with increasing CO₂ loading (uptake) and does not vary significantly with B functionalisation (ranging between 11.4-17.8 kJ mol⁻¹ at zero loading). Hence, the primary CO₂ adsorption mechanism for the majority of my materials is physisorption – although CO₂ could also form localised chemical bonds (chemisorption) with -NH₂ groups in the structure, to a lesser extent, due to the affinity of basic amine groups with acidic CO₂, as suggested in computational studies^{189,203,262}. An increased CO₂ uptake in B-CN materials, compared to pristine CN, has been previously reported in the literature (from 0.04 up to 0.35 mmol g⁻¹ at 25 °C and 1 bar for thermally exfoliated B-CN nanosheets)²⁶². Bulk CN-based materials usually adsorb less CO₂ than their 2D shaped counterparts, however my B-CN (11BA) sample has the

same CO₂ uptake as ultrathin nanoporous B-CN nanosheets, and outperforms other reported bulk and shaped (in nanosheets) B-CN^{189,262}.

6.4.3. Optoelectronic properties

To probe the optoelectronic properties of my materials, I employed several techniques including DRS UV-Vis spectroscopy, XPS valence band and work function measurements, APS, steady-state PL spectroscopy and TAS (**Figure 6.11**). Initially, to examine the effect of B functionalisation on light harvesting, I measured my materials using DRS UV-Vis (**Figure 6.11a**). All materials show similar curves and absorption edge (around 450 nm), and I conclude that B functionalisation does not affect light absorption significantly. However, sample B-CN (3B) exhibits significant absorbance even at higher wavelength compared to the 450 nm absorption onset of CN, potentially due to the agglomeration of B atoms in the structure. Using the Kubelka-Munk function, I converted the DRS UV-Vis data into Tauc plots to determine the indirect allowed bandgap transition²²⁰ (**Figure 6.11b**). By linear regression in the zoomed-in area (edge) of the Tauc plots (**Figure 6.11c**), I identified the bandgaps of the materials in the range 2.6-2.7 eV, which agrees well with previous reports^{187,189,288}. Band edge energies were determined using XPS valence band and work function, and APS measurements. Through XPS valence band analysis (**Figure 6.11d**), I identified the XPS valence band energy of the samples which ranges between 2.2-2.4 eV. I note that these energy levels need to be added to the work functions of the materials (**Figure B.12**) for the calculation of the true valence band position (E_v) vs vacuum (E_{vac}). Therefore, the calculated (from XPS) E_v varies from 5.6 to 6.2 eV. For comparison, I also measured the E_v of the materials using APS (**Figure 6.11e**). APS measurements performed at ambient conditions reveal somewhat deeper

E_V : 6.5 eV for CN, 6.7 eV for B-CN (3B), and 6.8 eV for B-CN (11BA), confirming the trend with B functionalisation. I calculated the band structures of the materials vs E_{vac} (eV), vs normal hydrogen electrode NHE (V) and vs saturated calomel electrode SCE (V), based on the bandgaps, XPS valence band and work function (**Figure 6.11f**). The band edge values align with literature for B-functionalised CN samples^{187,189,288}. Even though B functionalisation does not alter the light absorption (bandgap), it clearly shifts the band edges to deeper energy levels and brings the Fermi level (E_F) closer to the conduction band (E_C), increasing the n-type semiconductor behaviour. While this may be counterintuitive – given the electron deficiency of B compared to C and N –, the n-type behaviour can be justified by the previously suggested chemical features of the materials; my findings indicate an increased concentration of O atoms (electron-abundant compared to C and N) and the creation of B-O bonds, rather than B_C or B_N substitutions. Due to the decrease in conduction band reduction potential, this electronic band structure modification may prove to be problematic for photocatalytic CO_2 reduction, as the CO_2 activation potential (-1.9 V vs NHE) is higher than the conduction band potential of the materials (max -1.5 V vs NHE), especially for the B-CN samples.

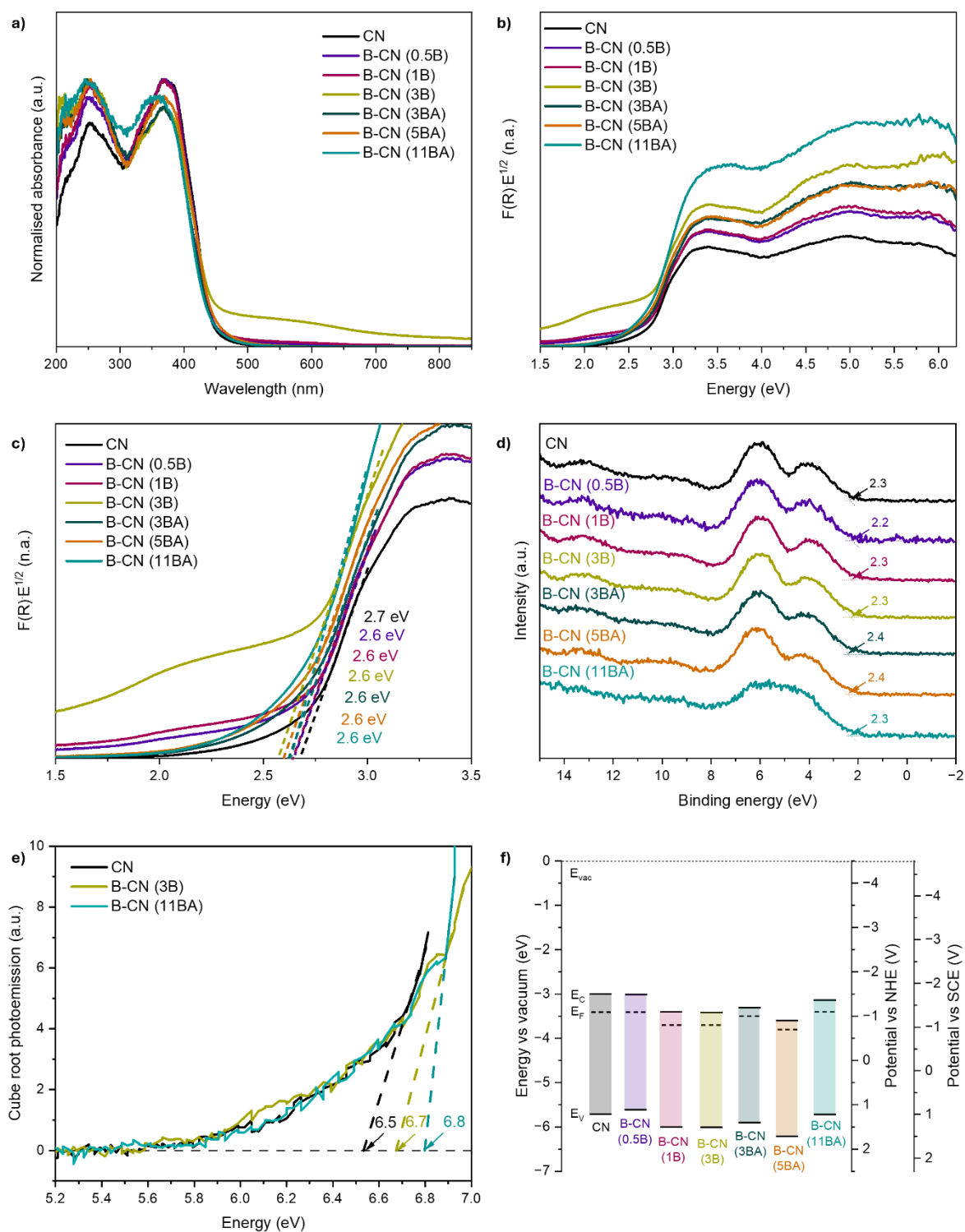


Figure 6. 11. Spectroscopic analyses of the pristine and B-functionalised CN samples to analyse optoelectronic properties: a) normalised DRS UV-Vis spectra, b-c) Tauc plots and zoomed-in area of Tauc plots, d) XPS valence band spectra, e) APS valence band spectra of CN, B-CN (3B) and B-CN (11BA), and f) electronic band structures vs vacuum, vs NHE and vs SCE.

To study the pattern of light emission upon charge carrier recombination, I measured the steady-state PL of selected materials: CN, B-CN (1B), B-CN (5BA) and B-CN (11BA) (**Figure 6.12a**). There is a drop in PL intensity with an increasing amount of B functionalisation, following the trend: CN > B-CN (1B) > B-CN (5BA) > B-CN (11BA). This gradual decrease of PL intensity could indicate: i) a relevant gradual decrease in electron-hole (e^-h^+) radiative recombination rate, hence the reduced light emission, ii) an increased propensity for the non-radiative recombination pathway, or iii) a combination of both i) and ii). Other than the drop in PL intensity, extra peaks are seen at 2.20, 2.39, 2.50, and 2.55 eV with increased B content – especially for B-CN (BA) samples. These extra peaks point to midgap states, which may act as trapping sites for excited electrons usually right below (*i.e.* energetically lower than) the conduction band, or right above (*i.e.* energetically higher than) the valence band. I fitted the experimental steady-state PL data using the Gaussian model²⁵¹ (**Figure B.13**). Using the Gaussian fit, the main PL peak for each material can be deconvoluted into two peaks: one peak corresponding to the bandgap energy (2.6-2.7 eV), and a second one approximately 0.25 eV lower than the bandgap energy (2.34-2.48 eV). Therefore, I suggest the main electron excitation states in my materials are the conduction band (emission E_1 in **Figure 6.12a**), and midgap states ~ 0.25 eV below the conduction band (emission E_2 in **Figure 6.12a**)²⁵¹. It needs to be noted here that the Gaussian model may not be the perfect fit for the PL data, as the emission is often not symmetric Gaussian. Therefore, the validity of my Gaussian analysis is arguable.

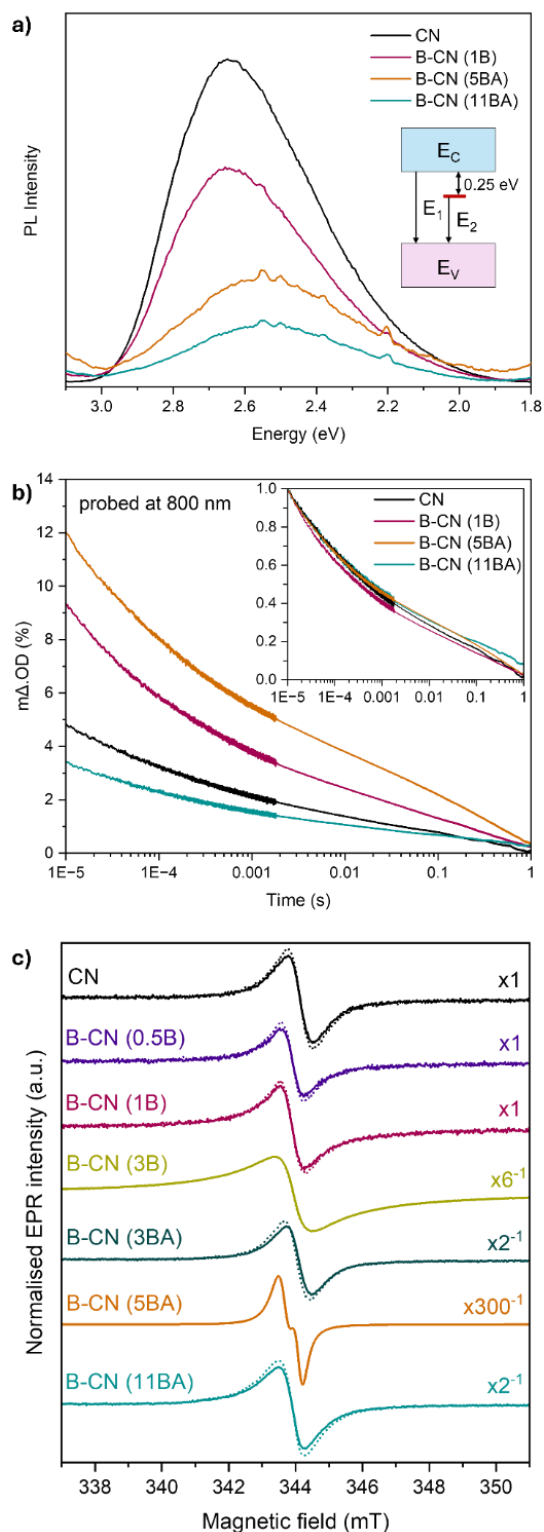


Figure 6. 12. Spectroscopic analyses of the pristine and B-functionalised CN samples to analyse exciton behaviour: a) steady-state PL spectra of CN, B-CN (1B), B-CN (5BA) and B-CN (11BA) samples, with indication of main light emissions in the inset, b) TAS decay profiles of

CN, B-CN (1B), B-CN (5BA) and B-CN (11BA) samples, with normalised profiles displayed in the inset, and c) EPR spectra of pristine and B-functionalised CN materials at room temperature in air, before (solid line) and after (dashed line) irradiation. Multiplication factors used to normalise the spectra to a similar scale are shown in the right side of the plot in c).

To further examine the exciton behaviour in the B-functionalised materials, I carried out, for the first time on B-CN materials, TAS measurements in air using a 355 nm laser source (**Figure 6.12b**). I then compared the results with and without the use of scavengers (TEOA, AgNO_3) (**Figures B.14-B.20**). Overall, the initial amount of charge carriers produced at 10 μs follows the trend: B-CN (5BA) = 12 m Δ .OD > B-CN (1B) $\sim$ 9 m Δ .OD > CN $\sim$ 5 m Δ .OD > B-CN (11BA) $\sim$ 3.5 m Δ .OD. Therefore, at this timescale, increasing B content (up to 5 at%) enhances the concentration of excited species, however this is reversed at higher B content (11 at%). Looking at the normalised TAS decay profiles (inset of **Figure 6.12b**), I do not see significant change in the charge carrier lifetimes upon B functionalisation. The half-times (*i.e.* time at which the initial TAS signal at 10 μs reaches 50% of its initial value) of the materials are: B-CN (11BA) = B-CN (5BA) = 590 μs > CN = 540 μs > B-CN (1B) = 340 μs . The charge carriers are long-lived, and their half-times are longer than some TiO_2 materials ($\sim$ 80 μs), other CN materials ($\sim$ 60-90 μs), and heterojunctions thereof (10-90 μs), probed at the same wavelength (800 nm) with μs -TAS^{247,254,302}. Charge carriers seem to be constantly mobile, and their potential energy changes over time. Hence, I conclude that B functionalisation does not affect significantly the carrier kinetics. The use of TEOA (a hole scavenger) seems to have a different impact on pristine CN and B-functionalised CN samples (**Figure B.20**). In the presence of TEOA, the amount of charge carriers produced by CN is increased, although their lifetimes are not affected, while for B-CN samples the amount of charge carriers is reduced, and their lifetimes

are extended. AgNO₃ (an electron scavenger) does not have the desired effect on any material, as it reduces the amount of charge carriers and does not influence their lifetimes. While I am the first to characterise charge carrier behaviour in B-CN materials using μ s-TAS, also including the effect of scavengers, a similar effect of TEOA and AgNO₃ on the concentration of charge carriers and their lifetimes has been reported previously for pristine CN²⁵¹. Specifically, similar to my case, it has been shown that in pristine CN the initial amplitude of electrons in the μ s scale is increased in the presence of TEOA, and decreased in the presence of AgNO₃, while exciton lifetimes are extended by TEOA presence, and not affected by AgNO₃ presence, respectively.

As an extra level of confirmation for the creation of photoexcited electron carriers in the materials, I performed EPR measurements at room temperature in air, before and after irradiation with a light source. The EPR signal intensity is proportional to the concentration of unpaired electrons in a material. Almost all materials show an increase in EPR signal intensity upon irradiation (**Figure 6.12c**), which can be attributed to the creation of excited electrons. The electrons move from sigma (σ) to pi (π) bonding (source of EPR signal) upon excitation, as suggested in the literature²⁹⁷. Samples B-CN (3B) and B-CN (5BA) are the only materials to not exhibit a difference in EPR signal upon irradiation. Notably, these two samples show major differences in chemistry as shown by the XPS and EPR analyses (described in **Section 6.4.1**) and display the highest EPR signal intensities under no illumination. This feature potentially indicates that the creation of excited electrons upon irradiation is hindered at higher defect concentration (as suggested by the higher unpaired electron concentration in dark conditions).

6.4.4. Photocatalytic CO₂ reduction

A few research groups have performed CO₂ photoreduction and reported superior photocatalytic activity of B-functionalised CN materials compared to the pristine one^{185,187,189,203,261–263}. In most cases, the materials were tested in the gas phase using H₂O as the electron and proton donor, and the main products were CO (up to 40.4 $\mu\text{mol g}^{-1} \text{h}^{-1}$) and CH₄ (up to 2.2 $\mu\text{mol g}^{-1} \text{h}^{-1}$) from reduction of CO₂, and H₂ (up to 4.4 $\mu\text{mol g}^{-1} \text{h}^{-1}$) from the competitive H₂O splitting reaction. In one case, B-CN materials were tested in liquid phase in an aqueous suspension, and the sole gaseous product was CH₄ (up to 42.5 $\mu\text{mol g}^{-1} \text{h}^{-1}$ under visible light)¹⁸⁷. Here, I tested the pristine CN and B-CN (11BA) samples for liquid phase batch CO₂ photoreduction, using H₂O as reactant, and conducted control tests (**Figure 6.13a** and **Figure 6.13c**). The main products in the gaseous phase are CO and H₂ – in accordance with literature. B-CN (11BA) produces similar amount of CO (0.9 $\mu\text{mol g}^{-1} \text{h}^{-1}$) and lower amount of H₂ (4.4 $\mu\text{mol g}^{-1} \text{h}^{-1}$) compared to pristine CN (0.8 $\mu\text{mol CO g}^{-1} \text{h}^{-1}$ and 39.5 $\mu\text{mol H}_2 \text{g}^{-1} \text{h}^{-1}$), therefore showing a higher selectivity to CO (17%) compared to CN (2%). Moreover, I notice CO is also formed in the absence of the catalyst ($\sim 0.014 \mu\text{mol h}^{-1}$) and when using CN with no irradiation ($\sim 0.008 \mu\text{mol h}^{-1}$). The CO production from these control tests accounts for > 80% of the CO production measured when using CN under normal reaction conditions (0.026 $\mu\text{mol h}^{-1}$). The limited activity of the B-CN compounds studied herein may be due to their optoelectronic properties, most specifically their deeper conduction band edge (**Figure 6.11f**). In addition, the availability of CO₂ molecules in an aqueous suspension (such as in my case) is a limiting factor to the reaction, as CO₂ solubility in pure H₂O in ambient pressure and temperature is minimal.

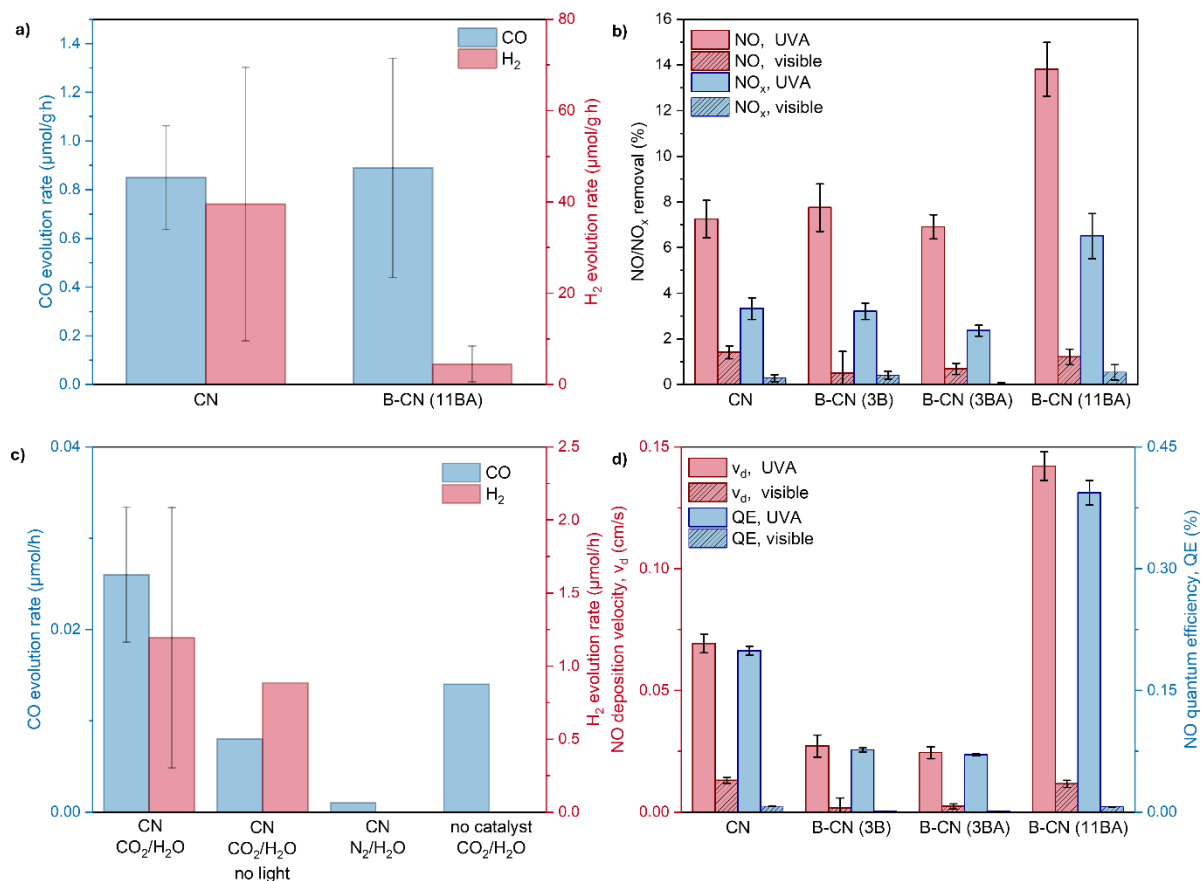


Figure 6. 13. Photocatalytic CO₂ reduction and NO_x removal results: CO and H₂ product evolution rates for a) pristine CN and B-CN (11BA) samples after 5 h liquid phase reaction under CO₂/H₂O, and c) pristine CN sample after 5 h liquid phase reaction under CO₂/H₂O + control tests (under CO₂/H₂O without irradiation, under N₂/H₂O, no catalyst under CO₂/H₂O). The left axis is scaled and assigned to CO evolution rate, while the right axis is scaled and assigned to H₂ evolution rate. b) NO/NO_x removal rates, and d) NO deposition velocities/quantum efficiencies for samples CN, B-CN (3B), B-CN (3BA) and B-CN (11BA). In d) the left axis is scaled and assigned to NO deposition velocity, while the right axis is scaled and assigned to NO quantum efficiency. The error bars in a-d) represent 95% confidence intervals.

6.4.5. Photocatalytic NO_x removal

Another light-assisted reaction of interest is photocatalytic NO_x (including NO/NO₂) removal, owing to its role in combating environmental pollution and lingering public health issues. In this reaction, the aim is to achieve high NO removal from the inlet air stream, whilst limiting conversion of NO to toxic NO₂ (*i.e.* low NO₂ selectivity) thus favouring conversion to non-toxic NO₃⁻ ³⁰³. I tested the CN, B-CN (3B), B-CN (3BA) and B-CN (11BA) materials for photocatalytic NO_x reduction according to the ISO BS 22197-1:2016 protocol, to investigate the effects of B functionalisation, choice of B precursor and B content (**Figure 6.13b** and **Figure 6.13d**). Almost all materials show similar NO removal rates (**Figure 6.13b**) under UVA light (6.9-7.8 %), except B-CN (11BA) whose removal rate is twice that of pristine CN and other B-CN samples (13.8 %). The removal of NO under visible light is minimal (<2 %) for all materials, with CN and B-CN (11BA) showing the best performance (1.4 and 1.2 %, respectively). As I mentioned, NO can be converted into NO₂ (undesired) and NO₃⁻ (desired). NO_x removal refers to the removal of both NO and produced NO₂ and is a direct measure of the efficiency of a photocatalyst, and an indirect measure of the selectivity to NO₂. Total NO_x removal under UVA light follows the trend: B-CN (11BA) (6.5 %) > CN (3.3 %) > B-CN (3B) (3.2 %) > B-CN (3BA) (2.4 %), while it is nominal under visible light with B-CN (11BA) showing the highest performance (0.5 %). NO₂ selectivity under UVA light follows the trend: B-CN (3BA) (64.9 %) > CN (53.0 %) > B-CN (11BA) (51.7 %) > B-CN (3B) (26.2 %). I also calculated the NO deposition velocity and quantum efficiency for my materials (**Figure 6.13d**). The NO deposition velocity/quantum efficiency under UVA light follow the same trend, where B-CN (11BA) (0.14 cm s⁻¹/0.39 %) > CN (0.07 cm s⁻¹/0.20 %) > B-CN (3B) (0.03 cm s⁻¹/0.08 %) > B-CN (3BA) (0.02 cm s⁻¹/0.07 %). To my knowledge, the use of B-functionalised CN materials has been studied twice before for photocatalytic NO_x removal^{261,264}. Wang et al. compared the NO removal and NO₂ selectivity

rates over bulk C_3N_4 , C_3N_4 hollow nanotubes and B-doped C_3N_4 hollow nanotubes with different B contents (although the B content is not specified). They reported enhanced NO removal (25-30 %) and low NO_2 selectivity (24-49 %) of B-CN nanotubes compared to pristine CN (nanotubes and bulk) under visible light irradiation. They also suggest a potential mechanism, where NO_x is primarily converted to NO_3^- through: i) a one-step reaction with photogenerated holes, and ii) a two-step reaction of O_2 with photogenerated electrons to form $^{\bullet}O_2^-$ that then reacts with NO to form NO_3^- ²⁶⁴. Jin et al. also present higher NO removal under visible light irradiation (25-26 %) for the B-doped samples²⁶¹. Overall, my selectivity rates are in accordance with literature, although my NO removal rates are lower than those reported for visible light activity. I note that the experimental conditions, sample morphology and B content are not the same in the two cases, and therefore a direct comparison is difficult. I can summarise that the choice of B precursor does not play an important role, however B-functionalisation at a high B content (11 at%) enhances the photocatalytic NO_x removal and efficiency. Based on literature, 1D CN-based structures (such as nanotubes) may be more promising candidates for this reaction than bulk form, however I encourage more extensive research be done in this field based on my findings on the influence of B content.

6.5. Conclusions

In this Chapter, I have successfully achieved **Objective 2**, and unravelled the influence of i) B functionalisation, ii) B content, and iii) choice of B dopant on the physicochemical, morphological, sorptive and optoelectronic properties of bulk CN, and explored the relationship between such properties and photoactivity through advanced characterisation. More specifically, I produced two sets of B-functionalised CN samples with varying B content

(0.5 – 11 at%), using two B precursors: amorphous boron or boric acid. Based on the nominal vs actual B content, I found that the amount of functionalisation is better controlled using boric acid, owing to its greater reactivity with melamine. I propose that B is integrated in the CN structure through B-O bonds – contrary to current reports in the literature claiming B_c substitution –, and additionally in B clusters when using elemental boron as precursor. Although I have shown homogeneity of B functionalisation at the bulk level, heterogeneities in both morphology and elemental dispersion occur in the nm to μm scale. High B content results in increased surface area and enhanced CO₂ adsorption, and B functionalisation lowers the band edges, without changing the bandgap of the material. All materials show a similar tri-s-triazine structure and light absorbance, however they exhibit different relaxation patterns and creation of mid-gap states. Charge carrier lifetime and decay behaviour was not significantly affected with B content, however, the concentration of charge carriers seen maximises at 5 at%. I notice differences in the concentration of unpaired electrons, which could be linked to the chemical structure changes caused by B integration from different precursors. Most materials show a change in EPR signal intensity before and after irradiation, an indication of excited electrons. I have also tested my materials for CO₂ photoreduction and photocatalytic NO_x removal and discovered that B functionalisation alone is not enough to make bulk CN an efficient standalone photocatalyst.

The scope of this study was the investigation of fundamentals, rather than optimisation. Building on this work, a way forward to test these materials in more favourable conditions would be to synthesise CN-based heterojunctions or add cocatalysts to overcome the CO₂ activation barrier, and use H₂O-CH₃OH or H₂O-TEOA solutions for the CO₂ saturation. It has been previously suggested in the literature that the enhanced CO₂ photoreduction activity of B-CN materials is due to their i) extended visible light absorption, ii) better charge carrier

separation and limited recombination rates, or iii) higher surface area and CO₂ uptake, compared to pristine CN. However, my findings and data do not support these claims. Overall, I encourage further research in the field, especially in the use of B-CN as part of heterojunction systems, where each redox half-reaction of the photocatalytic process can be driven by each component whilst improving charge carrier separation, or use alongside cocatalysts, where the kinetics of photocatalytic processes can be increased relative to the intrinsic recombination rate in B-CN.

6.6. Supporting information

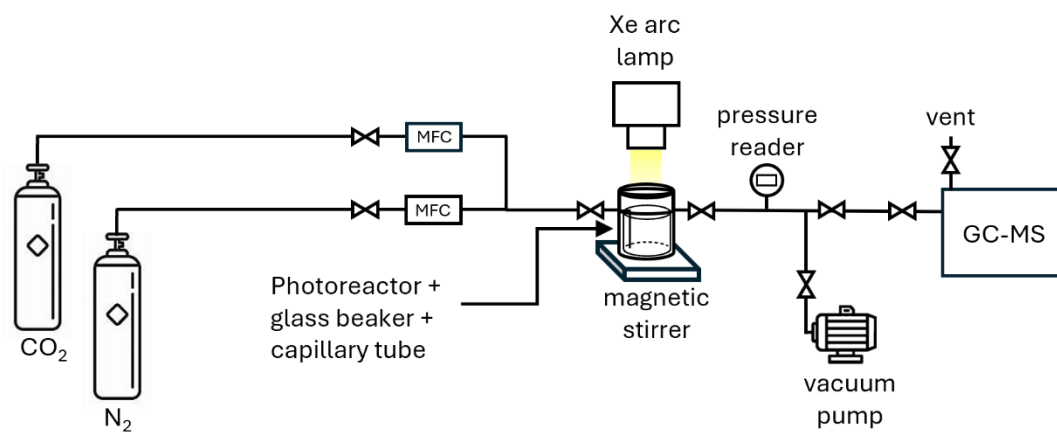


Figure B. 1. Schematics of the photocatalytic set-up used for CO₂ photoreduction tests in liquid phase.

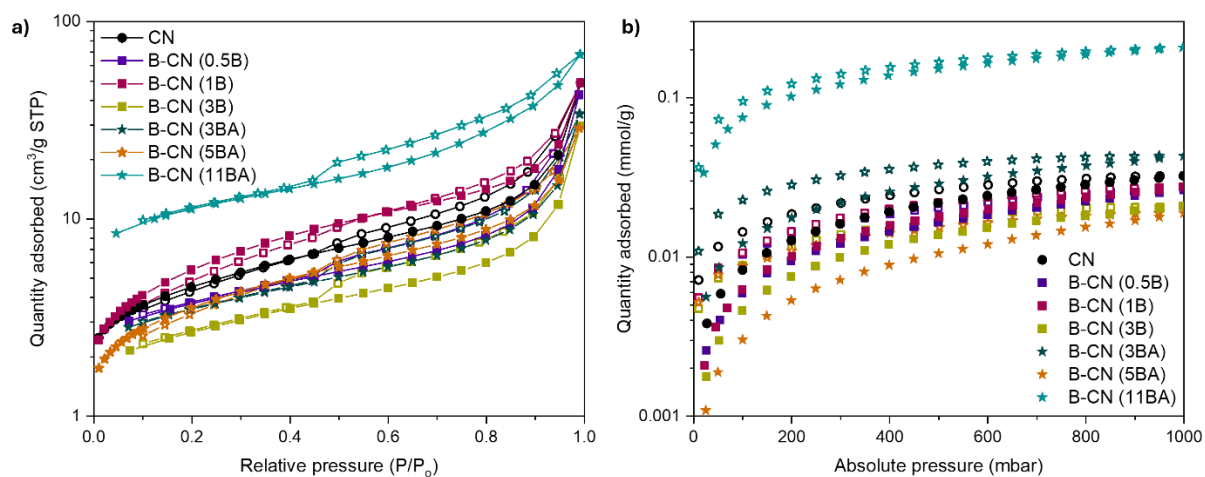


Figure B. 2. a) N₂ adsorption-desorption isotherms (-196 °C), and b) CO₂ adsorption-desorption isotherms (25 °C) of pristine and B-functionalised CN samples, in logarithmic scale (y-axis). Filled symbols represent adsorption, and hollow symbols represent desorption.

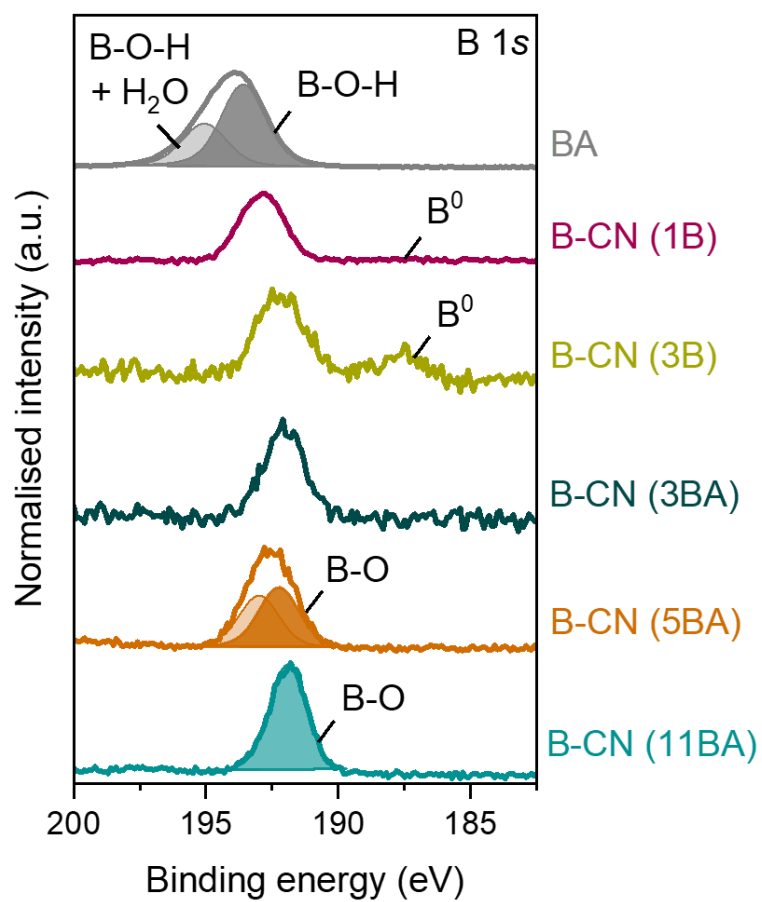


Figure B. 3. Enlarged XPS B 1s spectra of B-CN (1B), B-CN (3B), B-CN (3BA), B-CN (5BA) and B-CN (11BA).

Table B. 1. Full width at half maximum (FWHM) values of C 1s, N 1s, B 1s and O 1s fitted peaks of B-CN (11BA) sample, before and after fitting a secondary deconvoluted B peak.

	Spectrum	Fitted peak	FWHM (eV)
	C 1s	C-C	1.5
		C-N, C-O	1.5
		N-C=N, C=O	1.2
	N 1s	C-N=C	1.2
		N-(C) ₃	1.3
		N-H	1.3
	O 1s	O=C	1.7
		O-B	1.9
Before	B 1s	B-O	2.0
After	B 1s	B-O	1.8
		B-O-H (?)	1.8

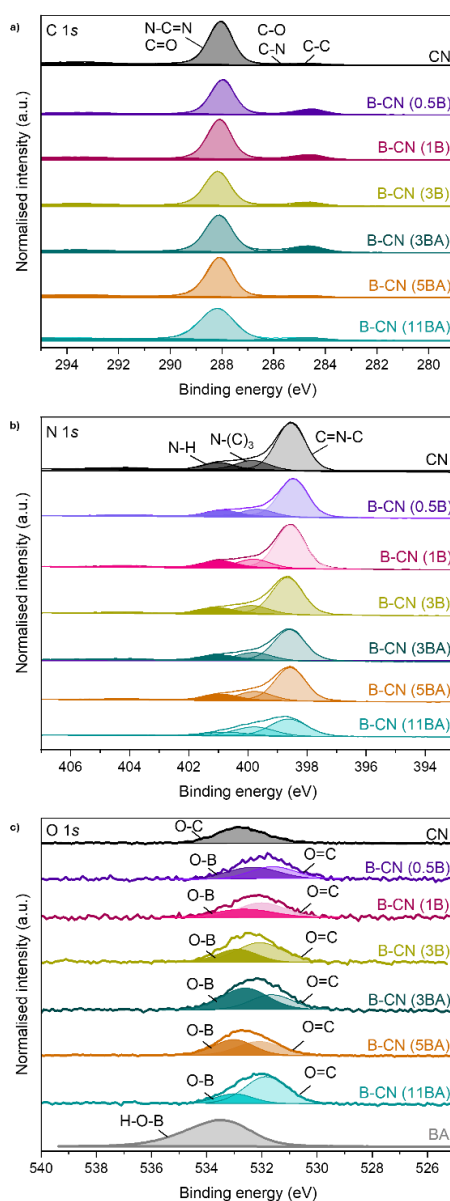


Figure B. 4. a) C 1s, b) N 1s, and c) O 1s XPS spectra of pristine CN and B-functionalised CN samples. The main bonds appearing in the C 1s spectra are similar between pristine and doped CN samples: N-C=N (~288 eV), C-N (~286 eV), and C-C (284.8 eV). The main bonds appearing in the N 1s spectra are also similar between pristine and doped CN samples: N-H (~401 eV), N-(C)₃ (~400 eV), and C=N-C (~398.5 eV). O 1s spectra change with the introduction of B-doping. The main O-C (~533 eV) peak in pristine CN shifts to a lower energy (~532 eV) for B-CN samples, which can be deconvoluted into two peaks: O-B (532.5-533 eV) and O=C (531.5-531.8 eV).

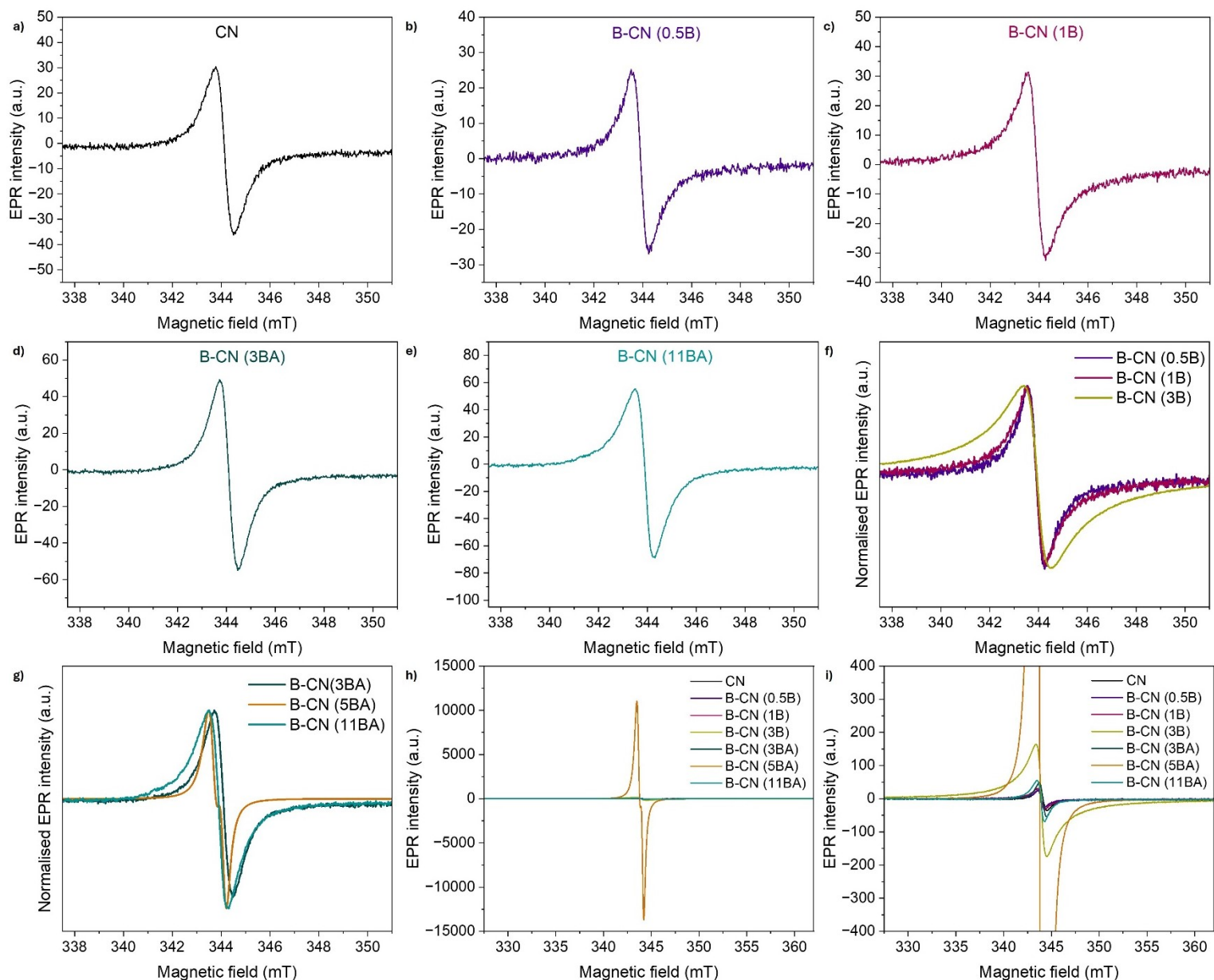


Figure B. 5. EPR measurements at room temperature in air of a) CN, b) B-CN (0.5B), c) B-CN (1B), d) B-CN (3BA), e) B-CN (11BA), f) B-CN (B) samples (normalised), g) B-CN (BA) samples (normalised), h) pristine CN and B-CN samples on the same scale, and i) zoomed-in pristine CN and B-CN samples on the same scale.

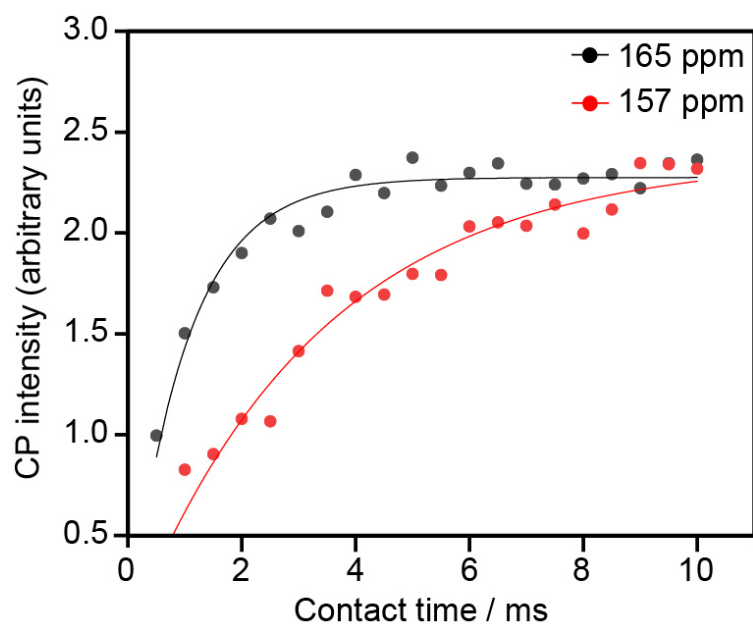


Figure B. 6. Plot showing the variation in the intensity of the two signals in the ^{13}C CP MAS NMR spectrum of CN as a function of contact time.

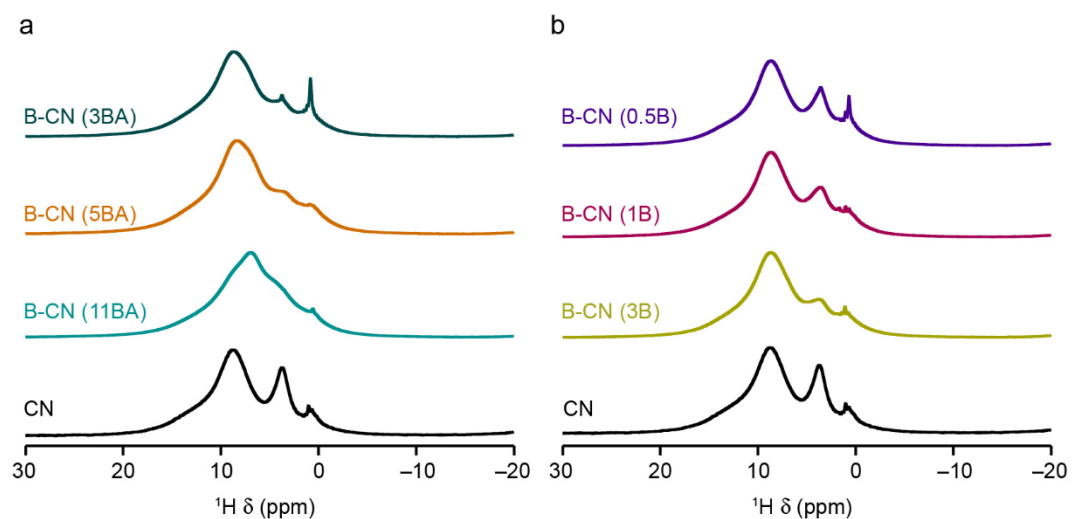


Figure B. 7. ^1H (9.4 T, 14 kHz) MAS NMR spectra acquired using DEPTH background suppression for pristine CN and a) B-CN (BA), and b) B-CN (B) samples.

Table B. 2. ^{13}C NMR parameters predicted using DFT for the two idealised models of CN shown in **Figure 6.8a** and melem.

Ordered CN			Disordered CN		Melem ($\text{C}_6\text{N}_7(\text{NH}_2)_3$)	
Species	Type	δ_{iso} (ppm)	Type	δ_{iso} (ppm)	Type	δ_{iso} (ppm)
C1	$\text{CN}_3(\text{e})$	178.9	$\text{CN}_3(\text{i})$	158.2	$\text{CN}_3(\text{i})$	156.7
C2	$\text{CN}_3(\text{i})$	161.6	$\text{CN}_3(\text{i})$	162.4	$\text{CN}_3(\text{i})$	157.4
C3	$\text{CN}_3(\text{i})$	162.4	$\text{CN}_3(\text{e})$	172.0	$\text{CN}_3(\text{i})$	155.9
C4	$\text{CN}_3(\text{e})$	178.4	$\text{CN}_3(\text{e})$	172.6	$\text{CN}_2(\text{NH}_2)$	167.2
C5			$\text{CN}_3(\text{i})$	161.4	$\text{CN}_2(\text{NH}_2)$	164.2
C6			$\text{CN}_3(\text{e})$	171.8	$\text{CN}_2(\text{NH}_2)$	164.7

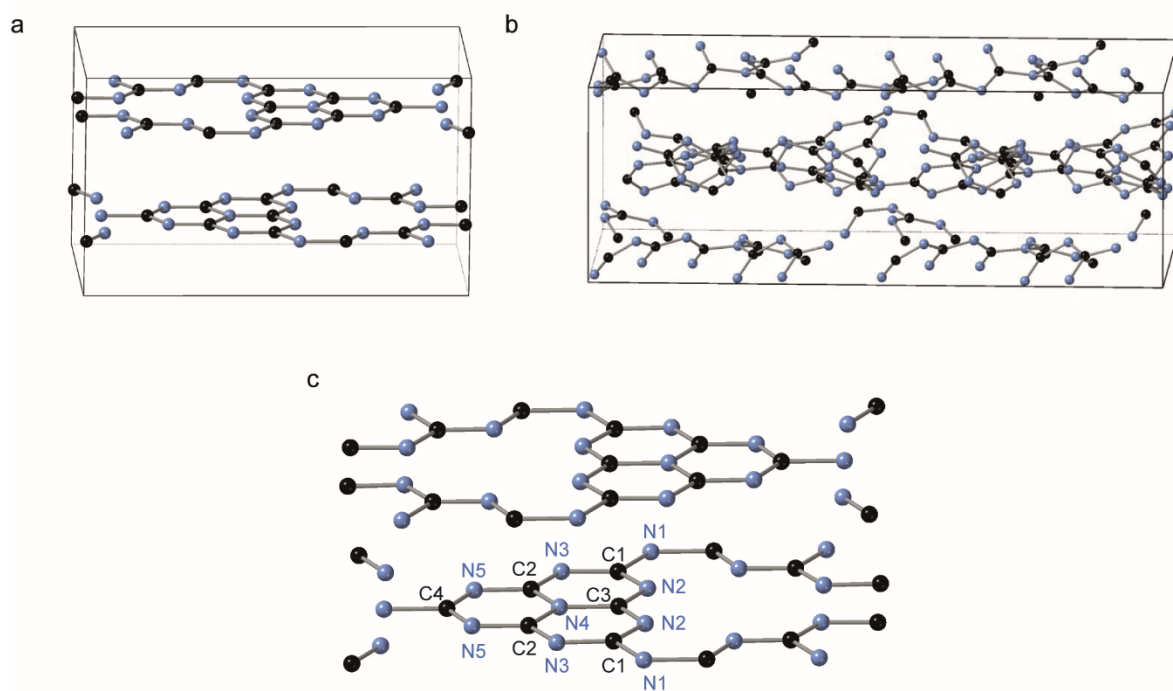


Figure B. 8. a) Ordered and b) disordered structural models of CN used for DFT calculations.

Note there are no NH_2 groups in these idealised models. c) Numbering scheme used in the DFT calculations for the structural model in a). (carbon = black, nitrogen = blue).

Table B. 3. Relative energies and ^{11}B NMR parameters from DFT calculations of six models of ordered CN shown in **Figure B.8a** with B functionalisation.

C site substituted for B	N site protonated	$\Delta\Delta E$ / eV	^{11}B NMR parameters		
			δ_{iso} (ppm)	C_Q / MHz	η_Q
1	2	0.0885	28.9	3.14	0.41
1	3	0.8140	27.8	3.17	0.38
2	3	1.2823	24.8	2.91	0.62
2	5	0.3669	28.0	3.01	0.54
3	2	0.4776	28.0	3.02	0.55
4	5	0.0000	27.7	2.96	0.48

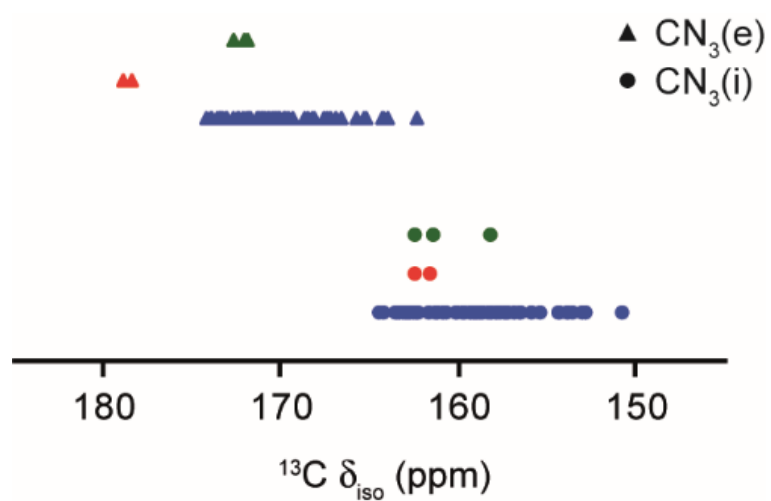


Figure B. 9. Calculated $^{13}\text{C } \delta_{\text{iso}}$ from ordered (red) and disordered (green) models CN, and for B-substituted ordered CN (blue). Carbons in $\text{CN}_3(\text{e})$ environments are denoted with triangles and those in $\text{CN}_3(\text{i})$ environments with circles.

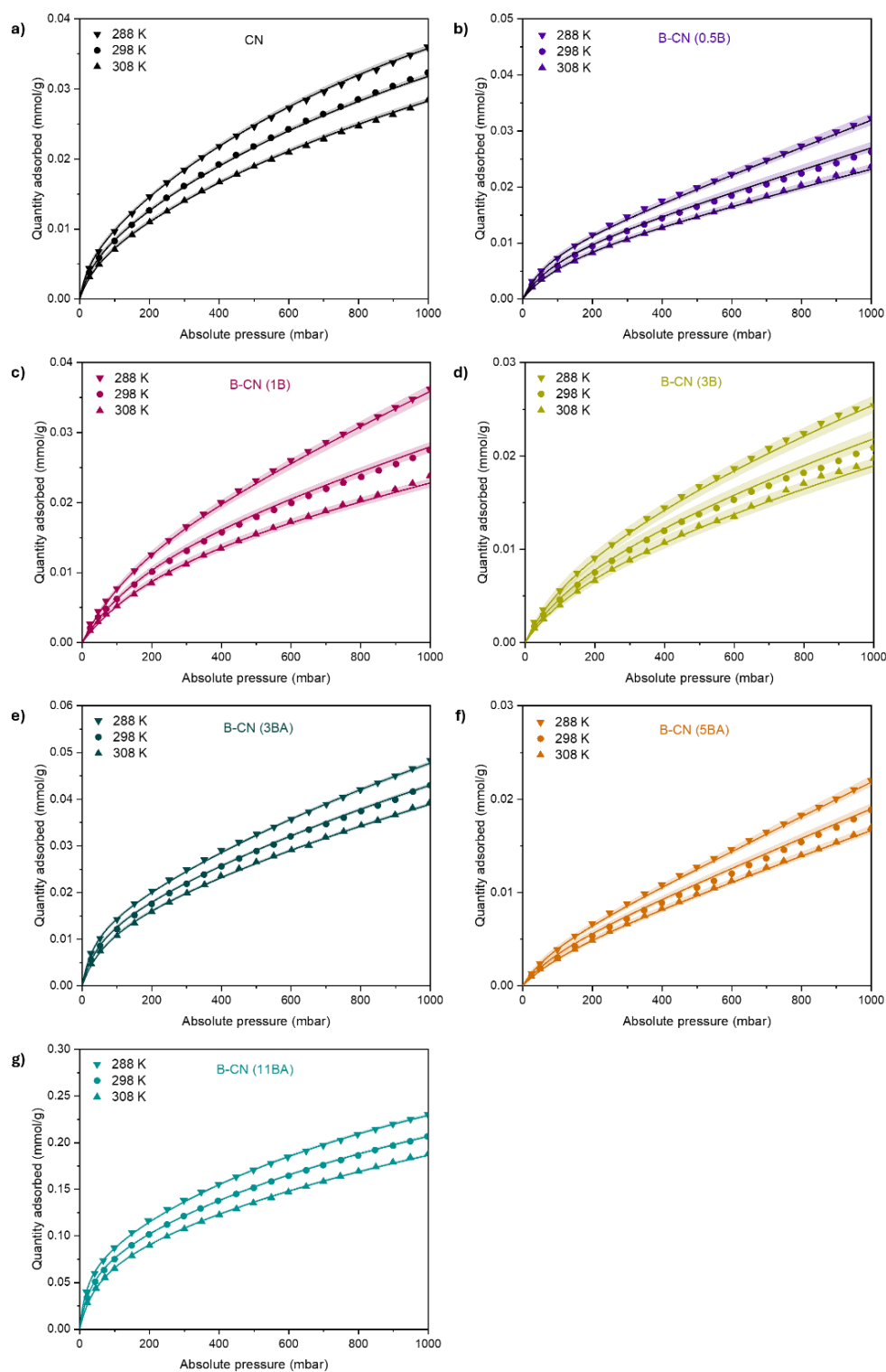


Figure B. 10. CO₂ adsorption isotherms measured at 15, 25 and 35 °C of a) CN, b) B-CN (0.5B), c) B-CN (1B), d) B-CN (3B), e) B-CN (3BA), f) B-CN (5BA), and g) B-CN (11BA) samples. Symbols represent data points, solid lines represent dual-site Langmuir (DSL) fitting, and shading represents confidence bounds.

Table B. 4. Dual-site Langmuir (DSL) coefficients, as derived from fitting experimental CO₂ adsorption data for pristine and B-doped CN materials (**Figure B.10**). Uncertainty values are presented in parentheses.

DSL coefficient	CN	B-CN (0.5B)	B-CN (1B)	B-CN (3B)	B-CN (3BA)	B-CN (5BA)	B-CN (11BA)
q_{sb} (mol kg ⁻¹)	0.07 (4.03·10 ⁻⁴)	8.91·10 ⁻³ (2.12·10 ⁻⁴)	0.02 (2.80·10 ⁻⁴)	7.78·10 ⁻³ (2.74·10 ⁻⁴)	0.15 (9.74·10 ⁻⁴)	3.98·10 ⁻³ (1.52·10 ⁻⁴)	0.07 (4.74·10 ⁻⁴)
q_{sd} (mol kg ⁻¹)	6.57·10 ⁻³ (1.07·10 ⁻⁴)	31.10 (0.46)	4.98 (0.10)	0.10 (2.16·10 ⁻³)	0.01 (1.44·10 ⁻⁴)	44.06 (0.56)	0.36 (1.77·10 ⁻³)
b_0 (bar ⁻¹)	6.80·10 ⁻⁴ (5.44·10 ⁻⁶)	1.22·10 ⁻³ (1.35·10 ⁻⁴)	0.03 (1.50·10 ⁻³)	0.06 (8.58·10 ⁻³)	1.48·10 ⁻³ (1.17·10 ⁻⁵)	9.97·10 ⁻⁴ (1.67·10 ⁻⁴)	7.56·10 ⁻⁵ (3.63·10 ⁻⁶)
d_0 (bar ⁻¹)	9.74·10 ⁻⁴ (1.15·10 ⁻⁴)	9.80·10 ⁻⁷ (1.45·10 ⁻⁸)	2.50·10 ⁻⁸ (5.00·10 ⁻¹⁰)	1.35·10 ⁻⁴ (3.24·10 ⁻⁶)	4.08·10 ⁻⁴ (2.88·10 ⁻⁵)	3.07·10 ⁻⁶ (3.88·10 ⁻⁸)	4.53·10 ⁻⁴ (3.15·10 ⁻⁶)
$-\Delta U_b$ (kJ mol ⁻¹)	16.65 (19.80)	22.26 (277.67)	12.37 (132.57)	11.40 (336.89)	12.78 (19.47)	22.43 (418.45)	31.98 (120.15)
$-\Delta U_d$ (kJ mol ⁻¹)	25.07 (295.77)	15.94 (36.49)	29.00 (49.07)	17.73 (59.08)	26.68 (176.08)	11.74 (31.32)	17.78 (17.21)

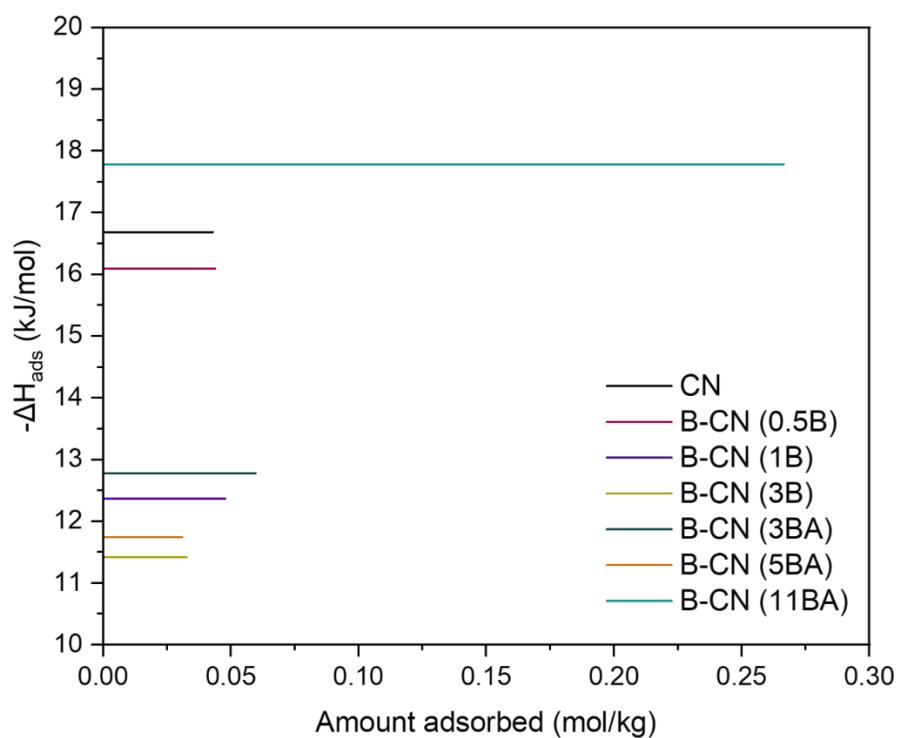


Figure B. 11. Isosteric heat of adsorption plotted against CO₂ loading for pristine and B-functionalised CN materials. Heat of adsorption was calculated by applying the DSL coefficients (**Table B.4**) on the Clausius-Clapeyron equation.

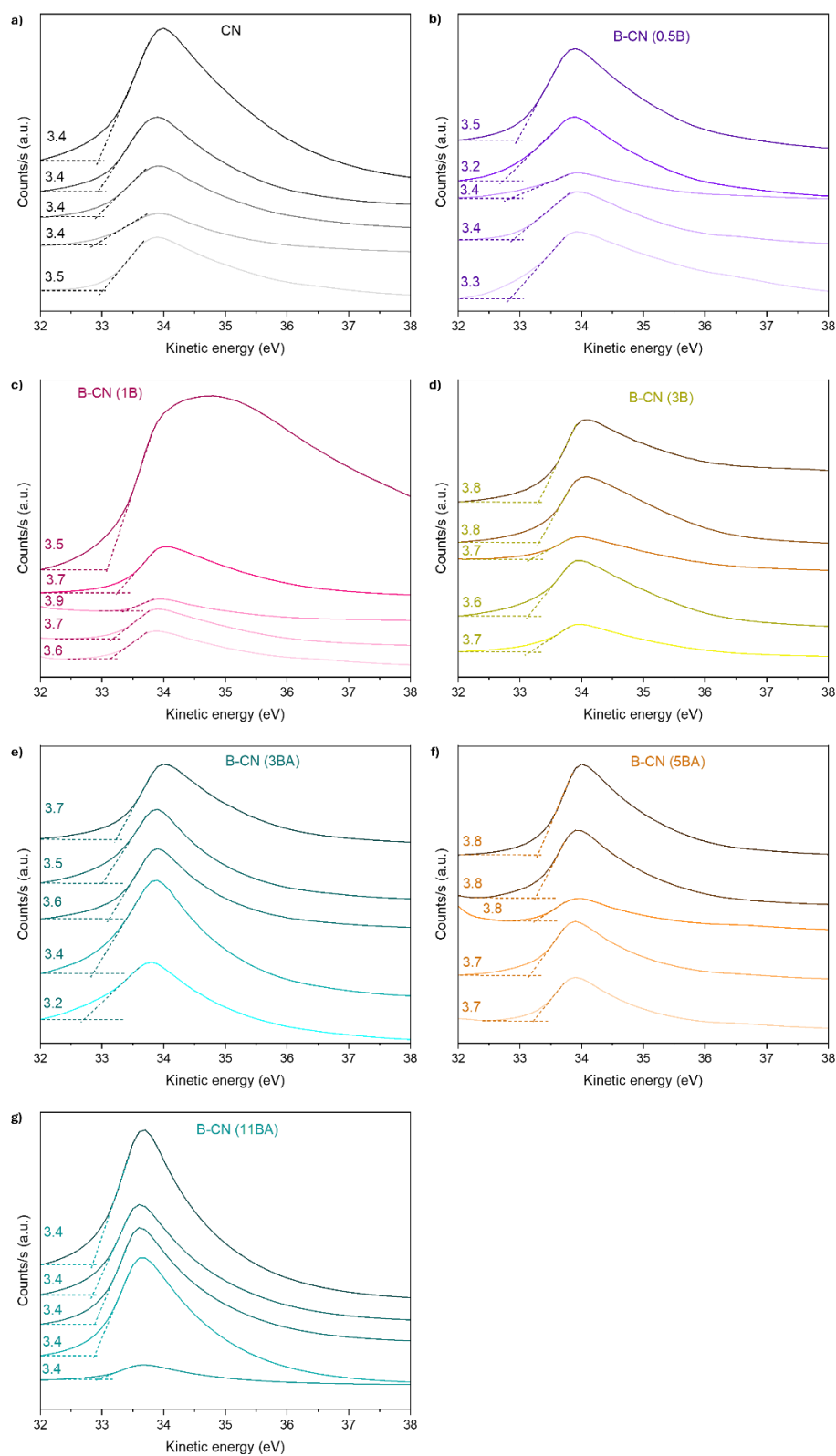


Figure B. 12. XPS work function data for a) CN, b) B-CN (0.5B), c) B-CN (1B), d) B-CN (3B), e) B-CN (3BA), f) B-CN (5BA), and g) B-CN (11BA). The work function for each sample was calculated by averaging the five indicated values from the five different points.

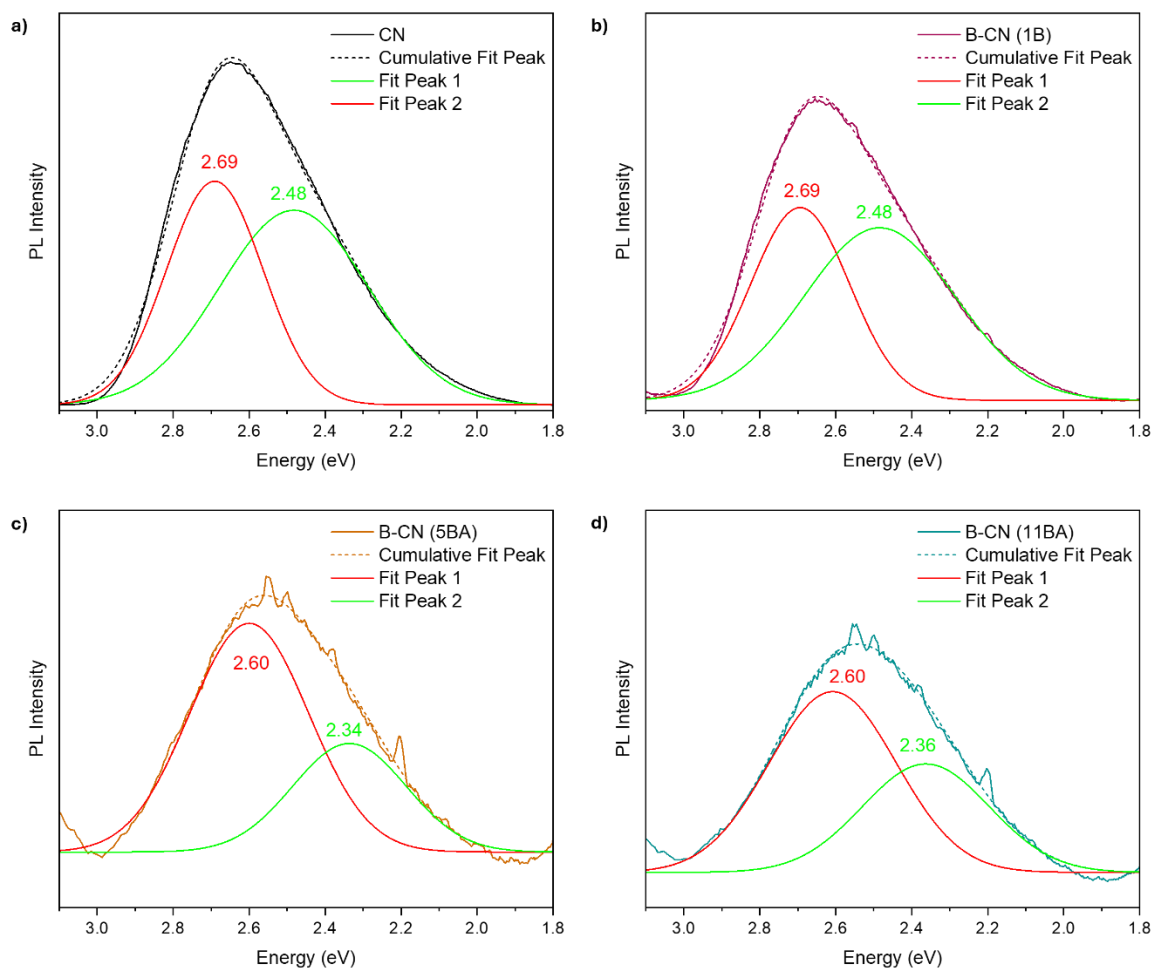


Figure B. 13. Steady-state PL data obtained upon excitation at 355 nm, fitted using the Gaussian fit for a) CN, b) B-CN (1B), c) B-CN (5BA), and d) B-CN (11BA). The main fitted peak for each sample can be deconvoluted into two peaks, presented as Fit Peak 1 and Fit Peak 2.

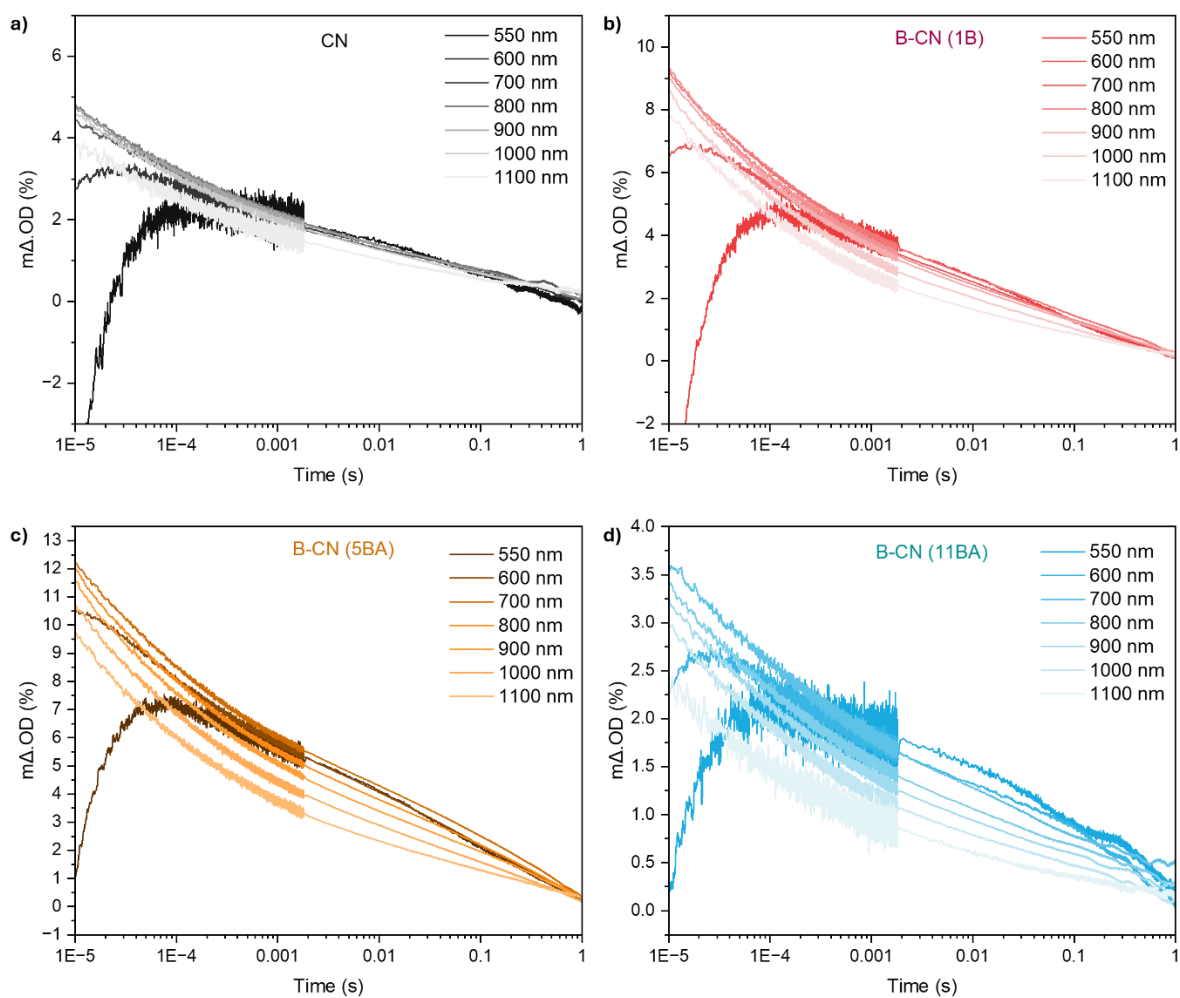


Figure B. 14. TAS decay profiles over time upon excitation at 355 nm, probed at 550-1100 nm for a) CN, b) B-CN (1B), c) B-CN (5BA), and B-CN (11BA).

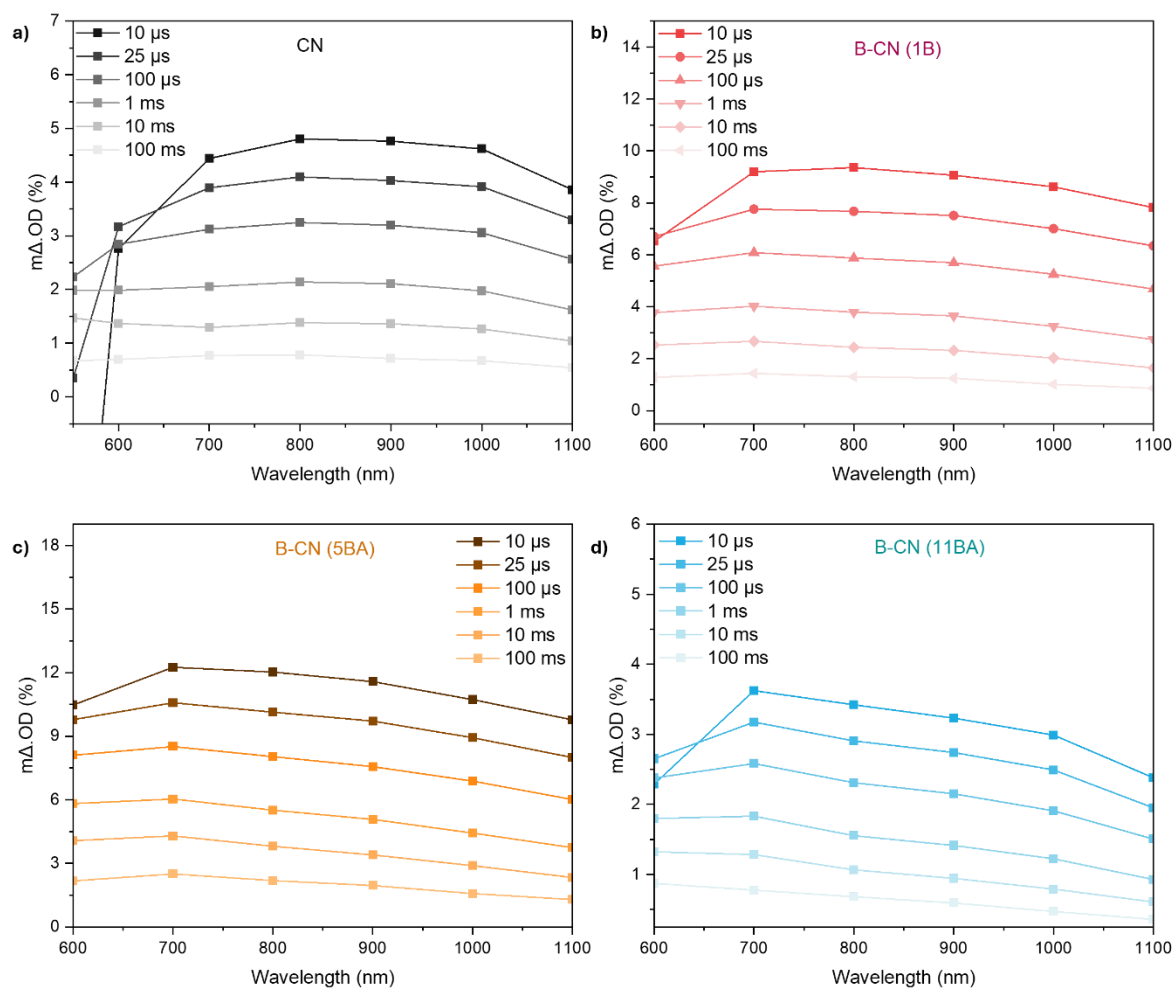


Figure B. 15. TAS data probed over 550-1100 nm, obtained upon excitation at 355 nm for a) CN, b) B-CN (1B), c) B-CN (5BA), and d) B-CN (11BA).

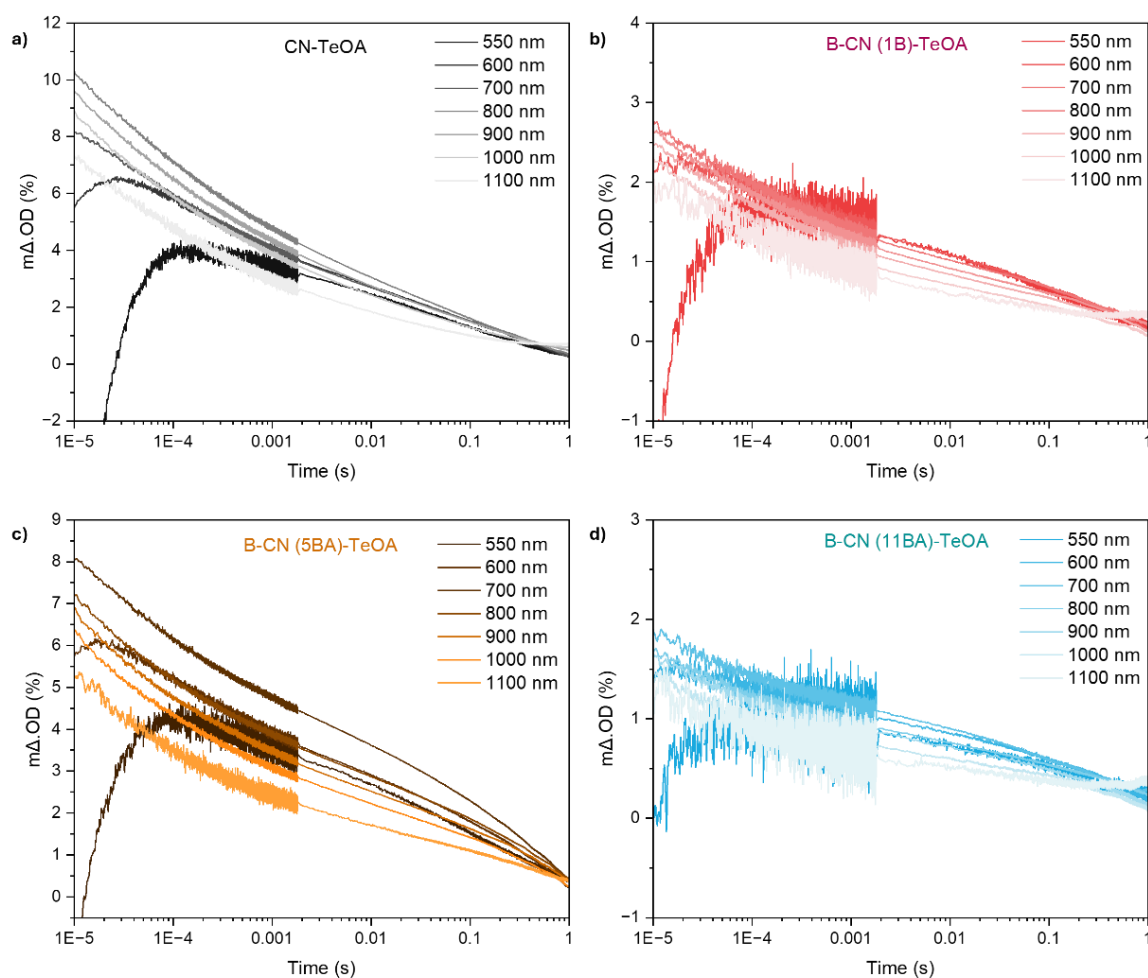


Figure B. 16. TAS decay profiles over time upon excitation at 355 nm, probed at 550-1100 nm for a) CN, b) B-CN (1B), c) B-CN (5BA), and B-CN (11BA), in the presence of hole scavenger TEOA.

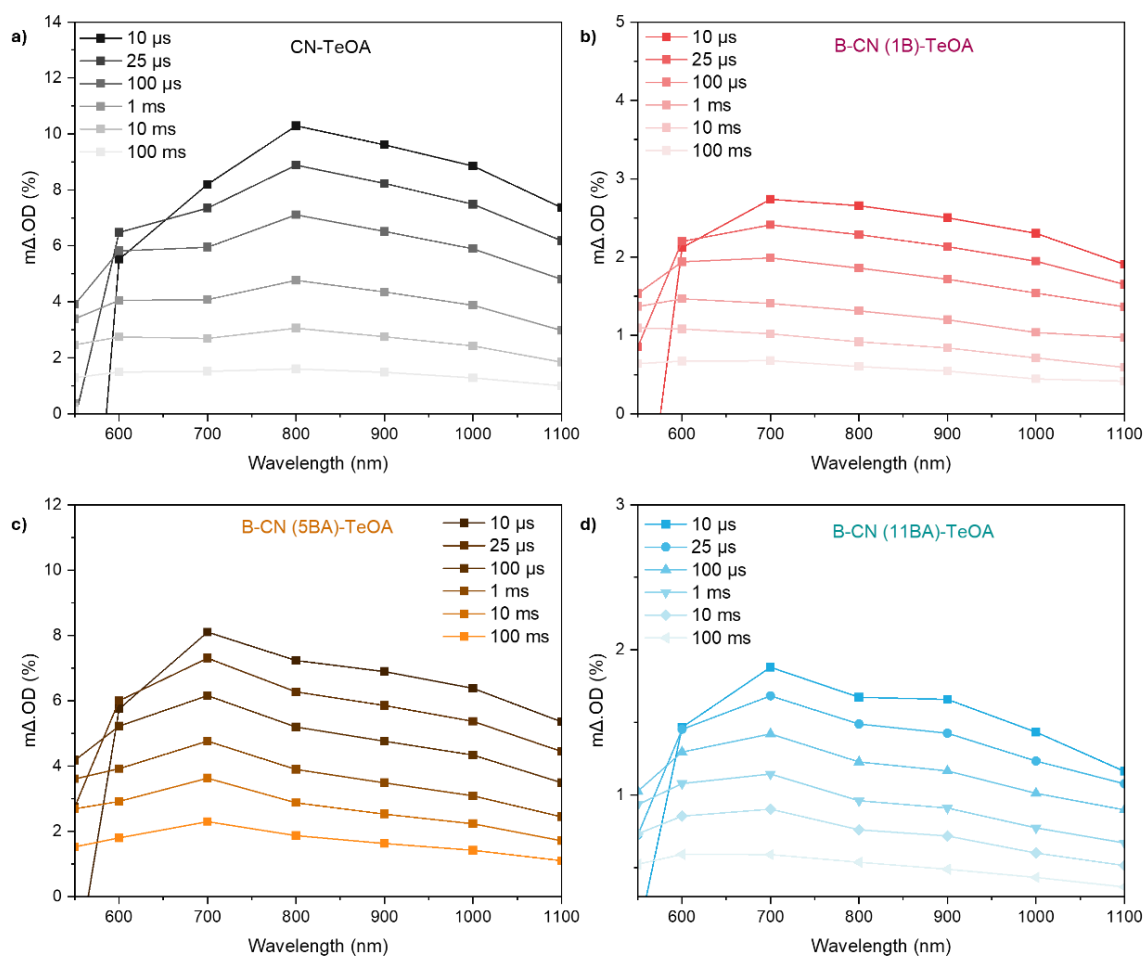


Figure B. 17. TAS data probed over 550-1100 nm, upon excitation at 355 nm for a) CN, b) B-CN (1B), c) B-CN (5BA), and B-CN (11BA), in the presence of hole scavenger TEOA.

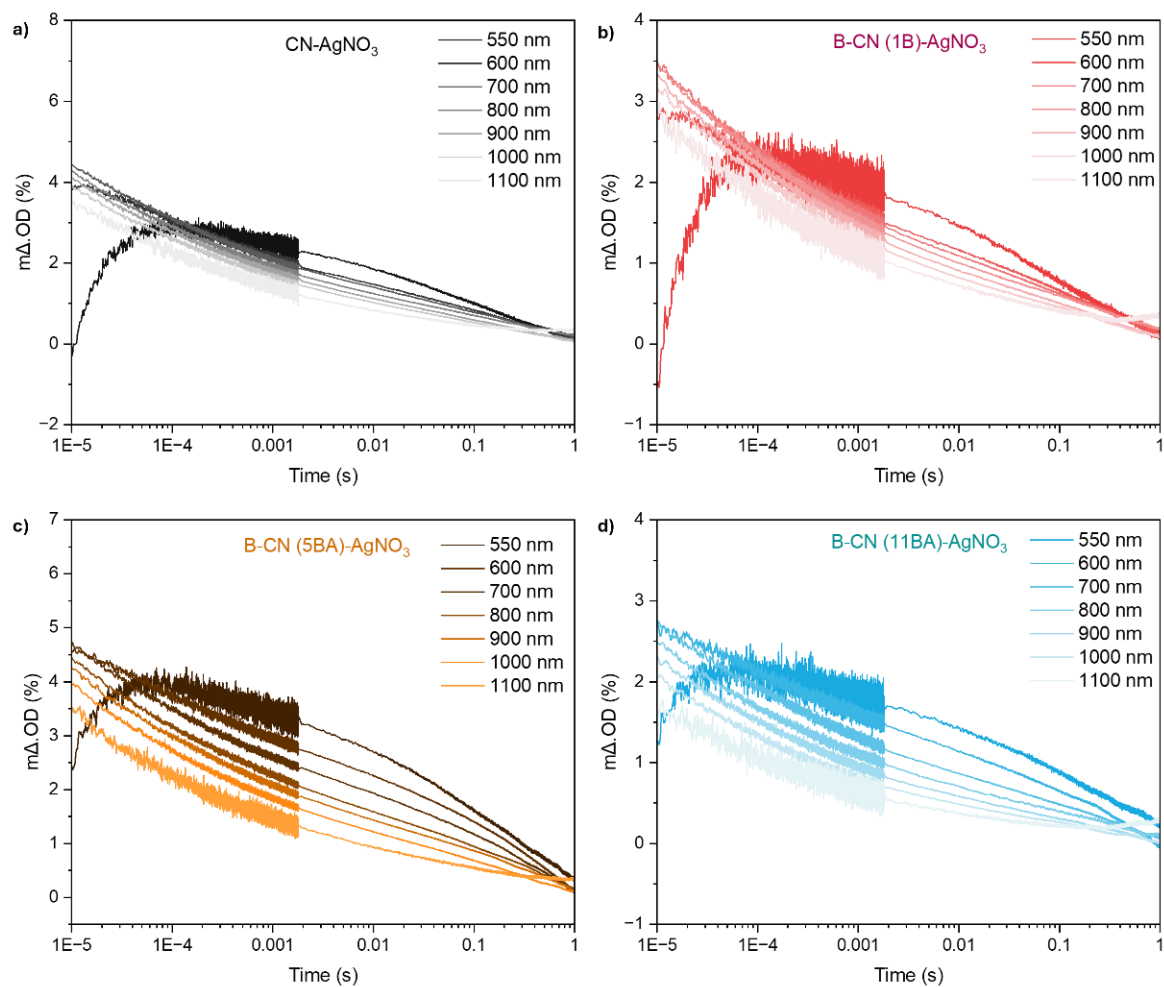


Figure B. 18. TAS decay profiles over time upon excitation at 355 nm, probed at 550-1100 nm for a) CN, b) B-CN (1B), c) B-CN (5BA), and B-CN (11BA), in the presence of electron scavenger AgNO₃.

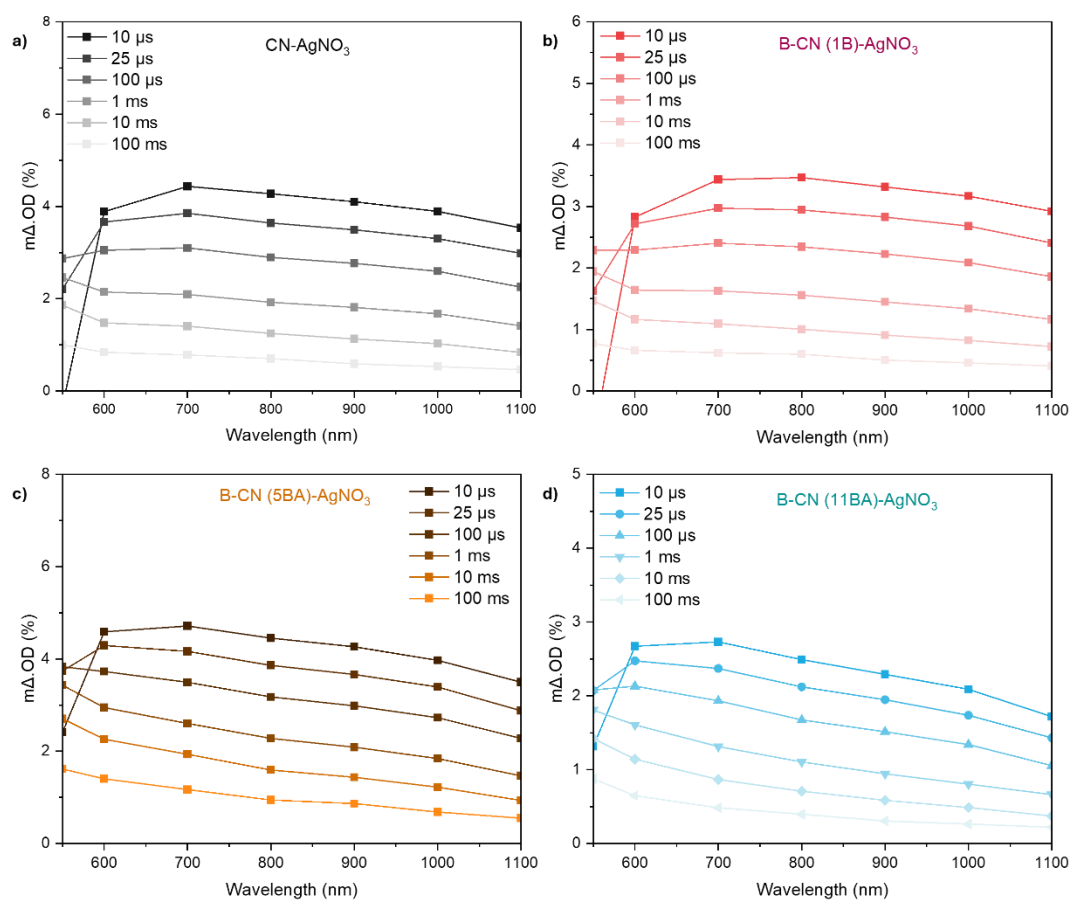


Figure B. 19. TAS kinetic data probed over 550-1100 nm, upon excitation at 355 nm for a) CN, b) B-CN (1B), c) B-CN (5BA), and B-CN (11BA), in the presence of electron scavenger AgNO_3 .

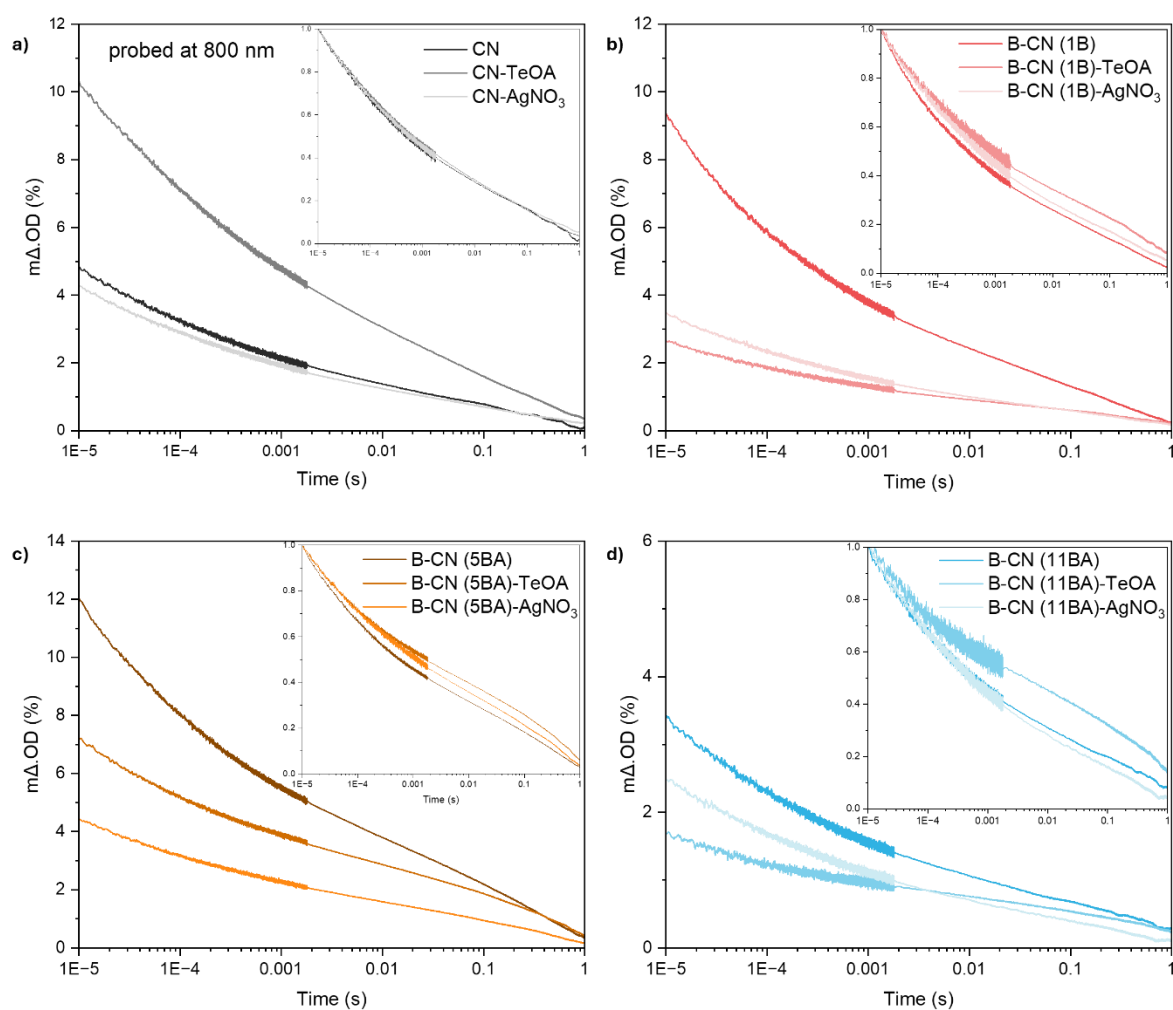


Figure B. 20. Comparison of TAS decay profiles over time upon excitation at 355 nm, probed at 800 nm for a) CN, b) B-CN (1B), c) B-CN (5BA), and B-CN (11BA), with and without use of scavengers TEOA and AgNO₃. The inner plots present the normalised TAS decay profiles, under the same conditions.

7. CO₂ PHOTOTHERMAL REDUCTION ON gC₃N₄-BASED

MATERIALS

All measurements in this Chapter have been performed by the author, unless otherwise stated.

Ms Aurelie Celerien (visiting MSc student, EPFL & Imperial College London) was a collaborator in this study, and carried out some of the photothermal CO₂ reduction experiments.

7.1. Introduction

The advantages and promising attributes of photothermal CO₂ reduction vs thermal and photocatalytic CO₂ reduction have already been discussed in **Section 2.2**. The comprehensive review in **Section 2.3** did not mention nonmetal-functionalised gC₃N₄ for CO₂ photothermal reduction, as there is very limited literature on gC₃N₄-based materials for this application, and previous reports have been restricted to the use of (bi)metallic dopants, metal alloys or cocatalysts (*e.g.* Mo, Ag, Au, Pt)³⁰⁴. Such systems have reached higher product (mainly CO and CH₄) yields from the photothermal CO₂ reaction compared to the pristine material, and even achieved the challenging C-C coupling leading to ethanol formation^{304–308}. This enhanced activity has been assigned to i) lowered kinetic barrier for the reaction, especially because of the externally applied thermal field, ii) further chemical transformations due to transport of plasmon heat to the surface reactants, and iii) extended light absorption due to the localised surface plasmon resonance (SPN) effect³⁰⁴. However, the question remains: can nonmetals, and specifically B, be used to functionalise gC₃N₄ for the CO₂ photothermal reduction? This literature gap was identified in **Chapter 3.1**, and bridging this gap was defined as **Objective 3**. To fulfil **Objective 3** of this thesis, I decided to select two thoroughly characterised gC₃N₄

materials (one pristine, reference sample and a B-functionalised sample) from **Chapter 6**, and test them for photothermal CO₂ reduction, for the first time. The materials that were selected and resynthesised for the purpose of this **Chapter 7** are CN and B-CN (11BA) (**Chapter 6**). CN was selected as the pristine reference sample, and B-CN (11BA) was selected as an interesting candidate due to its high B content and subsequent influence in chemical, sorptive, optoelectronic and photocatalytic properties.

To the best of my knowledge, the photothermal effect of B-functionalised gC₃N₄ has only been studied by one research group before, for the photocatalytic degradation of sulfamerazine²⁹¹. Elemental boron was used as a cocatalyst in different concentrations, and created an interface with gC₃N₄. In this study, by photothermal effect, the authors referred to the ability of elemental boron to convert light into heat and increase the reaction temperature (suspension temperature increase from ~38 °C to ~55 °C). They assigned the heat increase to enhanced light absorption compared to the pristine material, and to the subsequent conversion of the absorbed light.

The novelty of my work in this Chapter lies in i) the first reported use of B-functionalised gC₃N₄ materials for the photothermal CO₂ conversion, and ii) the examination of the combined effect of solar light and heat as externally applied drivers.

7.2. Materials

7.2.1. Synthesis of pristine CN

CN was synthesised using the same protocol as in **Section 6.2.1**. 10 g (0.08 mol) of melamine (C₃H₆N₆, 99.0%, Sigma Aldrich) was placed into an alumina crucible covered with lid and

heated in a muffle furnace up to 560 °C with a 10 °C min⁻¹ heating rate. The temperature was held for 4 h, and then the material was allowed to cool down naturally to room temperature. The obtained powders were ground using a mortar, and labelled CN.

7.2.2. Synthesis of B-CN

B-CN was synthesised using the same protocol as B-CN (11BA) in **Section 6.2.3**. 10 g (0.08 mol) of melamine and 0.70 g (0.01 mol) of boric acid (H₃BO₃, >99.5%, Sigma Aldrich) were mixed using a mortar. The mixture was placed into an alumina crucible covered with lid and heated in a muffle furnace up to 560 °C with a 10 °C min⁻¹ heating rate. The temperature was held for 4 h, and then the material was allowed to cool down naturally to room temperature. The obtained powders were ground using a mortar, and labelled B-CN.

7.3. Methods

7.3.1. Characterisation of chemical properties

FTIR and XPS were used to investigate the materials' chemistry and environment around B, C, N and O atoms, as described in **Chapter 4**.

7.3.2. Characterisation of structural properties

XRD and N₂ sorption (-196 °C) were used to investigate the materials' crystallinity and textural properties, as described in **Chapter 4**.

7.3.3. Characterisation of optoelectronic properties

DRS UV-Vis was used to explore the materials' light absorption range, and the materials' bandgaps were calculated based on Tauc plots, as described in **Chapter 4**.

7.3.4. CO₂ adsorption

The CO₂ uptake of the materials at 25 °C and up to 1 bar was measured using a volumetric sorption analyser, as described in **Chapter 4**.

7.3.5. Photothermal CO₂ reduction

The photothermal CO₂ reduction experiments were performed using the purpose-built set-up illustrated in **Figure C.1**, which includes a stainless steel photoreactor (17.7 cm³) equipped with a fused quartz window for irradiation, placed on a stainless steel plate equipped with a heating element (2-inch, 50 W, 220 V, RS PRO) and two Type K thermocouples (thermocouple/wire extension lead, 1 m length, 0.2 mm diameter, and mineral insulated thermocouple, 150 mm length, 0.5mm diameter, RS PRO), connected to a temperature control unit. Approximately 20 mg of sample was ground and dry-cast onto a stainless-steel holder (7.1 cm²), and the sample holder was placed inside the photoreactor. The bypass line, while isolating the photoreactor, was vacuumed down to ~0.013 bar. Then, CO₂ (10 cm³ STP min⁻¹, research grade, 99.999 %, BOC) and H₂ (30 cm³ STP min⁻¹, produced in a H₂ generator) were mixed and flown through the bypass line for ~5 min, and an initial measurement was taken. Afterwards, the photoreactor was heated to 200 °C under N₂ flow (40 cm³ STP min⁻¹, research grade, 99.9999 %, BOC). Once the temperature was reached, the photoreactor was vacuumed

down to ~ 0.013 bar, and CO_2 and H_2 (same mixture as described above) were flown for 30 min through the photoreactor. Finally, the photoreactor was filled with ~ 1.7 bar of the gas mixture and sealed. The sample was then irradiated for 5 h using a solar simulator equipped with a 100 W Xe arc lamp (Oriel LCS-100 solar simulator, Newport) at a distance of i) 11 cm or ii) 5 cm above the catalyst surface, providing the intensity of i) 1 sun power (100 mW cm^{-2}) or ii) 3 suns power (300 mW cm^{-2}). The gaseous products were detected and analysed using a GCMS-QP2020 NX gas chromatographer (Shimadzu) equipped with Rt-Q-Bond Plot column (30 m, 0.32 mm ID, 10 μm , Shimadzu) and molecular sieve SH-Msieve 5A plot column (30 m, 0.32 mm ID, 30 μm , Shimadzu) in series. Control experiments were performed: i) without irradiation (*i.e.* reverse water-gas shift reaction, RWGS), ii) with the stainless-steel holder and no sample, and iii) under a N_2/H_2 atmosphere.

To compare the photothermal effect to the pure photocatalytic effect, and to investigate a potential photothermal synergy, CO_2 photoreduction experiments were conducted in the same procedure as described above, excluding the heating under N_2 step.

Some of the experiments were conducted by Ms Aurelie Celerien (visiting MSc student, EPFL & Imperial College London).

7.4. Results & discussion

7.4.1. Reproducibility between batches

As previously mentioned, CN and B-CN (11BA) samples from **Chapter 6** (herein mentioned simply as CN and B-CN) were selected to be re-synthesised and tested for photothermal CO_2 reduction in this Chapter. Upon re-synthesising the materials, it is important to investigate the

synthesis' reproducibility pertaining to the materials' properties. Therefore, in this Section, 'old' (synthesised for **Chapter 6**) and 'new' (synthesised for this Chapter) batches of CN and B-CN are compared to each other using characterisation tools to probe their chemical, sorptive and optoelectronic properties.

Initially, I explored the existence of characteristic functional groups between 'old' (**Figure 7.1a**) and 'new' (**Figure 7.1b**) batches using FTIR. Indeed, the typical absorption bands for N-H/O-H ($\sim 3000\text{-}3300\text{ cm}^{-1}$), C=N/C-N ($\sim 1250\text{-}1700\text{ cm}^{-1}$) and heptazine rings ($\sim 750\text{-}900\text{ cm}^{-1}$) appear in all samples, indicative of their similar chemical structure^{264,285}. In addition, the XRD patterns of 'old' (**Figure 7.1c**) and 'new' (**Figure 7.1d**) batches point to the similarity in crystal structure (tri-s-triazine), with the same, unshifted main (100) and (002) planes, and secondary (101), (300) and (004) planes. Hence, d-spacing and π -stacking are maintained between the batches. Overall, the core chemical and crystal structure are maintained among batches.

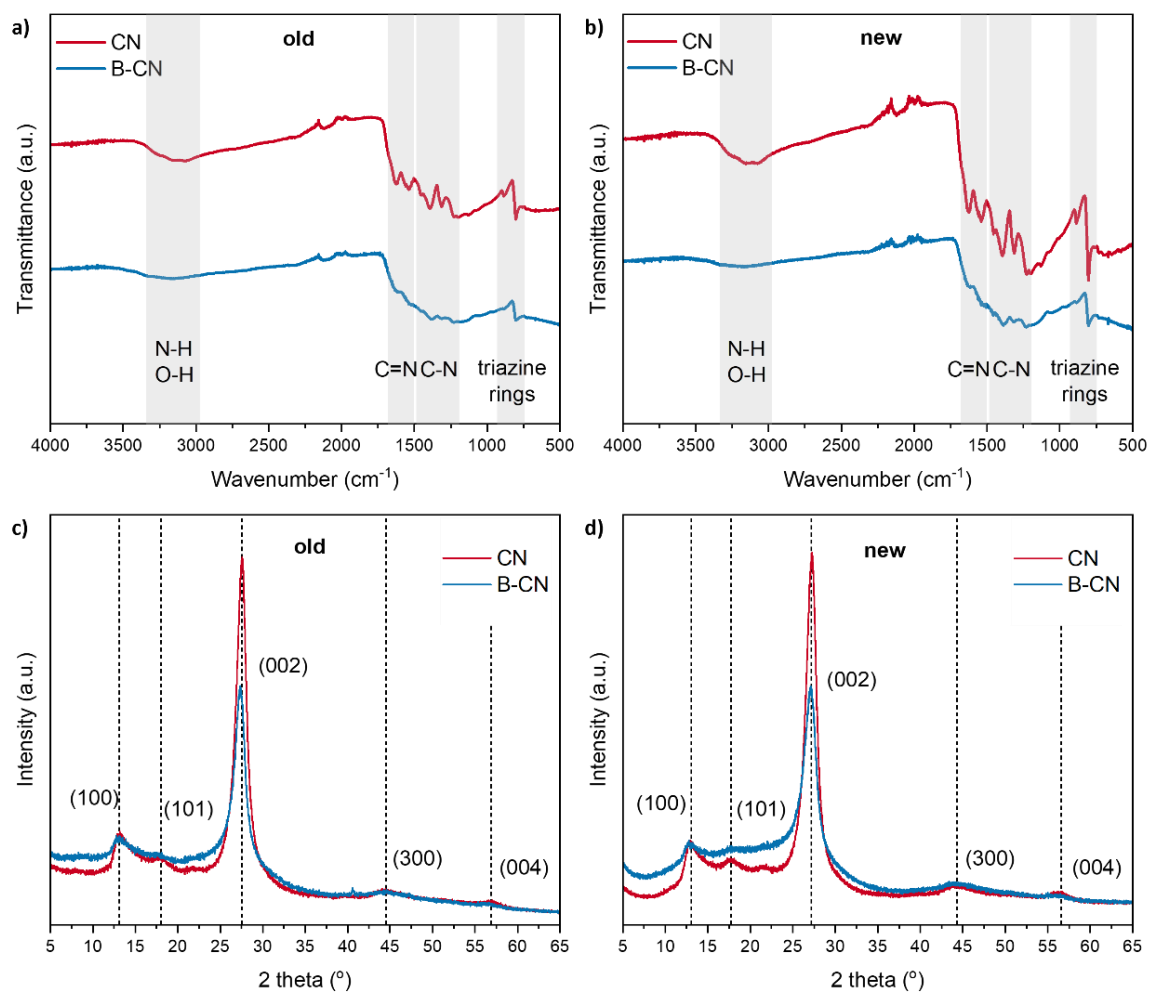


Figure 7. 1. a-b) FTIR spectra with highlighted IR absorption bands, and c-d) XRD patterns of ‘old’ (left) and ‘new’ (right) batches of CN and B-CN.

Next, I examined the porosity and sorptive properties of the two batches. Through N_2 sorption at $-196\text{ }^{\circ}\text{C}$, it is clear that the ‘old’ (**Figure 7.2a**) and ‘new’ (**Figure 7.2b**) batches show similar Type II/III isotherms with Type H3/H4 hysteresis loops, typical of materials with slit-like pores²⁸⁶ (as known from **Chapter 6**). The new batch shows a less pronounced desorption slope at $P/P_0 = 0.45$, and a higher amount of adsorbed N_2 , indicating a small difference in the pore network. The textural parameters of the materials, as derived from the N_2 sorption measurements, are presented in **Table 7.1** below. BET area and pore volume/pore ratio are in

the same order of magnitude between the two batches, with minor differences. B-CN still exhibits higher BET area (37-40 m² g⁻¹) and microporosity (25-31 %) than CN (S_{BET}:17-20 m² g⁻¹ and 16-18 % microporosity). The absolute CO₂ uptake values remain low for pristine CN (< 0.04 mmol g⁻¹), and in the same order of magnitude between both batches. B-CN samples exhibit a superior uptake (0.15-0.21 mmol g⁻¹) (**Figure 7.2c-d**). Similarly to **Chapter 6**, it is clear that functionalisation of CN with high B content results in stronger/more interactions with CO₂ due to increase in microporosity. I conclude that although different batches exhibit slightly different porosity and sorptive properties (these differences would be insignificant with more porous materials), a clear trend prevails.

Table 7. 1. Textural parameters of ‘old’ and ‘new’ batches of CN and B-CN, as derived from N₂ sorption measurements at -196 °C.

Sample	S _{BET} (m ² g ⁻¹)	V _{tot} (cm ³ g ⁻¹)	V _{micro} (cm ³ g ⁻¹)	V _{micro} /V _{tot} (%)
CN – old	17	0.076	0.012	15.8
CN – new	20	0.090	0.016	17.8
B-CN – old	40	0.106	0.033	31.1
B-CN – new	37	0.117	0.029	24.8

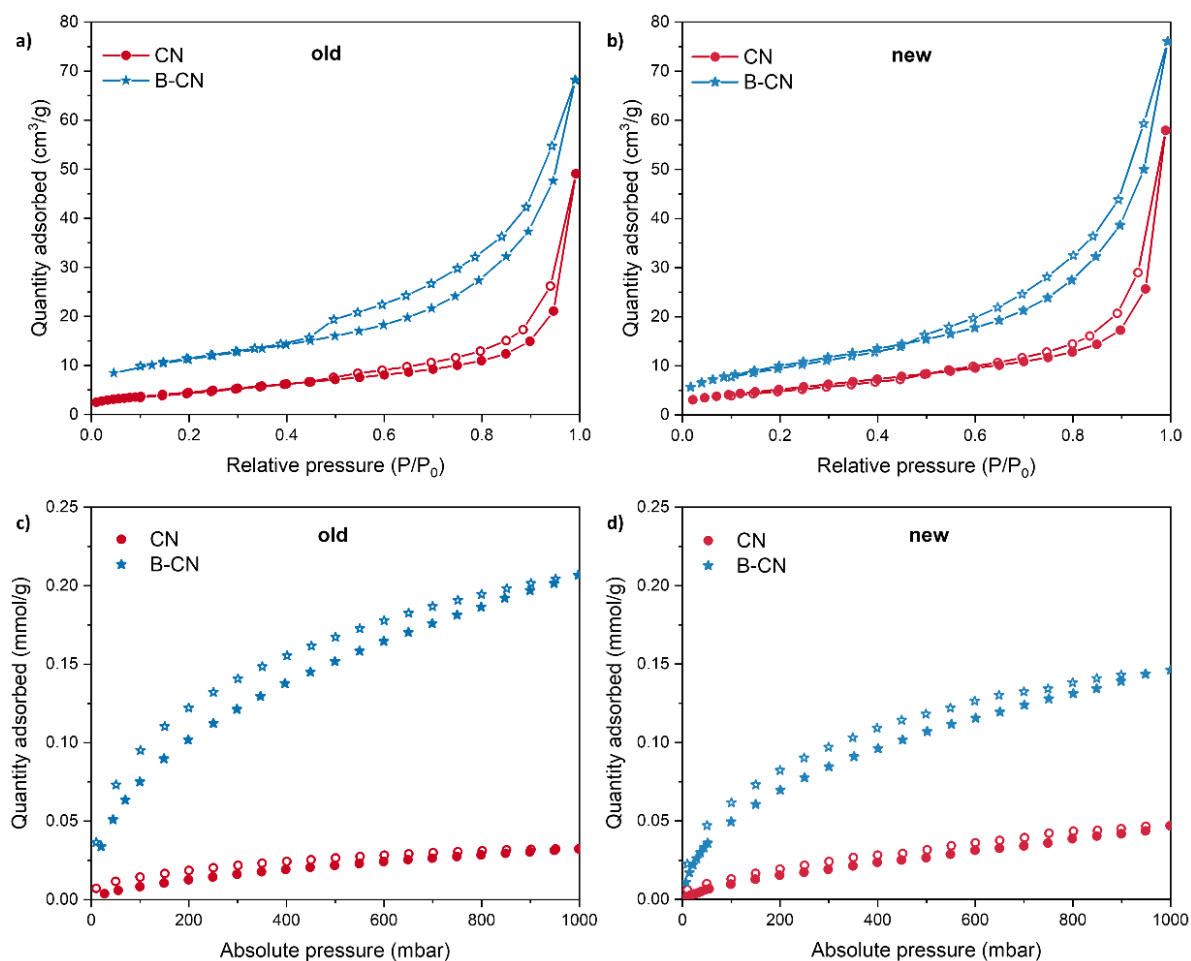


Figure 7. 2. a-b) N_2 sorption ($-196\text{ }^{\circ}\text{C}$) and c-d) CO_2 sorption ($25\text{ }^{\circ}\text{C}$) of 'old' (left) and 'new' (right) batches of CN and B-CN.

Moving forward, I wanted to inspect the reproducibility of elemental composition and chemical bonding around B, C, N and O atoms. Through XPS analyses on 'old' and 'new' batches, I indeed confirm the identical elemental composition (**Figure 7.3a**) for CN (48 at% C, 51 at% N, 1 at% O) and similar (within the XPS error margin) composition for B-CN (42-43 at% C, 38-41 at% N, 6 at% O, 11-13 at% B). B 1s spectra of B-CN materials show the same binding energy ($\sim 192\text{ eV}$) corresponding to B-O bonding⁶⁴ (**Figure 7.3b**). From C 1s spectra, CN and B-CN seem to have the same chemical bonding around C atoms: C-C ($\sim 285\text{ eV}$), C-N/C-O (~ 286

eV) and C=N/C=O (~ 288 eV) regardless of batch³⁰⁹ (**Figure 7.3c**). The same trend can be observed for the N environment from N 1s spectra: N=C (~ 398 eV), N-C (~ 400 eV) and N-H (~ 401 eV)³⁰⁹ (**Figure 7.3d**). As previously observed in **Chapter 6**, CN and B-CN show differences in O 1s spectra due to the different O coordination environments when B is introduced to the structure (O-C in CN, O=C and O-B in B-CN)⁶⁴. Although the main O-C peak in the new CN seems to be shifted by ~ 0.5 eV compared to the old sample, there are no shifts spotted in B-CN among different batches (**Figure 7.3e**). In conclusion, based on the XPS analyses, the synthesis of CN and B-CN samples appears reproducible with regards to chemical environment and elemental content.

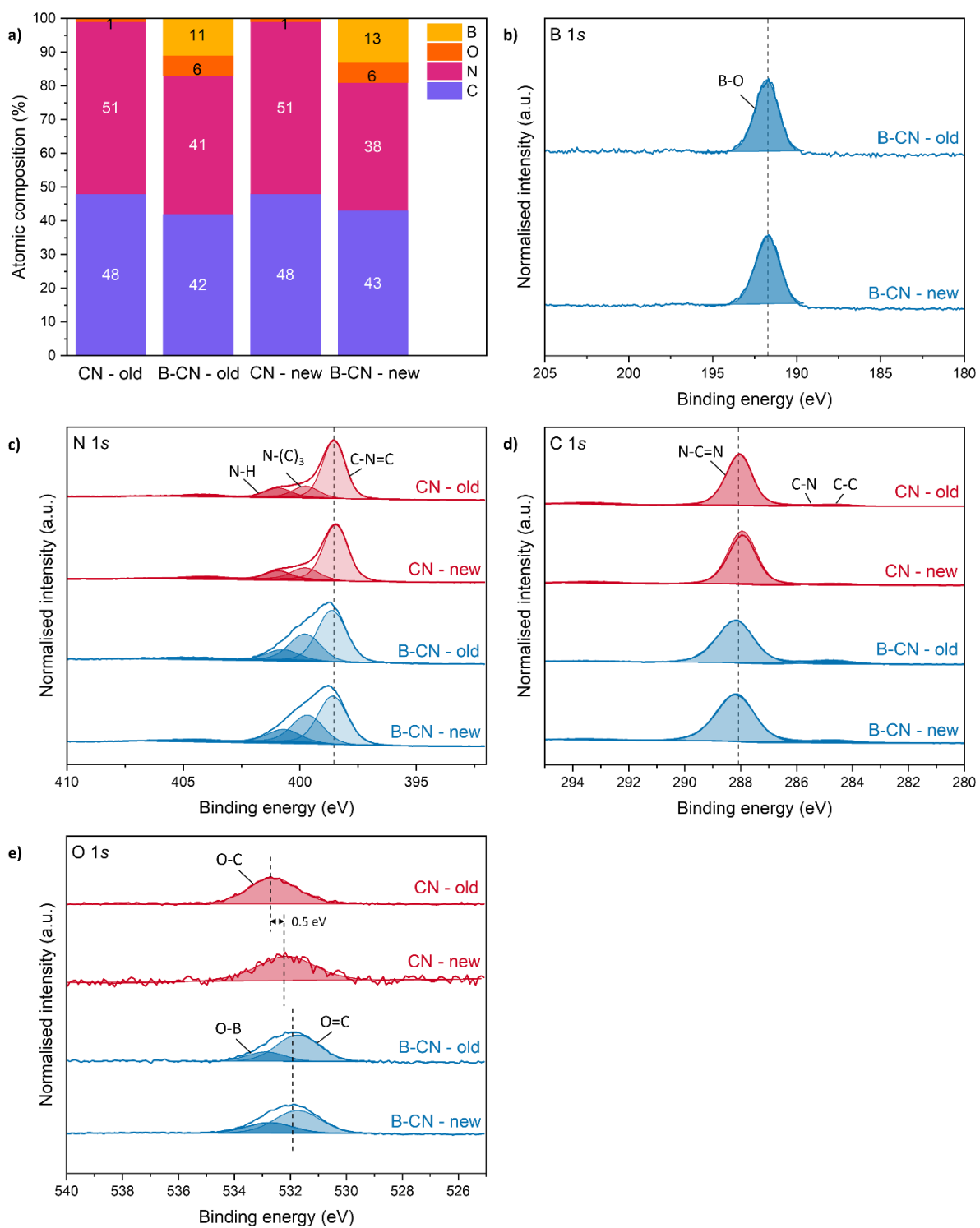


Figure 7. 3. XPS analyses of 'old' and 'new' batches of CN and B-CN. a) Elemental composition, b) B 1s, c) O 1s, d) C 1s, and e) N1s core level spectra.

To probe any deviation in the main optoelectronic properties of 'old' and 'new' batches of CN and B-CN, I used DRS UV-Vis spectroscopy. The light absorption curve and range, along with the absorption edge (~ 450 nm) remain unaffected between 'old' (**Figure 7.4a**) and 'new' (**Figure 7.4b**) samples. As in **Chapter 6**, I converted the DRS UV-Vis data into Tauc plots, using the Kubelka-Munk function, to determine the indirect allowed bandgap transitions^{220,288} (**Figures 7.4c-d**) which are unchanged. To calculate the bandgaps of the materials, I applied linear regression in the Tauc plots' edge. As expected, 'old' (**Figure 7.4e**) and 'new' (**Figure 7.4f**) batches show unaltered bandgaps (2.7 eV for CN, 2.6 eV for B-CN). Overall, there is reproducibility among samples in the light absorption behaviour, and I assume this is true for the remaining optoelectronic properties examined in detail in **Chapter 6**.

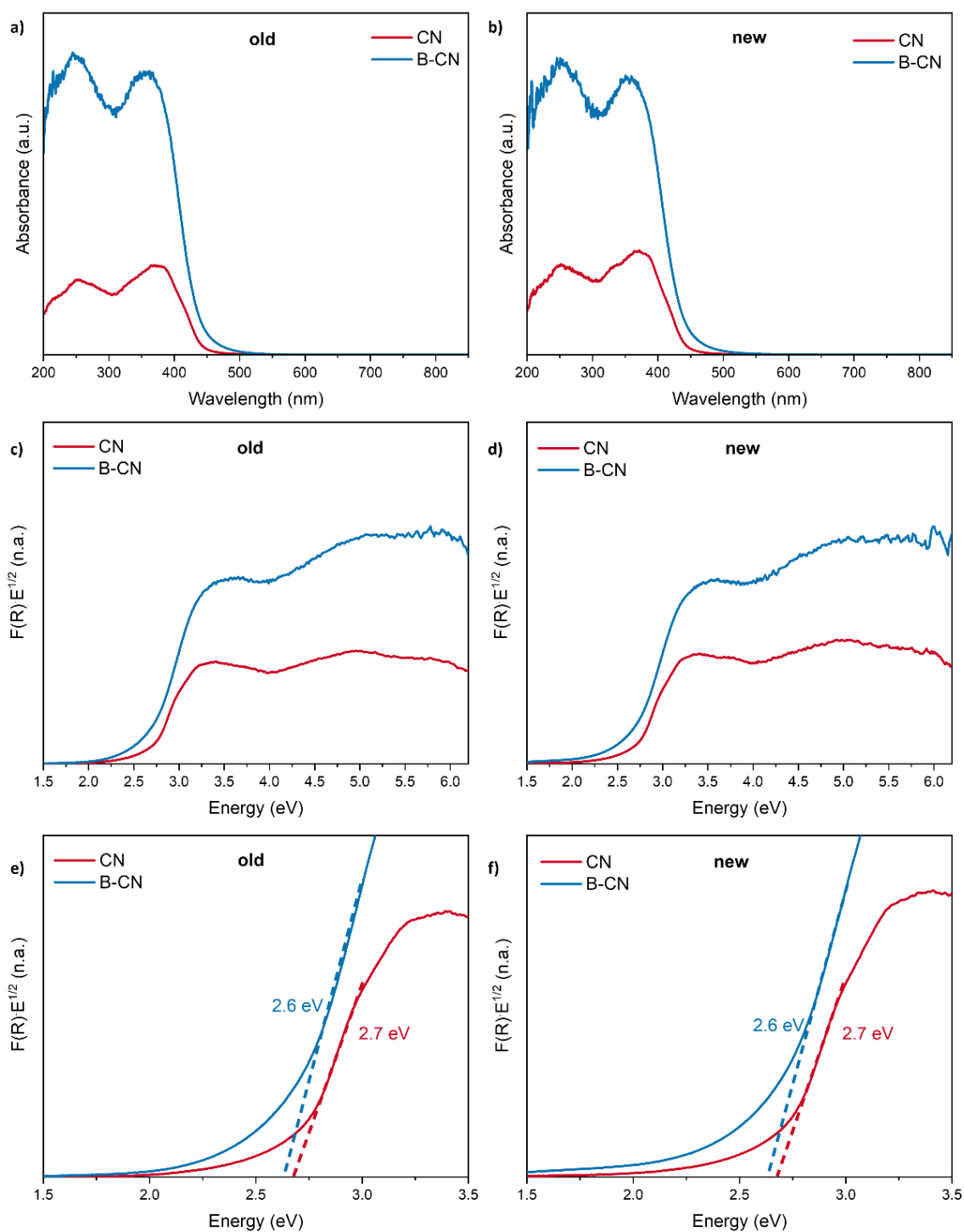


Figure 7. 4. a-b) DRS UV-Vis spectra, c-d) Tauc plots, and e-f) zoomed-in Tauc plots of 'old' (left) and 'new' (right) batches of CN and B-CN.

In general, encouraged by the reproducible results presented in this Section, I assume the CN and B-CN samples have similar chemical, structural, sorptive and optoelectronic properties as in **Chapter 6**. Therefore, existing characterisation can serve as basis and explanation for the activity of these materials for photothermal CO₂ reduction, which will be examined in the next Section.

7.4.2. Photothermal CO₂ reduction

I tested the newly synthesised CN and B-CN samples for gas phase photothermal CO₂ reduction at 200 °C in ambient pressure, using H₂ as proton donor. The main product from this reaction is CO, and the amount of produced CO after each experiment is presented in **Figure 7.5a** for CN, and **Figure 7.5b** for B-CN, respectively. It is noted here that the amount of produced CO is not normalised by mass of catalyst, for ease of comparison with control experiments with no presence of catalyst. Care was taken to use the same amount of catalyst for each experiment, and to perform the reaction for the same duration (5 h) so that the ‘non-control test’ results remain comparable. For context, **Table C.1** shows the evolution rates of CO and CH₄ (secondary product) in each experiment, normalised by experiment duration and mass of catalyst. As can be seen in **Table C.1**, during the measurements it was discovered that using different CO₂ sources affects the type of products formed. Use of CO₂ research grade (99.999 %, BOC) yields CO as the sole product, while use of CO₂ CP grade (99.995 %, BOC) results in formation of both CO and CH₄ – most likely due to the impurity traces existing in the CO₂ cylinder which can be converted into CH₄. Interestingly, for the same reaction conditions, the total CO yield when using CO₂ research grade equals the sum of CO and CH₄ yields when using CO₂ CP grade (see second and third row of **Table C.1**).

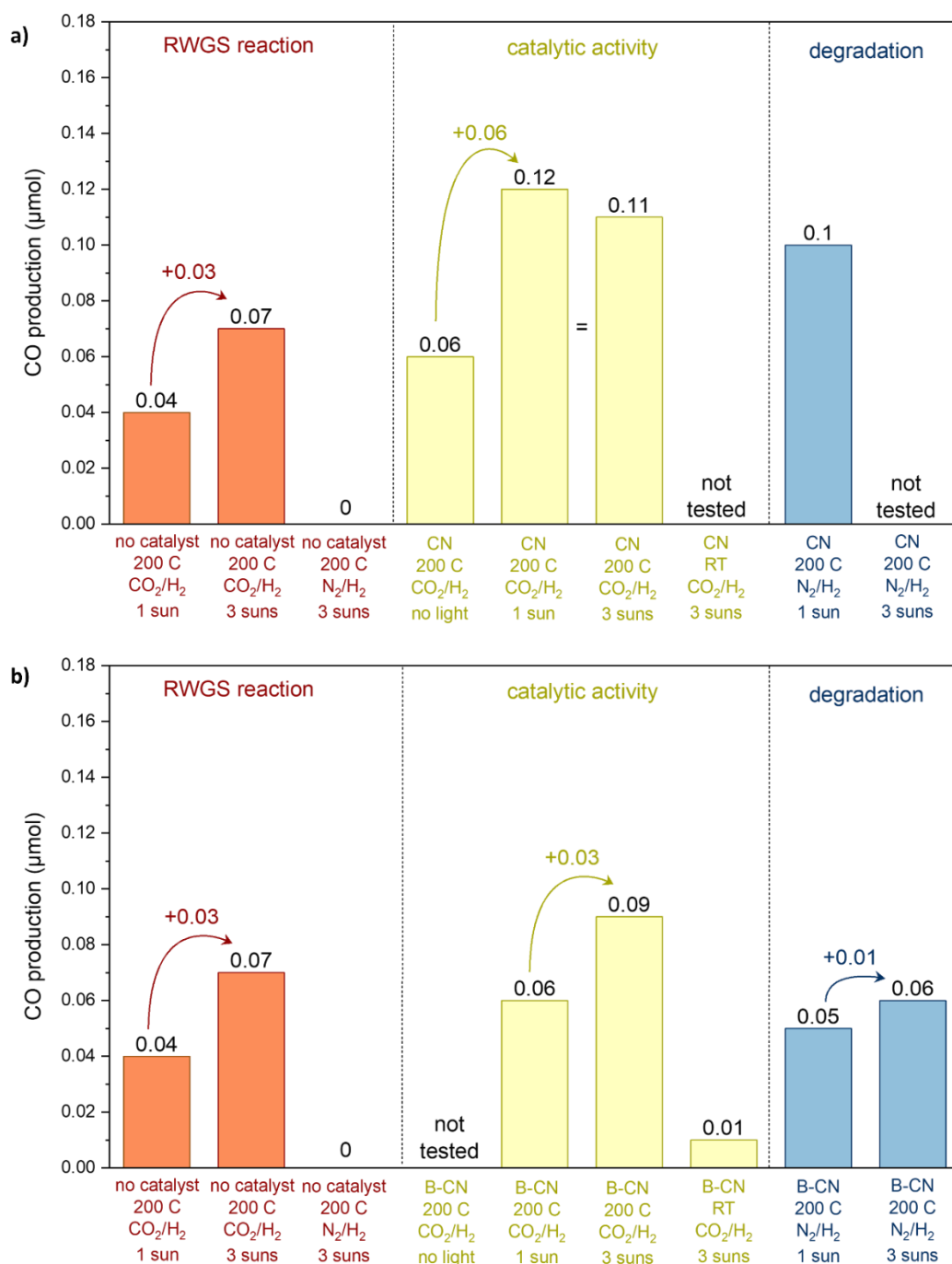


Figure 7. 5. CO₂ photothermal catalytic testing results at 200 °C with different irradiation conditions (*i.e.* 1 sun or 3 suns intensity), including control tests i) with no catalyst, ii) under heat with no irradiation (*i.e.* reverse water-gas shift reaction, RWGS) and iii) under heat and irradiation with inert gas mixture (*i.e.* under N₂/H₂ instead of CO₂/H₂) and photocatalytic tests (*i.e.* with irradiation at room temperature, RT), after 5 h reaction for a) CN and b) B-CN samples.

Initially, for CN, the photothermal CO₂ reduction results seem interesting. The production of CO doubles when moving from thermal (*i.e.* no irradiation) reaction (0.06 μmol) to photothermal reaction using 1 sun irradiation (0.12 μmol), which could point to a synergistic light-heat effect. However, the photothermal activity remains the same under 1 sun and under 3 suns irradiation (0.11 μmol CO), which is counterintuitive if solar energy indeed has an effect. Moreover, when performing experiments at 200 °C with no catalyst (*i.e.* reverse water-gas shift reaction, RWGS reaction), the CO production under 3 suns (0.07 μmol) is higher compared to the same reaction under 1 sun (0.04 μmol) – a rather minimal increase, which however is not apparent when adding CN. In addition to this, when considering that CN with (*i.e.* CO₂/H₂) and without the presence of CO₂ (*i.e.* degradation test, N₂/H₂) under the same conditions (200 °C, 1 sun) produces similar amounts of CO (0.12 and 0.10 μmol, respectively), it is likely that CO is not produced by the photothermal reduction of CO₂, but from side reactions. Having arrived at this conclusion, in the interest of time, complementary CO₂ photoreducing activity (under CO₂/H₂, no heat, 3 suns) and degradation (under N₂/H₂, 200 °C, 3 suns) tests with CN were not performed, as indicated in **Figure 7.5a**.

In the case of B-CN, the CO₂ photothermal activity increases from 0.06 to 0.09 μmol CO when moving from 1 sun to 3 suns irradiation, respectively. When comparing this to the negligible CO production (0.01 μmol) from CO₂ photoreduction (*i.e.* no heat) at 3 suns, it is assumed that there can be a synergistic effect between heat and light. However, the same increase is also spotted during RWGS reaction (+0.03 μmol CO), and smaller increase during degradation checks (+0.01 μmol CO) when moving from 1 to 3 suns. It is concluded that B-CN could potentially be an interesting candidate for photothermal CO₂ reduction under optimised conditions – given its different behaviour to change in irradiation conditions compared to CN. But, with the current results, the actual photothermal effect – if any – cannot be elucidated.

Having arrived at this conclusion, in the interest of time, the thermal CO₂ reduction activity (under CO₂/H₂, 200 °C, no irradiation) test with B-CN was not performed, as indicated in **Figure 7.5b**.

7.5. Conclusions

Two materials from **Chapter 6** [CN and B-CN (11BA)] were selected as interesting candidates for the photothermal CO₂ reduction application. In this Chapter, the reproducibility of the two samples when synthesised in different batches (CN – old vs CN – new, and B-CN – old vs B-CN – new) was investigated, with regards to the effects on fundamental chemical, sorptive and optoelectronic properties. It was proven that the synthesis of these specific materials is reproducible with acceptable accuracy, and the samples were further tested for gas phase CO₂ photothermal reduction. To my knowledge, this is the first time B-functionalised CN has been tested for the photothermal CO₂ reduction. Both materials produce CO as the main product. Pristine CN is not deemed appropriate for the CO₂ photothermal reduction, as there is no effect on the reaction performance upon increasing the incident light intensity, and the largest part of the ‘activity’ comes from material degradation. B-CN appears a more interesting material than CN for this application, as an increase in the incident solar energy leads to an increase of the CO production after CO₂ photothermal reduction tests, which could indicate a heat-light synergy. However, an analogous increase in CO production also happens in the absence of catalyst during the RWGS reaction. Overall, B-CN materials’ activity is minimal, and further work is required to establish the source of the produced CO, and then find optimised testing conditions.

7.6. Supporting information

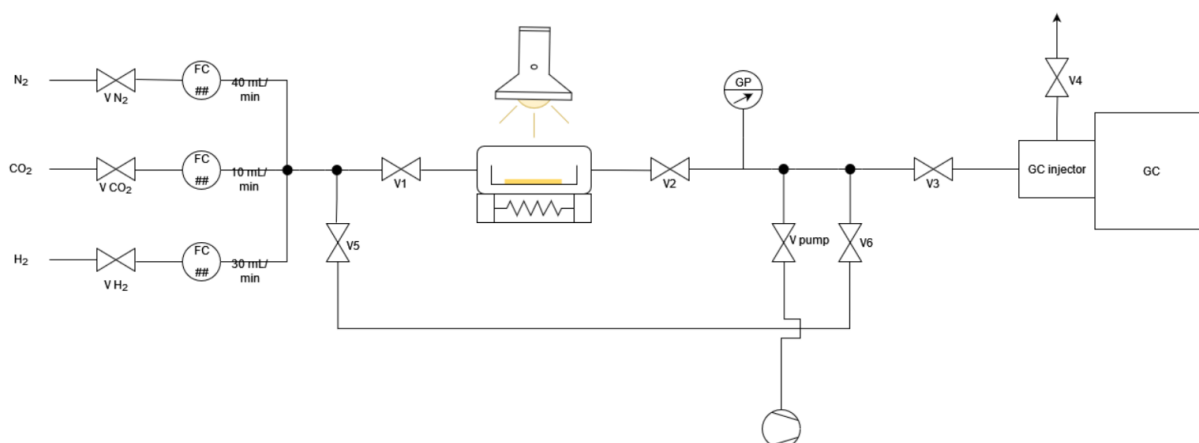


Figure C. 1. Schematic representation of the photothermal CO₂ reduction set-up. Produced by Ms Aurelie Celerien.

Table C. 1. CO evolution rates after CO₂ photothermal reaction under different conditions on CN and B-CN, including control tests. n.a. indicates non applicable, n.d. indicates not detected, and RT indicates room temperature.

Sample	Conditions	Irradiation (mW cm ⁻²)	Duration (h)	CO evolution rate (μmol g ⁻¹ h ⁻¹)	CH ₄ evolution rate (μmol g ⁻¹ h ⁻¹)
CN	CO ₂ /H ₂ 200 °C	n.a.	5	0.56	n.d.
CN	CO ₂ /H ₂ 200 °C	100	5	1.17	n.d.
CN	CO ₂ /H ₂ 200 °C	100	5	0.96*	0.21*
CN	CO ₂ /H ₂ 200 °C	300	5	1.06**	n.d.
CN	N ₂ /H ₂ 200 °C	100	5	1.05*	0.10*
B-CN	CO ₂ /H ₂ 200 °C	100	5	0.57*	0.07*
B-CN	CO ₂ /H ₂ 200 °C	300	5	0.92	n.d.
B-CN	CO ₂ /H ₂ RT	300	5	0.06	n.d.
B-CN	N ₂ /H ₂ 200 °C	100	5	0.42	n.d.
B-CN	N ₂ /H ₂ 200 °C	300	5	0.58	n.d.
n.a.	CO ₂ /H ₂ 200 °C	n.a.	5	0.01 μmol h ⁻¹	n.d.
n.a.	CO ₂ /H ₂ 200 °C	100	5	0.01*** μmol h ⁻¹	n.d.
n.a.	CO ₂ /H ₂ 200 °C	300	5	0.01 μmol h ⁻¹	n.d.
n.a.	N ₂ /H ₂ 200 °C	300	5	n.d.	n.d.

* CO₂ CP grade (99.995 %, BOC) was used instead of CO₂ research grade (99.999 %, BOC).

** Average of 2 tests.

*** Average of 3 tests.

8. CONCLUSIONS & FUTURE WORK

8.1. Conclusions

The aim of this thesis was to uncover the fundamentals surrounding the nonmetal functionalisation of semiconducting boron and carbon nitride photocatalysts for the CO₂ reduction reaction. This includes functionalising BN using P and S (**Objective 1**), and gC₃N₄ using B (**Objective 2**), and unravelling the (largely unknown) effects of such functionalisation on the relationship between chemistry – structure – functionality – photoactivity. Another aspect of my thesis was to test such functionalised materials for the rising light- and heat-assisted CO₂ reduction in gas phase, and probe any synergy between the two externally applied fields (**Objective 3**).

In **Chapter 5**, I studied the functionalisation of BN, which has traditionally been used in the ceramics/cosmetics industries (in its crystalline form), but only recently started being tested for photocatalytic reactions (in its tunable, amorphous porous form). I addressed **Objective 1** by exploring the effects of P functionalisation, including the choice of precursor and the nonmetal content, on the different porous BN properties. More specifically, through advanced characterisation, I investigated the relationship between P functionalisation and the chemistry, structure, CO₂ adsorption capacity, charge carrier behaviour and CO₂ photoreducing activity of BN. I added to and partly disproved previous literature, suggesting potential P-BN structures where P is interstitially connected to N atoms without necessarily replacing B. I showed that, while porous amorphous BN is inherently defective, P functionalisation causes further defects – the extent of which is P precursor-dependent. The creation of such structural changes leads to more ultramicropores and in turn increased CO₂ uptake (up to threefold ambient conditions up). In terms of electronic structure, the generated

defects act as charge carrier traps, extending exciton lifetimes but hindering their reaction with CO₂ and H₂ due to loss in mobility and potential energy. This was the first time P-BN materials were tested for the CO₂ photoreduction reaction, with no cocatalysts, co-dopants, junctions or sacrificial agents.

In **Chapter 6**, I worked with gC₃N₄ (or CN); a material widely used in photocatalytic reactions owing to its unique optoelectronic properties, albeit scarcely used as a standalone catalyst. The functionalisation of gC₃N₄ with B has been explored before but the isolated effects of this functionalisation (*i.e.* the characterisation/photocatalytic testing of the B-functionalised material, not decorated with cocatalysts/part of heterojunctions/tested with sacrificial agents) are rarely experimentally proven and remain a point of controversy. I addressed **Objective 2** by unravelling the influence of i) B functionalisation, ii) B content, and iii) choice of B precursor on the physicochemical, morphological, sorptive and optoelectronic properties of bulk gC₃N₄. My results suggested that the amount of functionalisation is better controlled when using boric acid as opposed to amorphous B as the precursor. In addition, the resulting chemical structure differs based on the precursor used. Through a combination of techniques, I argued that B does not replace N or C atoms in the structure but rather creates B-O bonds, as opposed to reported literature. I showed that it is the amount of B in the structure, rather than the choice of precursor, that enhances porosity and CO₂ uptake. While B integration does not extend light absorption, it does shift the material's electronic bands to deeper energies and introduces midgap states – most likely below the CB – which do not affect the exciton lifetimes. I tested the materials for CO₂ photoreduction and photocatalytic NO_x removal and discovered that B functionalisation alone is not enough to make bulk gC₃N₄ an efficient standalone photocatalyst, which does not agree with literature reports.

Wishing to boost B-CN materials' photoactivity, I experimented with heat- and light-assisted CO₂ reduction in **Chapter 7**. To address **Objective 3**, I tested for the first these materials for the photothermal CO₂ conversion. Initially, I confirmed the reproducibility in chemistry, structure, CO₂ adsorption and light absorption of pristine and B-functionalised CN when synthesised in different batches. Then, I discovered that the main product from the photothermal CO₂ reaction using both materials is CO, and a small amount of CH₄ can be produced when using lower-purity CO₂ reactant. While pristine CN was not deemed appropriate for the CO₂ photothermal reduction, B-CN appeared to be more interesting, as an increase in the incident solar energy caused increase of the CO production, potentially indicative of a heat-light synergy. However, an analogous increase in CO production was also noted during the RWGS reaction, therefore excluding a clear effect from B-CN's activity.

Overall, my PhD provided a thorough and multidisciplinary approach towards understanding fundamental physicochemical, optoelectronic, adsorptive and catalytic properties of functionalised carbon and boron nitrides. When testing these materials, I abstained from the use of precious metals and sacrificial agents which allows to uncover the "sole" effects of nonmetal functionalisation but also poses a bottleneck for the scalability of the reaction. I elucidated the functionality of P-BN and B-CN, and paved the way to tailoring these materials' properties towards targeted photocatalytic applications – and thus, designing enhanced photocatalysts.

8.2. Future work

En route to understanding the fundamentals, one can only acknowledge the significance of optimisation strategies to advancing the CO₂ photoreduction field. For this process to be

technoeconomically viable, we need the deployment of robust, scalable, efficient and sustainable catalysts, and we need to conduct research focused on achieving this target.

Envisioning this goal, further research on P-BN materials could include utilising the extended light absorption and the charge carriers' prolonged lifetimes – which are necessary to drive the kinetically challenging CO₂ reduction. I would hence propose future work on i) co-doping porous BN, *e.g.* with alkali metals or halogens, ii) decorating with transition metal cocatalysts, *e.g.* Co, Ni or Cu, and/or iii) creating heterojunction systems, *e.g.* with MOFs, perovskites or gC₃N₄. Another promising avenue could be forming (P-)BN quantum dots and hierarchical 3D structures (*e.g.* foams) as structure engineering shows great potential in gas phase photocatalytic applications. Importantly, probing the defect – charge carrier – photoactivity relationship through a combination of X-ray-based and ultrafast pump-probe techniques is vital for reverse-engineering enhanced BN materials.

With regards to gC₃N₄, it seems to be behaving better dispersed in a solution rather than in the gas phase. A way forward to test this material in more favourable conditions would be to overcome: i) the CO₂ activation barrier (*e.g.* by applying external fields, creating heterojunctions, adding cocatalysts), ii) the low CO₂ uptake (*e.g.* by structure engineering, doping), iii) the limited CO₂ solubility/saturation (*e.g.* by increasing the operating pressure, using H₂O-CH₃OH or H₂O-TEOA solutions), and iv) the degradation under irradiation (*e.g.* by coating, testing for a number of days, creating heterojunctions). Another interesting approach would be the semi-artificial CO₂ photoreduction, by combining the optoelectronic properties of gC₃N₄ with highly selective and efficient enzymes.

While the photothermal conversion of CO₂ did not work under the tested conditions and materials, it is a promising pathway. B-functionalised gC₃N₄ could be further tested to

investigate optimal reaction conditions, as on many occasions a material may not be active unless certain requirements are fulfilled. A more compelling candidate could be C-, O- or P-functionalised porous BN for this application, as it is thermally stable, porous and with a good CO₂ adsorption capacity.

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APPENDIX A. PERMISSIONS



Formation Mechanism and Porosity Development in Porous Boron Nitride
Author: Anouk L'Hermitte, Daniel M. Dawson, Pilar Ferrer, et al
Publication: The Journal of Physical Chemistry C
Publisher: American Chemical Society
Date: Dec 1, 2021
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Publication: Springer eBook
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