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**Advances in Phenyl-Modified Carbon Nitride: Towards Sustainable
Environmental Applications**

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*I shall be telling this with a sigh
Somewhere ages and ages hence:
Two roads diverged in a wood, and I—
I took the one less traveled by,
And that has made all the difference.*

-Robert Frost

Abstract

The advancement of human civilization through industrialization and technological development is undeniable, appearing boundless in its scope. However, these advancements come at a significant cost, borne by nature and the delicate ecological systems that are often harmed in the name of progress. The increasing frequency of natural disasters and the extinction of numerous species of flora and fauna have underscored the urgent need for environmental remediation, compelling policymakers to prioritize this critical issue. Consequently, the exploration of novel materials for environmental applications has become a pressing necessity. Among these, photocatalysis has emerged as a highly advantageous process, harnessing renewable light energy to drive reactions that transform harmful or unwanted substances into valuable products. In recent years, graphitic carbon nitride (g-C₃N₄)-based materials have gained significant attention for their photocatalytic properties, owing to their abundance, low toxicity, and environmental friendliness. Despite these advantages, g-C₃N₄ faces limitations such as high charge recombination rates and restricted visible-light absorption, which hinder its photocatalytic efficiency. To address these challenges, phenyl-modified carbon nitride (PhCN) has been developed as a promising alternative. PhCN retains the 2D layered structure and beneficial properties of g-C₃N₄ while offering enhanced stability through charge delocalization and superior visible-light activity. Although preliminary studies indicate the potential of PhCN, its research remains limited, and its full scope of applications has yet to be explored. Recognizing this gap, we aimed to utilize PhCN for a range of applications focused on environmental remediation. While literature highlights its promising photocatalytic performance, limitations in charge separation and stability persist, necessitating improvements. Our research sought to address these limitations through targeted structural and functional modifications. We investigated various synthesis routes and processes to enhance the photocatalytic activity of PhCN. These modifications were meticulously studied

to understand their impact on the structural and optical properties of the material. Through this work, we gained valuable insights into the nature and potential of PhCN, paving the way for its broader application in sustainable environmental technologies.

Firstly, the concept of photocatalysis is introduced in **Chapter 1**, and the importance of carbon nitride structures is emphasized. The possible structural modifications that can enhance the photocatalytic activity of carbon nitrides are discussed, and the state of the art in phenyl modification of carbon nitride is presented.

The first modification implemented on PhCN is presented in **Chapter 2**, where the detailed study of the generation of the 2D-2D hybrid photocatalyst PhCN/WS₂ and its application in hydrogen production under visible-light illumination is presented where WS₂ is utilized as an environment-friendly co-catalyst. The synthesis and characterization of 2D PhCN and 2D WS₂ via liquid-phase exfoliation are presented. The dependence of photocatalytic activity on the exfoliation medium is separately analyzed for PhCN, and the effect of WS₂ size on photocatalytic activity is examined.

In the 2nd PhCN modification, a series of phenyl-modified carbon nitride (PhCN) and TiO₂ (anatase) hybrids are synthesized, and the dependency of their visible-light-mediated photocatalytic efficiencies are investigated as a function of the mass ratio of the components and post-synthetic thermal treatment at different temperatures. This comprehensive study is presented as **Chapter 3**. A successful utilization of visible light for dual photocatalytic applications is demonstrated by the optimized hybrid, achieving complete degradation of the organic dye Rhodamine B and concurrent generation of H₂ gas. A correlation between the structural and optical properties of the hybrids is established and a charge transfer mechanism is proposed for the best-performing hybrid after mechanistic studies and advanced characterizations. The complex interplay of various structural and optical properties of the hybrid system that influence its photocatalytic behavior is emphasized in this chapter. A study on the application of PhCN/TiO₂ hybrid for deactivation of H1N1 virus in indoor conditions is presented as well.

The trial to advance the photocatalytic efficiency of PhCN is then done with doping of Boron into the framework of PhCN in **Chapter 4** with the formation of a new

material BPhCN whose new and modified properties are presented in detail with various structural and optical characterizations along with the photocatalytic dye degradation and H₂ production studies.

Lastly, all the results are summarized in **Chapter 5** with main takeaways followed by supplementary information accompanying particular chapters in the **Appendices**.

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List of Acronyms

PhCN	Phenyl-modified Carbon Nitride
HER	Hydrogen Evolution Reaction
OER	Oxygen Evolution Reaction
TMDCs	Transition-Metal Dichalcogenides
LPE	Liquid Phase Exfoliation
TEOA	Triethanolamine
XRD	X-ray Diffraction
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
DLS	Dynamic Light Scattering
PL	Photoluminescence
TRPL	Time-Resolved Photoluminescence
XPS	X-ray Photoelectron Spectroscopy
EDS	Energy Dispersive X-ray Spectroscopy
BET	Brunauer-Emmett-Teller
PLE	Photoluminescence Excitation
MB	Methylene Blue
MO	Methyl Orange
RhB	Rhodamine B
ROS	Reactive Oxygen Species
MDCK	Madin-Darby Canine Kidney

PFU	Plaque-Forming Units
MTT	3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide
DMEM	Dulbecco's Modified Eagle Medium
FBS HI	Fetal Bovine Serum Heat-Inactivated
IPA	Isopropanol
EtOH	Ethanol
BPhCN	Boron-doped Phenyl-modified Carbon Nitride
CEAP	Circular Economy Action Plan
IEA	International Energy Agency
WHO	World Health Organization
NHE	Normal Hydrogen Electrode
SPR	Surface Plasmon Resonance
CB	Conduction Band
VB	Valence Band
AOPs	Advanced Oxidation Processes
QDs	Quantum Dots
BN	Boron Nitride
BJT	Barrett-Joyner-Halenda Calculation
TGA	Thermogravimetric Analysis

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Chapter 1

Introduction

1.1. Motivation

Research focused on environmental applications is crucial to address pressing global challenges such as pollution, climate change, and resource depletion. With rising industrialization and population growth, ecosystems are under severe strain, necessitating sustainable solutions for water, air, and soil remediation. Innovative materials and technologies can mitigate environmental damage, ensuring clean energy, safe water, and reduced carbon footprints. By advancing eco-friendly processes and renewable energy sources, environmental research safeguards public health, biodiversity, and future generations. Moreover, it fosters a circular economy, reduces waste, and promotes sustainable development, aligning with global goals to create a balanced and resilient environment for all.

Water is fundamental to life on Earth, supporting ecosystems, human societies, and the global economy. It covers 71% of the planet's surface and is essential for various biological processes, including nutrient transport, temperature regulation, and photosynthesis in plants, which produce oxygen and sustain food chains¹. Freshwater resources are crucial for drinking, sanitation, agriculture, and industry, with agriculture alone consuming about 70% of the available freshwater, highlighting its role in food security.¹

Beyond human use, water maintains biodiversity in rivers, lakes, and oceans, supporting countless species.¹ Healthy ecosystems regulate water quality, prevent erosion, and help control floods, demonstrating water's role in environmental balance. Climate patterns are also driven by the water cycle, influencing weather and temperature on a global scale. Despite its abundance, only about 2.5% of Earth's water is freshwater, and an even smaller fraction is accessible for human consumption, making sustainable water management essential for future generations.¹

The UN World Water Development Report 2024 “Water for Prosperity and Peace” has emphasized water's essential role in achieving global stability and prosperity. The in-depth study has concluded that water scarcity, pollution, and inequitable access, can exacerbate food insecurity, disrupt livelihoods, and heighten social tensions, underscoring the need for universal access to safe water and sanitation as outlined in Sustainable Development Goal 6 of UN (to ensure the availability and sustainable management of water and sanitation for all by 2030).² The report advocates for water to be recognized as a fundamental human right that, when managed properly, contributes to peace and economic growth by supporting health, agriculture, and energy security.² Therefore, there is no doubt that water is equivalent to life on the Earth and is one of the most precious resources available to us.

In the modern age, rapid industrialization, urbanization, human population boom and agricultural activities have contributed significantly to the contamination of water sources with harmful organic pollutants, such as dyes, pharmaceuticals, and industrial chemicals, etc. These pollutants pose severe risks to both ecological systems and human health, as they often persist in the environment and are challenging to degrade by conventional treatment methods like- filtration, chemical treatment, adsorption, UV-treatment, etc. which can also be energy expensive and non-bio-friendly.³

In parallel, the world is facing an urgent need for clean, renewable energy sources as we shift away from fossil fuels to mitigate the effects of climate change. Hydrogen is recognized as a clean fuel, offering a high energy yield while producing only water as a byproduct when used.⁴ However, the current methods of hydrogen production like- natural gas reforming, coal gasification, electrolysis, etc. are energy-intensive and often rely on non-renewable sources, contradicting sustainability goals.⁴ The Global Hydrogen Review 2023 by the International Energy Agency (IEA) indicated that global hydrogen demand reached a historic high of 95 million tonnes in 2022, mainly driven by traditional applications in refining and chemicals. However, low-emission hydrogen usage remains minimal, with demand for this cleaner alternative struggling to scale up as costs remain high and policies lag.⁴ Despite ambitious plans, only a small portion of current hydrogen projects focuses on low-emission sources, highlighting a disconnect between supply and demand targets.⁴

Therefore, humanity is in a dire need of sustainable approaches which can mitigate reliance on fossil fuels, reduce greenhouse gas emissions, and lessen ecological degradation. More research is needed on renewable methods which can harness inexhaustible natural resources, such as solar or wind energy, minimizing harmful environmental impacts. The European Commission's new circular economy action plan (CEAP) aims to reduce the dependency on non-renewable natural resources for the development of humanity.⁵ Unlike the traditional linear economy, which follows a "use & throw" model, a circular economy emphasizes keeping materials in use as long as possible, extracting maximum value, and regenerating natural systems. This approach involves reusing, repairing, remanufacturing, and recycling products and materials, which helps conserve resources and reduce the need for virgin materials. This approach aligns well with waste-water utilization where waste becomes a resource, fostering resilience against resource scarcity and environmental degradation.⁵

The history of removal of contaminants from water resources dates back to the 1700s when the first water filters for domestic application were applied. These were made of wool, sponge and charcoal.⁶ In 1804 the first actual municipal water treatment plant designed by Robert Thom, was built in Scotland.⁷ British scientist John Snow pioneered the use of chlorine for water purification, laying the foundation for modern water disinfection.⁶ It was ultimately recognized that good taste and odor are not sufficient indicators of safe drinking water. Later, Dr. Fuller discovered that rapid sand filtration was significantly more effective when combined with prior coagulation and sedimentation processes.⁷ Over time, waterborne diseases like cholera and typhoid became increasingly rare as the practice of water chlorination gained widespread adoption globally.⁷ The physical separation methods were not enough to tackle the increasing chemical usage in the industries hence and the use of chemical methods threatened the aquatic and marine life and the whole

ecosystem which depended on them. As necessity is the mother of invention, scientific techniques were developed from 1900s which were target specific, more efficient and less harmful to the life on the Earth.⁷

Water softening, developed in 1903, emerged as an early method for water desalination, where cations were exchanged with sodium or other cations using ion exchangers.⁸ Techniques such as aeration, flocculation, and activated carbon adsorption were later introduced.⁸ In the 1980s, membrane technology for reverse osmosis was added, followed by the implementation of risk assessments after 1990.⁹ In modern times, various advanced scientific techniques are employed for environmental remediation, each tailored to address specific types of pollution effectively. Bioremediation, a process that uses microorganisms to break down organic pollutants in soil and water, is widely utilized for oil spills and industrial waste.¹⁰ Advanced Oxidation Processes (AOPs), such as ozone treatment and Fenton's reaction (using hydrogen peroxide and iron catalysts), generate hydroxyl radicals to oxidize and neutralize stubborn organic pollutants.¹¹ Nanotechnology leverages materials like carbon nanotubes and zero-valent iron nanoparticles, known for their large surface area and reactivity, to adsorb heavy metals and degrade pollutants.¹² Electrochemical methods, such as electrocoagulation and electrooxidation, are used to precipitate metals and degrade pollutants in wastewater with precision.⁸ Additionally, Phytoremediation, where plants like poplar and willow absorb or stabilize contaminants, is effective for managing soil and water pollution.¹⁰ These techniques combine efficiency, cost-effectiveness, and eco-friendliness, making them indispensable for sustainable environmental management

Another such approach- Photocatalysis, is a light-driven process that offers a dual solution to these environmental challenges.¹³ It allows for the decomposition of organic pollutants in water, thus contributing to pollution abatement, while providing a means of producing hydrogen in an environmentally benign manner.¹⁴ By harnessing solar energy, photocatalytic materials can offer an efficient and sustainable approach to address these pressing needs. Therefore, research on advanced photocatalytic materials is essential to refine sustainable solutions for environmental challenges.

1.2 Background

According to the IUPAC (International Union of Pure and Applied Chemistry) definition, photocatalysis is a process in which a material called photocatalyst absorbs light and initiates a chemical reaction to transform the reactants without being consumed in the reaction itself.¹⁵ In this process, the photocatalyst, upon illumination, generates electron-hole pairs, which then drive redox reactions on its surface, leading to transformations of substrates, such as pollutant degradation or hydrogen generation from water.¹⁶

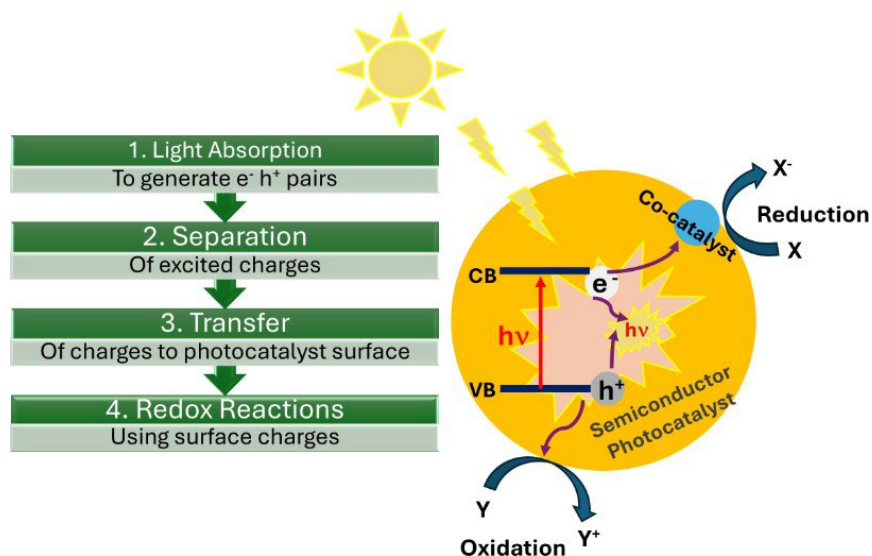


Figure 1.1 Schematic diagram of a typical photocatalysis.

To address the cause of environmental remediation through Photocatalysis, it is crucial to have a good understanding of the mechanism of function of photocatalysis. The schematic diagram of a typical photocatalytic process is shown in **Figure 1.1**.

Photocatalysts are semiconductor materials which can be activated only when incident by photons with energy equal to or more than their band gap/work function. The first property relevant to the photocatalytic activity of a semiconductor is its energy band configuration, which determines the absorption of incident photons, the photoexcitation of electron-hole pairs, the migration of carriers, and the redox capabilities of excited-state electrons and holes.¹⁷ When a photocatalyst is successfully excited, e^- - h^+ pairs are produced in it and the e^- s migrate to the conduction band (CB) of the catalyst where it can reduce any substrate whereas, the h^+ in the valence band (VB) can oxidize the species in contact.¹⁸ There are mainly two kinds of photocatalysis: 1. Homogeneous - where both the pollutant and the photocatalyst are in the same phase (liquid); 2. Heterogeneous – where they are in different phases (solid-liquid). Heterogeneous photocatalysis is a more popular method because of the ease of retrieving the catalyst after a cycle of reaction for further uses.¹⁴

An ideal photocatalyst should be:

- i. **Earth-abundant:** So that the raw materials utilized to produce it do not lead to expensive mining and handling charges and can be readily available.
- ii. **Visible-Light active:** To maximize energy use.
- iii. **Stable in performance:** By facilitating the generation and long-lived separation of electron-hole pairs which minimizes recombination, otherwise reducing the reaction efficiency.

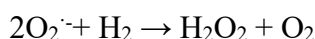
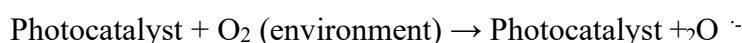
- iv. **Chemically and Structurally Stable:** To prevent degradation during the reaction.
- v. **Environment friendly:** For applications in environmental remediation and water treatment.
- vi. **With High Surface Area:** For more active sites for reactions, which enhances the photocatalytic activity.
- vii. **Cost-Effective:** To facilitate large-scale applications.
- viii. **Easily Recoverable and Reusable:** For making it practical for repeated cycles.

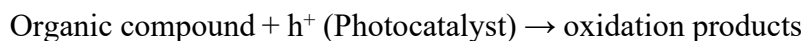
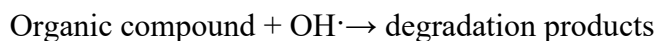
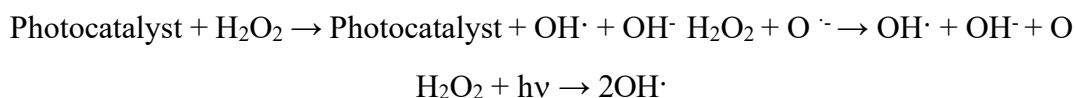
The current use of a wide range of photocatalysts encompasses, but are not limited to, the following environmental and energy-related transformations as follows:

- i. **Solar Water Splitting:** Splitting of water into hydrogen and oxygen using sunlight, which is vital for hydrogen fuel production, a clean and renewable energy source.¹⁹
- ii. **CO₂ Reduction:** Into useful fuels or chemicals, helping to reduce greenhouse gas levels in the atmosphere.²⁰
- iii. **Nitrogen Reduction:** Conversion of nitrogen to ammonia, which is essential for agriculture as it contributes to fertilizer production.²¹
- iv. **Organic Pollutant Degradation:** which can be used for purifying water contaminated by industrial effluents and toxic dyes.²²
- v. **Polymerization and Biomass Conversion:** Free radicals generated through photocatalysis are useful in polymerization processes and converting biomass into valuable chemicals, like aldehydes and acids.²³

These applications showcase the versatility of photocatalysis in supporting sustainable energy and environmental solutions. However, reports on photocatalytic systems always encounter one or two of the classic challenges- limited light absorption, high charge recombination, chemical instability, problems in scalability and product separation, which are the exact ideals for being a good photocatalyst¹⁹. Therefore, deeper studies with rigorous analysis must be done to look for materials which can satisfy all the requirements of being an ideal photocatalyst.

A typical process of photocatalytic degradation of organic compounds through heterogenous photocatalysis after the separation of charge carriers occurs via following reactions:²⁴





These reactions are useful for organic pollutant degradation. The most common pollutant degradation studies are carried on organic dye pollutants like Rhodamine B, Methylene blue, methyl orange, etc. The reactions are also responsible for the generation of H₂ and O₂ through water splitting. As the name suggests, water splitting reaction utilises H₂O to produce O₂ and H₂ through oxidation and reduction respectively. These reactions are separately known as hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). For HER to occur, the conduction band of the photocatalyst must be positioned at a more negative potential than the reduction potential of H^+/H_2 (0 V vs. NHE at pH 0), while the valence band must be positive enough to oxidize water.¹⁹ More often than not, co-catalysts, like platinum or other metals, added to the photocatalyst's surface to catalyze HER.¹⁹ They provide active sites that improve charge separation and lowers the activation energy for the hydrogen evolution step. A typical water-splitting reaction containing HER co-catalyst and OER co-catalyst can be represented by the following **Figure 1.2**.

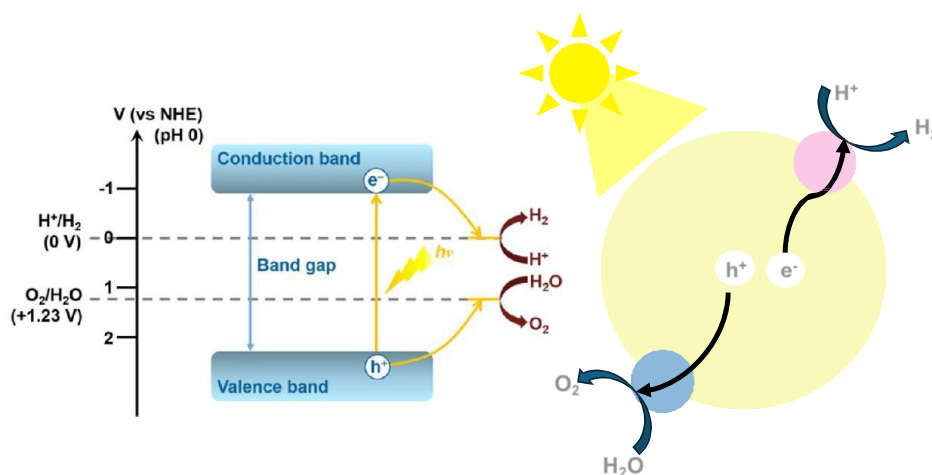
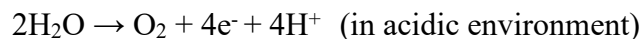


Figure 1.2 Schematics of a water splitting reaction.¹⁹ Adapted from Chem.Rev. 2020, 120, 2, 919–985 DOI: 10.1021/acs.chemrev.9b00201 Copyright © 2019 American Chemical Society. Reprinted with permission.

The Hydrogen evolution reaction (HER) pathway in photocatalytic water-splitting is:

$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (in acidic environment) $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (in basic environment)

The Oxygen evolution reaction (OER) pathway in photocatalytic water splitting can be written as:



Due to the multiple-functionality of a photocatalyst, various semiconductors have been explored as photocatalysts, including metal oxides like ZrO_2 , ZnO , V_2O_5 , TiO_2 , Fe_2O_3 , WO_3 , and CeO_2 , as well as sulphides such as CdS and ZnS .²⁴ Among these, TiO_2 has gained significant attention due to its effectiveness in breaking down organic pollutants in wastewater. In water-based applications, TiO_2 demonstrates a favorable balance between photocatalytic efficiency and stability but is not visible-light active.²¹ Visible light activity in photocatalysts enables the utilization of a larger portion of the solar spectrum, which predominantly consists of visible light (~43%) and only about 4-5% of UV.²⁵ Therefore, photocatalysts with visible light activity can harness sunlight more effectively, reducing the reliance on artificial UV light sources, making the process more energy-efficient and cost-effective. This enhanced activity under visible light is crucial for practical applications like water purification, hydrogen production, and air cleaning, as it enables these processes to operate efficiently under ambient sunlight conditions, promoting greener and more sustainable photocatalytic technologies.

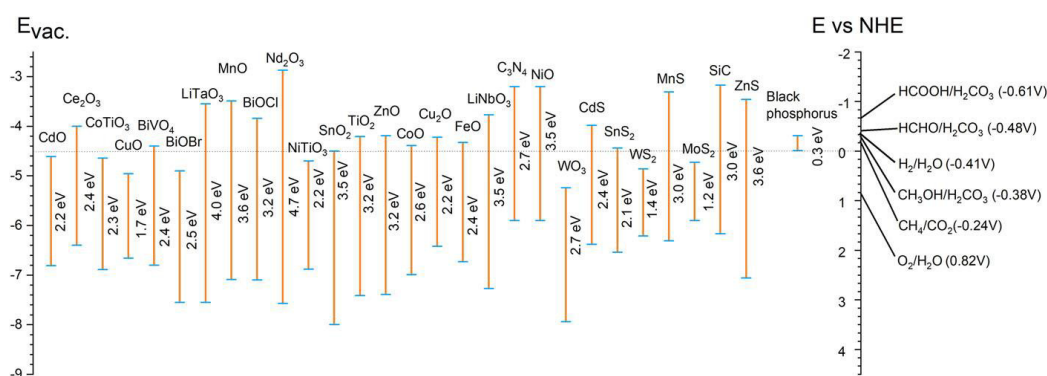


Figure 1.3 Band edge positions of different photocatalysts relative to various redox potentials at pH=7.²⁵ Adapted from APL Mater. 8, 030903 (2020) <https://doi.org/10.1063/1.5140497> Licensed under a Creative Commons Attribution (CC BY) license.

The utilization of visible-light component of the sunlight by a photocatalyst is dependent on its band gap. Additionally, specific redox potentials are required for particular reactions to take place. The **Figure 1.3** shows the band gaps with the band-edge positions of some of the most commonly studied photocatalysts relative to various redox potentials at pH 7.

Recently low dimensional materials have proven beneficial in photocatalysis due to their unique structural, electronic, and surface properties. Quantum dots, such as CdSe and carbon dots, exhibit size-dependent light absorption and emission. Their small size enhances charge separation, although issues like toxicity (for cadmium-based QDs) can limit their environmental applications.²⁶ Materials like Au and Ag utilize surface plasmon resonance (SPR) to capture a broader spectrum of light.¹⁷ The high surface-to-volume ratio of Two-dimensional (2D) materials provides abundant active sites for reactions, while their reduced thickness facilitates efficient charge carrier transport, minimizing recombination losses.^{27–29} These materials exhibit enhanced light absorption and tunable optical properties, making them ideal for visible light photocatalysis.²⁹ The quantum confinement effect in ultra-thin materials adjusts the bandgap for improved light utilization. Additionally, 2D materials can be easily doped or hybridized, enabling tailored properties for specific applications, such as water splitting, pollutant degradation, and CO₂ reduction.³⁰ They are beneficial in enhancing the efficiency of photocatalysis but are often costly. 2D materials like g-C₃N₄ and MXenes, offer high surface areas and adjustable bandgaps. However, challenges such as stability in reactions and issues in synthesis methods persist.¹⁴

The history of metal-free graphitic carbon nitride (g-C₃N₄) dates back to 1834, when Liebig discovered compounds like melamine, melem, melam, and melon, which were later identified as parts of triazine and tri-s-triazine structures.³¹ Liebig named the yellow powder, formed from the polymerization of potassium thiocyanate and aluminum chloride, "melon."³² However, due to limited characterization methods at the time, these compounds did not attract significant attention. In 1922, Franklin revisited these findings with improved characterization techniques. Despite this, research on g-C₃N₄ progressed slowly, largely because of its high chemical stability and insolubility in most reagents.³³ In 1989, Liu and Cohen discovered that β -C₃N₄ could achieve a hardness comparable to diamond by replacing silicon in β -Si₃N₄ with carbon, sparking renewed interest in g-C₃N₄ for theoretical and practical applications.³² Building on this, Teter and Hemley in 1996 proposed five forms of g-C₃N₄— α -C₃N₄, β -C₃N₄, pseudocubic-g-C₃N₄, cubic-C₃N₄, and g-C₃N₄. While α -C₃N₄, β -C₃N₄, pseudocubic-g-C₃N₄, and cubic-C₃N₄ exhibit impressive hardness, their low stability has hindered synthesis efforts.³² In contrast, g-C₃N₄ is relatively easy to synthesize, highly stable, and possesses semiconducting properties.

g-C₃N₄ is a conjugated polymer semiconductor composed of tris-triazine and/or heptazine units. The sp² hybridization of carbon and nitrogen atoms in g-C₃N₄ forms a π -conjugated electronic structure.³¹ With a moderate band gap of around 2.7 eV, g-C₃N₄ is capable of absorbing visible light at wavelengths approximately between 450 and 460 nm.³⁰ g-C₃N₄ is typically synthesized through thermal polymerization of nitrogen-rich organic compounds, such as urea, melamine, and cyanamide.³⁰ This simple synthesis process, conducted under mild conditions, allows to produce g-C₃N₄ with adjustable

compositional, electronic, and physicochemical properties. These tunable properties are essential for g-C₃N₄ use in photocatalytic applications, particularly in environmental remediation and energy conversion.

A breakthrough in metal-free photocatalysts occurred in 2009 when Wang and colleagues demonstrated that g-C₃N₄ could be used for photocatalytic hydrogen production under visible light.³⁴ This discovery ignited a surge in research, leading to a dramatic increase in publications on g-C₃N₄. While ongoing research continues to explore the catalytic mechanisms behind photoinduced redox reactions, graphitic carbon nitride (g-CN) has emerged as a promising metal-free photocatalyst. This two-dimensional (2D) conjugated polymer, made from nitrogen-rich, inexpensive organic materials, has drawn considerable interest due to its unique properties and simple synthesis. Over recent years, polymeric g-CN has been extensively studied as a versatile photocatalyst with applications in hydrogen production, CO₂ reduction, water purification, environmental remediation, and even artificial photosynthesis.^{30,35–37}

Despite this, g-C₃N₄ exhibits relatively low quantum efficiency in solar hydrogen production. The lower efficiency may stem from issues with charge separation and transfer due to imperfections in its structure or irregularities during crystal formation.³⁸ These structural defects can encourage electron-hole recombination at specific surface sites, which diminishes the photocatalytic performance.

Various methods have been utilized by researchers to modify the structure and band gap of g-C₃N₄ to amplify its photocatalytic yield. Some of the main methods can be summarized as below:

- i. **Elemental Doping:** Introducing non-metal elements (e.g., nitrogen, oxygen, sulphur) or metal ions (e.g., Fe, Pt) into the g-C₃N₄ structure modifies its electronic properties and reduces recombination rates.^{39,40} Non-metal doping generally narrows the band gap and enhances visible light absorption, while metal doping introduces defect states that improve charge separation.⁴¹
- ii. **Heterojunction Formation:** Creating heterojunctions by combining g-C₃N₄ with other semiconductors (e.g., TiO₂, ZnO) improves charge separation and broadens the light absorption spectrum.^{42–45} The different band positions in the heterojunction facilitate directional charge transfer, enhancing photocatalytic efficiency.
- iii. **Surface Modifications:** Adding co-catalysts like platinum (Pt) or modifying the surface with functional groups improves electron transfer and reduces the overpotential for catalytic reactions.⁴⁶ Surface modifications also increase the active sites for photocatalytic processes.
- iv. **Dimensional Reduction:** Reducing g-C₃N₄ to nanosheets or quantum dots enhances the surface area, boosts electron transport, and reduces the distance for charge carrier migration.^{47–49} This structural change results in a higher number of reactive sites and improved photocatalytic activity.
- v. **Defect Engineering:** Introducing structural defects (e.g., nitrogen vacancies) creates mid-gap states, reducing the band gap and enhancing visible light absorption.^{50,51} These defects also act as traps for charge carriers, which can help reduce recombination and increase the lifetime of photogenerated charges.⁵²

- vi. **Porous Structure Creation:** A porous g-C₃N₄ structure provides more surface area and light-scattering centers, enhancing light absorption and increasing active sites.^{53–56} Porosity also improves the accessibility of reactants, thereby boosting photocatalytic reactions.⁵⁷

All the above-mentioned techniques enhance the charge separations in g-C₃N₄ compounds and have significantly increased their photocatalytic performance. Recently, bulk modifications like co-polymerization, polycondensation, polymer blending and polymer linking have also been utilised to synthesise a modified carbon nitride structure which possesses the 2D layered structure of g-C₃N₄ but do not necessarily have a C₃N₄ composition.^{46,58}

The overall structure, electronic properties, and band gap is modified during the synthesis process from within the bulk material rather than just at the surface. This modification adjusts the conjugated network and can incorporate various functional groups throughout the entire g-C₃N₄ framework, leading to changes in its optical and electronic properties, thereby enhancing photocatalytic activity.³² Song et al. employed a straightforward copolymerization method using urea and polyethyleneimine (PEI) to introduce defects into the g-C₃N₄ structure.⁵⁹ Elemental C doping was done by Liu et al. through a copolymerization strategy with chitosan as carbon source.⁶⁰ Ho et.al developed copolymerization with 2,4,6- triaminopyrimidine (TAP) to precisely substitute one nitrogen atom with a carbon atom in the triazine ring of polymeric g-C₃N₄.⁶¹

In the last decade, the optoelectronic properties of g-C₃N₄ have also been explored and a phenyl-modified carbon nitride material has come out as a promising emitter with great visible-light applications, which in turn also improves the photocatalytic applications of the material.^{62,63} This modified polymorph of g-C₃N₄ was our material of interest and is discussed in the next section.

1.2. State-of-the-Art

The addition of phenyl groups to the carbon nitride framework alters the electronic structure and creates an extended π -conjugated system, which enhances light absorption, especially in the visible range.⁶⁴ Phenyl groups provide electron-rich aromatic rings that promote efficient charge transfer and reduce the recombination rate of electron-hole pairs.⁶⁵ This modification not only improves the photocatalytic efficiency of carbon nitride for applications such as hydrogen evolution and pollutant degradation but also increases its structural stability under reaction conditions.⁶⁶ In typical synthesis strategies, phenyl-modified carbon nitride (PhCN) is obtained through copolymerization methods, where precursors like melamine or urea are combined with phenyl-containing monomers, such as 2,4,6- triaminopyrimidine (TAP).^{61,67} This approach enables a controlled insertion of phenyl units into the g-C₃N₄ framework, resulting in a more versatile photocatalyst with tunable properties tailored for specific reactions. Through copolymerization and other defect engineering strategies, phenyl-modified carbon nitride emerges as a promising solution for various environmental and energy applications, combining the benefits of carbon nitride's stability with improved light absorption and charge dynamics provided

by phenyl groups. **Figure 1.4** shows the polymerization scheme of 6-phenyl-1,3,5-triazine-2,4-diamine to obtain phenyl-modified carbon nitride structure.

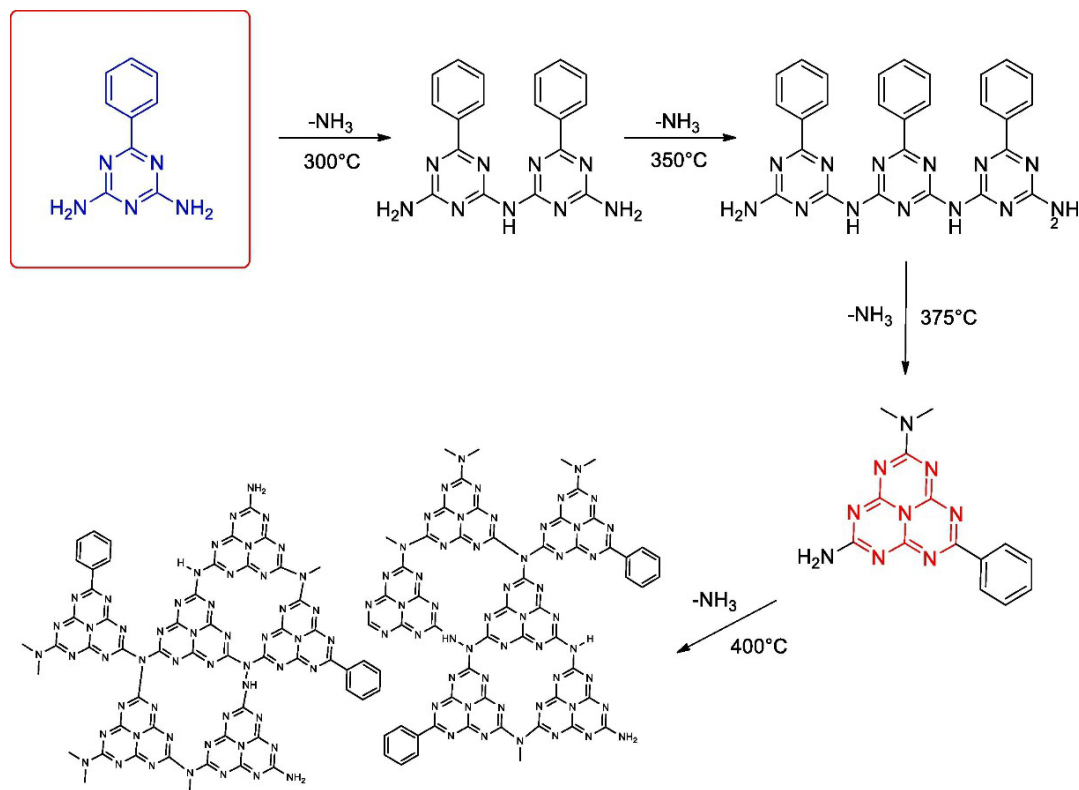


Figure 1.4 Thermal polymerisation of benzoguanamine to obtain PhCN.⁶⁴ Adapted from *Applied Surface Science*, (2020) 504, 144330. <https://doi.org/10.1016/j.apsusc.2019.144330> Copyright © 2019 Elsevier B.V. All rights reserved. Reproduced with permission.

The development of phenyl-modified carbon nitride (PhCN) as a better functional material, has led to several innovative approaches in its synthesis and structural design. Below are key advancements in the synthesis techniques and modifications that have been used to generate phenyl-modifications in g-C₃N₄:

i. Copolymerization and Defect Engineering

Copolymerization is one of the primary methods used to introduce phenyl groups into the g-C₃N₄ framework like in **Figure 1.4**. In this approach, different organic monomers, such as urea or melamine, are combined with phenyl-containing compounds like 2,4,6-triaminopyrimidine (TAP) to control the placement and concentration of phenyl groups within the structure.⁶¹ This process allows for the precise introduction of nitrogen defects, which act as charge traps, enhancing the separation of photogenerated electron-hole pairs and reducing recombination rates.

Recent studies have demonstrated that phenyl copolymerization not only modifies the electronic structure but also improves the stability of the resulting PhCN material under UV and visible light irradiation.^{68,69} Researchers have observed that the copolymerized PhCN shows improved photocatalytic efficiency compared to g-

C₃N₄, particularly in hydrogen evolution and pollutant degradation.^{70,71}

ii. Functional Group Integration

Another significant advancement is the integration of specific functional groups along with phenyl units to further enhance photocatalytic properties. Functional groups such as electron-donating (e.g., amino groups) or electron-withdrawing groups (e.g., sulfonates or carboxylates) can be introduced to tune the electron density and band structure of PhCN.⁷²⁻⁷⁴ These modifications enhance the material's visible light absorption and facilitate improved charge mobility.

For instance, studies have shown that introducing sulphate groups alongside phenyl units creates a dual modification, leading to enhanced light absorption and more efficient charge separation due to the establishment of electron pathways between interlayer sulphate groups.⁷³ This synergy results in higher hydrogen evolution rates, as the sulphate and phenyl groups collectively create a more negative conduction band and promote faster electron transfer across layers.⁷³

iii. Supramolecular and Molecular Engineering

Supramolecular assembly techniques offer precise control over PhCN's morphology and surface properties. This method allows for the formation of organized structures like nanotubes, nanosheets, or hollow spheres, which provide high surface areas and better exposure to light.⁷⁵ The enhanced surface area not only increases the number of active sites for photocatalytic reactions but also facilitates charge transport by shortening diffusion pathways for electrons and holes.⁷⁶

Phenyl-modified carbon nitride (PhCN) has proven to be an adaptable material for diverse photocatalytic applications, with significant improvements over unmodified carbon nitride in terms of stability, light absorption, and charge separation. The following are some of the main applications of PhCN in photocatalysis, demonstrating its versatility and effectiveness in both environmental and energy applications.

- i. **Degradation of Pollutants** found in wastewater and industrial effluents. The phenyl modification in carbon nitrides extends its light absorption into the visible spectrum, enabling it to harness more solar energy for breaking down persistent pollutants, such as dyes, pharmaceuticals, and pesticides.^{66,69,77} The stability of PhCN under harsh conditions also ensures consistent performance over multiple cycles, making it a practical solution for large-scale water treatment processes.
- ii. **Hydrogen Evolution Reaction (HER)**- Studies have shown that the incorporation of phenyl groups in carbon nitrides not only improves the charge separation process but also shifts the conduction band to a more negative potential, which is beneficial for HER.^{32,78} Recent reports have demonstrated that PhCN, when combined with appropriate co-catalysts like platinum (Pt), achieves high hydrogen generation rates

and quantum efficiencies, making it a competitive alternative to more expensive metal- based photocatalysts.⁷⁴

- iii. **Carbon Dioxide Reduction** to valuable chemicals, such as methane, methanol, and carbon monoxide, under light irradiation.⁷⁹ The phenyl modifications in g-C₃N₄ improve its electron-donating ability and enhance the selectivity for CO₂ reduction products by creating electron-rich sites.
- iv. Beyond traditional photocatalytic applications, PhCN is also being explored for **biosensing** and **environmental monitoring**.⁷⁶ The extended π - conjugation and tunable surface properties of PhCN make it suitable for detecting biological and environmental analytes.^{65,68} PhCN-based sensors benefit from high surface area, chemical stability, and improved signal transduction, making them promising for use in detecting organic pollutants and biomolecules at trace levels.

Some of the recent reports on the utilization of Phenyl- group incorporated carbon nitride in photocatalytic water remediation are summarised in the following **Table 1.1** :

Table.1.1 Recent advancements in phenyl-carbon nitride structures for photocatalytic water remediation.

Precursor	Synthesis method	Application	Efficiency	Year	[Ref]
Urea, Phenyl urea , Melamine	Co-polymerization	RhB dye degradation	k = 0.307 min ⁻¹	2019	⁷⁹
Melamine, 4-diamino-6-phenyl-1,3,5-triazine	Co-polymerization	H ₂ production	H ₂ evolution rate- 69.9 μ mol h ⁻¹	2017	⁸⁰
Melamine, Cyanuric acid, 2,4-diamino-6-phenyl-1,3,5-triazine	Co-polymerization	RhB dye degradation	16x g- C ₃ N ₄	2014	⁸¹
Urea, Phenyl urea	Co-polymerization	H ₂ production	535 μ mol h ⁻¹	2013	⁸²
Urea, Benzamide	Co-polymerization	H ₂ production, RhB dye degradation	2.38 mmolg ⁻¹	2016	⁸³
Urea, 4-Nitro- <i>o</i> -phenylenediamine	Co-polymerization	Bisphenol A degradation	K = 4.88 $\times 10^{-3}$ min ⁻¹	2024	⁷²
Melamine, PPDS	Hydrothermal-calcination	H ₂ production	8709.29 μ mol g ⁻¹ h ⁻¹	2024	⁷³

phenylguanidine carbonate	Polymerization-gelification-liquid exfoliation	chromium(VI) reduction	3055.9 mg g ⁻¹	2024	⁶⁶
Benzoguanamine	Polymerization – acid liquid exfoliation	Reduction of 4-nitrophenol	2.78×10 ⁻¹ min ⁻¹	2021	⁶⁹
2-aminobenzonitrile, melamine, cyanuric acid	Co-polymerization	Oxidation of Benzyl alcohol	94.5% under 8 h	2023	⁸⁴

As the above table shows, the photocatalytic activities of carbon nitrides in water could be enhanced a lot by the addition of a phenyl group to the polymeric structure. Due to the great enhancement of photocatalytic activity of phenyl-added-CN as compared to g-C₃N₄, more research should be focused on this material to address the existing challenges shown in **Figure.1.5** by further modifications in its structure.

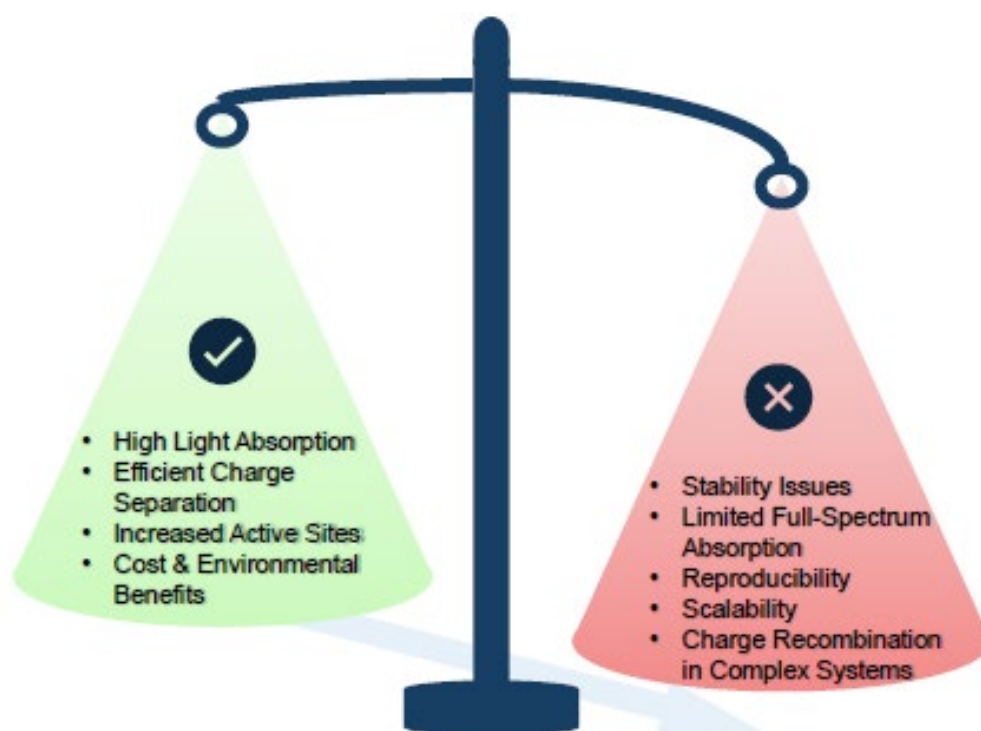


Figure 1.5 Comparing the advantage of PhCN over g-C₃N₄ and PhCN's demerits.

Therefore, we were intrigued about this material and planned to further explore its modifications in turn to observe an increased visible-light harnessing ability.

1.3. Objective

The main goal of this research is to enhance the photocatalytic performance of phenyl-modified carbon nitride (PhCN) for environmental applications.

Specifically, the research aims to develop advanced PhCN-based materials through targeted traditional modifications namely- exfoliation, addition of a co-catalyst, organic-inorganic heterojunction formation and elemental doping. These modifications are explored in-depth to understand the underlying mechanisms and the usability of the end products. These enhancements are focused on maximizing the efficiency of PhCN in environmental applications mainly focalised on organic

pollutant degradation, hydrogen fuel production and virus inactivation in practical conditions. Utilization of the solar spectrum through visible-light activity is one of the main concerns of this study. The study further seeks to address existing limitations in PhCN stability and photocatalytic performance, providing a pathway toward scalable, high-performance photocatalysts for clean energy and water remediation which could be cost-effective and biofriendly.

This is achieved by exploring three main strategies:

Optimizing PhCN structure for H₂ Production (Chapter 2): Through exfoliation and co-catalyst integration with 2D WS₂, this work aims to create a PhCN/WS₂ hybrid system that leverages enhanced visible-light-induced charge separation. This component of the research addresses the need for cost-effective, sustainable hydrogen production by using earth-abundant materials in place of noble metals and demonstrating their effectiveness in solar-driven hydrogen evolution.

Creating Advanced Heterojunctions for Pollutant Degradation and Viral Inactivation (Chapter 3): Developing a PhCN/TiO₂ heterojunction for the degradation of the industrial organic dye pollutant- Rhodamine B, utilization of the pollutant molecules of Rhodamine B for hydrogen production; and deactivation of H1N1 flu virus under visible light and ambient conditions, expands the potential applications of the PhCN photocatalyst. This system is designed to extend light absorption into the visible spectrum, enhancing photocatalytic performance and demonstrating multiple functionalities, essential for water treatment, sustainable fuel generation as well as indoor applications.

Modifying PhCN Through Boron Doping for Broadened Photocatalytic Applications (Chapter 4): By doping PhCN with boron, this component investigates the structural and electronic modifications introduced by boron, enhancing photocatalytic performance under visible light. The objective is to understand and leverage boron's effect on charge separation, light absorption, and surface reactivity, making PhCN suitable for a broader range of photocatalytic applications, including pollutant and contaminant removal in water.

Chapter 2

Integration of 2D WS₂ as a co-catalyst with exfoliated PhCN for enhanced visible-light H₂ fuel production.

Hazra, M.; Hoffer, M.; Fickl, B.; Ertl, A.; Myakala, S.N.; Eder, D.; Porcu, S.; Cherevan, A.; Bayer, B.; Ricci, P.C. Enhanced PhCN Nanosheet Stacking Order via WS₂ Linkers: A Metal Co-Catalyst Free 2D-2D Photocatalyst for Hydrogen Production. (under preparation)

Abstract

This chapter attempts to understand the effects of liquid phase exfoliation in PhCN and WS₂ and how their hybridization affects the photocatalytic HER. Structural, chemical and optical properties of exfoliated PhCN nanosheets are analysed and compared with the bulk properties. It is studied whether the changes induced by ultrasonication in the PhCN nanosheets is like the reported changes in g-C₃N₄. Moreover, this chapter attempts to analyse the effect of the presence of the phenyl group on the exfoliation process. The results indicate that the choice of solvent is crucial for effective exfoliation. The H₂ productivity under visible light irradiation is evaluated for all the systems and it is found that the steric hinderance, surface tension, polarity and boiling point of the solvents affect the resultant photocatalytic activity. It is to the best of our knowledge that for the first time, exfoliation of aromatic PhCN was carried out and exploited for hydrogen gas evolution. An understanding of supramolecular alteration of PhCN by ultrasonication is achieved through structural and optical characterizations. The results show an enhancement in the HER activity after exfoliation due to better charge separation. Then, the LPE of WS₂ is also studied with a green solvent and liquid centrifugal cascading is done to obtain different dispersions with varying monolayer concentrations and nanosheet sizes. The hybridisation of exfoliated PhCN with exfoliated WS₂ was performed because of its promising co-catalyst behaviour which shows 42 times more H₂ activity than otherwise. The results show that WS₂ can be substituted as a co-catalyst for visible light photocatalysis in the place of the noble metal 'Pt' and shows about 10% of the proficiency of Pt as a co-catalyst by mass. The effect of WS₂ size was also studied in the hybrid. The interaction between PhCN and WS₂ is studied which helped to propose the mechanism of action of the system obtained by a green synthesis procedure.

2.1. Introduction

The energy band structure and the structural conjugation system of g-C₃N₄ can be successfully modified with phenyl group addition for high H₂ generation under visible light irradiation according to Dai et al.⁷⁰ The modification of the band gap and low charge recombination helps in better photocatalytic HER performance of PhCN.⁷⁰ However, it still exhibits a high photoluminescence under visible-light and a low surface area and porosity which hampers the number of photocatalytic sites on PhCN.⁷⁷ Surface modification or structural modification of PhCN prior to hybridization can be an effective strategy to obtain higher yields of H₂. Exfoliation of a layered material is a fairly simple process compared to doping, creating defects and other chemical treatments which does not include expensive procedures and can be easily scalable.

There are several ways to delaminate bulk layered materials- thermal etching, chemical exfoliation, hydrothermal exfoliation, ultrasonic exfoliation, etc. A number of studies have explored this approach to obtain free-standing layers of g- C₃N₄ and have reported an improved photo-response, light absorption and water solubility which aids in photocatalytic applications.^{48,85-89}

In liquid phase exfoliation process, ultrasonic waves are utilized to expand and generate cavitation bubbles which penetrates the liquid medium in which the bulk material is suspended.⁴⁸ This process results in strong mechanical effects due to high temperature and pressure generated by the ultrasonic waves. LPE of g-C₃N₄ have been reported to enhance intrinsic photocurrent and have high PL quantum yield with high biocompatibility and non-toxicity.^{48,86,87,90} The ultrasonic exfoliation process also results in high surface area, large aspect ratios and reduced photoexcited charge carrier recombination.⁸⁵ Yang et al. also reported a homogeneous dispersion of C and N on these exfoliated nanosheets.⁹¹ These results are promising towards a high photocatalytic response of exfoliated PhCN. Cui et al reported enhanced photoresponse and high quantum yield of exfoliated PhCN suitable for bioimaging.⁶⁸ Mei et al used the liquid phase exfoliated PhCN to detect thiram in tap water.⁹⁰ Liu et al used the material for anti-counterfeiting applications.⁹² While all these reports discuss the stokes shift and quantum yield of exfoliated PhCN, there have been no reports on the HER study of exfoliated PhCN system.

It is very important to choose an ideal liquid medium to perform the exfoliation procedure. The surface energy of the solvent is extremely important for the exfoliation efficiency as the enthalpy of mixing is minimum when the nanosheets and the solvent have the same surface energy.⁹³

$$\frac{\Delta H_{Mix}}{V_{Mix}} \approx \frac{2}{T_{sheet}} (\delta_G - \delta_{sol})^2 \phi$$

The above equation gives the enthalpy of mixing ΔH , represents the energy of exfoliation whose lower value means higher exfoliation efficiency. Where, T is the thickness of the nanosheets, δ is the square root of component surface energy and ϕ is the volume fraction of nanosheets.

Therefore, choosing the right solvent is crucial to have unaltered structure of the starting material. It has been reported that liquid phase exfoliated nanosheets are highly crystalline when solvent with matching surface energy is used for the process which keeps the entire solution in a chemically stable state and does not let the solvent react with the nanosheets.⁹⁴ Various solvents like- water, iso-propyl alcohol, ethanol, formamide, methanol, acetone, etc. have been utilized for the exfoliation of g-C₃N₄ and it has been found with theoretical studies that the surface energy of g-C₃N₄ nanosheets are 115 mJ m⁻² but solvents with surface energy of approx. 40 mJ m⁻² also show efficient exfoliation.^{54,56,68,88,89,91,95} Hence, factors like steric repulsion, which is dependent on the size of the solvent molecules are also responsible for the exfoliation yield.

The evolution of H₂ gas via photocatalytic HER is dependent on the surface available to the photocatalyst and the number of active sites present on the surface per unit area.⁹⁶ The H₂ evolution happens at the surface by the consumption of the photoexcited charge carriers that reach there, and the kinetics of the surface chemical reactions determine the photocatalytic HER performance.¹⁹ Hence, it is important to understand the surface chemical reactions on the photocatalyst to maintain an optimum H₂ yield. According to Volmer-Heyrovsky mechanism, the formation of hydronium ion (proton) is the potential-determining step for H₂ evolution, but the hydronium ions are highly prone to reduction.¹⁹ Water molecules surrounding the photocatalyst are comparatively difficult to reduce due to the presence of strong O-H bonds in them. Several other side and back reactions can also compete with the HER and hamper the H₂ yield.¹⁹ Hence, co-catalysts are used to act as reaction sites by creating junctions and catalysing the preferred reactions. These materials also help in charge separation and boosts the reactions on the surface of the photocatalyst by lowering the activation energy of the reactions.^{97,98}

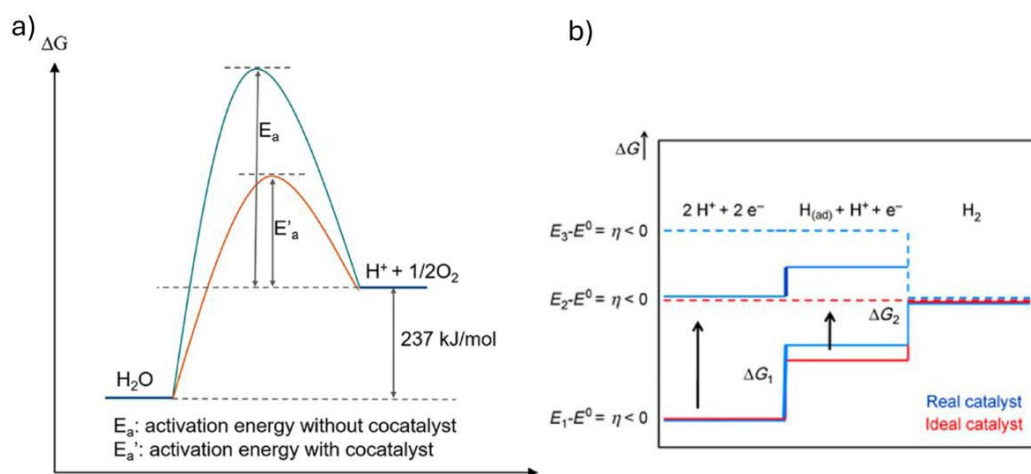


Figure 2.1 a) Schematic of the energy diagram for photocatalytic water splitting., b) Plots of Gibbs free energies of reactive species and of the chemisorptions of intermediates (horizontal lines) versus the reaction coordinate of HER. Blue lines and red lines indicate energetics of a typical (real) catalyst and ideal catalyst at three different electrode potentials (E_1, E_2, E_3), respectively. Dashed lines indicate energetics at the electrode potential at which all thermochemical barriers disappear. ΔG_i denotes the free reaction energy of the two elementary reaction steps. The red case corresponds to an overpotential-free catalyst. E° denotes the standard reversible electrode potential of the HER, η is the overpotential.¹⁹ Adapted from Chem.Rev. 2020, 120, 2, 919–985 DOI: 10.1021/acs.chemrev.9b00201 Copyright © 2019 American Chemical Society. Reprinted with permission.

Pt metal doping is vastly used for HER co-catalyst applications due to its large work-function which aids in reducing electron-hole recombination and results in an effective junction, but its high price prevents commercialization in large quantities.⁹⁹ Therefore, recent studies focus on noble-metal free co-catalysts for HER. Development of new co-catalysts should also consider the environmental impact of mining the constituent elements. A range of materials like- metal carbides^{29,100}, sulphides^{101,102}, phosphides¹⁹ and alloys^{19,103,104} have been used as co-catalysts for photocatalytic water-splitting to produce H_2 and O_2 . It has been stated that efficient electrocatalysts tend to act as good co-catalysts.⁷⁸ Among the abundant earth materials which are useful for co-catalysation, Metallic transition-metal dichalcogenides (TMDCs) are an emerging class of earth-abundant materials which are highly active and act as robust electrocatalysts for hydrogen evolution reactions (HER).^{38,102,105}

TMDCs are formulated as MX_2 where M stands for a transition-metal atom from group IVB to VIIB of the periodic table and X is a chalcogen atom like S, Se or Te.¹⁰⁶ The metal atom in TMDCs is sandwiched between the two chalcogen atoms hence a unit of TMDC consists of 3 atomic layers. They are 2D materials and have a layered structure where the interlayer bonds are weak van der Waals forces which then can be easily exfoliated to

extract monolayers and enhance photocatalysis by exposing more active sites on the edge and basal planes.¹⁰⁷

Many reports have been published which uses TMDCs as co-catalysts with different semiconductor photocatalysts eg. MoS₂/CdS³⁸, MoS₂/TiO₂, MoS₂/ZnInS₄¹⁰¹, WS₂/CdS¹⁰⁸, WS₂/g-C₃N₄¹⁰⁹, WS₂/Nb₂O₅¹¹⁰, MoSe₂/g-C₃N₄¹¹¹ etc. MoS₂ is the most studied TMDC for co-catalysation, but studies reveal that WS₂ has lower Tafel slope and an earlier overpotential which makes it more suitable for photocatalytic HER in addition to being less toxic and cheaper as compared to other TMDCs.³⁸

For our work, we chose to hybridise WS₂ as a co-catalyst with PhCN due to its high surface area, favourable electrochemical activity, photocatalytic and electronic efficiency, high carrier mobility, biocompatibility, and tuneable bandgap.¹¹² WS₂ occurs in 1T metallic phase and 2H semiconducting phase. The hexagonal (2H) bulk to monolayer transition leads to an indirect (less than 1.5 eV) to a direct band gap (more than 2 eV) transition depending on the synthesis technique used.¹¹³ Archana et al. reported high HER yield of CdS/WS₂ composite compared to MoS₂ substitution because of better ability of WS₂ to cover CdS surface with tighter contacts.³⁸ Photodeposition of WS₂ on TiO₂ has been reported to extend its visible light absorption.¹¹⁴ An impregnation-sulfidation approach was taken by Hou et al. to make WS₂/g-C₃N₄ (mpg-CN) composite which resulted in thin layered junctions and high HER activity.¹¹⁵ In recent years, WS₂ deposition on carbon nitrides have been studied well for photocatalytic applications. Most works have been carried out for organic pollutant degradation¹¹⁶, H₂O₂ production^{116,117} and electrochemical energy storage¹¹⁸ and photocatalytic HER¹¹⁹ (with 2H WS₂ as a photocatalyst) using this hybrid system. **Table 2.1** summarizes the reports of WS₂ utilized as a co-catalyst with carbon nitride-based systems for photocatalytic H₂ production. The use of 1T metallic WS₂ as co-catalysts is difficult to obtain as it has tendency to return to its 2H phase under high temperatures¹⁰⁷. Hence, it is important to use hybridization procedures which preserves the structure of both the components. Liang et al. reported a successful 1T-WS₂/g-C₃N₄ nanotube photocatalyst for high HER activity under 370nm irradiation via a simple grinding self-assembly procedure.¹²⁰ Hence, we used a simple self-assembly procedure to hybridise 2D WS₂ with our exfoliated PhCN pre-optimised for H₂ production.

Table 2.1 Reports on g-C₃N₄/WS₂ systems for photocatalytic H₂ production.

Hybrid system	Hybridisation procedure	HER activity	Light source	Ref.
Ag nanoparticles bridged g-C ₃ N ₄ and WS ₂	solvent evaporation and high temperature calcination	68.62 $\mu\text{mol h}^{-1}$	simulated sunlight irradiation	121
g-C ₃ N ₄ /WS ₂ sandwich WS ₂ /g-C ₃ N ₄	one-pot calcination Heating	599.7 $\mu\text{mol h}^{-1} \text{ g}^{-1}$ 257 mmol h^{-1}	300 W Xe lamp AM 1.5 solar simulator (100 mWcm ⁻²).	122 100
IT-WS ₂ /g-C ₃ N ₄	one-step calcination route.	10.08 $\text{mmol} \cdot \text{g}^{-1} \text{ h}^{-1}$	300 W Xe lamp	123
WS ₂ /2D-C ₃ N ₄	Self-assembly grinding	331.09 $\mu\text{mol h}^{-1} \text{ g}^{-1}$	300W Xenon lamp with an optical filter ($\lambda > 400 \text{ nm}$)	98
IT-WS ₂ /g-C ₃ N ₄	simple grinding method	1021 $\mu\text{mol h}^{-1} \text{ g}^{-1}$	$\lambda = 456 \text{ nm}$	120
IT-WS ₂ /NCN	In-situ stirring	1923.1 $\mu\text{mol g}^{-1} \text{ h}^{-1}$	300 W xenon lamp simulating solar irradiation	124
WS ₂ /g-C ₃ N ₄	One-pot synthesis (calcination-filtration)	154 $\mu\text{mol h}^{-1} \text{ g}^{-1}$	300W Xe Lamp	119
g-C ₃ N ₄ /WS ₂	One-pot synthesis	101 $\mu\text{mol g}^{-1} \text{ h}^{-1}$	300 W xenon arc lamp with a UV-cutoff filter ($\geq 420 \text{ nm}$)	125
WS ₂ /g-C ₃ N ₄	in-situ vulcanization	219.9 $\mu\text{mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$	($\lambda > 420 \text{ nm}$)	126
g-C ₃ N ₄ /WO ₃ /WS ₂	Growth of WO ₃ /WS ₂ on CN	3.83 $\text{mmol g}^{-1} \text{ h}^{-1}$	($\lambda > 420 \text{ nm}$)	43

$g-C_3N_4/C-TiO_2/WS_2$	Electrostatic self-assembly then annealing	985.8 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	300 W Xe lamp equipped with a UV light filter ($\lambda > 420\text{ nm}$) ¹¹⁴
$g-CN/WS_2(2H/1T)$	<i>in situ</i> gas-solid phase reaction	34.76 $\mu\text{mol}\cdot\text{h}^{-1}$	300W Xe Lamp working with a 420 nm cut off filter ¹²⁷
$g-C_3N_4/WS_2-Y$ (Y: Ni, Co)	Chemical reduction	0.249 $\text{mmol g}^{-1}\text{h}^{-1}$	Solar Simulator (with cut-off filter $\lambda \geq 420\text{ nm}$) ¹²⁸
$WS_2/WO_3/g-C_3N_4$	hydrothermal		300 W Xe lamp with cutoff filter allowing $\lambda > 420\text{ nm}$. ¹¹⁸

This chapter aims to study the results of ultrasonically exfoliated PhCN nanosheets and their properties compared to exfoliated $g-C_3N_4$. It is to establish whether the phenyl-modified system has the same effect of exfoliation as $g-C_3N_4$. For this, various solvents are utilized for the exfoliation process of PhCN to check for the best HER activity. The idea is to increase the HER productivity of the PhCN without losing its structural integrity with a simple and green method. The WS_2 is exfoliated with a similar LPE method, and a good monolayer yield is obtained. To conserve the 2D sheet structure of PhCN, post-loading of WS_2 via electrostatic self-assembly was performed. Then the interaction between exfoliated PhCN and mono/few-layered WS_2 was studied to understand the mechanism for photocatalytic HER. Due to its eco-friendly composition, sustainable synthesis, and environmental applications, PhCN/ WS_2 shows promise as a green material.

2.2. Materials and experiments

2.2.1. Chemicals required

Benzoguanamine ($C_6H_5(C_3N_3)(NH_2)_2$ (Ph-Triazine, 99%, Sigma Aldrich), Iso propanol (IPA, C_3H_7OH , %, Sigma-Aldrich), Ethanol (EtOH, from Chem-Lab NV), Deionised Water, H_2PtCl_6 (Fluka (Sigma Aldrich), Triethanolamine (TEOA, $N(CH_2CH_2OH)_3$, 98+%, Alfa Aesar).

2.2.2. Synthesis of exfoliated PhCN

1.9 g of benzoguanamine was put in a glass vessel and covered well to be put inside a furnace for heating at 400°C for 2 hours. The heating ramp was kept at $10^\circ\text{C}/\text{min}$. 50mg of as-prepared PhCN powders were taken in a 25ml glass vial and 15ml of the exfoliating solvent was added to it. The mixture was then sonicated using Sonorex Digitec DT 255 in an ice bath for 8 hours continuously (Appendix Figure A1). The suspension was then dried in vacuum at room temperature to obtain PhCN nanosheets. The powder was collected from the glass vial and named as $PhCN_{\text{solvent}}$. The solvents used were- i. IPA,

ii. EtOH and iii. H₂O. Hence, the 3 exfoliated samples were PhCN_{IPA}, PhCN_{EtOH} and, PhCN_{H₂O}.

2.2.3. Synthesis of 2D WS₂

2D WS₂ was produced via LPE in neat isopropanol in a temperature-stabilised ultrasonic bath (~ 0 °C), followed by centrifugation up to 4500 rpm for size selection.⁹³ WS₂ bulk crystals as starting material for LPE were self-made via direct solid-state synthesis of high-purity W and S powders in an evacuated quartz vial placed in a hot wall furnace at >1000 °C for >24 h. The obtained dispersion was named WS₂_1 and was further centrifuged at 2500rpm for 2 hours to obtain WS₂_2 dispersion (Appendix Figure A2).

2.2.4. Synthesis of PhCN/WS₂ hybrid

50mg of PhCN was exfoliated in 15ml IPA for 8 hours. Therefore, the concentration of the PhCN dispersion is 3.33mg ml⁻¹. According to the concentrations of WS₂ dispersions calculated by the extinction spectra, a certain volume of WS₂ dispersions were added to the PhCN_{IPA} dispersion so that the mass of WS₂ is 0.75mg which is 5% of PhCN wt. The suspension was then covered and stirred overnight. The IPA was then evaporated in ambient conditions. The dried powders were collected and named PhCN/WS₂_1 and PhCN/WS₂_2 depending on which WS₂ dispersion was used.

2.2.5. Photocatalytic HER tests

Hydrogen evolution tests were done with a gas-flow slurry type in-house reactor for the detection of continuous production of H₂ gas from the PhCN samples for 5 hours under illumination of 445nm through an LED lamp. The online gas analyser (X-Stream, Emerson Process Management) equipped with a thermal conductivity detector (TCD) was used for the quantification of H₂ detection respectively. The argon flow was kept at 15ml min⁻¹ throughout the experiment. The concentration of the catalyst is kept at 10mg/ml with 0.1M TEOA sacrificial agent and 1% Pt cocatalyst through photodeposition.

HER tests with the PhCN/WS₂ hybrids were done in a home-made glass batch reactor with 0.1M TEOA as the sacrificial agent and 2 mg of the photocatalyst. The concentration of the photocatalyst was kept at 1mg/ml. The irradiation was done with 445nm and 365nm LED sources. 1% Pt was used in the case of reference measurements without WS₂.

2.2.6. Characterization

Powder XRD measurements were carried out using a Bruker D8 Advance diffractometer in Bragg Brentano geometry with CuK α source. For samples containing only PhCN, the scan speed was kept at 0.4°min⁻¹ with a step size of 0.02°. Samples containing WS₂ were measured with a scan speed of 2.3°min⁻¹ and a step-size of 0.05°.

Spectrum Two **FT-IR** Spectrometer from Perkin Elmer was used to acquire the infrared spectra of all the hybrids and pristine samples (LiTaO₃ detector, scan range 4000-400cm⁻¹). The resolution was 0.5 cm⁻¹. All the measurements were done in attenuated total reflectance mode with 10 spectra averaging.

For **Raman spectroscopy** of powder samples with PhCN, BW-TEK: i-Raman® Plus, Fiber coupled Raman system at 1064 nm was used at room temperature. Acquisitions were taken for 8000ms with 20 % LASER intensity. The system has a resolution of 1cm^{-1} .

WS₂ does not show any Raman response with 1064nm excitation, therefore 532nm LASER was used for the measurements related to WS₂. Sol Instruments: MS750 series Monochromator-spectrograph, was used for MicroRaman with 1800 gr/mm grating at room temperature. The system is coupled with a prototyped chamber from NuovaCm (Italy). The LASER intensity was kept at 20%. For the WS₂ solid sample measurement 10x objective was used and the acquisition was taken for 10s with 20 scans. The reported spectrum is the average value. The spectral resolution was 0.6 cm^{-1} .

The same equipment was used for the measurement of Raman spectra of the liquid dispersions WS₂_1 and WS₂_2 with a liquid sample holder of cylindrical shape of height 1mm and radius of 4mm printed by a 3D printer at our laboratory. The LASER was focused on the surface of the liquid sample (Figure A3 in Appendix A) as suggested by Backes et al.⁹³ and the acquisitions were made for 30s with 20 scans averages. The spectrum of only IPA was also measured under the same conditions and to eliminate the peaks arising from IPA.

Dynamic Light Scattering (DLS) measurements were performed with LS Spectrometer™ II for studying the hydrodynamic radii and particle size distributions in the WS₂ dispersions. The instrument had an angular resolution of 0.05° .

SEM was recorded on a FEI Quanta 250 Field-Emission-Gun-SEM, equipped with an Everhardt-Thornley secondary electron detector. The device was operated at an electron acceleration voltage of 10 kV at a working distance of about 5 mm. The powder samples were sprinkled on a carbon tape adhered to the aluminium sample stud and then extra powder was dusted off before the measurement

Transmission Electron Microscope TEM JeolJEM 1400 Plus was used for bright field imaging of PhCN nanosheets under ultra-high vacuum conditions. The powder PhCN samples were dispersed and then sonicated for 10 minutes in their respective solvents of exfoliation before drop-casting them onto the Cu TEM grids. The grids were then dried under ambient conditions before measurements were taken.

The TEM images of PhCN/WS₂_1 were obtained with a FEI TECNAI F20 transmission electron microscope equipped with a field emission gun and a GATAN Rio16 CMOS camera. For **EDX** analysis a EDX (EDAX Apollo XLTW SSD) detector was used. The TEM was operated at 200 kV acceleration voltage. The sample with WS₂ was prepared on a copper holey carbon-coated grid (Plano, 200 mesh). The powder was dusted onto the grid and then a drop of IPA was put to uniformly disperse the sample on the grid.

N₂ physisorption was measured at 77 K using a Micromeritics 3Flex. Samples were vacuum outgassed at 120°C for 10 hours. Surface area was calculated using the Brunauer-Emmet-Teller (BET) equation. The measurements used in this research were acquired by Dr.rer.nat. Shaghayegh Naghdi from TU Wien, and their contribution is deeply appreciated.

UV-Vis light absorption measurements of solid samples were obtained by diffuse reflectance spectroscopy utilizing a UV-Vis-NIR Jasco spectrophotometer Spectrometer. Measurements were performed by using a PbS solid-state photodetector. The reflection configuration measures the diffuse reflection of the sample with respect to a KBr reference that is considered to have 100% reflectivity. The Kubelka-Munk equation was applied to extract the absorption features.

The excitation spectra of WS₂ dispersions were measured in the same equipment using the liquid sample configuration. The reference and sample cuvettes were filled with IPA to measure the baseline of the experiments. Then the sample cuvette was changed to WS₂_1 and WS₂_2. The scan speed was kept at 100 nm min⁻¹ with a step-size of 1nm. The dispersions were diluted before the measurements to minimize scattering and prevent saturation of the absorption measurements. The dilution factor was then multiplied before reporting the concentrations of the dispersions.

Three-dimensional fluorescence mapping was performed using a with a 450 W xenon lamp as the excitation source (Horiba Ltd., Kyoto, Japan) Spectrofluorometer FP-8550ST jasco. The maps were collected in very low sensitivity mode using an excitation range of 300–500 nm with a 5 nm spectral bandwidth for excitation and emission.

Spectrofluorometer FP-8550ST jasco was used for the **Measurements for scattered light** intensity by WS₂ suspensions, which were done in an integrating sphere in a cuvette of 1mm thickness with an incident light of 315nm using the previous instrumentation. Emission mode was used with 2.5nm Em and Ex bandwidth 2.5 nm with a response of 0.2 sec

Time-resolved photoluminescence (TR-PL) measurements were performed by exciting the samples by an optical parametric amplifier (Light Conversion TOPAS- C) pumped by a regenerative Ti:Sapphire amplifier (Coherent Libra-HE, Coherent Inc., Santa Clara, CA, USA). The repetition frequency was 1 kHz, and the PL signal was recovered by a streak camera (Hamamatsu C10910, Hamamatsu Photonics, Hamamatsu City, Shizuoka Pref., Japan) equipped with a grating spectrometer (Princeton Instruments Acton SpectraPro SP-2300, Teledyne Princeton Instruments, Trenton, NJ, USA). Time windows used were 1μs, 200ns and 50ns for excitation wavelengths at 360nm and 410nm. The LASER power was maintained at 10μW for all measurements.

2.3. Results and Discussion

2.3.1. Photocatalytic H₂ production enhancement by exfoliation of PhCN

Reported studies have concluded that the liquid phase exfoliation process yields a suspension with a wide nanosheet size distribution and does not strictly lead to suspended monolayers or few-layers.¹²⁹ Centrifugation of the suspension after ultrasonication results in the sedimentation of heavier particles but does not guarantee the elimination of smaller/lighter bulk particles from the suspension as centrifugation is mass specific rather than layer number specific.⁸⁹ Therefore, we did not proceed with a centrifugation procedure after the LPE step. As being environmental-friendly and “green methodology” of synthesis were our top concerns, we opted for three solvents for the exfoliation of PhCN which are harmless towards the environment, easy to eliminate, and were previously reported ideal for the exfoliation of g-C₃N₄ systems.⁹¹ Triethanolamine (TEOA)- a common sacrificial agent used with carbon nitride systems in water splitting, was used in our experiments. The exfoliated PhCN powders were not further suspended in dispersion medium (liquid) after drying to avoid mixing of the dispersion medium with the sacrificial agent TEOA, which would have complicated the HER dynamics.

The 3 exfoliated PhCN samples- PhCN_{H₂O}, PhCN_{EtOH} and PhCN_{IPA}, were compared with the Bulk PhCN and characterised in the following way.

XRD

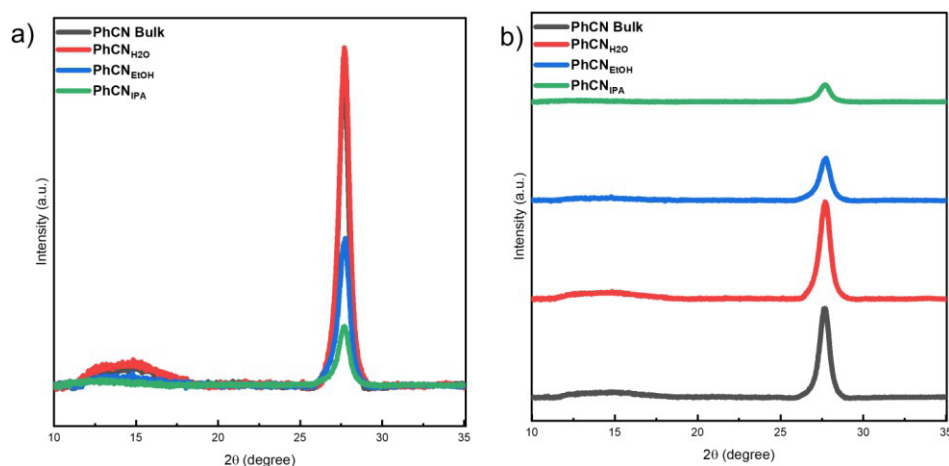


Figure 2.2 XRD data of PhCN Bulk and its exfoliated counterparts a) unstacked, b) stacked

The X-ray diffractograms of the PhCN samples are shown in **Figure.2.2**. The broad peak from $11.5\text{--}18^\circ$ was ascribed to an in-plane structural repeating motif of tri-s- triazine units and indexed as the (100) peak.⁹⁵ The peak at 27.7° was assigned to interlayer stacking of the conjugated aromatic segments with 0.2 nm distance and indexed as the (001) peak of the stacked aromatic system.⁶⁴ There is no shift in the reflection at 27.7° in the exfoliated samples which shows that the interlayer distance stays the same. For exfoliated samples in IPA and EtOH, the intensity of this peak diminishes which indicates a successful exfoliation process as the number of stacked sheets are lowered.^{68,86,90} However, the sample exfoliated in H_2O shows increased intensity of the (001) peak meaning that more planes were aligned in the same position and the exfoliation process might have not been successful. The broad peak at $\sim 15^\circ$ also diminishes after the sonication process meaning that there was also an in-plane breakage of the bonds during the sonication process except for $\text{PhCN}_{\text{H}_2\text{O}}$ suggesting no perpendicular breaking of sheets during the exfoliation. Through pseudo-voigt peak fitting, we found that there is a broadening observed in the exfoliated samples which could be due to increased disorder and induced strains in PhCN from exfoliation (Appendix Figure A4) . The increase in the FWHM of the main peak in the exfoliated PhCN samples indicates a decrease in the crystallite size, which also shows the effectivity of the LPE procedure.

FTIR

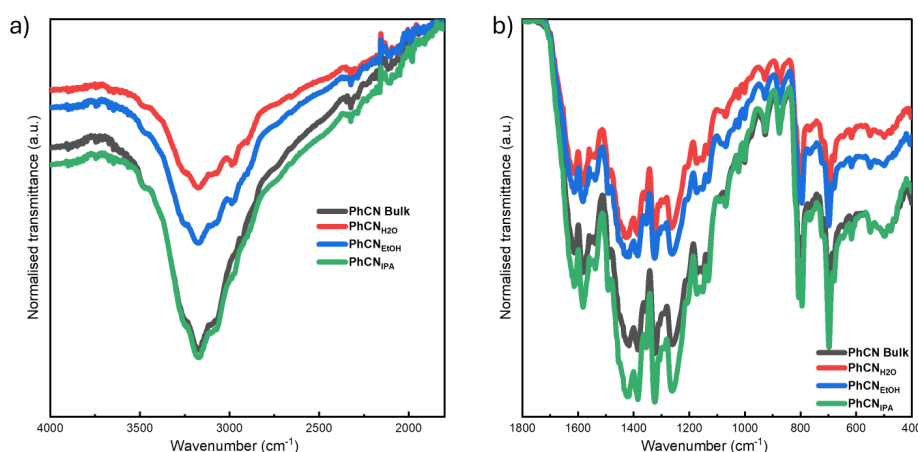


Figure 2.3 Normalised FTIR spectra of PhCN Bulk and the exfoliated counterparts. The normalization is done for the transmittance maxima for each sample which lies at 1824 cm^{-1} . a) x-axis $4000\text{--}1800\text{ cm}^{-1}$ and b) x-axis $1800\text{--}400\text{ cm}^{-1}$.

In the **Figure 2.3**, the PhCN shows a broad peak at $3500\text{--}3000\text{ cm}^{-1}$ for N-H and O-H stretching resulting from the partial hydrogenation of N and adsorbed water species respectively.^{85,95,130} The region from $1600\text{--}1200\text{ cm}^{-1}$ shows multiple peaks from C-N stretching and C-N

heterocycles.^{70,85,95,130} The characteristic breathing mode of the tri-s-triazine units shows at 810 cm^{-1} .^{70,85,95} The peak at 700 cm^{-1} shows the out of plane bending mode of C-H from the phenyl rings.⁷⁰ The exfoliated samples show all the characteristic peaks of PhCN without any introduction of new absorbance peaks. This proves that the chemical structure of PhCN is not harmed by the solvents during the ultrasonic treatment. The exfoliation in H_2O and EtOH lead to lower intensity of absorption related to all the species. PhCN_{IPA} shows higher absorption from aliphatic and aromatic C-N, C-C and C-H bonds. The FTIR results show that the exfoliation of PhCN in water, ethanol and isopropanol do not change its chemical composition.

RAMAN

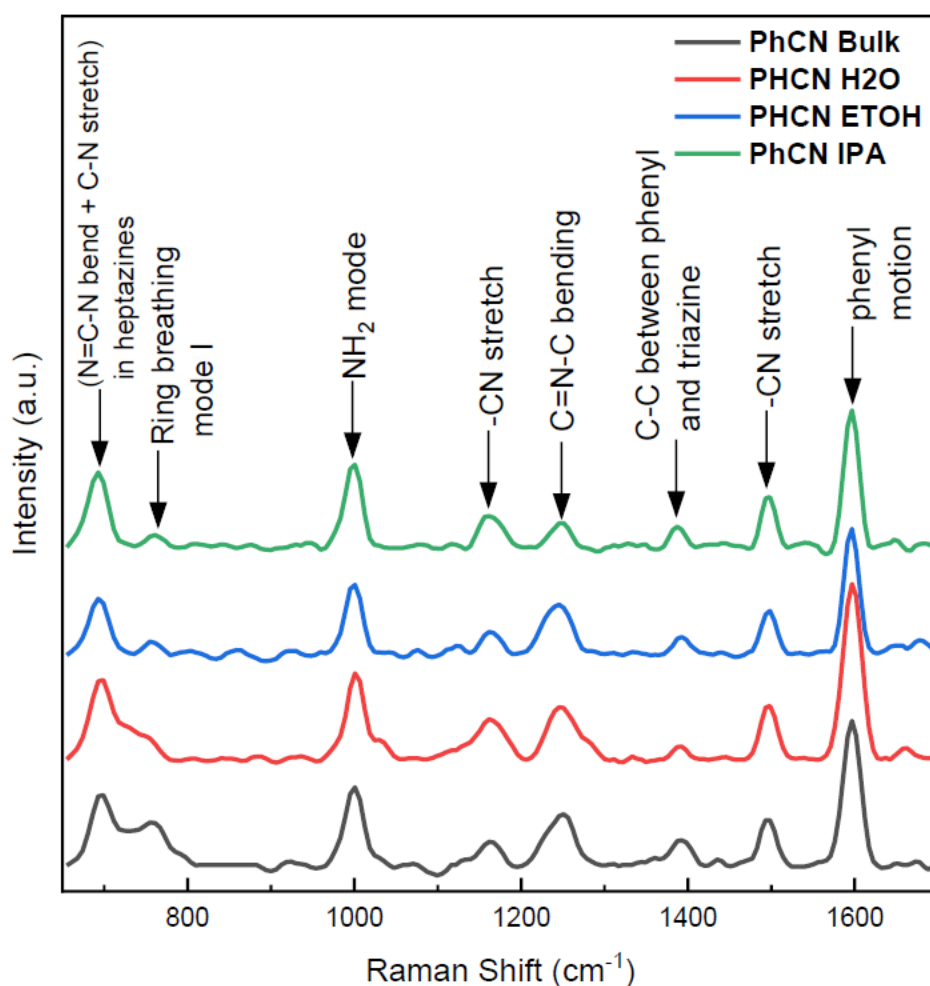


Figure 2.4 Raman spectra of PhCN Bulk with its exfoliated counterparts.

Table 2.1 The ratio of Ring breathing mode I intensity I_{rbl} to the intensity of the phenyl motion raman peak of all the samples.

Sample	Phenyl motion mode intensity (I_{ph})	Ring breathing mode I intensity (I_{rbl})	(I_{rbl})/(I_{ph})
PhCN	542.6	157.5	0.29
PhCN _{H2O}	659.1	77.7	0.12
PhCN _{EtOH}	466.6	44	0.09
PhCN _{IPA}	514	37	0.07

The structure of the samples was again investigated by Raman spectroscopy with 1064 nm LASER excitation. All the PhCN samples, bulk and exfoliated, show identical peaks ensuring that the molecular vibrations present in PhCN bulk are not lost completely due to exfoliation process (**Figure 2.4**). No new molecular species were detectable from Raman analysis. The spectra show typical polymeric carbon nitride peaks. Ring breathing mode I is shown at 760 cm^{-1} .⁴⁹ The peak at 693 cm^{-1} corresponds to the combined effect of N=C-N bending and C-N stretching in the heptazine rings due to loss of symmetry. Enhancement in this mode shows breaking of the polymeric units by exfoliation. -CN stretch at 1150 cm^{-1} and 1493 cm^{-1} is observed for PhCN.⁴⁹ The phenyl group motion at 1601 cm^{-1} was the most prominent peak followed by NH_2 mode at 1000 cm^{-1} in the spectra.⁶⁴ The conjugated stretching vibration (C-C) between the phenyl ring and the triazine ring is shown by the peak at 1392 cm^{-1} .⁶⁴ The C=N-C bending is observed at 1256 cm^{-1} .⁴⁹ **Table 2.2** shows comparison of intensities of the Raman modes related to phenyl group motion and heptazine ring breathing. The loss of ring breathing with respect to the phenyl motion indicates an in-plane cleavage during the liquid phase exfoliation.

SEM/EDS

The morphology of carbon nitrides has a big impact on their photocatalytic activity.¹³¹ PhCN exhibits blocky morphology where the 3D arrangement appears as chunks of PhCN on top of each other which may indicate low exposed surface area as seen in **Figure 2.5a**. The exfoliated PhCN nanosheets show an interconnected structure with higher space between the particles which may have better adsorption capacity and greater number of active sites for enhanced photocatalytic performance.⁵⁶ The layered structure is visible for PhCN_{H2O} and PhCN_{IPA} in **Figure 2.5b,c**, where PhCN nanosheets appear like a staircase with nanosheets layered on top of each other. The change in the morphology can arise from breaking of van der Waals force in between the sheets leading to exfoliation by the ultrasonic waves and breaking of sheets in the perpendicular direction.⁸⁵ PhCN exfoliated in IPA shows a crimped paper-like structure which can be suitable for generating higher surface area and for contact with the sacrificial agent during hydrogen evolution reaction. The morphology of the exfoliated PhCN samples are alike and detailed differences between them could not be observed with SEM.

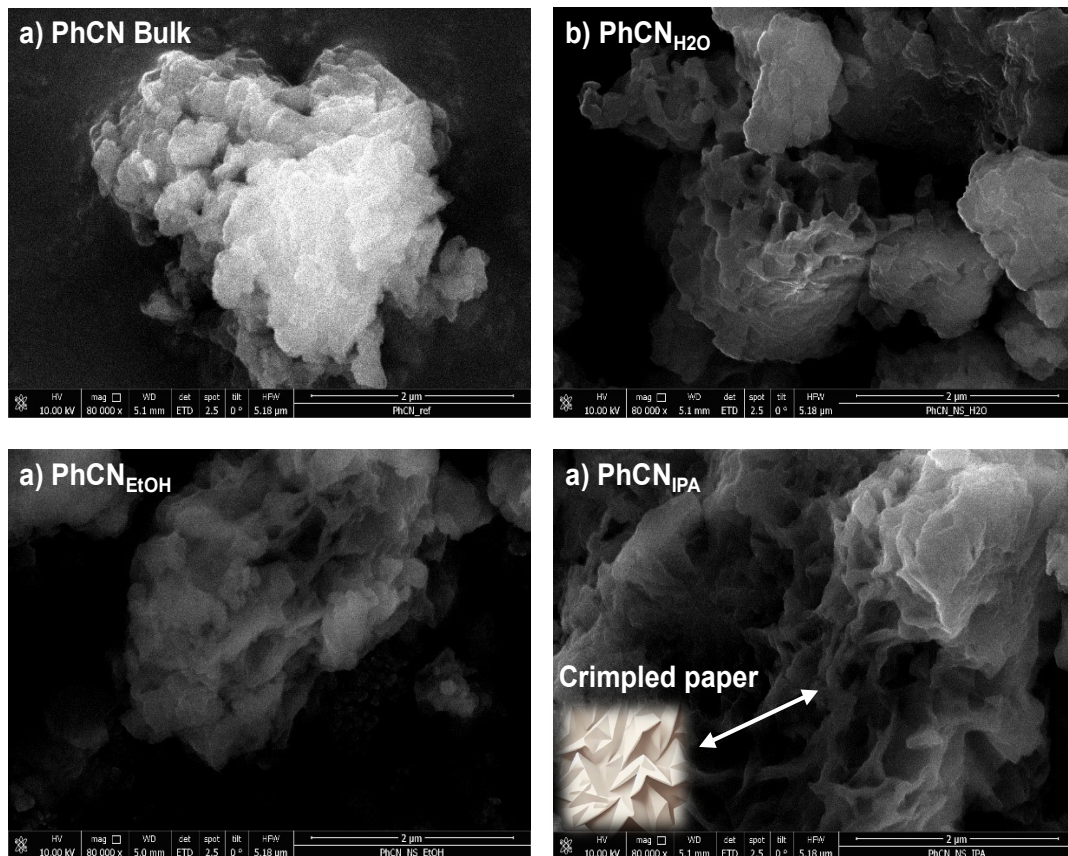


Figure 2.5 SEM micrographs of the PhCN Bulk compared to the exfoliated samples.

TEM

The TEM imaging of PhCN bulk shows the existence of nanosheets (**Figure 2.6**) which mimic the $g\text{-C}_3\text{N}_4$ structure.^{43,131,132} The PhCN exfoliated in water shows more dense packing than the starting material, while $\text{PhCN}_{\text{EtOH}}$ and PhCN_{IPA} show fewer number of nanosheets stacked on top of each other as they appear more translucent to the electron beam. The bulkier and more cloudy appearance of $\text{PhCN}_{\text{H}_2\text{O}}$ should be because of rearrangement of PhCN nanosheets while drying at room temperature. Water has a higher boiling point of 100°C which poses difficulty for it to get evaporated fast in the ambient conditions giving the nanosheets a slow and long process to interact with each other. On the other hand, the alcohol was rapidly evaporating and did not allow the restacking of the PhCN nanosheets. Through LPE, it was possible to get PhCN nanosheets with less compact stacking in the case of EtOH. and IPA.

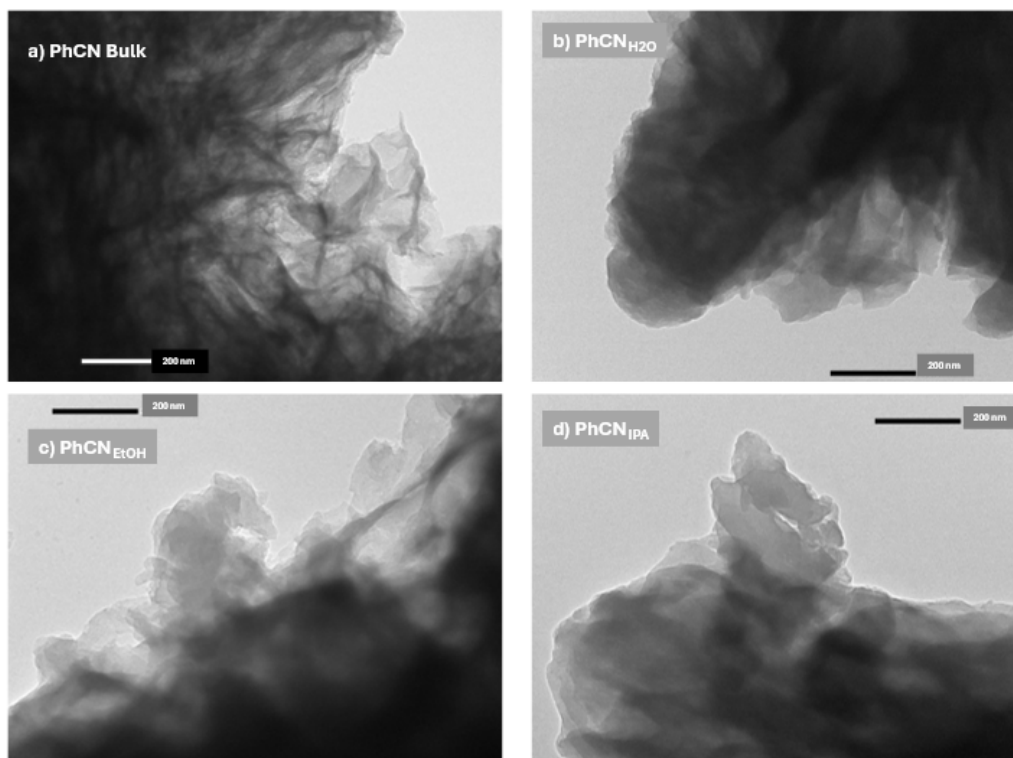


Figure 2.6 TEM images of the a)PhCN Bulk and the exfoliated PhCN in different solvents.

DRS

The UV-Vis absorption spectra of all the samples are shown in **Figure 2.7a**. All the samples have similar behaviour where there is an onset of absorption of visible light at 800 nm which increases significantly for higher energies than 500 nm. PhCN shows an absorption edge at 470 nm before exfoliation process which is blue shifted for PhCN_{H₂O}, PhCN_{EtOH} and PhCN_{IPA}. This blue-shift is due to size effects which are responsible for increasing band gap as evident in the Tauc plots in **Figure 2.7b**.⁶⁸ This is a quantum confinement effect caused by the small size and thickness of the PhCN nanosheets.^{48,86} There is a minor difference in the vis-light absorption of the exfoliated PhCN samples which is in the order IPA>EtOH>H₂O. A higher absorption of visible light can lead to generation of a higher number of excitons and an easier activation of the material for photocatalysis.²⁵ The increase in band gap indicates a better charge separation medium and a possible lower charge recombination which could aid in photocatalysis. A shift of the valence band towards more positive value leads to an improved mobility of photogenerated holes which favours photooxidation.⁸⁶

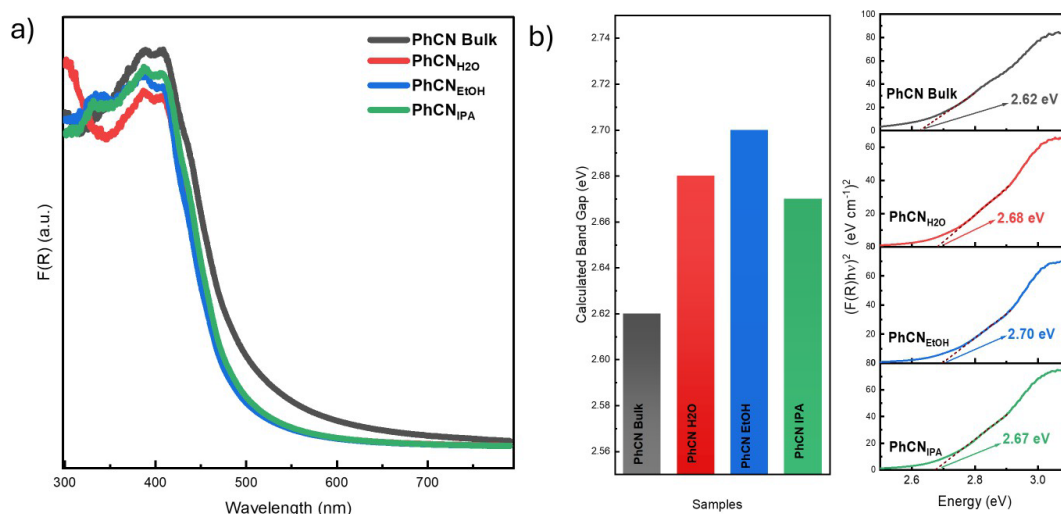


Figure 2.7 a) UV-Vis absorption spectra, b) calculated band gaps of the samples and Tauc plots

Steady-state Photoluminescence

The steady-state photoluminescence of the samples were measured via 3D fluorescence mapping of all the samples excited from 300 nm to 500 nm under identical conditions. In **Figure 2.8a**, Bulk PhCN shows a broad fluorescence spectra peaking at 529 nm for a range of 300-500 nm excitation. When 3D fluorescence mapping is done for the exfoliated PhCN samples, it is observed that the emission counts were increased by a low factor which has also been reported in the case of g-C₃N₄.⁸⁹ The increase in the fluorescence counts in the exfoliated samples show that the radiative recombination of the charge carriers has increased for both UV and Visible-light excitations. The enhancement of PL counts is due to the minimization of defects per particle due to the small size.⁶⁸

The **Figure 2.9** shows fluorescence spectra of the samples extracted from the 3D mapping data at 365 nm excitation and 445 nm excitation. For the 445 nm excitation, there is no shift of the maximum emission wavelength of PhCN after exfoliation indicating that the energy levels responsible for the luminescence are the same after exfoliation. While there was a red shift of ~2 nm in 365 nm excitation for PhCN exfoliated in H₂O and IPA, this red shift can be related to surface defect states appeared from the prolonged ultrasonication.⁶⁸ PL is highly affected by the surface to bulk ratio of the material where the surface effects are masked if the bulk material is in high quantity.⁶⁸

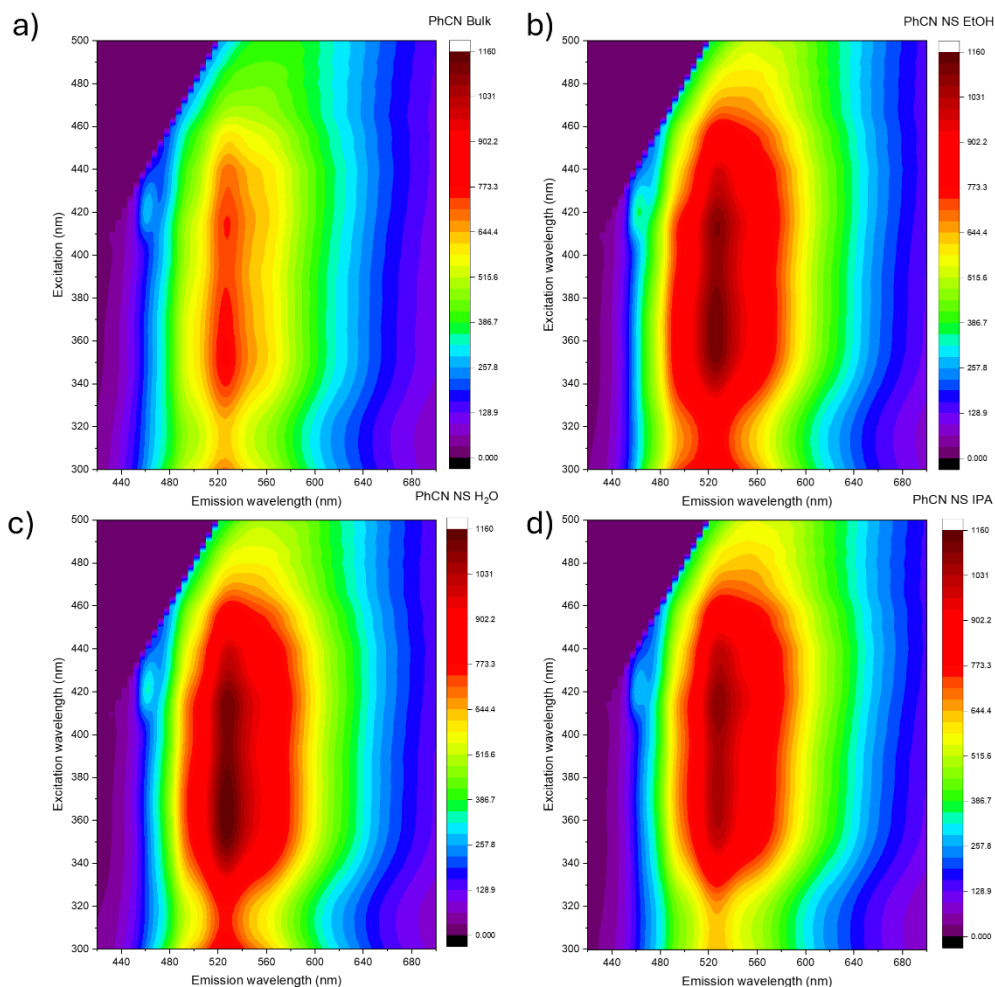


Figure 2.8 3D fluorescence mapping of PhCN samples excited from 300nm to 500nm with the same acquisition and plotting conditions.

The Em_{max} for the PhCN samples were all ~ 529 nm hence PLE spectra was extracted from the PL Maps for this emission shown in **Figure 2.10**. We see that the counts are always higher for exfoliated samples than the bulk PhCN for any excitation wavelength. PhCN has two major emission channels – at ~ 350 nm and 414 nm with comparable PL intensities. When exfoliated, the UV channel undergoes red shift to 365nm for $PhCN_{H_2O}$ and $PhCN_{EtOH}$, and 375nm for $PhCN_{IPA}$. The channel in vis- light spectra stay intact but becomes dominant for $PhCN_{IPA}$

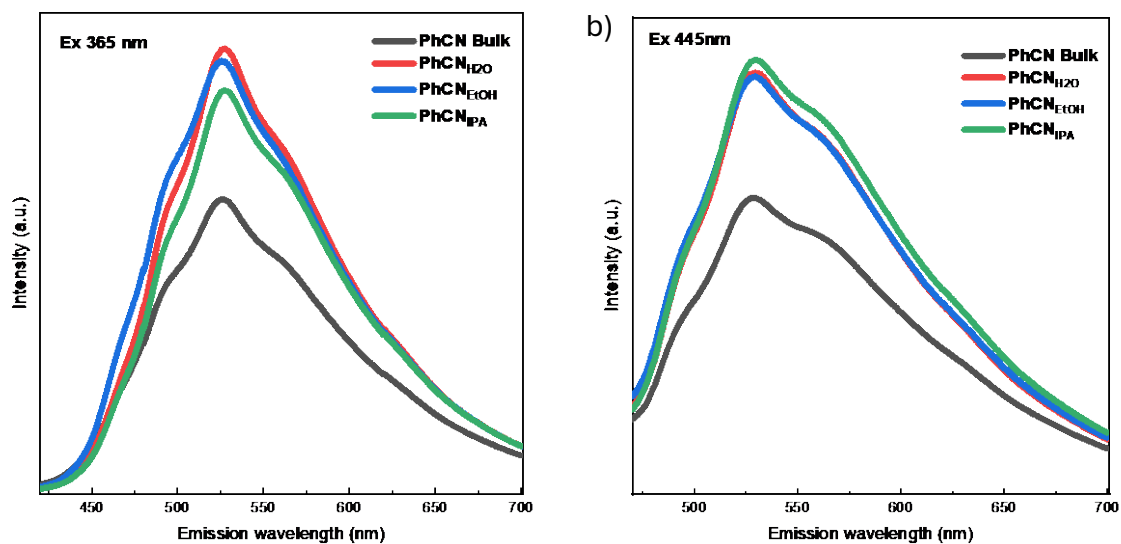


Figure 2.9 Photoluminescence spectra of PhCN Bulk and the exfoliated samples excited at a) 365nm and b) 445nm.

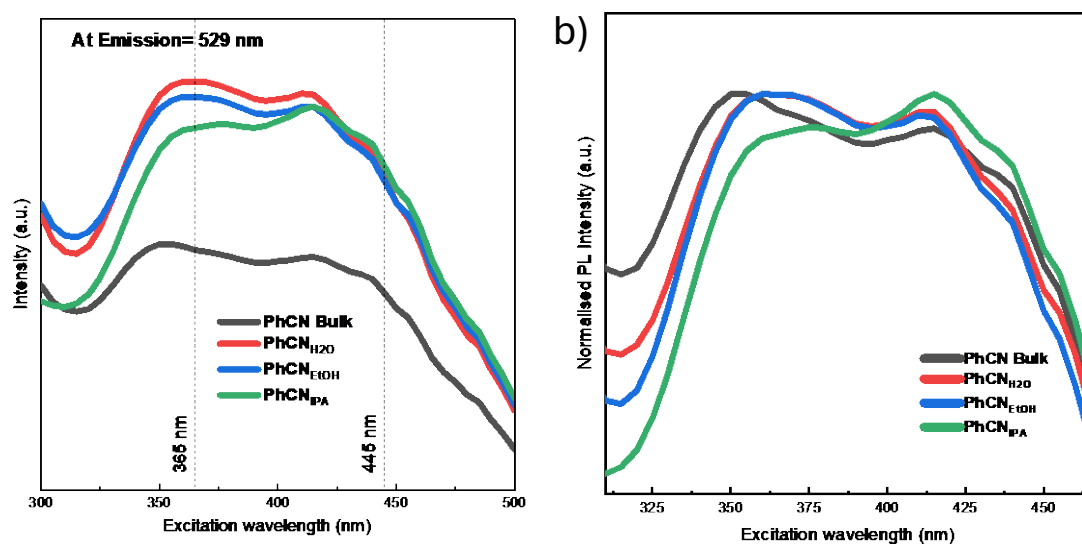


Figure 2.10 PLE spectra of the samples extracted from the 3D maps at the emission wavelength of 529nm .a), the same PLE spectra normalised to the maxima of each dataset respectively.

Time-resolved Photoluminescence (TRPL)

Time-resolved PL spectra were recorded for all the samples with an excitation of 360nm and 410nm excitation wavelengths in the 50ns, 200ns and 1ms time windows which are shown in **Figure 2.11 a,b,c,d,e,f**.

For PhCN bulk, comparing the time-decay behaviour in different time regimes for 410nm excitation gives an idea about the fast decay kinetics of the system. By previous studies it has been reported that the PhCN has two decay components at ~150ns and ~40ns.⁶⁴ When excited with 360nm, the PL spectra of the PhCN bulk system does not change neither does the time decay profile. Instead, a time- dependent spectral profile change was observed for the same acquisition. Comparable to g-C₃N₄, PhCN also shows at least two spectral contributions- the high energy one from σ^* level and another from π^* level.⁷⁷ The spectral study shows that the high energy contribution decays fast which in-fact is again comparable to g-C₃N₄. The fast decay of the high energy contribution is due to the non-radiative interaction among the planes which lead to non-radiation recombination of charge-carriers. As this non-radiative interaction decreases, radiative recombination of charge-carriers increases which is shown by the following equation-

$$\frac{1}{\tau_i} = \frac{1}{\tau_{Ri}} + \frac{1}{\tau_{NRI}} = Y_{Ri} + Y_{NRI}$$

From the **Figure 2.11b,d**. It can be observed that the exfoliated samples show a slower decay of the fluorescence which can arise from the decrease in the non- radiative component of the equation above and an increase in the radiative component which is proven by the fluorescence maps. Even for a longer time scale, the exfoliated samples show loss of non-radiative emission which indicates a high stability of excitons in the aromatic system.⁶⁸ The slower recombination rates of photogenerated charge-carriers in the exfoliated samples can be due to the enhancement of band gap as shown in the Tauc plots in **Figure 2.7b** which in turn is beneficial for photocatalytic activity. The time-dependent spectral properties and the time-decay behaviour in different time regimes of the exfoliated samples are analogous to the bulk PhCN.

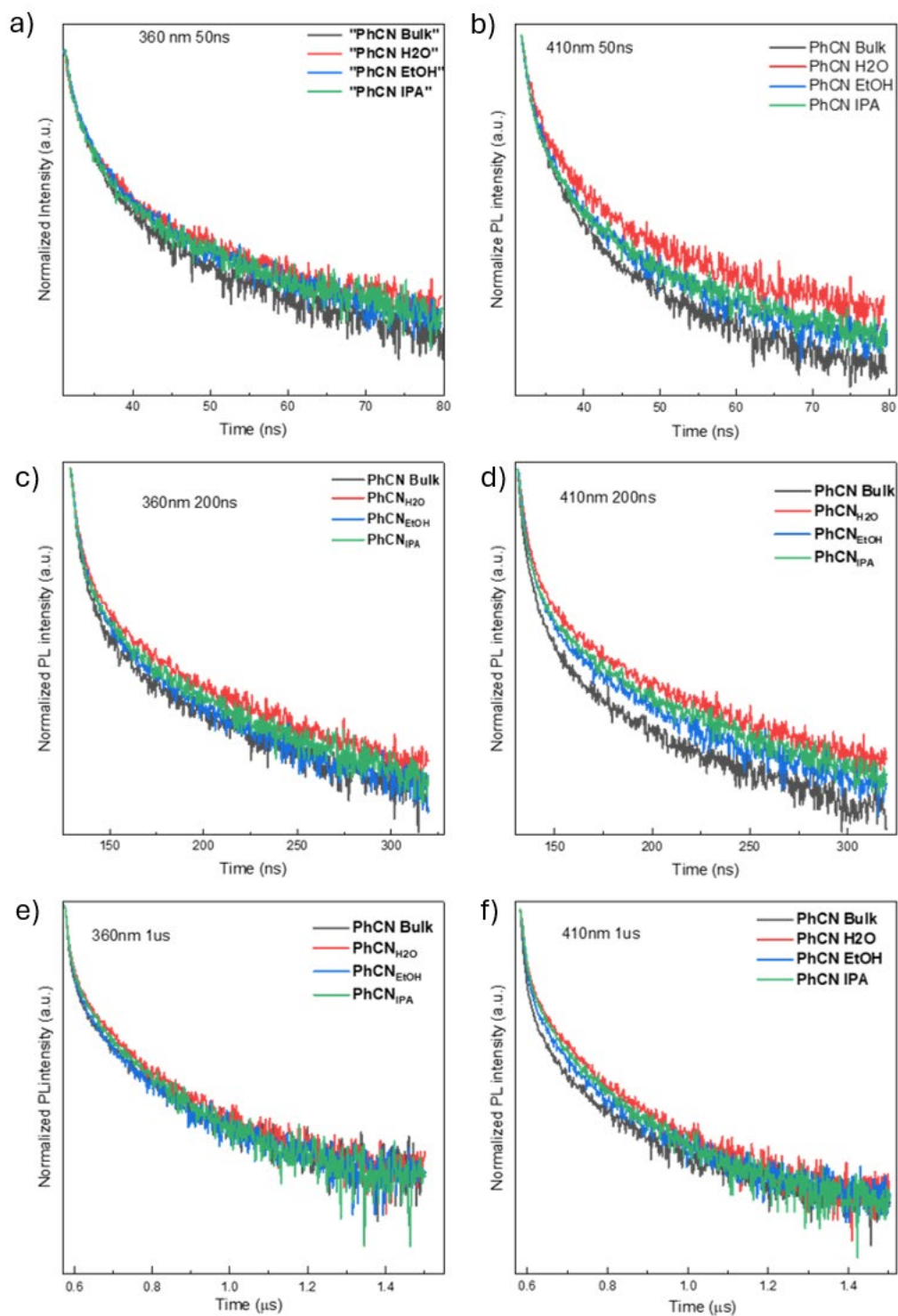


Figure 2.11 TRPL spectra of the PhCN bulk and all exfoliated PhCN samples excited at 410nm b), d), f) and 360nm a), c), e) with time windows 50ns, 200ns, 1 μ s.

Hydrogen Evolution Test

The H₂ evolution efficiency of the exfoliated samples was compared with that of the unexfoliated PhCN (PhCN Bulk) under a continuous illumination of 445nm LED for 5 hours. The results are shown in **Figure 2.12** and summarized in **Table 2.3**.

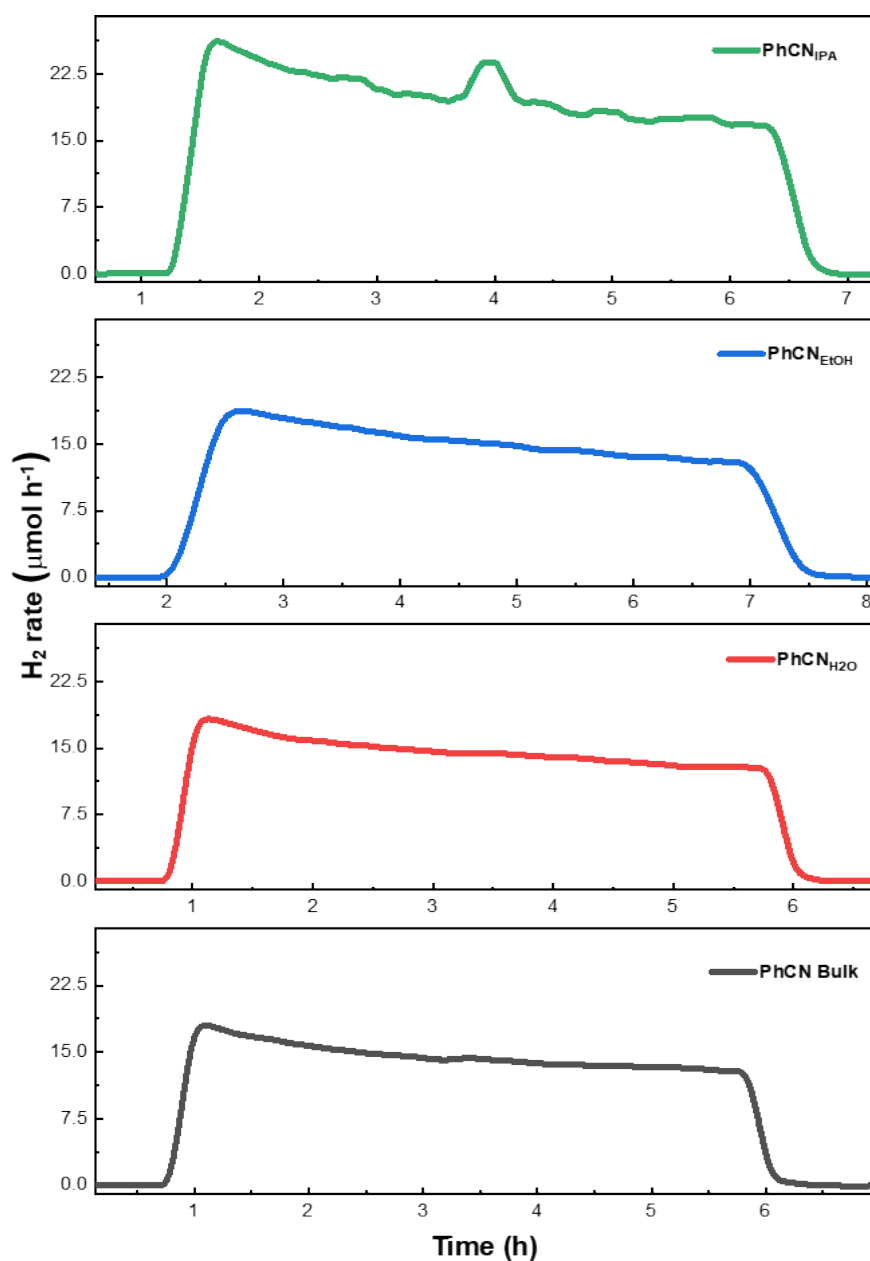


Figure 2.12 HER flow tests of PhCN Bulk and exfoliated samples under 445nm LED irradiation. The data points are adjacent averaged with 50 points window.

Table 2.3 Hydrogen gas production activities of the samples shown in Figure 2.12

Sample Name	Overall activity ($\text{mmol g}^{-1} \text{h}^{-1}$)	HER Deactivation rate ($\text{mmol g}^{-1} \text{h}^{-2}$)	Amount of H_2 produced after turning off lamp (mmol)
<i>PhCN Bulk</i>	1405.7	112.1	1.19
<i>PhCN_{H2O}</i>	1443.3	121.7	1.17
<i>PhCN_{EtOH}</i>	1557	136.9	5.67
<i>PhCN_{IPA}</i>	2000	218.2	2.24

The process of exfoliation shows an improvement in the HER activity of the PhCN samples. The PhCN_{H2O} shows similar H₂ evolution properties as that of the bulk PhCN ensuring an unsuccessful exfoliation procedure as suggested by XRD. On the other hand, the samples exfoliated in alcohol show considerable increment in the HER activity. PhCN_{IPA} shows the highest HER activity of 2000 mmol g⁻¹ h⁻¹ in 5 hours with the highest deactivation rate for H₂ production. The bump in the H₂ activity of PhCN_{IPA} in **Figure 2.12** is due to a bubble entering the detector. All the samples show a very slow deactivation of the catalyst with time which might be from the degradation of the Pt co-catalyst.¹³³ Some amount of H₂ was always produced after the illumination was turned off in all the samples. PhCN_{IPA} and PhCN_{EtOH} show a higher amount of H₂ production after the lamp was turned off. This may be attributed to a better charge-separation due to increased bandgap or, higher number of excitons from greater PL. These results show that the exfoliation process has indeed increased the photocatalytic hydrogen production of PhCN with high dispersibility in the sacrificial agent. The presence of -OH groups on the surface of the samples exfoliated in alcohols might create a synergy with the TEOA.¹³⁴ The increase in the band gap values due to size effects in the exfoliated samples lead to higher redox capabilities which contributes to a better charge separation and eventually better H₂ production. The ultrasonication process induces irregularly stacked PhCN planes as shown in the XRD which improves the interfacial charge transfer which further increases the dissociation of singlet excitons to respective charge carriers which may lead to a better H₂ production efficacy when combined with the higher redox potential.⁴⁷

IPA was also regarded as an ideal solvent for the exfoliation of bulk g-C₃N₄ due to its surface energy (~40 mJ m⁻²) which is close to that of g-C₃N₄.⁹¹ Nanosheet rearrangement during the drying process is a menace which reduces the surface area of the material. Therefore, choosing a low boiling solvent is important which will evaporate faster and give less time to the PhCN sheets to aggregate. High surface tension of water leads to reaggregation of the PhCN nanosheets which shows a low surface area and lower exfoliation effectivity as shown by BET and XRD data. In

PhCN_{H₂O}, the H₂O was not able to escape from within the layers of PhCN nanosheets and the remnants of it stayed there as shown in the FTIR data which made the PhCN nanosheets tightly bound with hydrogen bonds which also hampered the excitonic movements interplanar movements which lead to a slower PL decay.

The XRD and Raman results showed the highest level of exfoliation in PhCN_{IPA} which was also the case for g-C₃N₄ by previous study which declared IPA to be a better exfoliation agent than EtOH.

Hence, we conclude that IPA acts as the best green solvent which could exfoliate PhCN nanosheets to yield better H₂ activity. The next step is to obtain high-quality WS₂ exfoliated nanosheets to create the PhCN/WS₂ hybrid which shall not require a noble metal to act as an additional catalyst.

2.3.2. LPE of WS₂ co-catalyst

Home grown WS₂ powder was sonicated in pure IPA in an ultrasonic bath to obtain liquid phase exfoliated WS₂. The mixture was then centrifuged to let the heavier particles settle down and the supernatant was taken out to be purely exfoliated WS₂ nanosheets. The obtained suspension of WS₂ nanosheets in IPA was named WS₂_1, which was centrifuged further to obtain the supernatant WS₂_2. By principle, WS₂_2 should consist lighter and fewer layered WS₂ nanoflakes than WS₂_1.

The WS₂ nanosheet suspensions are studied in the following way-

UV-vis absorption spectroscopy

According to Backes et al., UV-vis spectroscopy is the most straightforward way to characterize nanosheet dispersions obtained through LPE as it can give information about the phase/polytype of the material, its concentration and the nanosheet size and thickness.⁹³ The extinction spectra of the WS₂ suspensions can help in estimating the amount of WS₂ present in them along with the dimensional confinement effects. The extinction coefficient is given by the Beer-Lambert Law:

$$-\log_{10}T = \varepsilon Cl$$

Where, T is the transmittance measured during the UV-vis absorption measurements, ε is the extinction coefficient, C is the concentration of the nanosheets in the suspension and l is the side length of the cuvette.

This extinction coefficient is dependent on the material and the wavelength and comprises both absorption and scattering information. Hence,

$$\varepsilon(\lambda) = \alpha(\lambda) + \sigma(\lambda)$$

where α and σ are coefficients of absorption and scattering respectively (also dependent on the incident wavelength).

Hence, it is important to calculate the concentration of the nanosheets first before estimating the extinction coefficient. For this purpose, we measured the absorbance of the WS₂_1 and WS₂_2 samples using an integrating sphere with 315nm excitation.

In the absence of scattering, absorbance is given by:

$$A = \frac{T_0 - T}{T_0}$$

Where T_0 is the transmittance for the reference sample and T is the same for the nanosheet dispersion. If we assume that the solvent IPA does not lead to any scattering by its own,

$$A = 1 - T$$

Paton et al. showed that for a diluted solution, the absorbance A can also be shown as ¹³⁵

$$A = \frac{\alpha(\lambda)Cl}{\log 2.72}$$

Where the absorbance A is dependent on the incident wavelength and is described as the ratio of radiant power absorbed to the incident radiant power on the sample. The value of absorbance for 315nm incident light was recorded for WS₂_1 and WS₂_2 dispersions using an integrating sphere. By using the value of absorption coefficient of WS₂ at 315nm predicted by Paton et.al.,¹³⁵ we could successfully calculate the concentration of WS₂ nanosheets for our dispersions as shown in **Table 2.4**. Using these values of concentration in the Beer-Lambert law for the transmittance measurements, we show the extinction spectra of the WS₂ species in **Figure 2.13a**.

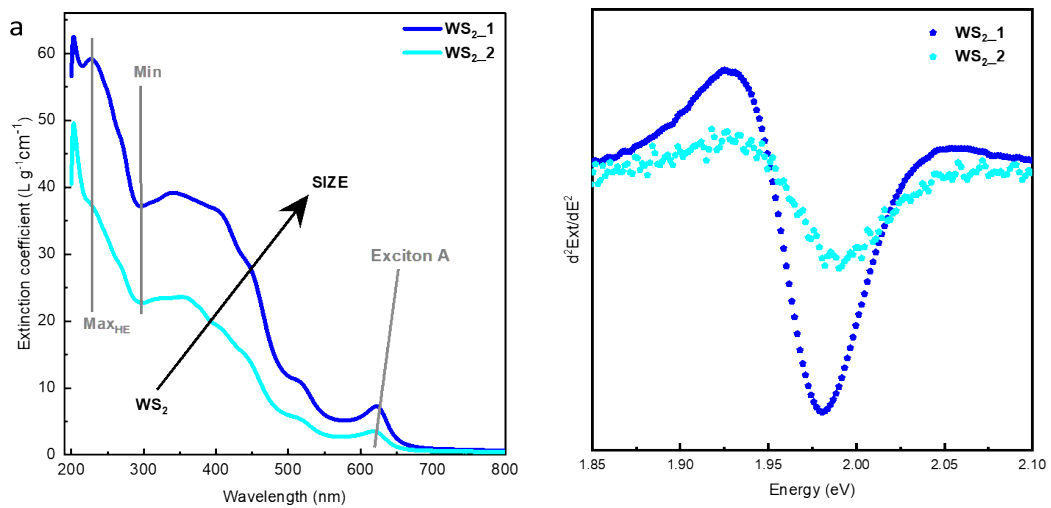


Figure 2.13 a) Extinction spectra of the exfoliated WS₂ samples. b) The Second derivatives of the A-exciton plotted versus energy for WS₂.

The peaks A at ~630nm and B at ~530nm arise from optical transitions at K point of the Brillouin zone.¹⁰⁹ WS₂ is known to show spin orbital coupling of the top of the valence band which is evident by the energy difference between A and B excitonic transitions. At ~470nm, we can observe the excitonic transitions from multiple points near Γ point of the Brillouin zone denoted as C. The A-exciton peak results from a direct optical transition between the highest point of the valence band and the lowest point of the conduction band.¹³⁶ Therefore, the energy associated with this peak indicates the band gap of the WS₂ nanosheets obtained.⁹³ For WS₂_2, the position of A is blue shifted due to quantum confinement in thinner/ lighter nanosheets. The liquid cascade centrifugation process

shows to yield a lower concentration of WS₂ along with lower sized nanosheets as evident from the spectra.⁹³ We can observe a change in the profile of the absorption along with a shift in the characteristic peaks of the extinction spectra for the material. These changes arise due to the confinement of electron in two-dimension causing a change in the excitonic transition energies and a shift of bandgap.⁹³ Nanosheet edge-effects can also lead to a spectral change as the scattering coefficient is size dependent and the extinction coefficient is different for the edge and the center of a nanosheet due to their electronic distinction.¹³⁷ Hence, the extinction spectra can also give a good comparison of the lateral size of the nanosheets in the dispersions. The average lateral size of the WS₂ flakes were estimated using the extinction spectra with the following equation:¹³⁸

$$\langle L \rangle = \frac{1000 \frac{Ext_A}{Ext_{Min}} - 7.6}{2.8}$$

where $\langle L \rangle$ is the mean nanosheet length of the WS₂ nanosheets, Ext_A is the extinction intensity at exciton A peak $\sim 620\text{nm}$ and Ext_{Min} is the same at the local minima at 295nm . **Table 2.4** shows the obtained values of the mean nanosheet length for the two dispersions. So, we can see that further centrifugation lead to the removal of bigger WS₂ nanosheets. In addition to this, we calculated the nanosheet thickness (N) in the two dispersions using the equation:

$$N = 6.35 \times 10^{-32} e^{\lambda_A/8.51}$$

Where λ_A is the wavelength corresponding to the excitonic A transition from the double derivative plot of extinction spectra shown in **Figure 2.13b**. The results are tabulated in **Table 2.4**. and shows that the liquid centrifugal cascading process leads to lighter nanosheets with fewer layers.

Table 2.4 Calculated WS₂ monolayer concentration and mean nanosheet length and thickness of the WS₂ nanosheets through UV-Vis extinction spectra of the exfoliated samples.

	Concentration (g l ⁻¹)	Mean nanosheet length (nm)	Thickness of the nanosheets (number of layers)
WS ₂ _1	0.744	67	5.6
WS ₂ _2	0.432	52	4.2

Dynamic Light Scattering (DLS)

Based on the Brownian motion of dispersed particles in a solvent, a relation between the speed of the particles and their hydrodynamic radius can be given by the Stokes-Einstein equation:

$$D = \frac{K_B T}{6\pi\eta R_H}$$

Where, K_B is the Boltzmann constant, T is temperature, η is the viscosity of the dispersant and R_H is the hydrodynamic radius. Lotya et al. correlated this value of the hydrodynamic radius with the lateral size of exfoliated WS_2 sheets by the formula:

$$\langle L \rangle = (0.07 \pm 0.03)R_H^{(1.5 \pm 0.15)}$$

Where $\langle L \rangle$ is the mean lateral size of the exfoliated nanosheets.

Table 2.5 summarises the DLS data of WS_2_1 and WS_2_2 dispersions.

Table 2.5 Summary of DLS data of the WS_2 dispersions.

	<i>Peak 1</i>	<i>Peak 2</i>	<i>Peak 3</i>
<i>WS₂_1</i>	Weight %: 0.06987 Mean Peak Position : 9.500E-002 nm	Weight % : 4.07976 Mean Peak Position : 9.524E-001 nm	Weight % : 95.85037 Mean Peak Position : 4.212E+001 nm
<i>WS₂_2</i>	Weight of Peak % : 7.04434 Mean Peak Position : 5.274E- 001nm	Weight of Peak % : 92.95566 Mean Peak Position : 2.544E+001nm	--

It can be observed that the liquid centrifuge cascading resulted in a dispersion with particle with a lower hydration sphere radius. This hydration sphere radius is proportional to the lateral size of the flakes which are considered to be rectangular. **Figure 2.14** shows the intensity particle size distribution of the WS_2_1 sample where a small peak centered at 0.9 nm could be from the presence of monolayers of WS_2 or residues. By calculating the lateral size of the WS_2 nanosheets in our dispersions using the equation¹³⁹ provided by Lotya et al. we get the values $(19.13 \pm 8.82)\text{nm}$ and $(10.62 \pm 5.01)\text{nm}$ for WS_2_1 and WS_2_2 respectively. Interestingly, these values do not match with the UV-Vis spectra-oriented values. This could be due to the difference in the measurement acquisition geometry which was side scattering for our measurements and was back-scattering for the measurements done. This shows that the angle of measurement changes the obtained

DLS size distribution. However, the DLS data shows that WS₂_2 has smaller nanosheets than WS₂_1.

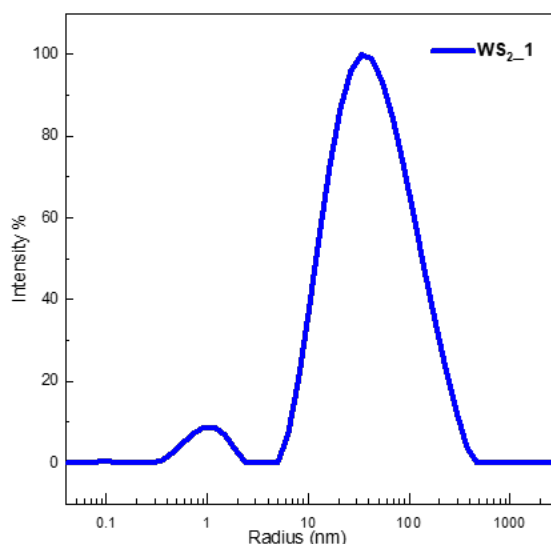


Figure 2.14 Intensity particle size distribution measured from the DLS technique for PhCN/WS₂_1 hybrid.

Raman and PL Spectroscopy

Raman spectroscopy is a highly effective technique for examining phonons and their interactions with electrons in 2D materials.¹⁴⁰ In WS₂, the two main Raman peaks, E_{2g}¹ and A_{1g}, correspond to the in-plane vibrations of tungsten (W) and sulphur (S) atoms and the out-of-plane vibrations of the sulphur atoms, respectively.¹⁴¹ It is widely recognized that the frequencies of these modes shift as the material's thickness changes and the difference in their frequencies can provide an idea of the number of layers present.¹¹⁶ Resonant Raman scattering in 2D materials, in particular, is known to be dependent on the number of layers.¹¹³ After exfoliation, when the WS₂_2 was created by centrifugation of WS₂_1, the obtained sediment was used for our Raman and PL measurements. We find the E_{2g}¹ mode at 343 cm⁻¹ and the A_{1g} mode at 410 cm⁻¹ as shown in **Figure 2.15**. We find a difference of 67 cm⁻¹ between these two modes which is indicative of the presence of 2 or more layers of WS₂.¹⁴² The intensity ratio of E_{2g}¹ to A_{1g} come out to be 1.03 which is a good indicator of presence of monolayers of WS₂ as for greatly exfoliated samples the E_{2g}¹ mode has higher intensity with respect to the A_{1g} mode.¹⁴²

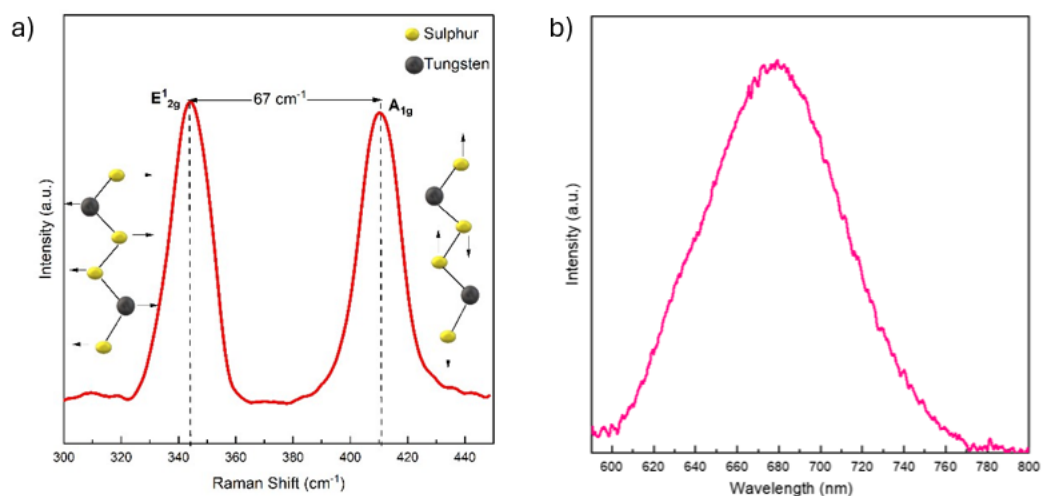


Figure 2.15 The a) Raman spectra of restacked WS₂ sample after centrifugation, b) PL spectrum of the same sample. Both are measured with 532nm LASER.

When assessing the output of liquid-phase exfoliation (LPE), both the size of the nanosheets and their optical properties, such as photoluminescence (PL), are key factors.¹⁴¹ PL can be used as a gauge of the sample's quality. For instance, it has been shown that only monolayer WS₂ with a sufficient lateral size (>25 nm) exhibits the characteristic excitonic emission associated with direct bandgap monolayers.¹⁴³ Moreover, lattice defects are expected to broaden or reduce the photoluminescence signal. Exfoliated WS₂ is known to show a strong emission signal at ~620nm due to the direct band gap transition of exciton A, which tends to be absent in bulk WS₂¹³⁷ due to an indirect semiconductor like behaviour. **Figure 2.15b** shows the PL spectrum of our WS₂ sample excited with a 532nm LASER. The spectrum is a perfect Gaussian profile centred at 677nm. The presence of high intensity PL shows the success of LPE of WS₂. The red shifted PL could arise from a red-shifted and intensified A exciton emission, originating from edge defects. This phenomenon has already been documented at around 650 nm in both monolayer and few-layer WS₂ nanosheets produced via liquid-phase exfoliation (LPE).¹⁴¹ This effect can be attributed to the natural tendency of excitons in WS₂ to accumulate in certain regions of the lattice, resulting in a stronger PL signal. The pronounced exciton localization in these areas leads to a higher exciton binding energy, which in turn causes the PL emission to occur at lower energy.

This analysis is in accordance with the UV-vis spectra of the two WS₂ dispersions where the size-selected dispersion WS₂_2 showed smaller lateral size of the nanosheets. The centrifugation step led to sedimentation of longer nanosheets with higher edge defects and lower lattice defects which is evident from the PL spectrum of the sediment. This step also eliminated a percentage of monolayers from the dispersion. Hence, the centrifugation of dispersions may not be layer number selective but is mass and size selective.

2.3.3. Hybridization of PhCN with WS₂

After successfully exfoliating PhCN and WS₂ in isopropanol, and studying their structural and optical properties, we proceeded to create a 2D-2D hybrid by combining them together. Since both the components are exfoliated, they must have more interlayers distances and reduced stacking. This might help WS₂ to enter in-between the PhCN nanosheets and have a greater contact with the system enhancing the catalytic sites. Therefore, the preservation of 2D nanosheets in their non-agglomerated form was essential. Procedures which include a thermal treatment, may harm the 2D structure of the nanosheets of WS₂ and end up curled. This in turn could also hamper the interaction between the two components of the hybrids so we selected the simplest pathway to hybridise 2 materials spontaneously- electrostatic self-assembly. If successful, this process would also hint on the inherent attraction of the two components of the hybrid and a long term stability. Various parameters like- assembly medium, medium volume, retrieval method and after retrieval heat treatment were optimised to get the final hybridisation method which turned out to be the simplest one too- self-assembly in IPA with the two separate dispersions followed by vacuum drying at room temperature. It was observed that the noble metal Pt had a great synergy with IPA but WS₂ as a co- catalyst had a better synergy with TEOA as a sacrificial agent during HER. The amount (volume) of WS₂ dispersion's injection in PhCN_{IPA} was chosen to be 5% of PhCN by weight after careful evaluation through HER measurements.

So, two hybrid samples were prepared- one using WS₂_1 dispersion with PhCN_{IPA} dispersion called PhCN/WS₂_1 and the other using WS₂_2 called as PhCN/WS₂_2. Both the hybrid samples have 5 wt% WS₂ in them but the later one has a higher concentration of smaller WS₂ flakes in it.

XRD

As observed in **Figure 2.16.**, the X-ray diffractograms of the two hybrids and the references. PhCN_{IPA} shows two peaks, (100) plane at 14.4° for the in-plane packing and (001) plane at 27. 7° for the interplanar stackings of the aromatic rings as showed in the first section of results.¹¹⁹ The WS₂ b1 shows peaks at 14.3, 28.9, 39.7, 43.9, 49.7, 59.8 for the planes (002), (004), (103), (006), (105) and (110) (JCPDS 02-0131),^{121,126,144} . The diffraction peaks from the WS₂ show the formation of 2H P63/mmc space group phase of WS₂.^{42,144} The most intense reflection was of (002) family of planes from WS₂.

The hybrids PhCN/WS₂_1 and PhCN/WS₂_2, show the major peaks from both the constituents- PhCN and WS₂. Reflection position corresponding to PhCN (001) at 27.7° is conserved but the (002) WS₂ reflection at 14.4° shifts to 13.9°

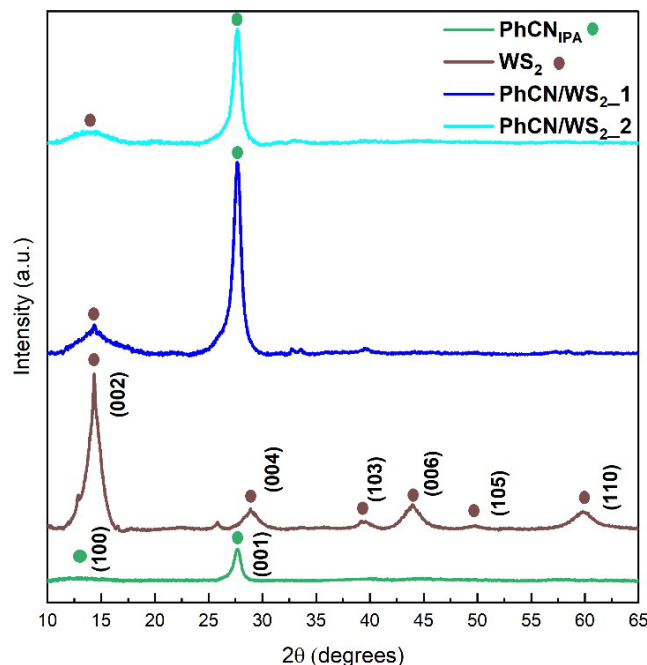


Figure 2.16 XRD data of the PhCN/WS₂ hybrids compared with the precursors

in PhCN/WS₂_2. This shift can be due to the (100) lattice overlapping of PhCN with the (002) planes of WS₂ in the hybrid. The intensity of the peak corresponding to WS₂ is of very low intensity in the hybrids and the peak for PhCN is of a greater intensity due to the presence of PhCN in excess mass in the hybrids. As the doping concentration of WS₂ is very low, we cannot observe all the other peaks corresponding to it in the hybrids. Compared to the precursors, the hybrids show a low crystalline peak of WS₂ with a substantial increase in the FWHM which can arise from intercalation of PhCN nanosheets in between the WS₂ sheets which reduces the stacking order in WS₂. The intensity of the peak at 27.7° increases with hybridization, likely due to the increased stacking of PhCN layers. This stacking is facilitated by the presence of -OH groups on the surface of PhCN, which interact with WS₂ nanosheets. When the FWHM of this peak of PhCN is compared in the hybrids, it was found that PhCN/WS₂_2 had broader peak than PhCN/WS₂_1. Therefore, smaller WS₂ flakes led to smaller crystallites and lower order. These interactions suggest that WS₂ may act as a bridge between the PhCN sheets, enhancing the structural alignment and layer stacking. There were no additional peaks found which confirms the presence of both the components without the formation of a composite. Using the Bragg's Law-

$$2d \sin\theta = n\lambda$$

where θ is the angle of XRD reflection, n is the order of reflection, λ is the incident beam wavelength, we can compute the spacing between the planes given as d . **Table 2.6** summarises the d spacing obtained for our samples using Bragg's law.

Table 2.6 The d -spacings of samples calculated via XRD data.

Sample	Interlayer spacing PhCN	Interlayer spacing WS ₂
PhCN _{IPA}	0.32 nm	---
WS ₂	---	0.62 nm
PhCN/WS ₂ _1	0.32 nm	0.62 nm
PhCN/WS ₂ _2	0.32 nm	0.64 nm

FTIR

FTIR absorption study was done on the samples as shown in **Figure 2.17**. As discussed previously, PhCN showed a broad peak at 3500-3000 cm⁻¹ for N-H and O-H stretching; vibration of stretching of aromatic C-N rings at 1250 to 1750 cm⁻¹;

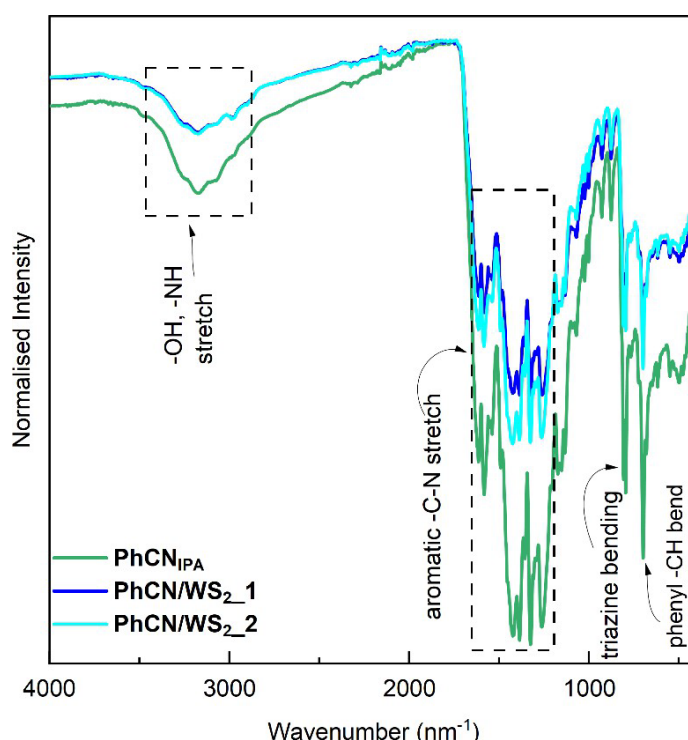


Figure 2.17 FTIR spectra of PhCN_{IPA} with the two hybrids with WS₂.

out-of-plane bending of triazine ring at 807cm⁻¹; out of plane bending mode of C- H from the phenyl rings at 700 cm⁻¹.⁷⁰ All of the absorption peaks of PhCN were observable in

the hybrids with WS₂. We could not observe any peaks of WS₂ for IR spectroscopy region 4000-400 cm⁻¹ in the case of the hybrids.¹²⁵ This could be because of the low concentration of WS₂ present in the hybrids and the non-polar nature of W-S bond.⁴²

It can be observed that the hybrids have lower absorption of the infrared light for all the peaks as compared to PhCN_{IPA}. This can be due to the presence of strong WS₂ linking in-between the PhCN sheets which dampens the molecular vibrations.^{124,126} The broadband at 2800-3400 cm⁻¹ also becomes less prominent in the hybrids which can hint towards the restriction of vibrations of the uncondensed amino groups of the defect sites of the aromatic ring present on the surface due to the presence of WS₂.¹²¹ There was no loss of peaks characteristic to PhCN after hybridization which indicates a preservation of the PhCN chemical structure in the hybrids. The FTIR results show a successful interfacial interaction of WS₂ on the surface of PhCN.

Raman Spectroscopy

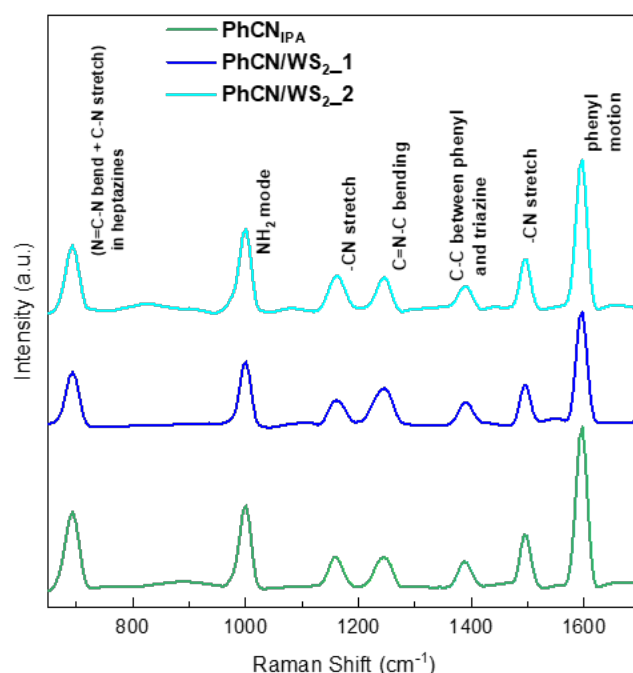


Figure 2.18 Raman spectra of the PhCN_{IPA} and hybrids with WS₂.

The Raman spectra of the samples were collected with 1064nm NIR LASER shown in **Figure 2.18**. According to the existing literature, 532nm LASER acts as the best excitation source to obtain the Raman fingerprint in WS₂ samples,^{108,116,141,145} but the presence of PhCN in our hybrids leads to a high photoluminescence when excited with 532nm. This fluorescence masks the Raman signal from WS₂ which is already very faint due to the low

concentration of WS₂ in our hybrids. WS₂ does not show any RAMAN peaks with 1064nm excitation hence no peaks related to WS₂ were observed in the hybrids. All the Raman peaks related to PhCN were observed in the hybrids- N=C-N bend + C-N stretch in heptazines at 692 cm⁻¹, - NH₂ mode at 1000cm⁻¹, -CN stretch at 1161 cm⁻¹, C=N-C bend at 1245 cm⁻¹, C-C between phenyl ring and triazine at 1392 cm⁻¹, -CN stretch at 1493 cm⁻¹, and phenyl motion at 1596 cm⁻¹.^{77,146} No shifts were observed for these peaks in the hybrids. This shows that there is no change in the vibrational response of the PhCN after electrostatic assembly with WS₂.

XPS

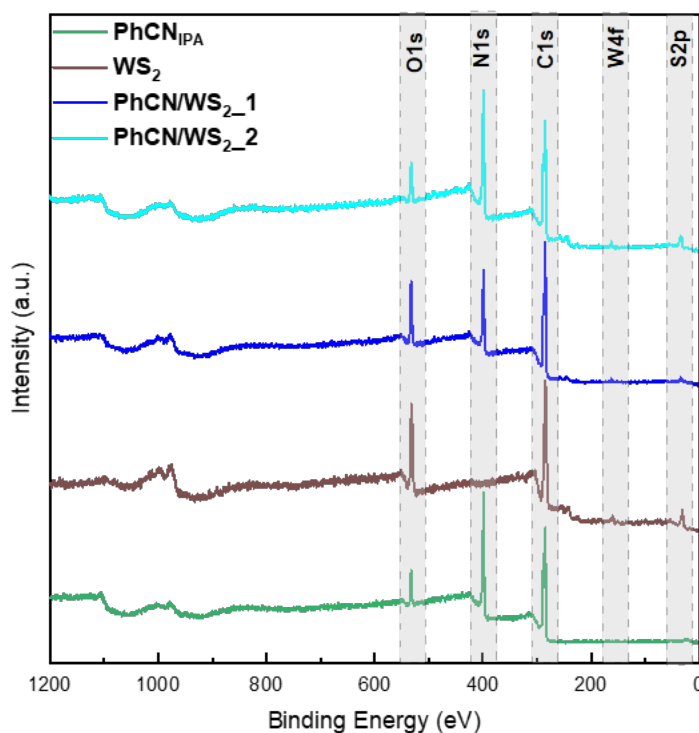


Figure 2.19 XPS survey spectra of PhCN/WS₂ hybrids and the precursors.

To verify the chemical species in our samples, we conducted X-ray photoelectron spectroscopy. The survey spectra of all the samples are shown in **Figure 2.19**. The hybrids show C, N, O, W and S species which indicate a successful hybridization of PhCN with WS₂. The signals from W and S are low probably due to a low mass % of WS₂ in the hybrids. **Table 2.7** shows the atomic concentration percentage of the key species present on the surface of the samples- N, W, and S along with the surface atomic ratio of W to N. The hybrid PhCN/WS₂_1 showed a considerable lower % of N on the surface probably

due to the accumulation of WS₂ and an increased O species concentration indicating oxidation but there was no shift in the N1s position. Interestingly, PhCN/WS₂_2 shows a higher WS₂ content on the surface than the other hybrid. There was an increase of 0.5eV in the B.E. of N1s for PhCN/WS₂_2. The S2p spectra does not show any oxidation and resembles a metal sulphide peak¹⁴⁴. This peak was also shifted towards higher binding energy by 2eV for PhCN/WS₂_1 and 2.5 eV for PhCN/WS₂_2 which could be due to the vicinity of N atoms. The XPS data confirms a successful hybridization of the two components and the presence of WS₂ on the surface of the hybrid.

Table 2.7 Atomic% of different elements found on the surface of the samples through XPS

<i>Sample</i>	<i>%N (atomic)</i>	<i>%W (atomic)</i>	<i>%S (atomic)</i>	<i>W:N ratio</i>
<i>PhCN_{IPA}</i>	28.7	0	0	0
<i>WS₂</i>	0	1	2.3	1
<i>PhCN/WS₂_1</i>	19.3	0.2	0.8	0.01
<i>PhCN/WS₂_2</i>	27.5	0.8	1.3	0.03

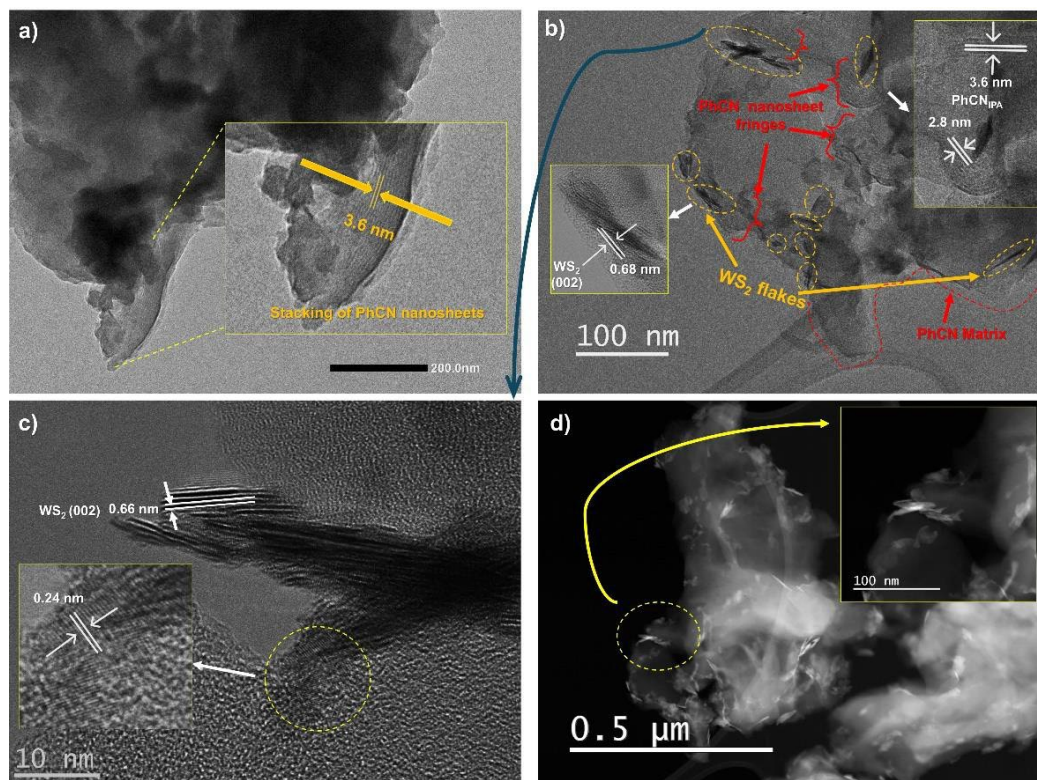


Figure 2.20 a) TEM image of PhCN_{IPA}, b),c) PhCN/WS₂_1 HRTEM images and d) STEM imaging of PhCN/WS₂_1.

The morphology of samples was characterized by TEM, HRTEM and STEM shown in **Figure 2.20**. The PhCN_{IPA} shows a layered morphology with a interlayer fringes of 3.6 nm which is highly expanded probably due to exfoliation or depicts a long- range order . The hybrid PhCN/WS₂_1 shows the presence of long WS₂ flakes integrated in the PhCN matrix in **Figure 2.20b**. A number of differently sized but long WS₂ nanosheets with a mean lateral size of 50nm were embedded in PhCN nanosheets as confirmed by the UV-Vis calculations in the previous section. In the right inset of **Figure 2.20b**, we can see the lattice fringes of PhCN sized 2.8 nm and 3.6 nm which are modified reflections similar to the ones seen in PhCN_{IPA}. The increase in this d-spacing represents changes in in-plane periodicity due to the addition of WS₂. In the left inset of **Figure 2.20b**, we can see the (002) lattice planes of WS₂. **Figure 2.20c** shows a WS₂ flake with varying lattice spacing for the (002) reflections which correspond to the interlayer spacing between WS₂ layers in 2H structure. A family of planes parallel to (002) at the head of the flake was found to be 0.22nm apart which can be associated with (100) reflection for in-plane atomic spacing (distance between W and S atoms of layer). Another set of fringes corresponding to (101) reflection of WS₂ characteristic of the ordered atomic spacing within the basal planes is

observed running through the wings of the flake. The same region of the hybrid was also undergone Scanning TEM dark field imaging in **Figure 2.20d**. The Z-contrast image shows bright images for W containing species and it has been observed that the hybridization through self- assembly was successful as a high number of WS₂ flakes could be observed.

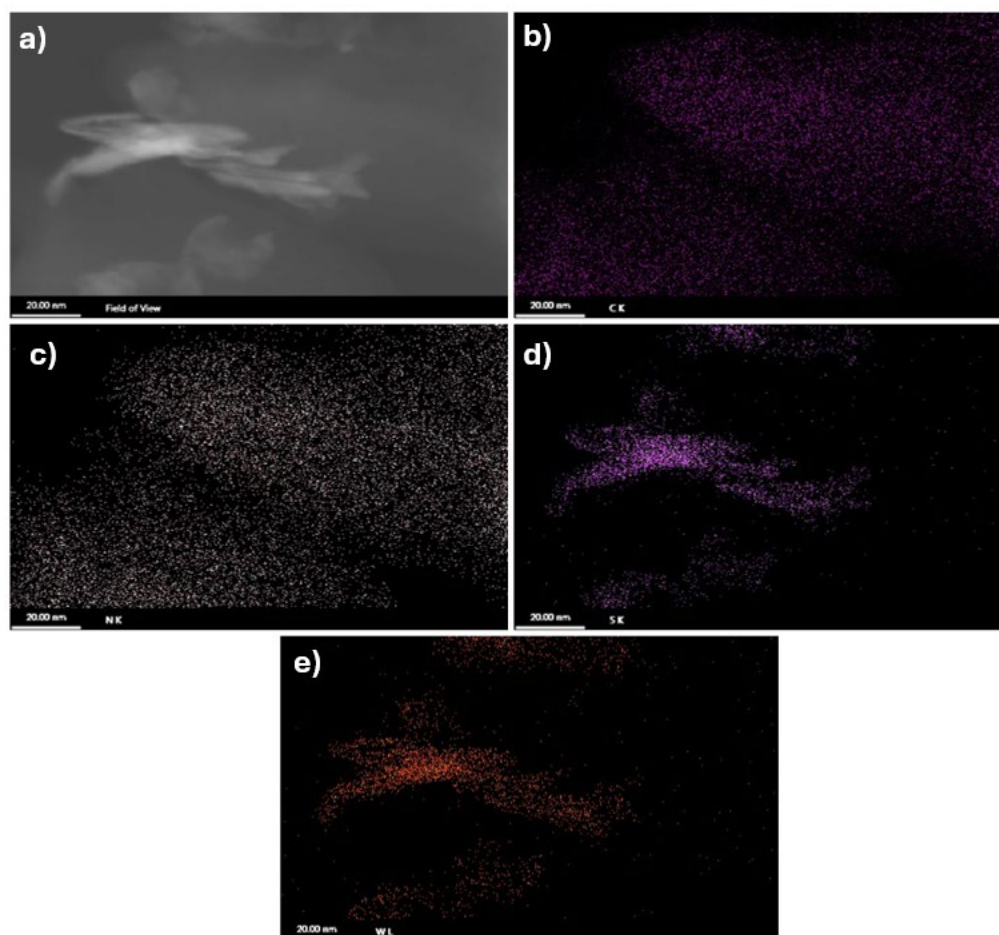


Figure 2.21 TEM-EDS mapping of the PhCN/WS₂_1 sample showing a)micrograph, K lines of b)Carbon, c)Nitrogen, d)Sulphur, and e)Tungsten.

We performed EDS mapping of the same flake region as of STEM image inset and the results can be seen in **Figure 2.21 (a-e)**. C and N species are observed to surround the W and S containing part of the hybrid. Hence HRTEM, STEM and EDS mapping showed a successful integration of WS₂ 2H phase in the PhCN nanosheets with a greater structural interaction.

HER tests

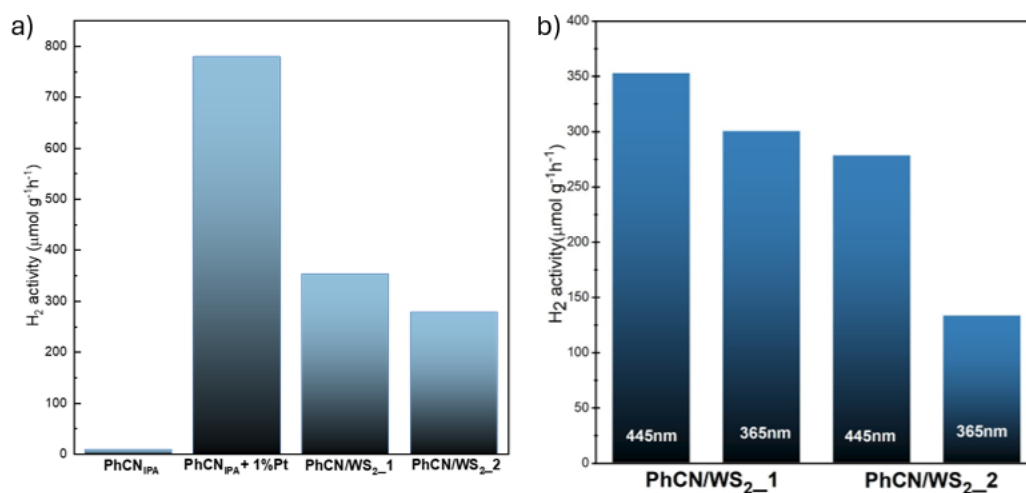


Figure 2.22 HER batch tests run for 1 hour a) study of the success of co-catalysation of WS₂, b) Comparing the H₂ activity of the hybrids in UV and visible light excitations

Hydrogen evolution tests were performed in a batch reactor with 15°C jacket cooling under 445nm and 365nm for the samples. 0.1M TEOA was used as the sacrificial agent. Injections were made every hour to the gas chromatography machine. From **Figure 2.22a** we can observe that the PhCN_{IPA} did not show any effective H₂ production in 1 hour without the presence of a co-catalyst under 445nm radiation but showed a high H₂ production activity with 1% photodeposited Pt which is the most efficient noble metal co-catalyst used for these kinds of measurements. When hybrids PhCN/WS₂_1 and PhCN/WS₂_2 were used for the same measurement, we saw the successful utilization of WS₂ as a co-catalyst showing an impressive 45% and 35% of the activity shown by the Pt co-catalyst, respectively. The HER activity of both the hybrids were then studied for a duration of 6 hours under 445nm irradiation **Figure 2.23 a**, which showed that the hybrid PhCN/WS₂_1 always produces more H₂ than the other. The same experiment was carried out under 365nm LED lamp and the same trend of a higher H₂ production by PhCN/WS₂_1 was observed in **Figure 2.23b**. It indicates that PhCN/WS₂_1 could be assigned as containing the ideal co-catalyst structure- longer and thicker WS₂ flakes. The difference between the activities of the two hybrids appeared more distinct under UV irradiation. Both the hybrids show a lower HER activity under 365nm as shown in **Figure 2.22b**. For comparison, HER measurements were carried out for PhCN_{IPA} and PhCN Bulk under 365nm (Appendix A Figure A6). It was observed that the bulk PhCN's HER activity got diminished under 365nm irradiation but the exfoliated sample PhCN_{IPA} showed an enhancement in the same.

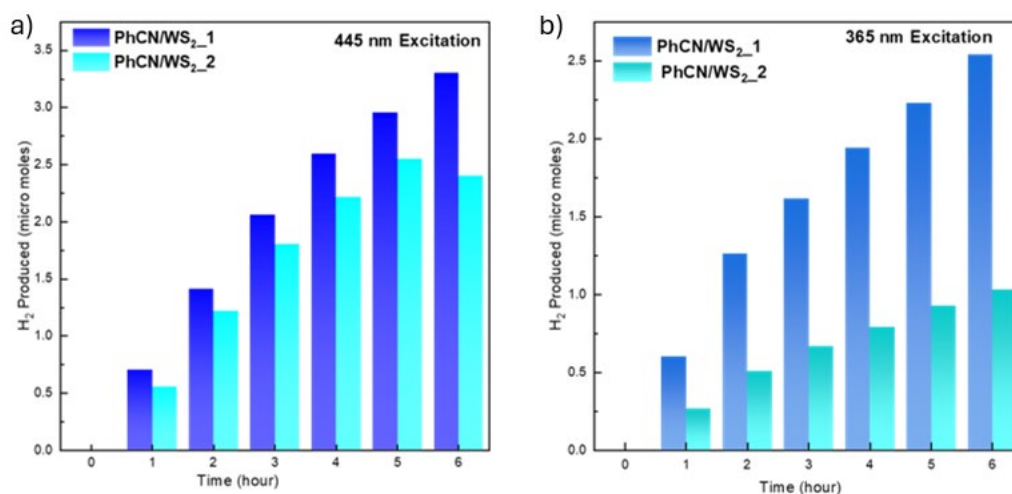


Figure 2.23 6 hours batch HER test for both PhCN/WS₂ hybrids under a)445nm, and b)365nm.

Undoubtedly, the H₂ production of PhCN_{IPA} was higher than the bulk counterpart even in UV radiation. This could be attributed to the higher charge recombination in PhCN_{IPA} under visible-light than the UV excitation region in the fluorescence maps shown in the previous section. Since the photoluminescence properties of carbon nitride compounds are linked to their stacking order^{69,146,147}, it can be expected that higher stacking of the nanosheets on top of each other, which is the case for the hybrids with WS₂ evident with the structural characteristics, may result in a higher charge recombination under UV light. So, the HER tests show the presence of WS₂ in the hybrid was indeed of a co-catalyst with incredible performance compared to the traditional Pt and that bigger and longer WS₂ flakes are ideal to hybridise with PhCN as they appear less on the surface of the material and more in between the PhCN sheets as evident from the XRD and XPS analyses. The hybrid PhCN/WS₂_1 shows an H₂ production activity of 353.2 $\mu\text{mol g}^{-1}\text{h}^{-1}$ under 445nm LED light. It shows a very stable production of H₂ for 6 hours with 7

μmol of H₂ produced every hour. The deactivation of this sample was checked after 18hours of 445nm irradiation, and it was found to have a deactivation rate of only 9.62 $\mu\text{mol g}^{-1}\text{h}^{-2}$. From the HER flow tests shown in the previous sections with PhCN samples- it was seen that the Pt degrades very rapidly with time and irradiation which hampers the stability of the photocatalyst. On the other hand, WS₂ not only lowered the Gibb's free energy for H₂ production but also stabilised the system for a longer period with a consistent H₂ generation. To better understand the charge separation and charge transfer dynamics between PhCN and WS₂ in the hybrid systems, we perform the following analyses:

UV-Vis Absorption

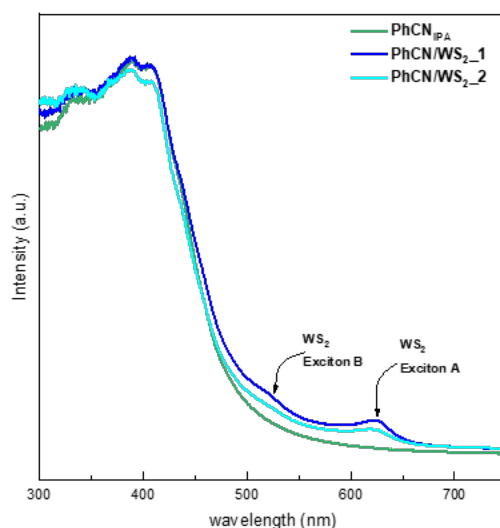


Figure 2.24 UV-vis absorption spectra of PhCN_{IPA} and hybrids with WS₂.

The UV-Vis spectra of the samples are shown in **Figure 2.24**. The absorption edge of PhCN_{IPA} was found at 464 nm corresponding to 2.67 eV. The hybrids showed presence of a good percentage of exfoliated WS₂ monolayers on the surface, through the distinct peaks of exciton A and B.⁹⁸ The presence of peak A ensures the direct band gap transitions in WS₂ with the lowest energy excitonic transition of 1.99 eV (622 nm).¹²³ The visible-light absorption was visibly enhanced and showed a weak-coupling between the two components. Tauc plots were used to estimate the band-interaction between the two components of the hybrids shown in **Figure 2.25a,b**. When hybridised with WS₂, the band gap shifted to 2.64 eV in PhCN/WS₂_1 and 2.65 eV in PhCN/WS₂_2. These results show a successful interface formation between PhCN and WS₂ nanosheets for charge transfer. In the previous section it was seen that the PhCN Bulk's band gap was found at 2.62 eV and then increased to 2.67 eV for PhCN_{IPA} due to quantum confinement effects. It is known that carbon nitride like layered materials show a dependency of band gaps on interplanar distances. Increased stacking leads to increased band gap and vice-versa. Therefore, the integration of WS₂ with PhCN leads to better visible light absorption and a lower band gap ideal for solar light utilization probably by decreasing the interplanar distance by being an interlink.

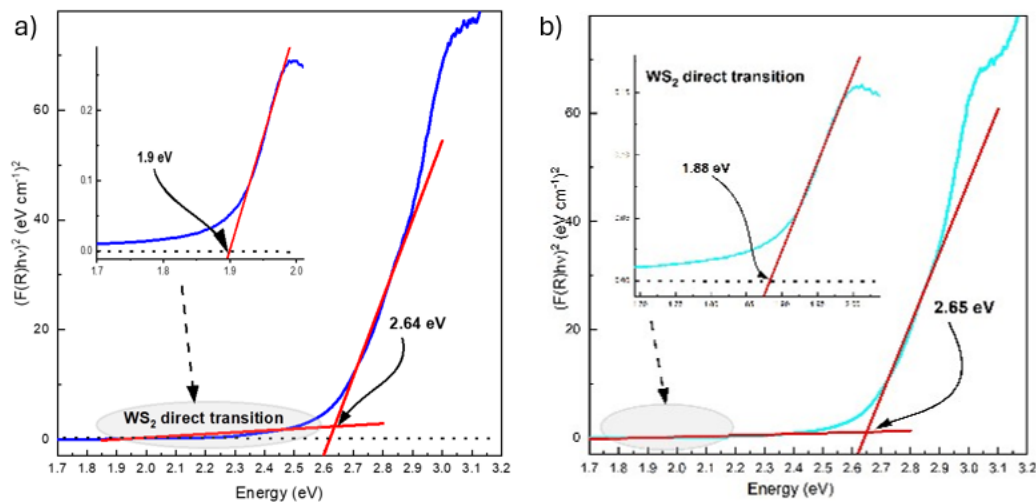


Figure 2.25 Tauc plots for a) PhCN/WS₂_1 and b) PhCN/WS₂_2.

Steady-state Luminescence

From previous studies, we know that PhCN shows a broad emission spectrum peaking at ~525nm. This fluorescence arises from the formation of excitonic species which are approximated by the quantum model of PhCN where it is considered as a particle⁶⁴. In this quantum model approximation, the optical electron is confined within the aromatic ring system, which is treated as a linear box. As the size of this box increases, the energy gap between the highest occupied and lowest unoccupied orbitals decreases and leads to a red shift; the opposite of this is also viable.⁷⁷ We study the fluorescence of the samples by exciting them from 300nm-500nm and recording the emission as shown in **Figure2.26**. When exfoliated in IPA the radiative recombination of the charge carriers increased in PhCN but there were no observable shifts in the spectra. When hybridised with WS₂, PhCN shows a reduced intensity of fluorescence. This quenching effect is indicative of the presence of a co-catalyst which serves as an electron acceptor (in our case- WS₂), reducing the number of charge carriers that recombine radiatively within the photocatalyst. The PL intensity in the descending order is as: PhCN_{IPA}, PhCN/WS₂_2, PhCN/WS₂_1, PhCN bulk. It was also observed that the spectra are broader for PhCN_{IPA} than the bulk counterpart. When hybridised with WS₂, the PL spectra become sharper. These observations show that the fluorescence of the hybrids tend to follow the trends of the bulk counterpart- in a way to revert the effects of exfoliation. This is due to the WS₂ linking in between the PhCN sheets which improves the stacking order.

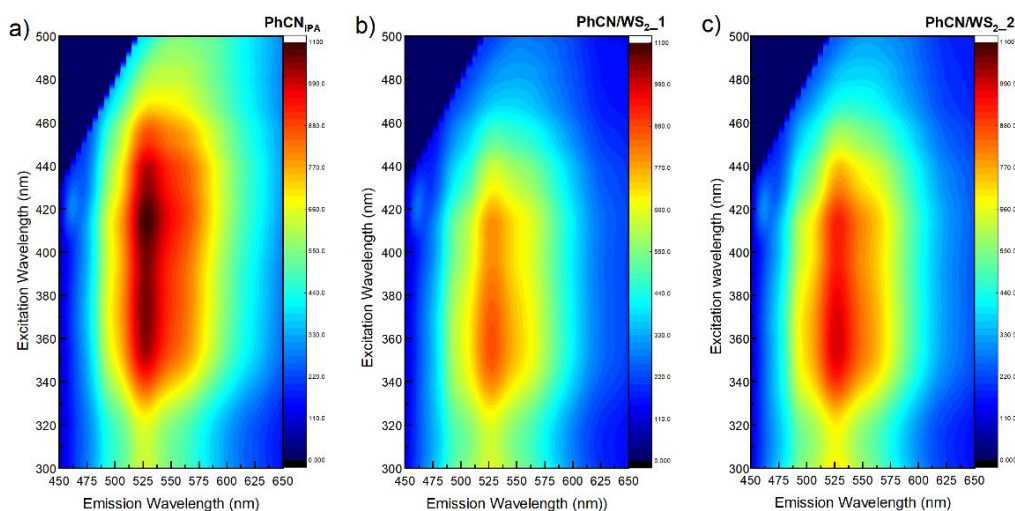


Figure 2.26 3D fluorescence mapping data of a) PhCN_{IPA}, b) PhCN/WS₂_1, and c) PhCN/WS₂_2.

The PL spectra of carbon nitride compounds can result from various contributions⁶⁴. The existence of multiple energy level contribution in PL leads to a broader light absorption spectrum and indicates the presence of multiple energy levels which could trap the charge carriers and lead to a prolonged fluorescence. The study of each contribution and changes in the fluorescence activity could yield valuable insights on the hybridization process and the charge-recombination dynamics in PhCN. Hence the PL spectra of the samples were gaussian fitted to have 4 different contributing species as shown in the **Figure 2.27 (a-c)**. We observed a substantial change in the contributing species resulting to the cumulative PL spectra which is summarised in **Table 2.8**.

Table 2.8 Summary of the band contributions shown in Figure 2.27.

<i>Samples</i>	Band 1 Area	Band 2 Area	Band 3 Area	Band 4 Area
<i>PhCN_{IPA}</i>	77.06237	156.1516	92.675	160.576
<i>PhCN/WS₂_1</i>	51.2886	127.7316	71.66938	150.06756
<i>PhCN/WS₂_2</i>	59.6166	143.12761	82.08266	173.73508

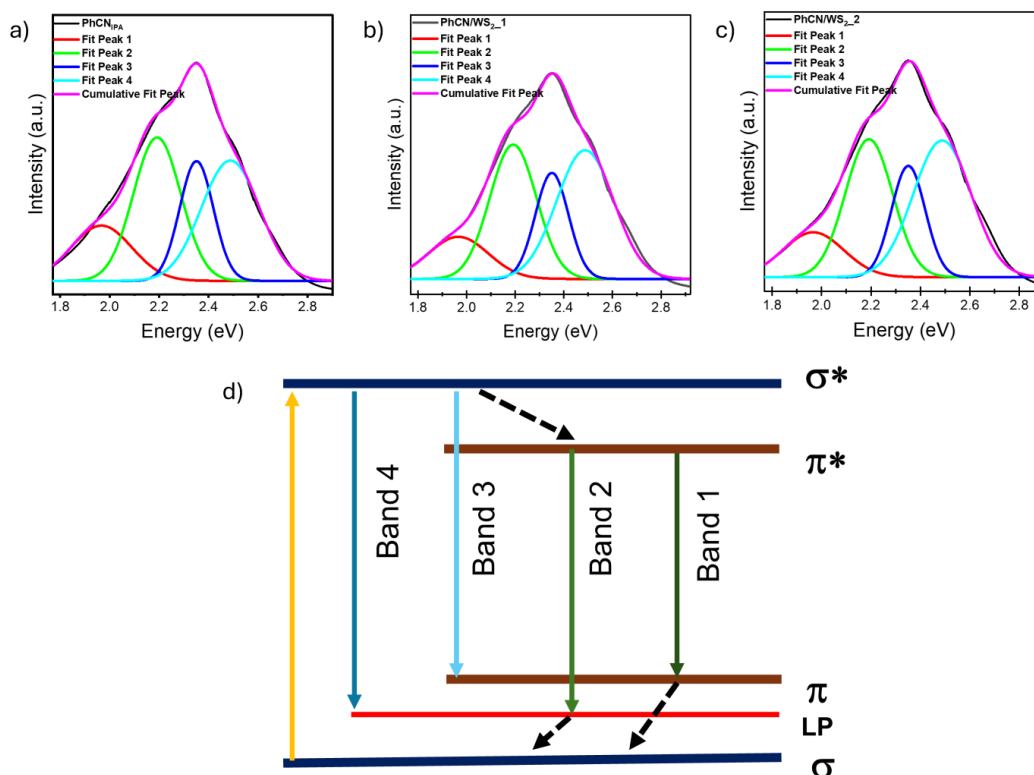


Figure 2.27 Deconvoluted Photoluminescence contributions under 360nm excitation of **a) PhCN_{IPA}**, **b) PhCN/WS₂_1**, and **c) PhCN/WS₂_2** and **d) the band assignments of the PL emission.**

The four contributing bands for the PL in PhCN were assigned to different emission mechanisms as shown in **Figure 2.27d**. The lowest energy transition was from $\pi^* \rightarrow \pi$ followed by $\pi^* \rightarrow \text{LP}$, $\sigma^* \rightarrow \pi$ and the highest energy emission from $\sigma^* \rightarrow \text{LP}$. It can be observed that the higher energy contribution increases, and the lower energy contribution decreases for the hybrids. This phenomenon was observed at all excitation wavelengths and could be explained by the absorption and energy band changes in the hybrids. The WS₂ facilitates electron transfer from PhCN, effectively reducing the likelihood of lower-energy recombination events (associated with defects or trap states). This reduction in low-energy emissions indicates that fewer electrons recombine through defect-related pathways, favouring more efficient charge separation and transfer to the cocatalyst.

The maximum emission wavelength (cumulative peak in **Figure 2.27**) remained unchanged before and after the hybridization process, even though the band contributions varied. This indicates that the intrinsic band structure of the primary photocatalyst (PhCN) was not altered by the addition of WS₂, as confirmed by the UV-Vis spectra. This consistency ensures that any observed changes in the PL spectra are attributed to modifications in charge dynamics due to the presence of WS₂. The PLE spectra of the

hybrids were obtained for this E_{max} (maximum emission wavelength) value in **Figure 2.28a**. The PL counts were lower for the hybrids than that of PhCN_{IPA} for all excitation wavelengths which means that the charge carriers are transferred to WS₂ in lower energy excitations. The overall profile of the PLE of PhCN_{IPA} did not change with hybridisation with WS₂ which confirms the optical integrity of PhCN_{IPA} and does not indicate any new energy level formation or any new emission channel formation. However, a shift in the dominant emission channel was observed after hybridization. For PhCN_{IPA}, the emission channel at 420 nm exhibited stronger fluorescence compared to the channel at 360 nm. In contrast, for the PhCN/WS₂ hybrids, the emission channel at 360 nm became more dominant, surpassing the fluorescence intensity of the 420 nm channel. The PLE spectra was normalised to the peak position at 420nm which serves as the maxima for PhCN_{IPA} PLE spectrum in **Figure 2.28b**. We could clearly observe the dominance and the effectiveness of higher energy wavelengths in yielding radiative recombination in the hybrids with WS₂. This could be due to higher effective optical band gap of the hybrids which leads to higher-energy (shorter-wavelength) transitions which is the result of incorporation of WS₂ which facilitates electron transfer from the PhCN (as supported by UV-Vis spectra).

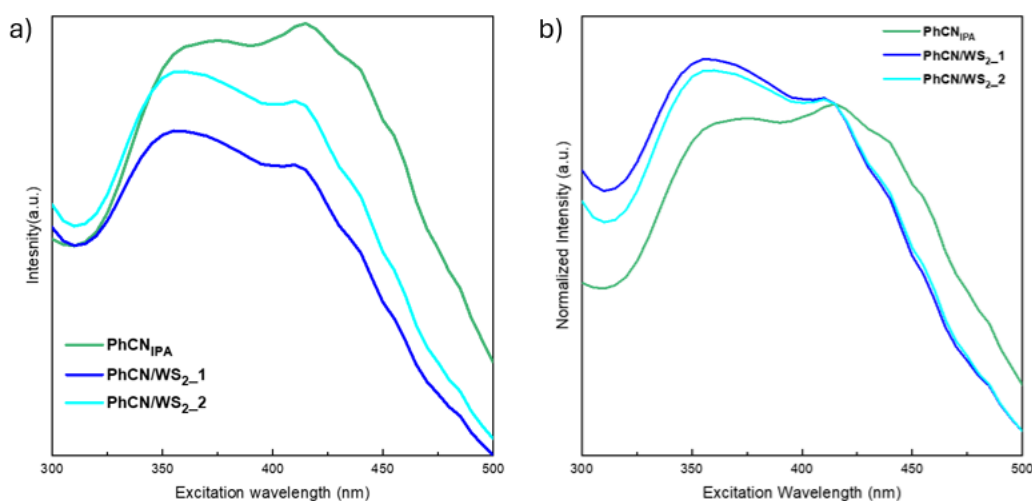


Figure 2.28 a) PLE spectra of PhCN_{IPA} and hybrids with WS₂ at emission 529nm, b) Normalised PLE to the maxima of PhCN_{IPA}.

The WS₂ cocatalyst acts as an electron or hole acceptor, pulling charge carriers away from the photoexcited sites on PhCN, which can lead to a quenching in PL intensity. This is because fewer charge carriers recombine radiatively within the PhCN matrix, decreasing the overall emission signal.

Time-Resolved Photoluminescence

The introduction of new recombination pathways, charge separation, and potential quenching effects can be seen through the time-resolved photoluminescence (TRPL) spectrum. Therefore, we measured the time-decay of fluorescence of our samples under 410nm and 360nm excitation with 50ns and 1 μ s time-windows for both. It was observed that the TRPL spectra of the hybrids show identical profiles to that of PhCN_{IPA} shown in **Figure 2.29** and any change in the lifetimes are not obvious.

On the other hand, the HER results showed the successful property of WS₂ as a co-catalyst in the PhCN/WS₂ hybrids which indicates an effective interaction between the two components which should be observable in TRPL results. The increase in the higher energy component in PL spectra dictated that the emission came from higher energy states, which can be associated with more efficient recombination pathways as higher energy radiative recombination are not energetically preferred by a system. The density of states at higher energies is lower, and these states often have fewer available transitions for radiative recombination.¹⁴⁸ Therefore, the radiative recombination from these levels is very fast. This should lead to shorter carrier lifetimes in TRPL.¹⁴⁹ According to that notion, the incorporation of 2D WS₂ cocatalyst must facilitate a very rapid charge transfer. From previous studies, it has been noted that the recombination from σ^* levels (high energy component in PL) in PhCN are known to be of sub-nanosecond range.⁴⁹ This would mean the initial charge separation occurred so quickly that the TRPL measurement within 50 ns could not capture the transfer but only the subsequent recombination events. Hence, a faster lifetime was not observed in the hybrids with the used time windows. PhCN_{IPA} shows the loss of high energy fluorescence components with time as seen in the time-spectral analysis. This phenomenon is also present in the hybrids, so the presence of WS₂ does not in any way change the dynamics within the PhCN but only acts as an electron sink for a better charge separation. From the photoluminescence studies we can observe that the radiative recombination in the hybrids was higher for 360nm excitation which led to a diminution of the H₂ production by the hybrids under 365nm LED as compared to that under 445nm LED.

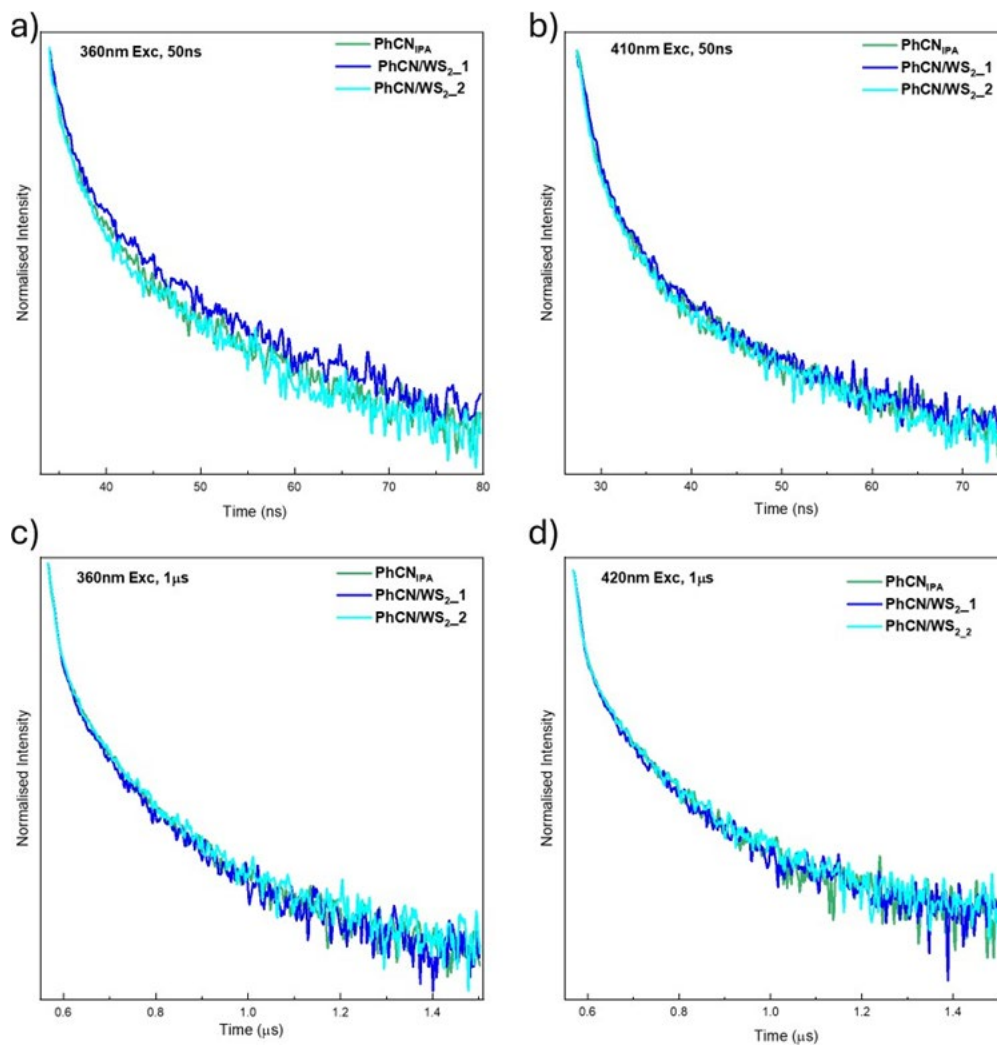


Figure 2.29 TRPL spectra of PhCN_{IPA}, and PhCN/WS₂ hybrids measured with a) 360nm excitation and 50ns time window, b) 410nm excitation and 50ns Time window, c) 360nm excitation and 1ms time window, and d) 420nm excitation and 2ms time window.

2.4. Conclusion

The liquid phase exfoliation of PhCN was carried out in different green solvents- IPA, EtOH and H₂O and the best HER activity was observed by the PhCN exfoliated in IPA. It was found that the boiling point and the surface tension of the exfoliation medium plays a big role in obtaining successfully exfoliated products. The LPE process preserved the structural and chemical properties of PhCN and only altered the morphology and optical characteristics which affect the photocatalytic performance. The exfoliated samples showed an increase in the band gap and a higher fluorescence. The increase in the band gap led to a better charge separation which led to a higher HER activity. This study underscores the role of solvent selection in achieving successful exfoliation and maintaining material stability. Using isopropyl alcohol (IPA) as an exfoliating agent enabled a more effective dispersion of PhCN and WS₂ nanosheets, which not only supported the exfoliation process but also preserved the integrity of the materials' structure. This choice of solvent, with properties closely matching the surface energy of PhCN, was essential for creating stable suspensions that minimized reaggregation and maximized the surface area for catalytic reactions. IPA was found to be a good exfoliation medium for WS₂ as well with a high yield.

This chapter has successfully demonstrated the use of liquid-phase exfoliation in obtaining exfoliated PhCN and monolayered WS₂ and their hybridization for enhanced photocatalytic hydrogen evolution under visible-light irradiation. The 2D-2D hybrid formed between PhCN and WS₂ was found to be instrumental in promoting efficient charge separation, which minimized electron-hole recombination and prolonged photoluminescence decay times. This improved charge separation is attributed to the tighter contact through WS₂ interlinking of PhCN nanosheets and efficient electronic interaction between PhCN and WS₂, allowing for quicker electron transfer from the conduction band of PhCN to WS₂ and thereby decreasing the Gibb's free energy for H₂ production. Moreover, it was established by the success of self-assembly that WS₂ and PhCN spontaneously align themselves to form a hybrid structure where WS₂ interlinks the PhCN nanosheets. The longer and bigger WS₂ flakes proved to act as a better co-catalyst as compared to smaller flakes.

The introduction of WS₂ as a co-catalyst provided a cost-effective alternative to noble metals like platinum, with the study showing its capability to function as an effective electron sink, thus amplifying the overall HER activity of PhCN under visible light irradiation. It was observed that longer WS₂ flakes yielded a better heterostructure formation with PhCN and thereby better co-catalyzation. The hybrid system was tested to be more stable than Pt co-catalyzed system with the same PhCN photocatalyst which adds to the advantages of using this earth abundant material instead of noble metals for photocatalytic HER. The selectivity of the hybrid towards visible-light activity suggests a great solar spectrum utilization. Hence, the hybrid PhCN/WS₂_1 resulted to be a sustainable answer for H₂ production and solar energy utilization.

Chapter 3

Heterojunction Formation with TiO₂ for the Degradation of Rhodamine B, H₂ Production and Viral Deactivation Under Visible Light.

Hazra, M.; Porcu, S.; Myakala, S.N.; Rabl, H.; Eder, D.; Cherevan, A.; Ricci, P.C. Elucidation of Core-shell Structure in Phenyl Grafted g-C₃N₄/TiO₂ Nanohybrids for Visible-light Mediated H₂ Production with Simultaneous Rhodamine B Degradation. ACS Applied Nanomaterials 2025.(accepted)

Porcu, S.; Maloccu, S.; Corona, A.; Hazra, M.; David, T.C.; Chiriu, D.; Carbonaro, C.M.; Tramontano, E.; Ricci, P.C. Visible Light-Mediated Inactivation of H1N1 Virus Using Polymer-Based Heterojunction Photocatalyst. Polymers 2023, 15, 2536. <https://doi.org/10.3390/polym15112536>

Abstract

This chapter presents a comprehensive study of the structural and functional characteristics of the PhCN/TiO₂ hybrid. The semiconductor-semiconductor heterojunction system, PhCN/TiO₂, was previously synthesized in our laboratory for photocatalytic dye degradation under visible light illumination. However, a complete understanding of the mechanism of action of this photocatalytic system was lacking.

The first part of the chapter presents the optimization of the hybrid system using four different mass ratios of the precursors and varying post-solvothermal annealing temperatures (three different temperatures and one untreated sample). The objective was to understand the effects of mass ratio and thermal treatment on the photocatalytic activity of this hybrid system, as well as their implications for its structural and optical properties. Through a detailed study of the 16 hybrid samples (4 × 4 combinations) using advanced experimental techniques such as TEM, XPS, and TRPL, we devised a scheme for TiO₂ crystallization on the surface of PhCN. A novel gradient core-shell structure was

discovered, whose evolution depended on the synthesis conditions and ultimately influenced the photocatalytic efficiency of the system. The photocatalytic activities of the hybrids were evaluated for Rhodamine B dye degradation under visible light illumination. The best-performing hybrids were further tested for H₂ evolution. Mechanistic studies revealed the potential for dual-functional photocatalysis, enabling simultaneous H₂ generation and Rhodamine B degradation. This dual functionality was tested with the best-performing hybrid, yielding positive results.

In the second part of this chapter, the PhCN/TiO₂ hybrid was applied for disinfection, focusing on the use of visible-light components in indoor settings. A series of tests were conducted to assess the cytotoxicity of this system on healthy liver cells. It was found that certain concentrations of hybrids do not harm healthy cells but prevent their infection by the H1N1 flu virus. Viral inactivation was achieved under both light and dark conditions, highlighting the potential use of this material as an active disinfectant in indoor environments where UV lighting is scarce.

3.1. Introduction

Dual-functional photocatalysis (DFP) has emerged as a promising method for the simultaneous degradation of industrial pollutants in wastewater and clean fuel production, offering an enhancement over traditional photocatalysis.¹⁵⁰ This approach allows for both the oxidative breakdown of water pollutants and hydrogen fuel generation through proton reduction under light exposure. DFP thus makes efficient use of both photogenerated electrons and holes in a photocatalyst, aligning with circular economy principles by transforming waste into valuable resources, such as solar fuels.⁹⁹

In recent years, innovative DFP materials have been developed, including metal-organic frameworks, metal-sulfide composites, TiO₂-based hybrids, and graphitic carbon nitride (g-C₃N₄) composites.^{150–155} When g-C₃N₄ is combined with TiO₂, it provides exceptional visible-light responsiveness, while TiO₂ itself is known for its chemical stability, abundance, and eco-friendliness.⁴⁰ Research on g-C₃N₄/TiO₂ hybrids has shown promise across applications including phenolic degradation, dye removal, antibiotic breakdown, photo-electrocatalysis, oxygen reduction reactions (ORR), viral disinfection, and hydrogen evolution reactions (HER).^{77,156–161} Special attention has been given to core-shell structured photocatalysts, which exhibit enhanced activity due to their high surface-to-volume ratios and effective charge transfer.^{160,162,163} However, a TiO₂ core with a g-C₃N₄ shell can limit active site interaction with pollutants and reduce visible-light absorption due to the shell shielding effect.

This study aims to develop a PhCN/TiO₂ hybrid system with a PhCN core and TiO₂ shell, creating a more interconnected network that improves charge migration from the sensitizer to the TiO₂ surface, thereby enhancing photocatalytic efficiency. Crafting an optimal photocatalyst requires a thorough understanding of its structural, chemical, and

optoelectronic characteristics, which can be optimized through synthesis techniques and various treatments.

In this work, we detail the stepwise design of a photocatalyst composed of phenyl-modified carbon nitride (PhCN) and anatase TiO₂, focusing on the evolution of structural and optoelectronic properties in relation to photocatalytic behavior. We propose that the TiO₂ growth on PhCN surfaces modifies the latter's chemical structure, influenced by the TiO₂ crystallization level, which can be managed via thermal treatment. High-pressure treatment of PhCN was found to induce surface changes that alter its structural and optical properties. A series of PhCN/TiO₂ hybrids with varying mass ratios were synthesized through a solvothermal method, with interactions characterized by diverse techniques. We also systematically examined how annealing at different temperatures impacted these interactions. Energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) revealed a 'gradient core-shell structure' in the hybrids. Extensive dye degradation tests using Rhodamine B (RhB) and hydrogen evolution reaction (HER) tests showed that this gradient structure maximizes the photocatalytic interaction with pollutant molecules.

Lastly, a type II heterojunction charge-transfer mechanism is proposed to explain the superior performance of the PhCN/TiO₂ hybrid for the simultaneous RhB degradation and H₂ generation. This work, to our knowledge, is the first to use a phenyl-modified carbon-nitride-based hybrid photocatalyst in dual-functional photocatalysis.

Furthermore, a separate study is carried out with the PhCN/TiO₂ hybrid for the disinfection of the virus H1N1 in the presence of only visible-light. This study explores the potential of Phenyl Carbon Nitride/TiO₂ (PhCN/TiO₂) for indoor photocatalytic disinfection under visible light, focusing on energy-efficient LEDs. This process relies on the activation of the photocatalyst by the incident light which generates reactive oxygen species (ROS) capable of damaging viral lipids and nucleic acids. This damage leads to a loss of viral structural integrity, preventing infection and replication. Photocatalytic inactivation offers a chemical-free approach, potentially making it safer and more environmentally friendly than traditional methods and is effective against a broad range of viruses. The hybrid system PhCN/TiO₂ shows potential as an effective virucide, particularly for inactivating H1N1 under visible light irradiation.

3.2. Materials and Methods

3.2.1. Materials

2,4-diamino-6-phenyl-1,3,5-triazine (C₆H₅(C₃N₃)(NH₂)₂, Ph-Triazine, 99%, Sigma Aldrich), Titanium tetrachloride (TiCl₄, 99%, Sigma-Aldrich), Absolute ethanol (C₂H₅OH, 96%, Alfa Aesar), Rhodamine B (RhB, C₂₈H₃₁ClN₂O₃, 95%, Sigma-Aldrich), Methylene Blue (MB, C₁₆H₁₈ClN₃S, Millipore Corp), Methyl Orange (MO, C₁₄H₁₄N₃NaO₃S, Sigma-Aldrich), Sodium azide (NaN₃, Sigma-Aldrich), Chloroform (CHCl₃, Sigma-Aldrich), Isopropanol (IPA, C₃H₇OH, %, Sigma-Aldrich),

Silver nitrate (AgNO_3 , Carlo Erba) and Triethanolamine (TEOA, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, 98+%, Alfa Aesar). All chemicals were used as received without further purification.

The Madin-Darby canine kidney cells (MDCK-2 ATCC® CRL-2936™, sourced from Merck in Darmstadt, Germany) were cultured in DMEM supplemented with 10% heat-inactivated Fetal Bovine Serum (FBS HI) and 1% Kanamycin sulfate. The influenza virus strain A/Puerto Rico/8/34 (H1N1) was propagated within these MDCK-2 cells. A total of 4×10^6 cells were seeded in a 75 cm² flask with 20 mL of complete medium and incubated at 37°C with 5% CO₂ for 24 hours. After incubation, the supernatant was removed, and the cells were rinsed with 10 mL of PBS before being infected with 1 mL of viral dilution (m.o.i. 0.01) in DMEM containing 1% Kanamycin. Following a one-hour infection period, 10 mL of maintenance medium (DMEM + 1% Kanamycin + 1% FBS HI) was added, and the infection was allowed to proceed for 72 hours. The cells were then cryolyzed through three cycles of freezing at -80°C for 30 minutes, followed by thawing at 37°C for 30 minutes. Cellular debris was removed by centrifuging at 3000 G for 20 minutes, and the supernatant containing the viral stock was stored at -80°C. The viral stock was subsequently titrated using a plaque assay.

3.2.2. Preparation of Phenyl modified carbon nitride

The phenyl-modified Carbon nitride (PhCN) was prepared by heating 1 g of 2,4- diamino-6-phenyl-1,3,5-triazine powder (Ph-Triazine) in a closed glass container in a muffle furnace at 400°C for 2 hours in the presence of air. The heating rate was kept at 10°C/min and the cooling at 5°C/min.

3.2.3. Preparation of Titania reference samples

Four TiO₂ samples were prepared via solvothermal method in 20ml ethanol and TiCl₄ (0.25ml, 0.5ml, 1.1ml and 2ml) for reference measurements. The TiO₂ prepared with 1.1ml TiCl₄ was annealed at 230°C, 300°C and 450°C.

3.2.4. Preparation of hybrid photocatalysts

The PhCN (100mg) was stirred at room temperature for 30 minutes in 20 ml of ethanol after which TiCl₄ (0.25, 0.5, 1.1, 2 ml) was added to it dropwise and the suspension was further stirred at room temperature for 2 hours. The resulting mixture was then transferred into a teflon autoclave and heated at 180°C for 8 hours. Following the reaction, the products were filtered and subjected to multiple washing steps with deionized water and absolute ethanol. The washed samples were then dried at 60 °C for 12 hours. The 4 hybrid nanopowders were named as A_RT, B_RT, C_RT and D_RT according to the mass ratio PhCN:TiO₂ – 2:1, 2:6, 2:13 and 2:30 respectively. Each sample underwent analysis both in its pristine state and after annealing at 230°C, 300°C, and 400°C. Consequently, the hybrids are named as A_temperature, B_temperature, C_temperature and D_temperature.

3.2.5. Photocatalysis tests

Dye degradation

The photocatalytic performance was assessed using a white commercial LED bulb (white LED 11 W, 6mW/cm²) as the light source. Before light irradiation, the suspension containing 50mg of photocatalyst and 50ml dye RhB/MB/MO (10 mg·L⁻¹) were stirred in dark for 30 min to ensure absorption–desorption equilibrium. Throughout the photodegradation process, 2 mL aliquots were collected every 60 min. The aliquots were then centrifuged and the residual concentrations of RhB were analyzed using the Beer-Lambert Law.

Active radicals quenching experiments.

The extend of the presence of reactive oxygen species (ROS) namely- OH, ¹O₂, O^{•-2}, h⁺ and photogenerated e⁻ is investigated via their scavengers- IPA, NaN₃, CHCl₃, TEOA and AgNO₃ respectively. The reaction conditions were kept identical to the dye degradation tests with 1mg/1ml concentration of catalysts in 0.02mM RhB solution and an excess of 1mM of the quenchers were added to the system individually for a comparative study between the radicals. These tests were also carried out with different concentrations of IPA-1mM/1.3M/6M and TEOA- 1/10/100mM.

Hydrogen evolution reaction tests

Home-made closed type reactors were used to test the hydrogen evolution ability of the hybrids. 2mg of each hybrid was dispersed in 2ml of 0.1M TEOA with 1wt%Pt and was illuminated 4cm away from the side by an LED light source(Thorlabs) centered at 445 ± 20 nm. Before the illumination, the reactor (with the reactants) was purged with argon (flow rate 5ml min⁻¹, MFC from MCC- Instruments) for 15min to eliminate any environmental gases within the head space of the reactor. The concentration of H₂ produced by the reaction in 1 hour was measured by gas chromatography (Shimadzu) through a Dielectric-Barrier Discharge Ionization Detector (BID detector). The temperature of the reactor was kept constant at 15C throughout the reaction by a water cooling system (LAUDA) with a continuous stirring of the reaction system at 550rpm.

A gas-flow slurry type home-made reactor with a different geometry was used for the detection of continuous production of H₂ gas from the best photocatalyst in the series for 40 hours. The online gas analyser (X-Stream, Emerson Process Management) equipped with a thermal conductivity detector (TCD) and photometric non-dispersive IR sensor, was used for the quantification of H₂ and CO₂ detection respectively. The argon flow was kept at 15ml min⁻¹ throughout the experiment. The concentration of the catalyst is kept at 10mg/ml and rest of the reaction conditions are kept the same as before.

For the simultaneous RhB degradation with HER, the concentration of the catalyst was kept at 10mg/ml in 0.02mM/0.1mM RhB solution with 1wt% Pt. The reaction conditions

were the same as that of initial tests. Gas injections for GC were done at every hour after illumination.

3.2.6. Cytopathic Effect Assay on MDCK-2 Cells

The cytopathic effect was evaluated using two sets of 2×10^4 cells per well, which were seeded in two separate 96-well plates with complete medium and incubated overnight. The following day, the supernatant was discarded, and the cells were treated with serial dilutions of the photocatalyst, ranging from 10 ng/mL to 0.01 mg/mL. Cells were either shielded with aluminum foil or exposed to white light for two hours, then incubated at 37°C with 5% CO₂. After 72 hours, 20 µL of MTT (3- (4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide) dissolved in PBS at a concentration of 7.5 mg/mL was added to each well, and the plates were further incubated at 37°C with 5% CO₂ for 1 hour. The supernatant was then removed, and the cells were lysed with 100 µL/well of a solution containing 10% 2-Propanol, 0.004% Triton-X-100, and 0.0004% HCl. Absorbance was measured at 570 nm using a Victor Nivo5 plate reader (PerkinElmer, Waltham, MA, USA).

For viral titration by plaque assay, 4×10^5 MDCK-2 cells per well were seeded in 12-well plates with complete medium. The next day, the supernatant was removed, and cells were treated with a serial dilution of the virus in DMEM alone and incubated for 1 hour. The virus was then removed, and each well was covered with 2 mL of immobilizing medium (DMEM with 1% Kanamycin, 0.1% trypsin, and 1% low-melting agar) and incubated for 72 hours. Afterward, the immobilizing overlay was discarded, and cells were stained with 0.8% crystal violet in 50% ethanol, followed by plaque counting through visual inspection.

For the viral infectivity reduction assay of PhCN/TiO₂ on the MDCK-2 cell line, 600 PFU of Influenza Virus strain A/Puerto Rico/8/34 (H1N1) were incubated with a 1.25 mg/mL suspension of PhCN/TiO₂ in DMEM alone, alongside a control solution without PhCN/TiO₂. The solution was divided into two parts: one was irradiated, while the other was kept in the dark for two hours. Viral titer differences were then assessed by plaque assay.

3.2.7. Characterization techniques

X-ray diffraction patterns were collected at room temperature by using a Rigaku Miniflex II diffractometer with θ -2 θ Bragg-Brentano geometry with Cu K α ($\lambda = 1.5418$ Å), radiation at room temperature. The scan speed was kept at 0.5° min⁻¹ with a step-size of 0.04°.

Spectrum Two **FT-IR** Spectrometer from Perkin Elmer was used to acquire the infrared spectra of all the hybrids and pristine samples (LiTaO₃ detector, scan range 4000-450cm⁻¹). The resolution was 0.5 cm⁻¹. All the measurements were done in attenuated total reflectance mode with 10 spectra averaging.

Raman spectroscopy was conducted using an MS750 spectrograph (Sol- Instruments) with a 600 gr/mm grating and an incident excitation from a 785 nm laser source focused via a 10× Olympus objective lens, with an approximate laser power of 1×10^{-2} W/cm². No discernible heating effect on the samples was observed. The measurements were carried out at room temperature, with a spectral resolution of 1 cm⁻¹.

A PerkinElmer **Thermogravimetric** analyser 8000 (Waltham, USA), was used to measure the mass loss with temperature in an aluminium oxide (Al₂O₃) crucible under air with a ramp rate of 10 °C min⁻¹.

All measurements were carried out on a custom-built SPECS **XPS-spectrometer** equipped with a monochromatized Al-K_α X-ray source (μFocus 350) and a hemispherical WAL-150 analyser (acceptance angle: 60°). The received powder samples were placed onto the sample holder using double-sided carbon tape.

Pass energies of 100 eV and 30 eV and energy resolutions of 1 eV and 50 meV were employed for survey and detail spectra respectively (excitation energy: 1486.6 eV, beam energy and spot size: 70 W onto 400 μm, angle: 51° to sample surface normal, base pressure: 3×10^{-10} mbar, pressure during measurements: 7×10^{-9} mbar).

Data analysis was performed using CASA XPS software, employing transmission corrections (as per the instrument vendor's specifications). For all elements Shirley backgrounds and the corresponding Scofield sensitivity factors were utilized. Charge correction was performed by shifting the adventitious carbon peak (C-C peak) to 284.8 eV binding energy (BE).

All content values shown are in units of relative atomic percent (at%), where the detection limit in survey measurements usually lies around 0.1-1 at%, depending on the element. The accuracy of XPS measurements is around 10-20% of the values shown.

SEM studies were carried out using a Carl ZEISS Auriga microscope equipped with an energy dispersive X-ray spectroscopy (EDX) detector or an ESEM FEI Quanta 200 microscope operating at 30 kV. Point EDS is measured with different beam energies-10keV, 15keV, 20keV, 25keV and 30keV for non-heat treated samples A,B,C and D. All the powder samples were sprinkled on the carbon tape adhered on the aluminium sample stub and then excess of powder was dusted off.

Transmission Electron Microscope TEM JeolJEM 1400 Plus was used for bright field imaging of TiO₂ nanoparticles and the PhCN/TiO₂ as-prepared hybrids under ultra-high vacuum conditions. The samples were put on the Cu grid with a drop of EtOH which was then dried under ambient conditions.

N₂ physisorption characterization was performed using a Micrometrics ASAP 2020 Porosimeter at 77 K. Surface area and pore-size distribution were calculated by the Brunauer-Emmett-Teller and Barret-Joyner-Halenda methods, respectively.

PL measurements were performed with an excitation wavelength of 405nm LASER coupled to an Avantes Sensilne Avaspec-ULS-TEC Spectrometer with an optical fiber. The measurements were recorded for a spectral range of 300-900nm with a 100ms time window.

Three-dimensional fluorescence mapping was performed using Horiba Jobin Yvon Fluoromax-3 with a 450 W xenon lamp as the excitation source (Horiba Ltd., Kyoto, Japan). The maps were collected with an excitation range of 300–600 nm and an emission range of 400–800 nm with a 2 nm spectral bandwidth for excitation and emission and a 10% filter at the excitation slit.

Time-resolved photoluminescence (TR-PL) measurements were performed by exciting the samples with 410nm by an optical parametric amplifier (Light Conversion TOPAS-C) pumped by a regenerative Ti:Sapphire amplifier (Coherent Libra-HE, Coherent Inc., Santa Clara, CA, USA). The repetition frequency was 1kHz, and the PL signal was recovered by a streak camera (Hamamatsu C10910, Hamamatsu Photonics, Hamamatsu City, Shizuoka Pref., Japan) equipped with a grating spectrometer (Princeton Instruments Acton SpectraPro SP-2300, Teledyne Princeton Instruments, Trenton, NJ, USA).

Absorption measurements of solid samples were obtained **by diffuse reflectance spectroscopy** utilizing a UV–Vis– NIR Agilent Technologies Cary 5000 Spectrometer (Santa Clara, CA, USA). Measurements were performed by using a PbS solid-state photodetector. The reflection configuration measures the diffuse reflection of the sample with respect to a KBr reference that is considered to have 100% reflectivity. The Kubelka-Munk equation was applied to extract the absorption features.

The absorbance spectra of the dye solutions were obtained by the same instrument with a liquid sample holder and absorbance was calculated from transmission.

3.3. Results and Discussion

3.3.1. Detailed study of PhCN/TiO₂ hybrid for dual-functional photocatalysis.

Pristine hybrids PhCN/TiO₂ were prepared by increasing the amount of TiCl₄, and were denoted as A_RT, B_RT, C_RT and D_RT in the order of increasing Ti content, where RT stands for room temperature denoting the non-annealed samples. Subsequently, each of these hybrids containing different ratios of PhCN:TiO₂ were further annealed at 230°C, 300°C and 400°C, denoted as A_230, A_300, A_400; B_230, B_300, B_400 and so on.

The study of the interaction between the two components of the hybrid and their dependence on the mass ratio and annealing temperature is studied through the following techniques-

XRD

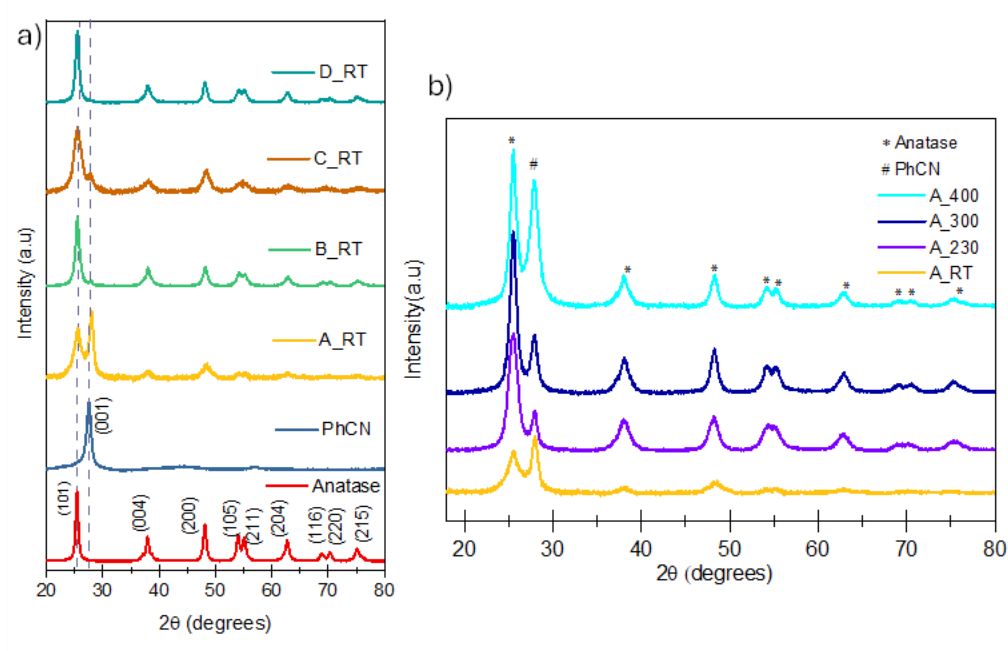


Figure 3.1 XRD data of a) as -prepared PhCN/TiO₂ samples with pristine PhCN and TiO₂, b) hybrid A series.

The characteristic reflection of PhCN at 27.5° corresponding to (001) depicts the interplanar stacking of the system.⁷⁰ All the as-prepared hybrids show the presence of titania in its anatase phase, without any contribution of brookite or rutile phases,⁴⁰ which can be attributed to the hydrolysis conditions of TiCl₄ in a high pH environment at 180°C known to promote anatase growth.¹⁶⁴ The diffraction from PhCN dies down with increasing TiO₂ content in the hybrids due to the lowering concentration of the PhCN component.¹⁶⁰ The hybrids with lower TiO₂ content also show the PhCN characteristic peak at ~27.9° shifted from its original angle in pristine PhCN (**Figure 3.1a**). This shift towards higher 2θ can be a result of decrease in the interplanar spacings of its nanosheets because of high pressure treatment in the autoclave. The same effect was observed when

PhCN was treated at the same temperature, pressure, and duration in an autoclave as the hybrids without the Ti precursor (**Figure B1**). The XRD peaks of TiO₂ in the hybrids also exhibit a minor shift towards higher 2 θ when compared to the characteristic peaks of the pristine anatase. This shift in the crystallographic planes of TiO₂ can be attributed to its interaction with PhCN structure.⁴⁰ In comparison to this, no further shifts are observed between the samples containing different ratios of PhCN:TiO₂, nor after annealing at different temperatures (**Figure 3.1b**). The average crystallite sizes calculated using the Scherrer equation ranges from 5 -14 nm for the hybrids (**Figure B2**). It is observed that the crystallite size always grows with annealing temperature for all the hybrids. According to the degree of crystallization calculated by the XRD data (**Figure B3**), we see an increase in the crystallinity of the hybrid from A_RT to B_RT and similar values for hybrids B_RT, C_RT and D_RT. This could imply that the TiO₂ has the highest degree of crystallization for the hybrid B ratio because hybrid C and D do not show appropriate increase in the % crystallinity in the hybrid system even after possessing a significantly high amount of Ti precursor during the solvothermal treatment. Since the synthesis conditions were the same for all the hybrids, it can be said that the TiO₂ did not find enough solvent molecules for immediate hydrolysis which slowed the process and the total time for the reaction was not enough for the crystallization of Ti species.¹⁶⁵

ATR-FTIR

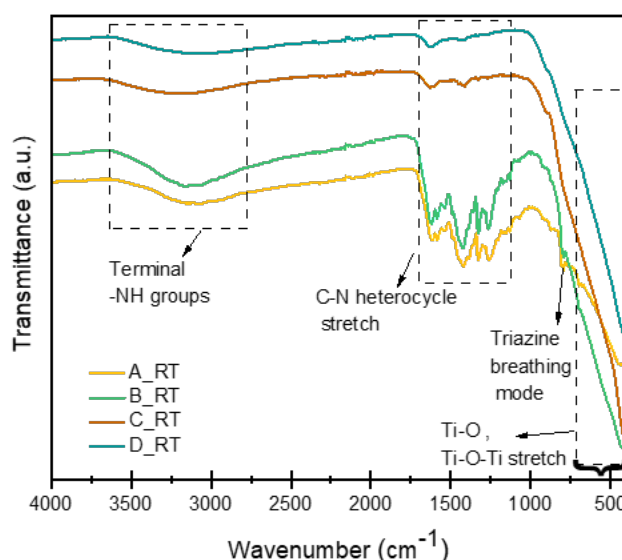


Figure 3.2 FTIR spectra of PhCN/TiO₂_RT hybrids.

The chemical composition of the PhCN/TiO₂ hybrids was studied by attenuated total reflection IR absorption spectroscopy (ATR-FTIR) (**Figure 3.2**). Pristine PhCN shows the characteristic peaks of sp³ C-N vibrations at 1383, 1324 and 1250 cm⁻¹, and sp² C=N vibrations at 1611 and 1534 cm⁻¹, well in agreement with reported literature (**Figure B4**).¹⁶¹ The band at 810 cm⁻¹ shows the breathing mode for triazine units in PhCN¹⁶¹ – confirming its incorporation – whereas the broad peak in the range of 3500-3000 cm⁻¹ corresponds to the terminal N-H groups and adsorbed water molecules in PhCN.¹⁶⁶ **Figure 3.2** shows the successful formation of TiO₂ in the hybrids visible from the appearance of a broad absorption in the low- wavenumber region at 483 cm⁻¹, corresponding to the Ti-O vibration.¹⁶¹ All hybrids show a broad band between 3500 and 2800 cm⁻¹ corresponding to the terminal N- H groups of the PhCN with a decrease in intensity with increasing TiO₂ loading. Moreover, the band 1300-1200cm⁻¹ corresponding to an aromatic amine gets weaker alongside other aromatic bond vibrations in samples containing higher titania content, showing a loss in the PhCN structure. When annealed, the hybrids show less surface adsorbed water molecules, lower contribution of sp³ C-N and sp² C=N vibrations along with a stronger Ti-O stretching related to the higher degree of crystallization of the anatase phase and high amounts of TiO₂ (**Figure 3.3**).

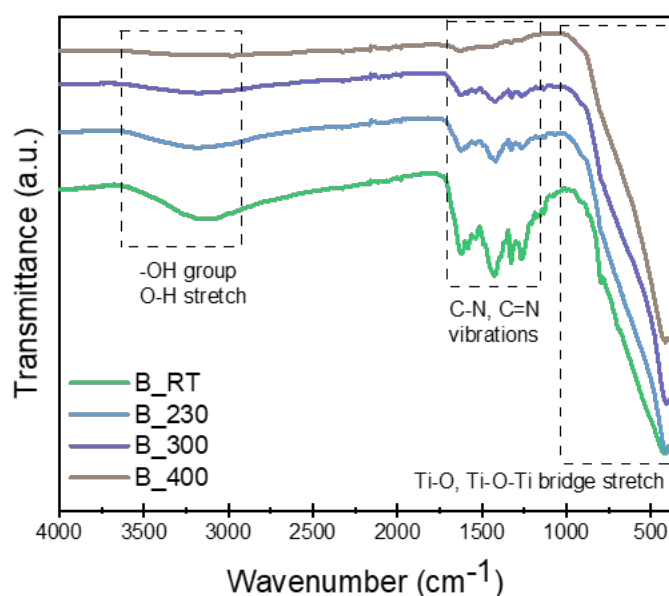


Figure 3.3 FTIR spectra of hybrid B series.

TGA/ DTG

Next, the thermal stability of the pristine components and the hybrids was studied via thermo-gravimetric analysis (TGA) by heating them from room temperature until 700°C in synthetic air (**Figure 3.4**). PhCN shows a sharp mass loss starting from 500°C and losing 100% of its mass via thermal oxidation until 650°C, while pure TiO₂ shows no change in mass in this temperature range.¹⁵¹ The autoclave treatment of PhCN barely alters the nature of the TGA curve (**Figure B7a**). In the as-prepared hybrids, a similar mass drop is observed in the same temperature range, attributed to the PhCN decomposition, and was used to calculate the fraction of PhCN present in these hybrids (Table S1). Interestingly, the amount of PhCN in the as-prepared hybrids calculated by the TGA results are lower than the amounts expected from the synthesis conditions. This result indicates a possible loss in the pristine form of PhCN during the hybrid formation via solvothermal treatment. On the other hand, TGA curve of hybrid sample annealed at 400°C (**Figure B7b**) show much lower mass loss due to the presence of highly crystalline TiO₂.

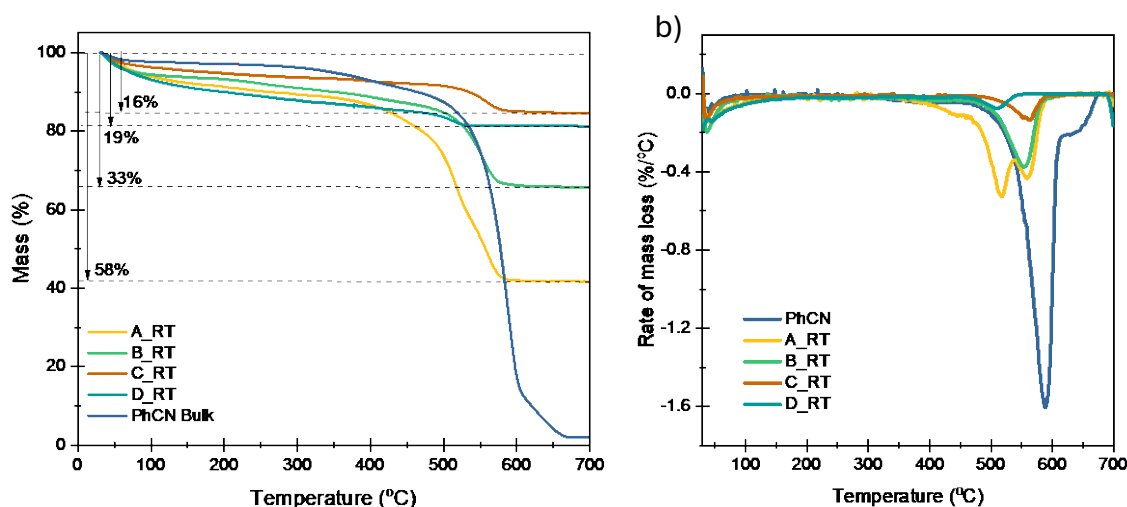


Figure 3.4 Data of as-prepared PhCN/TiO₂ hybrids with PhCN Bulk, a) TGA and, b) DTG.

The **Figure 3.4b** shows the differential analysis of the TGA of the as-prepared samples compared to PhCN where the rate of mass loss can be observed and negative peaks. It can be observed that PhCN has the highest mass loss rate due to the presence of organic components which are susceptible to heat and temperature. There is one major dip which can be observed in all the as-prepared hybrids and is characteristic to PhCN. The TiO₂ in

the hybrids also interacts with the temperature and as the amount of TiO_2 increases, this decomposition of PhCN occurred at a lower temperature. In the sample A_RT, we could observe another peak at a lower temperature which could be attributed to any defect phase interaction between TiO_2 and PhCN. As would be seen in the TEM images, the crystallization of TiO_2 was underdeveloped in the A_RT hybrid which may indicate remnants of TiCl_4 or $\text{Ti}(\text{OH})$ species which when interacting with PhCN undergoes decomposition for TiO_2 formation.

XPS

XPS was employed to elucidate the surface composition and nature of the chemical bonds present in the hybrids. In PhCN C1s spectra (**Figure B8**) the chemical bonds $\text{N}=\text{C}-\text{N}$, $\text{C}-\text{NH}_x$ and $\text{C}=\text{C}$ are observed at 288.7 eV, 286.02 eV and 284.6 eV respectively.¹⁶⁶ The N1s spectra of PhCN (**Figure 3.6b**) shows characteristic peaks of $\text{C}-\text{N}=\text{C}$, $\text{N}-(\text{C})_3$, $\text{C}-\text{NH}$, and pi-excitation, at 398.15, 399.43, 401.23, and 404.51 eV respectively.⁷⁰ The XPS indicates a successful phenyl-modification of carbon nitride according to previous reports.³⁴ The survey spectra of hybrids A_RT, B_RT, C_RT and D_RT show the presence of species from both - PhCN and TiO_2 (**Figure 3.5**). With increasing titania loading in the hybrid, the Ti peaks strengthen and the N1s peak weakens. The calculated atomic % of N depreciates with increased titania loading in the samples and an increase in Ti% is also observed (**Table B2**). We observe a shift of 0.7 eV in the N1s edge of the hybrids towards lower binding energies as compared to PhCN (**Figure 3.6b**) indicating the presence of a more electropositive atom which we attribute to the Ti-neighbour in the hybrids.¹⁶⁷ Furthermore, we also see an increasing contribution from the $\text{C}-\text{N}=\text{C}$ signal and a decreasing contribution from the $\text{N}-(\text{C})_3$ component with the increase in TiO_2 content.

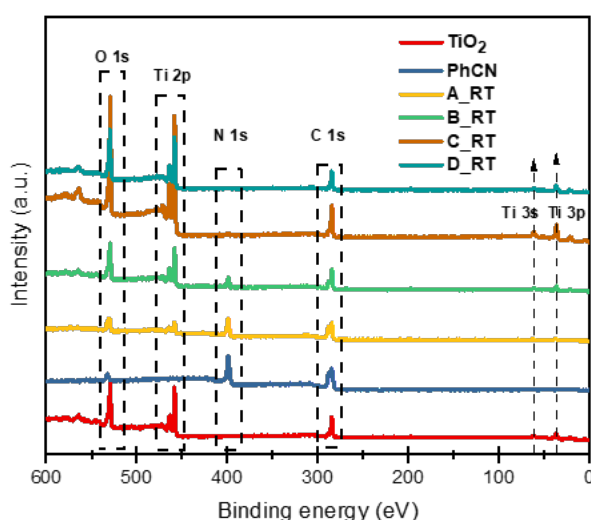


Figure 3.5 XPS survey spectra of as-prepared PhCN/ TiO_2 hybrids with the precursors.

This implies that when titania grows onto the surface of PhCN, it may hamper the degree of polymerization in PhCN and thus hinder the integrity of the heptazine structure. The peak related to the N-(C)₃ bond of the hybrids shifts towards higher binding energy with higher TiO₂ content indicating a successful perturbation of the aromatic carbon nitride structure due to the presence of Ti which agrees with FTIR and TGA studies. On the other hand, the N1s spectra is very weak for C_RT and D_RT hybrids which is due to enhanced crystallization of TiO₂ on the surface (**Figure B9**) as suggested by the XRD data.¹⁶⁷ The Ti 2p spectra (**Figure 3.6a**) of TiO₂ anatase shows peaks at 458.44 (Ti2p_{3/2}) and 464.14 eV (Ti2p_{1/2}) with a symmetric line shape and a spin orbit splitting of 5.7 eV corresponding to the Ti⁴⁺ state.¹⁶⁸ The Ti2p spectra at 458.3 eV is observable in all the as prepared hybrids indicating the presence of TiO₂ on the surface (**Figure 3.6a**). The Ti2p_{3/2} peak position in the hybrid A_RT shifts to a lower binding while it stays alike to pristine TiO₂ in hybrids B_RT and D_RT. This is due to the higher fraction of PhCN (i.e., N atoms) in the hybrid A_RT and comparatively much lower fraction of PhCN in the hybrids B_RT and D_RT. We could suggest that Ti sites on the surface of A_RT are well surrounded by a high number of electronegative N atoms causing the shift. When annealed at 400°C, the nitrogen % in hybrid B drops to a lower value and the N1s spectrum becomes very weak (**Figure B10**) indicating loss of N related bonds due to annealing, at the same time Ti2p spectra of B_400 shows a shift of 0.1 eV towards lower binding energy (**Figure B11**) due to the removal of electron rich N atoms from its vicinity. A higher count for Ti 2p signal is also observed, showing enhanced crystallization of TiO₂ in the annealed hybrid.¹⁶⁷

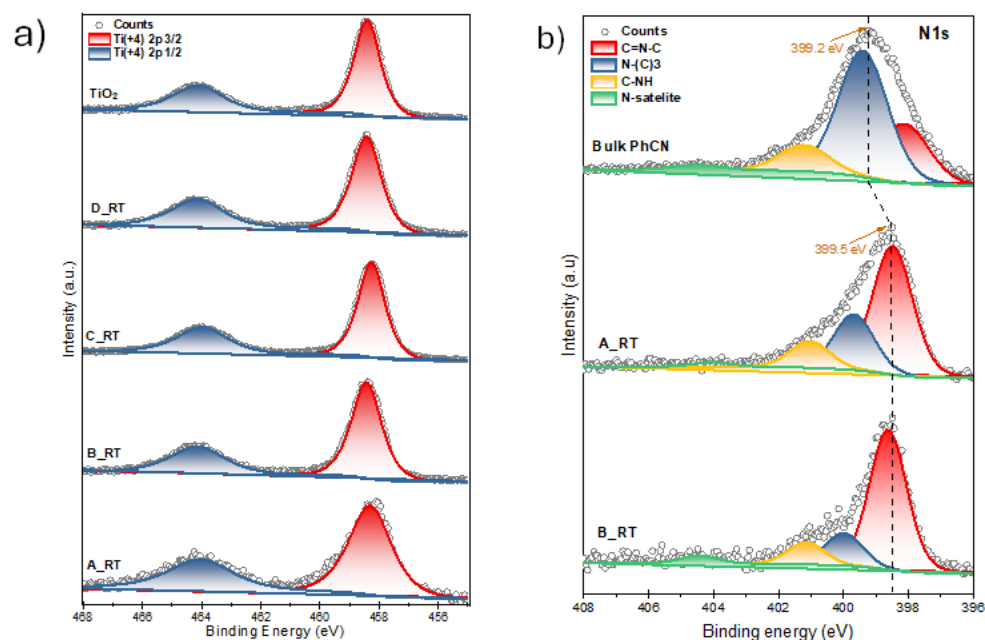


Figure 3.6 XPS edge of a)Ti2p and b) N1s

SEM

Scanning electron microscopy (SEM) images show the evolution of the hybrid morphology occurring with increasing titania loadings. They show smaller particle size and agglomeration with increasing TiO_2 loading in the hybrids which is consistent with the SEM images of TiO_2 nanoparticles prepared with identical amounts of Ti precursor under identical solvothermal process. When annealed, the hybrids do not show any considerable size changes through the SEM images while for pristine TiO_2 nanoparticles, we observe an increase in the particle size. In addition, the SEM images of PhCN treated in the autoclave show larger distribution of particles with smaller diameters, which can enhance the surface area available for TiO_2 for nucleation.

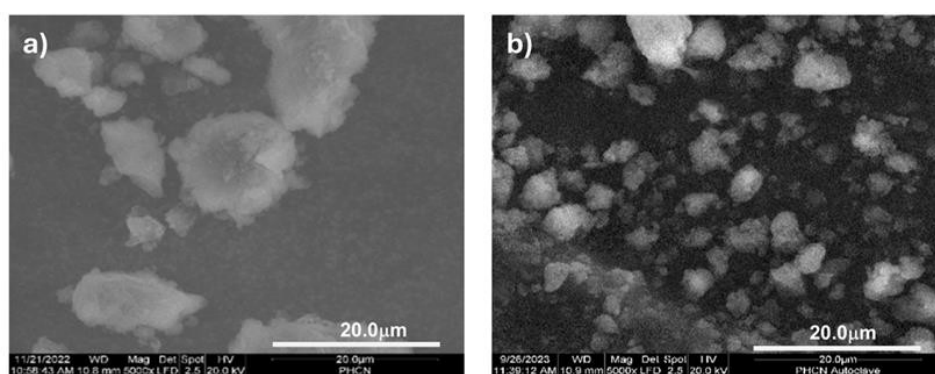


Figure 3.7 SEM image of a) PhCN Bulk and b) PhCN autoclave treated.

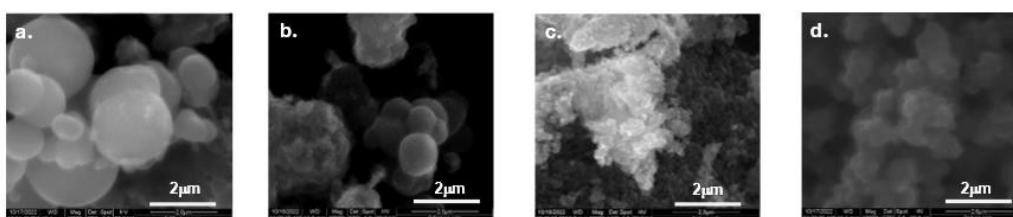


Figure 3.8 Sem Images of a) A_Rt, b) B_RT, c) C_RT and d) D_RT.

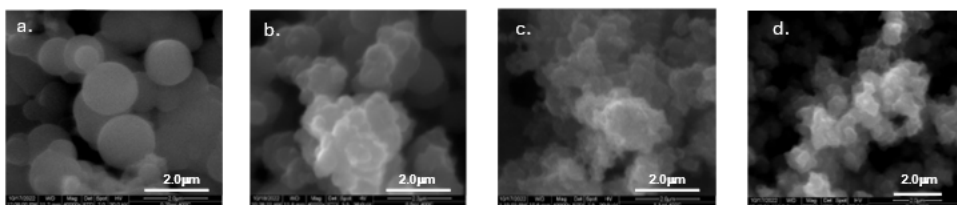


Figure 3.9 SEM images of a) A_RT, b) A_230, c) A_300 and d) A_400.

EDS

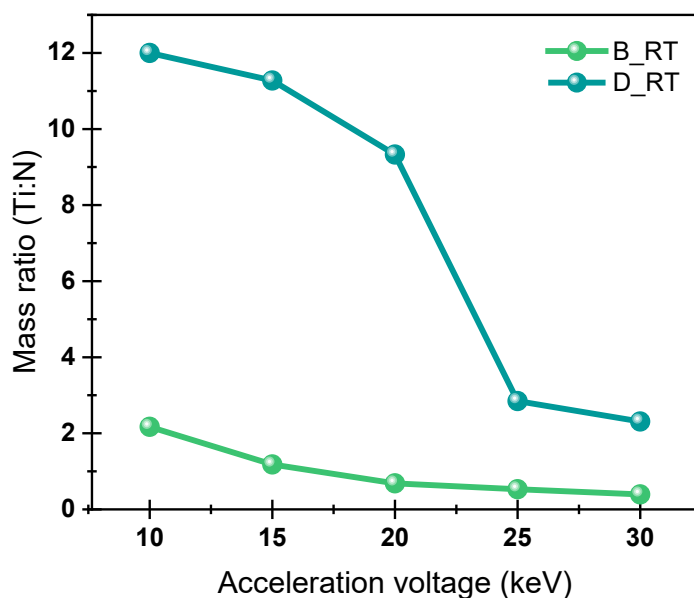


Figure 3.10 Atomic ratio of Ti and N in the hybrids B_RT and D_RT

Next, we conducted detailed energy-dispersive X-ray spectroscopy (EDS) point analysis with varying electron beam energy and observed the gradient of N from PhCN and Ti from TiO_2 in the hybrids. The hybrids B_RT and D_RT were penetrated by electrons with increasing acceleration voltages providing us the weight ratios of the constituent elements (Ti and N) at corresponding depths of the material. The amount of Ti decreases with increasing depth in both samples, showing a gradient and confirming the major presence of TiO_2 on the PhCN surface as shown by XPS results. Meanwhile D_RT, in which the amount of Ti precursor was five-fold higher, shows higher percentage of Ti at greater

depths of the sample. It must be noted that N was detected in both the hybrids at all acceleration voltage settings. This indicates a continuum of carbon nitride in-between the TiO_2 particles which ensures a strong connection between the two components – a structural characteristic favourable for charge transfer.

TEM

Transmission electron microscopy (TEM) analysis was done to unravel the structural properties of the hybrids. The TEM images of TiO_2 nanoparticles show the presence of nano-crystallites, which further grow upon annealing at different temperatures. PhCN shows a typical g- C_3N_4 like structure with irregularly curved layers and tremella-like appearance. When autoclaving with low amounts of TiCl_4 , the PhCN nanosheets become tightly overlapped with each other due to the high pressure and display minimal to no presence of TiO_2 crystallites. As the amount of Ti precursor is increased, we see the crystallization of TiO_2 around the PhCN nanostructures in the hybrid B_RT where we can observe intermeshed PhCN and TiO_2 on the surface. TEM images clearly show that the TiO_2 forms a layer around the irregular PhCN structures. B_RT exhibits a gradient core-shell morphology wherein the core of closely stacked PhCN nanosheets are decorated with small TiO_2 nano-crystallites all around the perimeter without large agglomeration. It is possible to observe a continuous network of PhCN with TiO_2 in the hybrid B_RT with a possible porous structure. However, further increasing the TiO_2 loading results in inhomogeneous agglomeration spots of TiO_2 encapsulating PhCN as evident in sample C_RT and D_RT. Additionally, we also observe breakage and random ordering of PhCN nanosheets in these samples. Furthermore, the effect of annealing the hybrids is identical to that as observed in TiO_2 nanoparticles. Hybrid A_400 shows TiO_2 nano-crystallites even when they were not observable in the as-prepared sample A_RT. These observations show that the ratio of the precursors and the employment of thermal treatment plays an important role in the morphology of a hybrid system.

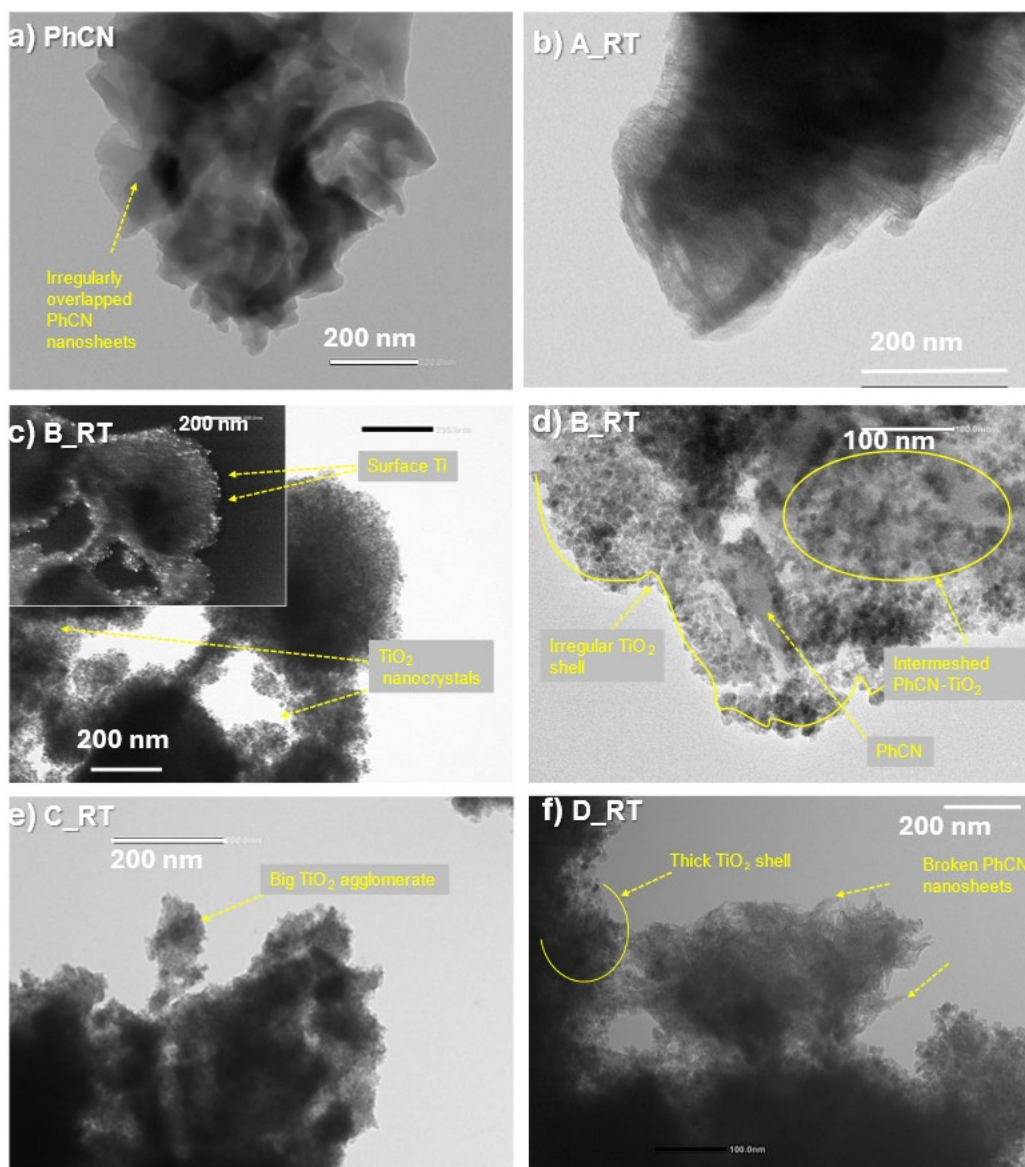


Figure 3.11 TEM images of a) Pristine Bulk PhCN, b) hybrid A_RT, c),d) hybrid B_RT with dark field image inset at c), e) hybrid C_RT and f) hybrid D_RT

Physisorption

The surface area of pristine TiO₂ nanoparticles shows a slight decrease with increased annealing temperatures (**Table 3.1**), accompanied by a reduction in micro- and mesopores, ultimately resulting in a predominantly macroporous material (**Figure B15**). In contrast, PhCN itself is non-porous, with a low surface area of 5.9 m²/g (**Figure B16**). However, in the PhCN/TiO₂ hybrids, the porous TiO₂ outer shell contributes to significantly higher porosity (**Table B4**). Additionally, we observed that as the TiO₂

loading in the hybrids increases, so does the surface area, consistent with SEM images that reveal smaller particle sizes with higher TiO₂ content. When annealed, the hybrids exhibit a similar trend to pure TiO₂ nanoparticles, showing a decrease in surface area, as reflected in both BET analysis and SEM images (**Table B3**). This pattern likely results from the densification of the TiO₂ shell around the PhCN core during thermal treatment. Through these results, it can be said that the structural evolution of PhCN/TiO₂ hybrids is synonymous to the structural evolution of TiO₂ nanocrystals present in them which is the fruit of TiO₂ crystallization on the surface of pristine PhCN during the solvothermal synthesis.

Table 3.1 BET and BJT calcuted surface area and pore volumes respectively of TiO₂ nanoparticles.

S.no	TiO₂	Pore diameter (nm)	Pore specific volume (cm³g⁻¹)	Specific surface area (m²g⁻¹)
1	Pristine	3.66	0.22	101.57
2	230°C	4.95	0.20	120.58
3	300°C	5.83	0.20	91.68

Structural evolution of PhCN/TiO₂ hybrids

From the FTIR, TGA and XPS studies we can conclude the loss in the PhCN's heptazine integrity with increasing TiO₂ content in the hybrids. We thus propose that the nucleation of TiO₂ happens on the surface of stacked PhCN sheets and as the crystallization takes place during the solvothermal treatment; it cleaves some of the PhCN nanosheets on the surface of the matrix as shown in TEM (**Figure 3.11f**). With an increase in the dosage of Ti precursor, more PhCN sheets are cleaved without any formation of Ti-C or Ti-N bonds as corroborated by XPS C1s and N1s spectra and more TiO₂ crystallites are formed around the PhCN particles. The XPS, EDS and TEM studies show the presence of a PhCN core and a PhCN-TiO₂ layer around it in the hybrids. With higher TiCl₄ dosage, nucleation is prevented, and the TiO₂ growth is slowed down due to less availability of the free water content needed in the hydrolysis.¹⁶⁹ A similar trend is observed in the annealed hybrids. The

extensive growth in the size of TiO₂ crystallites due to annealing leads to more rupture of PhCN nanosheets and the big crystallites form an outer shell shielding the PhCN core from the neighbouring environment. A schematic of this proposed structural evolution is given in **Figure3.12**.

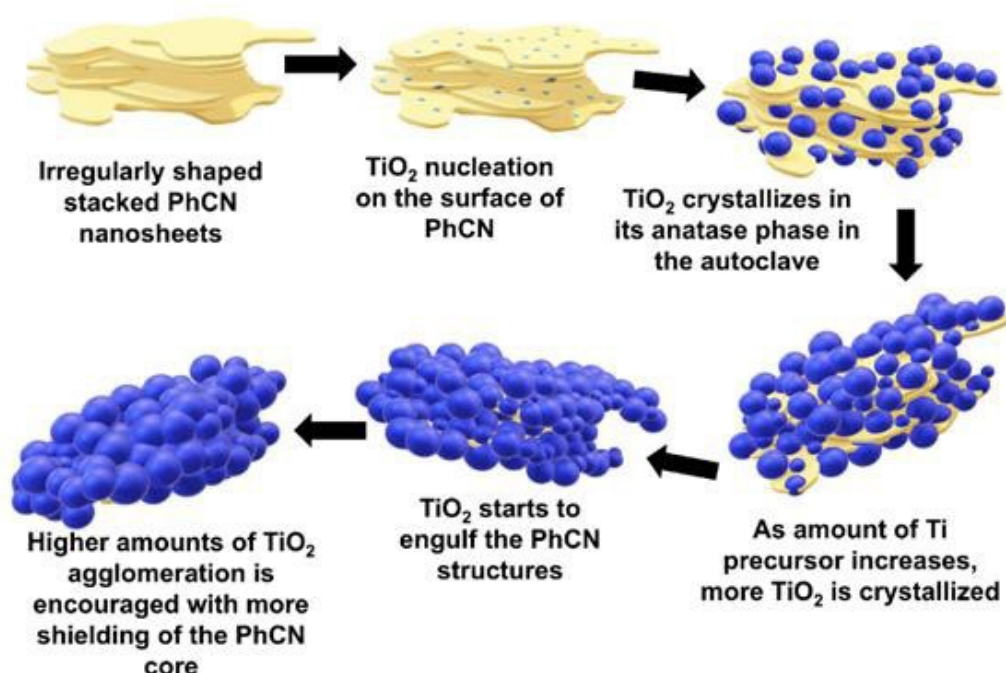


Figure 3.12 A schematic representation of core-shell evolution of PhCN/TiO₂ hybrids.

DRS

The light-absorption behaviour of the solid hybrids was studied with diffuse-reflectance spectroscopy (DRS) to shed light on the interaction between the PhCN and TiO₂ semiconductors and the Kubelka-Munk transformation function was used to estimate the optical band gaps of the materials (**Figure B18-B21**). The reflection configuration measures the diffuse reflection of the sample with respect to a KBr reference that is considered to have 100% reflectivity. As shown in **Figure 3.13a**, TiO₂ absorbs from wavelengths lower than 400nm corresponding to a band gap of 3.2 eV, while PhCN shows considerable absorption in the visible range with a bandgap of 2 eV. The autoclave-treatment of PhCN widens its bandgap to 2.3 eV and reduces the visible-light absorption (**Figure 3.14**). The as-prepared hybrids show light absorption extended throughout the visible range and a clearly visible absorption edge of TiO₂ at 390 nm (**Figure 3.13a**). The differential analysis of the absorption spectra of the as-prepared hybrids do not show any new optical band at energies lower than the energies of the absorption edge of either of the component indicating a case of a weak coupling, or the *photoinduced electron transfer*¹⁷⁰ where, the absorbed photons might result in the excitation of electron in the PhCN's HOMO to LUMO followed likely by a fast transfer to the conduction band of TiO₂. The absorption of the hybrids is controlled by the gradient core-shell structure,

where a thick TiO_2 shell (in the case of C_RT and D_RT) shows low visible light absorption, a shell with equal distribution of PhCN and TiO_2 (B_RT) shows intermediate visible-light absorption and, low TiO_2 on the surface (A_RT) shows visible-light absorption identical to PhCN. When a hybrid is annealed, it loses the concentration of N atoms from it as observed through XPS analysis. A loss in the N atoms in carbon nitride leads to a loss in its visible light absorption.¹⁵⁹ This trend is most prominent in hybrids with highest TiO_2 content- hybrid D series (**Figure 3.13b**)

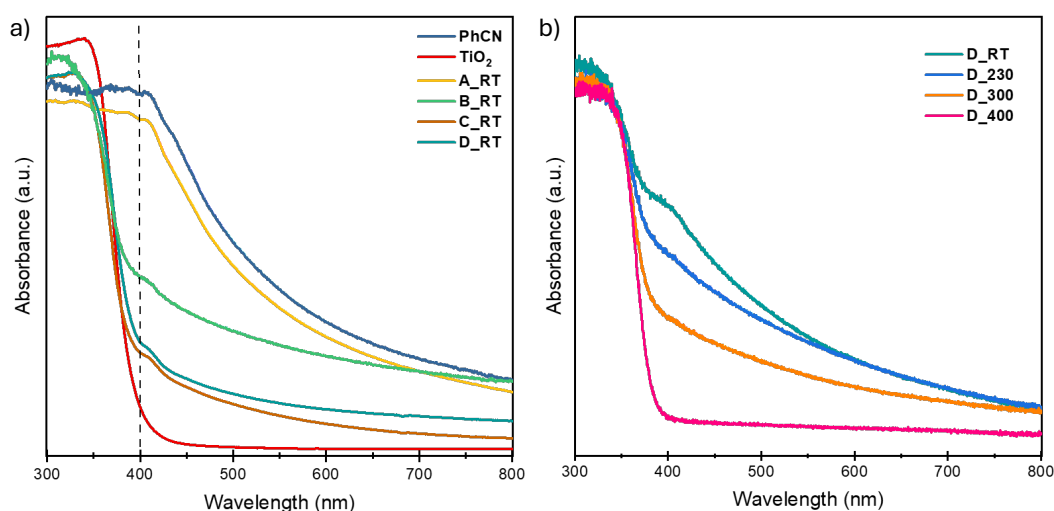


Figure 3.13 DRS data of a) as-prepared hybrids with the pristine PhCN and TiO_2 b) DRS of hybrid series D.

where we can observe the sample annealed at higher temperature showing absorption spectra identical to TiO_2 due to a highly crystallized and thick outer TiO_2 shell and low availability of N atoms from the PhCN. The reduction in the surface area and porosity of TiO_2 nanoparticles with annealing according to the BET data, also suggests a lower interaction of outer shell TiO_2 with PhCN and in turn less heterojunction formations which can also hamper the visible-light absorption. The optical bandgaps of the hybrid A series (**Figure B18-B21**) show no TiO_2 contribution in RT and 230°C annealing but show the same when annealed at higher temperatures. The tauc plots of B,C and D series (**Figure B18-B21**) show similarities with TiO_2 band gap values as all of them contain titania in much higher ratios than hybrid A. A tentative increase in optical bandgap of the hybrids can be observed when TiO_2 amounts are increased.

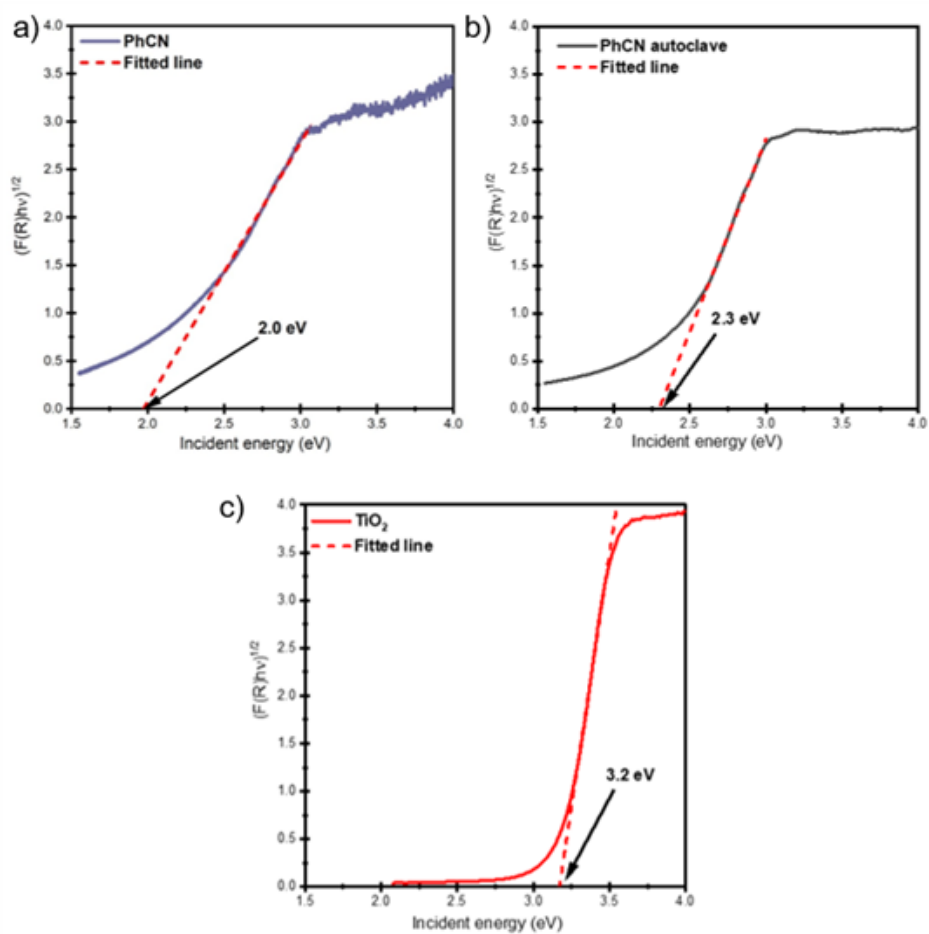


Figure 3.14 Tauc plots of a) PhCN, b) PhCN autoclave treated and c) TiO_2 .

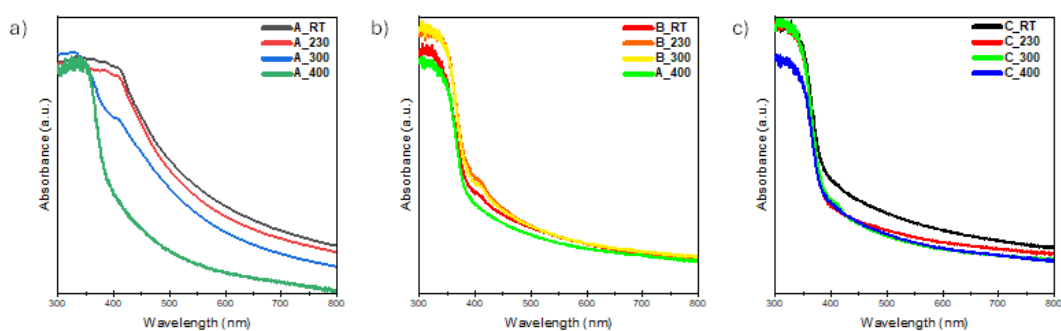


Figure 3.15 UV-vis absorption spectra (DRS) of a) hybrid A series, b) hybrid B series, c) hybrid C series.

Steady-state fluorescence

To study the excited state of the hybrid systems, we mapped the photoluminescence (PL) spectra of our samples with respect to excitation wavelength ranging from 300-600nm. The emission from bulk PhCN, consists of a broad emission between 450 and 650 nm peaked at 525 nm with a large excitation maximum between 350 and 420 nm (**Figure 3.16a**). This broad emission from PhCN is a function of generated excitonic species (bound $e^- - h^+$) and not separated e^- and h^+ . The autoclave treatment of PhCN generates higher luminescence counts without any variation in the photoluminescence excitation range (**Figure B22**). It is observed that the profile of emission from PhCN does not change with the excitation wavelength, and it has the same PL profile under both UV and visible excitation (**Figure 3.16a**). This arises from the localization of excitons in the disordered regions of the material where the presence of phenyl groups introduces additional states that facilitate the trapping of excitons, leading to the formation of self-trapped excitons (STE).¹⁴⁸ The excitation- emission maps of the as-prepared hybrids (**Figure 3.16**) show overall decrease in photoluminescence with increasing TiO_2 content. This quenching of PL indicates a reduced recombination of charge-carriers and a successful charge separation in the hybrids. The as-prepared samples also show a blue shift of the peak maximum (about 500 nm) and a restricted range of the excitation spectrum between 360 and 420 nm due to the high absorption of the UV energy by the TiO_2 component in the hybrids as shown by the UV-Vis absorbance spectra. It must be noted that only the emission from excitations below the wavelength 390 nm (the absorption edge of TiO_2) should have any absorption contribution from TiO_2 . The PL spectra of B_RT also show a blue shift in the emission maxima which might be due to a higher contribution from the recombination from σ^* energy level of the PhCN⁷⁷. When the annealed hybrids were measured for PL, could not observe any photoluminescence counts under the same measurement conditions as the RT samples. This could be due to the presence of more crystalline TiO_2 in the annealed samples which quenches the PL of PhCN.

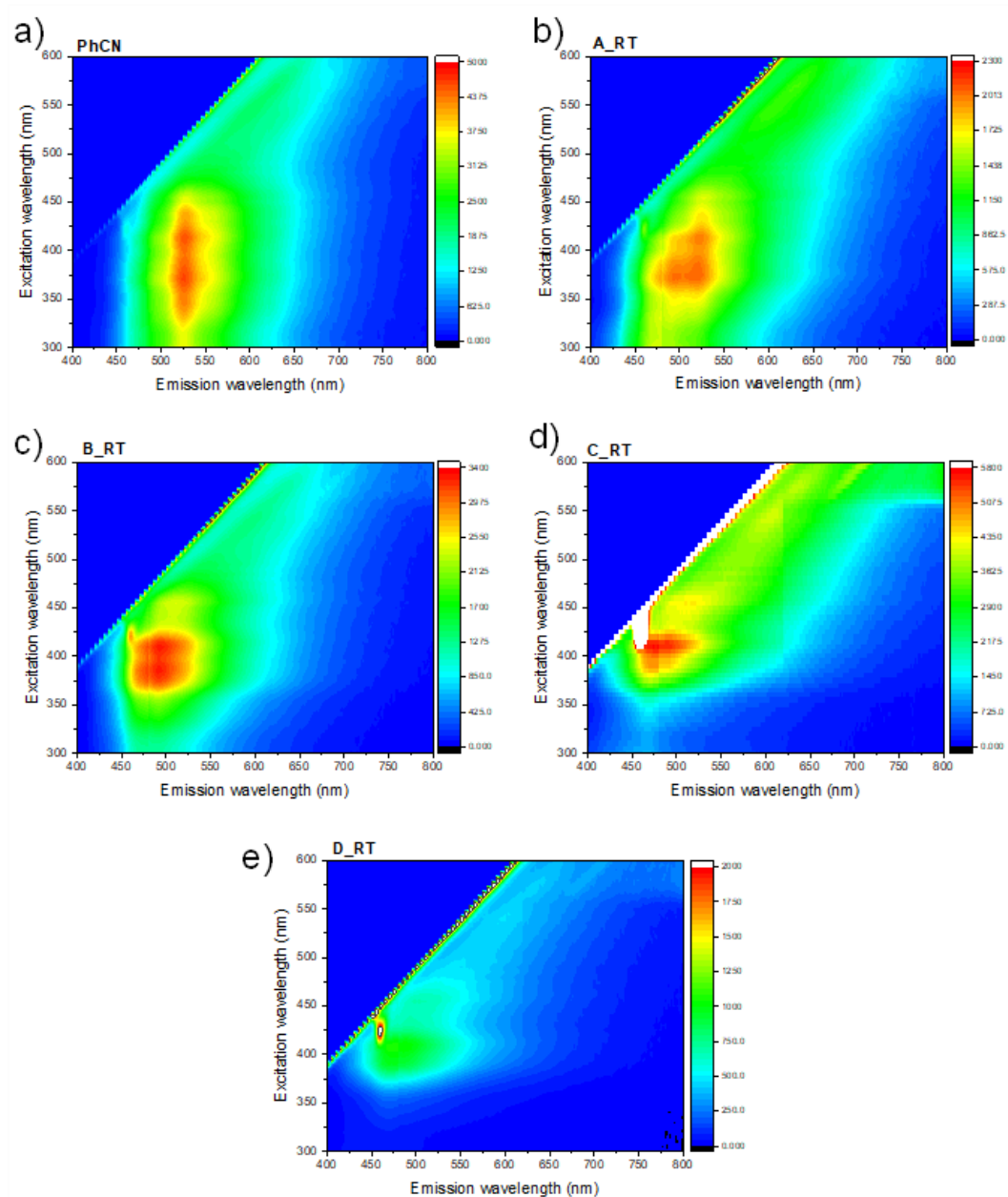


Figure 3.16 3D fluorescence maps of a) pristine PhCN, b) hybrid A_RT, c) hybrid B_RT, d) hybrid RT, and e) hybrid D_RT.

Time-Resolved Photoluminescence

The trapping of excitons on a timescale of picoseconds to nanoseconds, followed by slower relaxation processes in the microsecond region¹⁴⁸ can be studied by the time-resolved photoluminescence (TRPL) measurements. Generally, the time decay behaviour of excitons in PhCN can be well reproduced by three time- exponential curves with time decay of 35 ns, 150 ns and 750 ns.⁶⁴ The decay time profiles can be modelled using a multi-exponential decay function:

$$y = \sum_i A_i e^{-\frac{t}{\tau_i}} \quad (1)$$

The experimental time-resolved luminescence data relate to the recombination probability from the excited states through the equation:

$$\gamma_{tot} = \gamma_{rad} + \gamma_{NR} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{NR}} = \frac{1}{\tau_{tot}} \quad (2)$$

Here, $i=1$ or 2 γ_{tot} represents the overall recombination probability from the excited state, with γ_{rad} and γ_{NR} being the probabilities for radiative and non- radiative recombination, respectively. τ_{rad} and τ_{NR} are the respective lifetimes of the radiative and non-radiative pathways, and τ_{tot} , the overall decay time, is determined experimentally through the fitting procedure. Hence the observed decrease in the recombination kinetics in the PL is due to the presence of the increased probability of non-radiative path. This effect can be well observed in **Figure 3.17**, where a faster decay is observed from the σ^* level of the PhCN. All the hybrid samples show a faster kinetics, related to the presence of new non-radiative channels (**Figure 3.17**). The increased efficiency in the charge transfer mechanism in sample D_RT is due to the higher number of active organic sites. D_RT has most of the PhCN surface in close contact with titania generating the efficient charge transfer. The thermal treatment of the hybrids leads to low photoluminescence which did not provide enough counts for a TRPL measurement. The optical characterization results show a successful charge-separation and charge transfer in the case of the as-prepared hybrids indicating that the hybrid structure has been achieved only by the solvothermal process without further annealing.

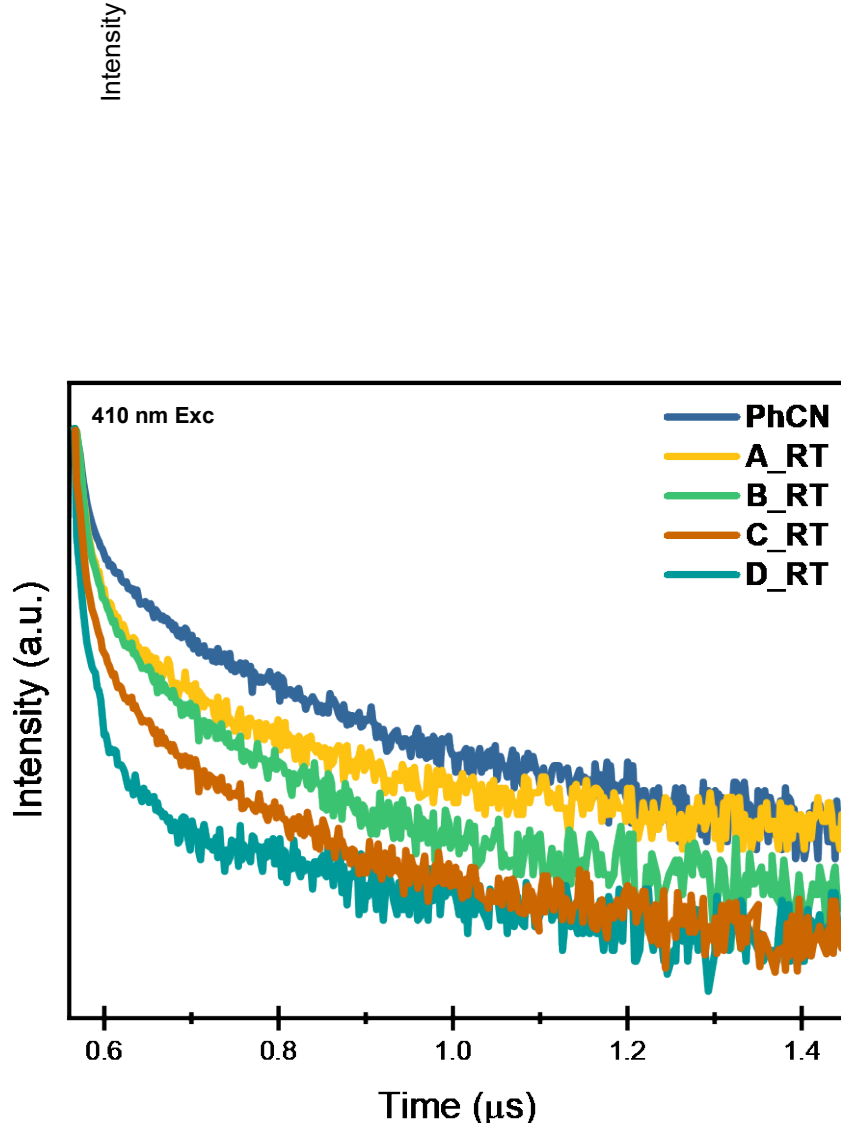


Figure 3.17 TRPL spectra of as-prepared PhCN/TiO₂ hybrids with pristine PhCN.

Photocatalytic Dye Degradation Tests

Rhodamine B (RhB) is an organic synthetic dye that is both harmful towards the ecosystem and extremely carcinogenic in nature causing various diseases in the human population. Therefore, it was selected as a model dye pollutant first, due to its high abundance and second, due to its excellent stability in industrial wastewater making its treatment difficult via other conventional methods. The photocatalytic performances of the PhCN/TiO₂ hybrids were evaluated by monitoring their oxidative properties of RhB dye under visible light irradiation. To evaluate their photodegradation performance, dye concentration profiles were measured as a function of time under illumination using a commercial white LED with a sharp emission at 445 nm. The tests were done in the presence of O₂ in ambient conditions. 2ml aliquots were taken every hour after illumination. 0.02mM concentration of dye was used for all degradation studies. Before illumination, the dye-photocatalyst system was kept in dark for 30 minutes to attain adsorption-desorption equilibrium. The effect of light on the dye was also studied without the presence of photocatalyst to look for any photodegradation.

Control experiments were performed with RhB to establish its interaction with our light source. **Figure B23** showed no photo-degradation of RhB dye under visible light irradiation. The photocatalytic degradation of RhB dye by PhCN and TiO₂ is shown by the **Figure B24 a and b** respectively. PhCN could degrade only 28.4% of the 0.02mM RhB solution in 7h while TiO₂ could degrade only 7% of it. The photocatalytic tests with RhB and the PhCN/TiO₂ hybrids showed successful visible-light active photocatalytic degradation. (**Figure 3.19a, b, c**). The photodegradation performance was found to be in the order of A_RT < D_RT < C_RT < B_RT along with the pseudo-first-order rate constants of $0.6 \times 10^{-2} \text{ min}^{-1}$, $2.3 \times 10^{-2} \text{ min}^{-1}$, $1.4 \times 10^{-2} \text{ min}^{-1}$ and $0.80 \times 10^{-2} \text{ min}^{-1}$ respectively calculated by using Langmuir-Hinshelwood kinetic model. The photocatalytic performance of hybrid B degrades with annealing at higher temperatures and the as-prepared hybrid has the highest activity. For the photocatalysts annealed at 400°C, hybrid B_400 showed the highest rate constant of $6.2 \times 10^{-3} \text{ min}^{-1}$ followed by hybrids A_400, C_400 and D_400 which is the order of their increasing TiO₂ content.

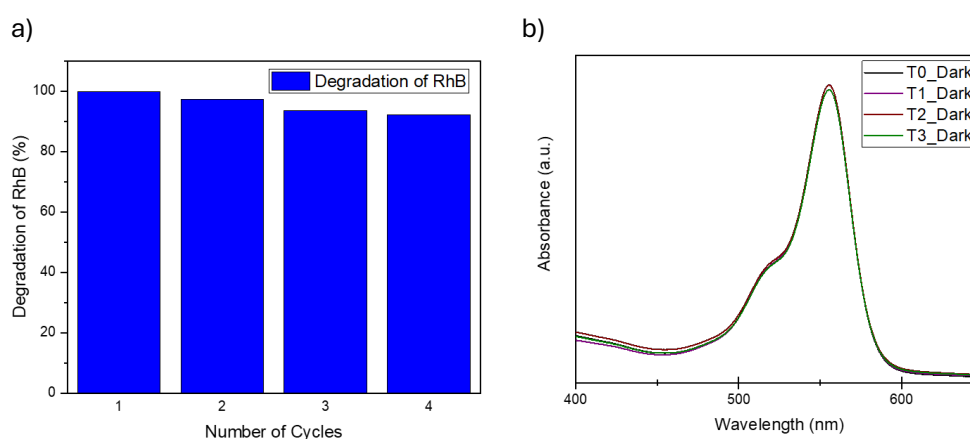


Figure 3.18 a) Recyclability tests done with B_RT, b) dark test for hybrid B_RT with RhB.

The observed trends in the degradation of RhB can be related to the morphology and structure of the hybrids revealed from TEM images where the less availability of TiO₂ on the surface can lead to worst photocatalytic performance for hybrid A, followed by an optimum level of interaction between PhCN and TiO₂ in hybrid B and an excess of TiO₂ agglomeration leading to a reduction in active catalytic surface for hybrids C and D.⁴⁰ When the hybrid B is annealed at different temperatures, the crystallinity of TiO₂ increases with the temperature alongside the band gap leading to lower RhB degradation. The core-shell structure shown by the EDS analysis, TEM and XPS shows that the sample series C and D have agglomeration of TiO₂ on the surface of PhCN, which shields the PhCN core and hampers the visible-light absorption and charge transport in-between PhCN and TiO₂ leading to a lower photocatalytic activity than B. On the other hand, A series samples

have an underdeveloped core-shell structure and a very low fraction of TiO_2 which hampers its photocatalytic activity. As the hybrids with ratio C and D are annealed, they grow in crystallite size which increases the transport route of the charge carriers and diminishes the photocatalytic efficacy in addition to increasing the bandgap. Since all the as-prepared samples have smaller crystallite sizes of TiO_2 , they perform better than their annealed counterparts. The unannealed hybrids have better visible-light absorption with smaller bandgap which increased their light response. Through this detailed study, one could argue that the best performing photocatalyst is in its unannealed phase because of the superiority of solvothermal synthesis as a facile method to generate crystalline anatase hybrids with good crystallinity which has enough active sites to refrain further heat treatment.⁴⁵ The tendency of the moderate ratio of PhCN/ TiO_2 (hybrid B) to outperform others indicates an optimised interaction between the PhCN core and the TiO_2 porous envelope suggesting the highest degree of charge extraction with lowest recombination rates.

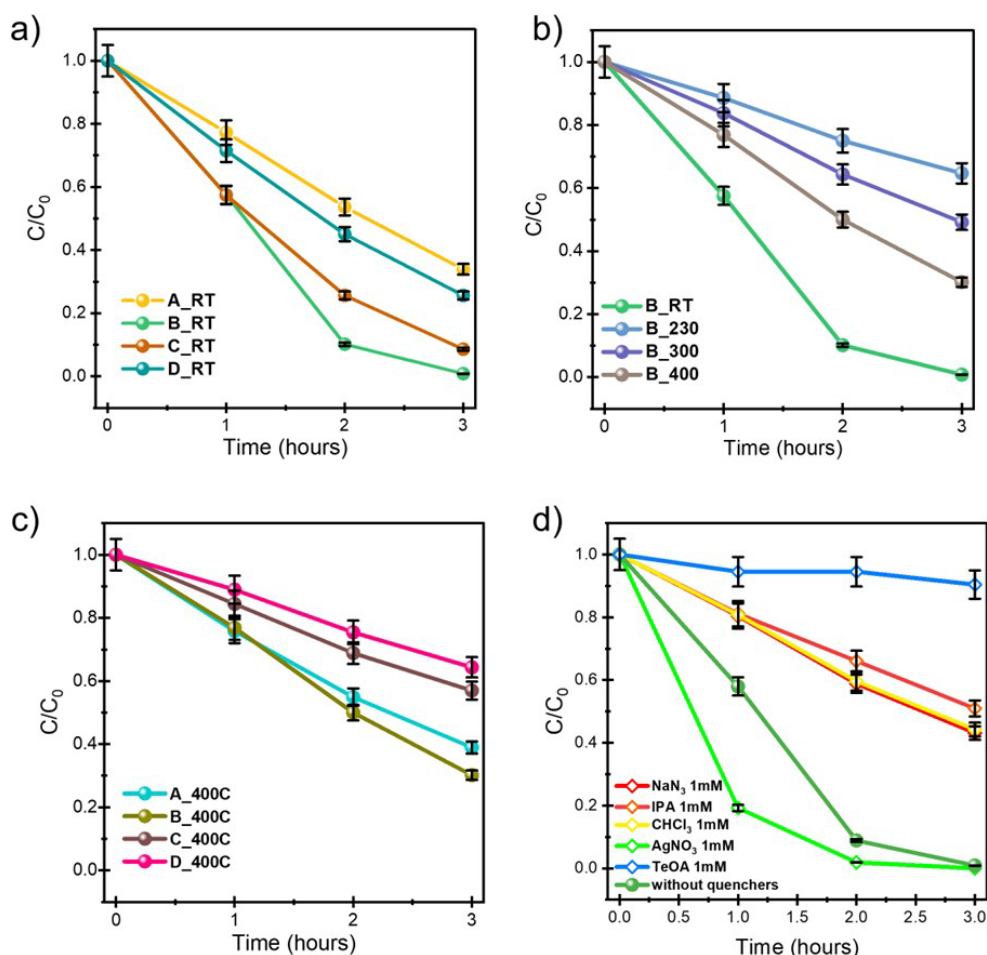


Figure 3.19 a),b),c) Photocatalytic degradation of rhodamine B dye by the PhCN/ TiO_2 hybrids under visible light illumination. ;d) Quenching of the degradation of Rhodamine B by B_RT through radical scavengers

The observed substantial decrease in the photocatalytic ability of all the hybrids when annealed at 400°C is likely related to the sintering of TiO₂ at higher temperatures and the corresponding loss of its active surface area along with the loss in the integrity of PhCN due to TiO₂ crystallization. In addition, when there is agglomeration of TiO₂ on the surface of PhCN core, it gets shielded from the incident light and cannot generate charged carriers. Recyclability tests were done for the best performing hybrid B_RT till 4 cycles of RhB degradation without observing any loss in the photocatalytic activity indicating its excellent stability (**Figure 3.18a**). The test in the dark (**Figure 3.18b**) shows that the removal of RhB by B_RT is solely due to photocatalysis without a major contribution from adsorption which enhances the reusability of the hybrid B_RT after a cycle of dye removal. All the above-mentioned discussion implies that we have successfully generated a hybrid which can be easily commercialised due to use of cheaper and readily available chemicals, ease of synthesis, reusability and practicality. Our hybrid is compared with some other advanced materials for the degradation of RhB in **Table 3.2**.

To investigate the main oxidation species responsible for the degradation of RhB dye, the identification of reactive oxygenated species (ROS) produced during the reaction is essential. For this, quenching tests were performed with 1mM solution of radical scavengers namely: NaN₃, IPA, CHCl₃, AgNO₃ and TEOA for the species O₂¹, OH^{*}, O₂^{*}, photogenerated e⁻, and h⁺ respectively (**Figure 3.18d**). The tests were performed in identical conditions to that of the dye degradation tests.

It was observed that all the ROS were present during the intermediate reactions for RhB degradation. NaN₃ and CHCl₃ show identical quenching suggesting the origin of singlet oxygen and the superoxide radical from identical pathways. AgNO₃ accelerates the degradation of RhB, where Ag enhances the e⁻-h⁺ separation process which was confirmed by the degradation of RhB dye by AgNO₃ in the absence of the photocatalyst (**Figure B25**). The quenching by IPA is higher than O₂²⁻ quencher and it acts as one of the major species for RhB degradation as evident by detailed quenching tests (**Figure B26**) where 50% v/v IPA shows complete stoppage of the photocatalytic dye degradation. Amongst all, the use of TEOA hampers the photocatalytic degradation to the highest extent and stops the process completely when added at 100mM concentration (**Figure B27**). This shows that the photogenerated holes were the predominant ROS responsible for the RhB degradation. The degradation of methylene blue (MB) and methyl orange (MO) dyes were also checked under visible-light illumination with hybrid B_RT as shown in **Figure B28 a,b**. It was observed that B_RT did not interact with MB either by photocatalytic degradation or adsorption, while MO was substantially adsorbed (60%) in 30mins by B_RT along with a red shift. Since MO is an anionic dye and MB is a cationic dye, the tests suggest that the surface of B_RT photocatalyst is positively supported by the abundance of holes. The red shift in the absorbance spectra of MO could be attributed to the polarity of the photocatalyst as MO is sensitive as a pH indicator. The pH of the reaction plays a significant role in influencing the photocatalytic degradation efficiency of the PhCN/TiO₂ hybrid. In general, pH adjustments can enhance or suppress the formation of reactive oxygen species (ROS), such as hydroxyl radicals, which are critical for the degradation of RhB as shown by the quenching tests. The addition of a weak base

like TEOA can raise the pH of an acidic environment but it resulted in complete quenching of RhB degradation in our case. Conversely, the addition of the hydroxyl radical quencher IPA lowers the pH, but it also inhibited photocatalytic RhB degradation, though to a lesser extent.

Table 3.2 Reports on photocatalytic degradation of rhodamine B dye

Photocatalyst	Rate constant (/min)	Light source	Limitation	Ref
PhCN/TiO₂	0.023	Commercial 11W white LED	No data with real wastewater	Our research
TiO₂ nanostructure	0.120	UV	Low activity in visible light	22
Quinazoline-derivative dyesensitized - TiO₂	0.0226 0.0146	UV and Vis	Low degradation rate	169
chlorophyll/TiO₂:W composite	0.00694 after 30mins	UV–VIS light by turning on a Xenon lamp (75 W)	Low utilization of visible light and low rate constant	170
g-C₃N₄/BaBi₂Nb₂O₉	0.02056	Simulated solar light	Lower degradation rate constant and use of toxic element Ba	171
Bi₂MoO₆/MIL-88B(Fe)	0.0364	350 W Xe lamp with a 420 nm cutoff filter	Use of expensive Mo	172
BiOBr/BiFeWO₆	0.031	300W Xe lamp	Cost-prohibitive use of W	173
SiO₂/g-C₃N₄/BiOBr/Bi	0.0708	4.75W Xenon lamp with an ultraviolet light filter	Use of many precursors and lengthy synthesis procedure with possibility of release of metal ions in water	44
SnO₂ quantum dots decorated NiFe₂O₄ nano plates	0.0242	100-W solar simulator with a UV cut-off filter ($\lambda > 400$ nm)	Toxicity of Sn and Ni	174

Photocatalytic H₂ production Tests

After evaluating the oxidative potential of our hybrids, we tested to the photocatalytic performance towards their sacrificial hydrogen evolution reaction (HER). Due to the higher dye degradation abilities of the as-prepared hybrids, only A_RT, B_RT, C_RT and D_RT were selected for the HER tests. The tests were conducted using a home-made closed reactor system with a constant temperature of 15°C through water jacket cooling, 1wt% photo deposited Pt as the co-catalyst and 445nm LED illumination .

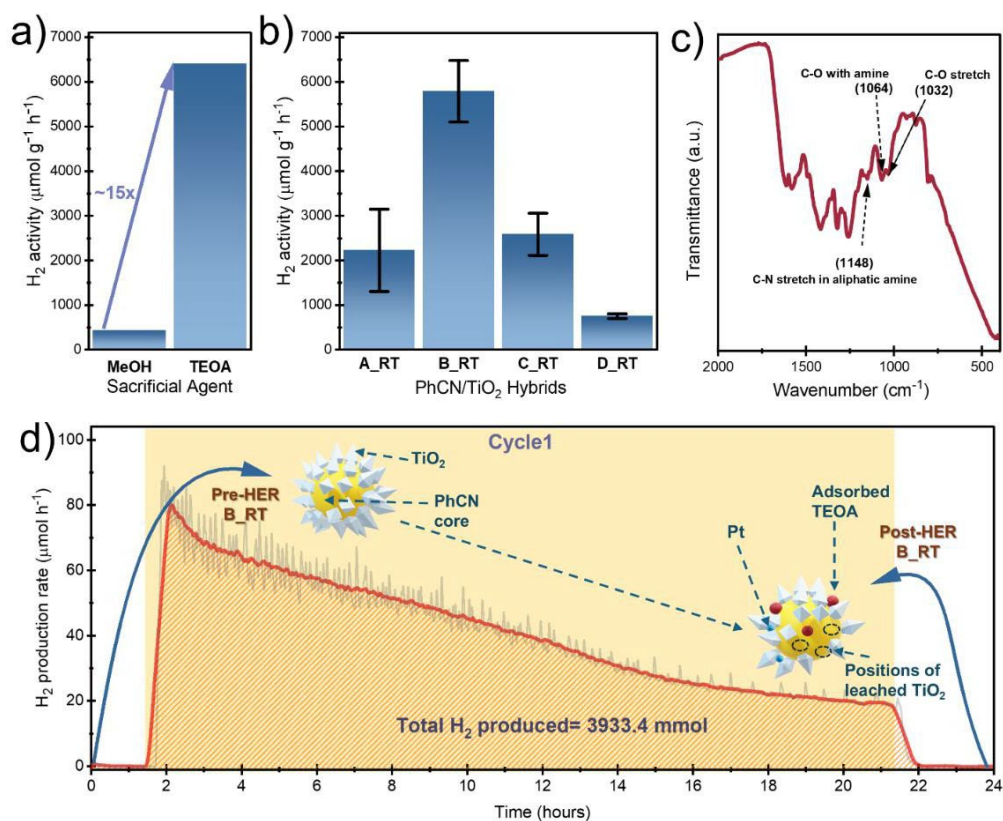


Figure 3.20 a) HER tests for sacrificial agent; b) HER tests of as-prepared hybrids; c) FTIR transmittance spectra of B_RT post flow HER test; d) Flow HER activity of B_RT for 1day.

Hybrid B_RT was used to test two sacrificial agents, MeOH and TEOA, which are widely reported as an efficient sacrificial agent for TiO₂ and carbon nitrides, respectively.¹⁷⁷ We observed that B_RT produced 15 times more H₂ in the presence of 0.1M TEOA as compared to MeOH (**Figure 3.20a**), thereby suggesting that the holes are effectively scavenged from the PhCN part of the hybrid and not TiO₂. Therefore 0.1M TEOA was employed for the rest of the HER tests of all the as-prepared hybrids (**Figure 3.20b**). Like the RhB degradation tests, hybrid B_RT showed the highest HER activity among the as-prepared hybrids at an impressive 5789 $\mu\text{mol h}^{-1}\text{g}^{-1}$. **Table 3.3** compares the H₂ production abilities of recently reported g-C₃N₄ based advanced photocatalysts. Compared to the case of the as-prepared PhCN (**Figure B29**), B_RT produces ~6.5 times more H₂ which can be ascribed to the successful formation of heterojunctions with TiO₂ enhancing charge separation as shown by the PL measurements. Since the holes are scavenged from the PhCN core, D_RT shows the lowest H₂ production due to shielding of the PhCN core by a thick TiO₂ outer cover and further leading to inaccessibility of holes to the electron donating TEOA. The HER results validate the superiority of the gradient core-shell structure of the PhCN/TiO₂ hybrid where loss of porosity and interaction with surrounding molecules lead to lower photocatalytic activity in the case of A_RT and C_RT.¹⁷⁸

The HER ability of the best performing hybrid B_RT was further evaluated with the help of an in-flow online H₂ detection system over a period of 44 hours (**Figure B30**). The rate of hydrogen production was measured continuously for 44 hours instead of doing hourly injections. **Figure 3.20d** shows the first 24 hours of the test in 1st illumination cycle. The initial rate of hydrogen production was measured around 80 $\mu\text{mol h}^{-1}$ during the first ~40 min of illumination using a 445nm LED. However, following this, the photocatalytic rate was found to decrease gradually to ~19.2 $\mu\text{mol h}^{-1}$ over the course of 21 hours, which could be attributed to the agglomeration, growth, and potential leaching of the Pt nanoparticles on the surface of the hybrid, as observed by similar studies on TiO₂/Pt photosystems.¹³³

To understand the process of deactivation of the hybrid, XRD, ATR-FTIR and XPS were performed on the hybrid B_RT post the flow HER reaction. XRD analysis showed all the characteristic reflections corresponding to PhCN and TiO₂ anatase, as observed in the pristine B_RT (**Figure B31**). The IR absorbance of the photocatalyst after the flow tests showed the formation of aliphatic C-O and C-N bonds and enhancement of -OH and -NH stretches as compared to as-prepared B_RT (**Figure 3.20c**). These new absorbance peaks arise from the sacrificial agent used i.e., TEOA which is present in excess amounts (0.1 M) and may have adhered to the porous surface of our hybrid. Survey spectra obtained from XPS analysis (**Figure 3.22**) confirms the presence of C, O, N and Ti on the surface of the post-HER hybrid. A minor increase in the counts in the 70-72 eV region was observed suggesting the presence of small amount of Pt⁰ on the surface.¹³³

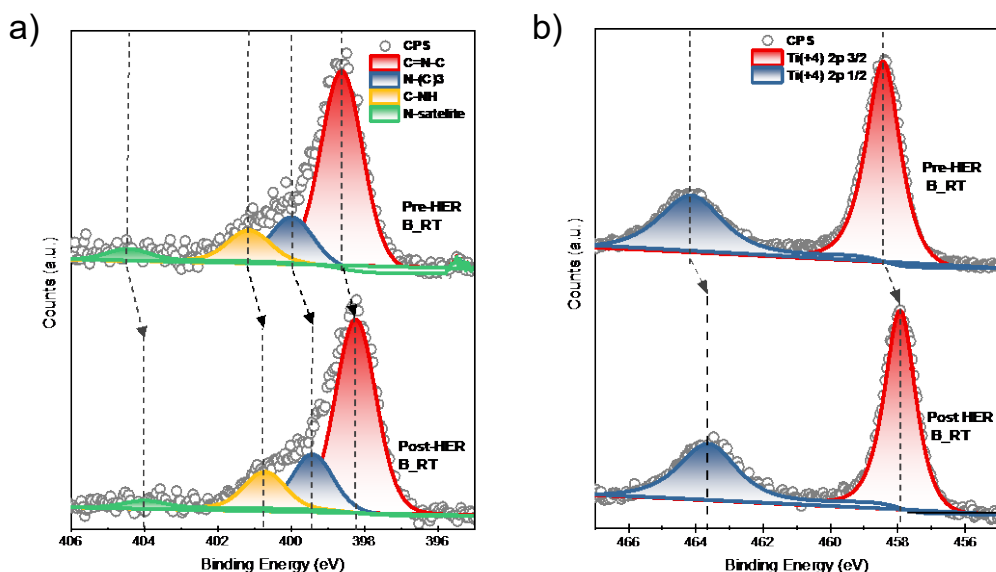


Figure 3.21 a),b) XPS N1s and Ti2p edges of B_RT post 2 day continuous HER test respectively.

However, due to the porous nature of the hybrid, it might be possible that some of the PtCl_6^{2-} from the photo deposition process seeped into the pores of the hybrid at the PhCN/TiO₂ interface, which is not detectable by outer surface sensitive XPS.¹³³ The atomic concentration% quantification show an increase in the amount of N, a decrease in the amount of O and a substantial decrease in the Ti amounts from 10% to 4% in the post HER hybrid, which might suggest leaching of TiO₂ nanoparticles into the solution or a changing morphology of the hybrid. The N1s spectrum (**Figure 3.21a**) shows a shift of 0.3eV and Ti2p (**Figure 3.21b**) showed 0.5eV shift, both towards lower binding energy in the post HER B_RT. All these observations indicate a partial reduction of the TiO₂ on the surface of the hybrid during the H₂ production.¹⁷⁹

Based on these results, we propose that this reduction of TiO₂ happens due to the surge of electrons flowing from PhCN to TiO₂. When illuminated using visible light, the photogenerated electrons from the PhCN go towards the TiO₂ (as in a type II scheme photocatalyst **Figure 3.25**) to increase the electron density around it causing the shift towards a lower binding energy. At the same time the lone pairs on N from the amine group of TEOA surrounds the PhCN resulting in the enhancement of electron density around N. While there have been a few reports studying such behaviour^{133,179,180}, where the Ti-O bond is fractured during the photoreduction process creating oxygen vacancies and thereby recombination centres¹⁸⁰, it requires a reducing environment, and our experiments were carried out in a continuous gas flow system which deems this scenario to be highly unlikely.

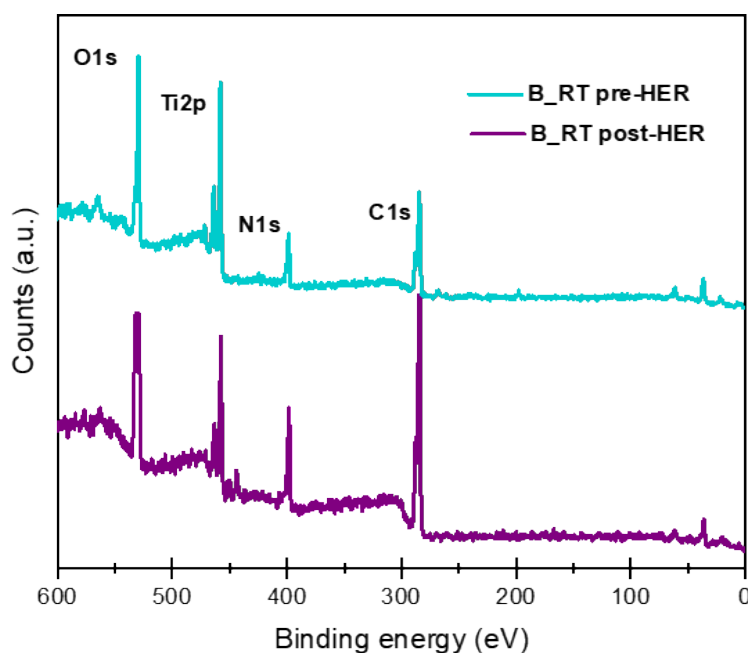


Figure 3.22 XPS survey of hybrid B_RT post 44 hours HER flow test.

Table 3.3 Recent advancements in photocatalytic H₂ production in g-C₃N₄ based systems¹⁸¹

Photocatalyst	Light source		H ₂ activity ($\mu\text{m g}^{-1}$)	Reaction conditions
PhCN/TiO ₂ (our work)	445nm LED		5789	2mg catalyst, TEOA solution, Pt co-catalyst
CuFe ₂ O ₄ /g-C ₃ N ₄	200W lamp	Xe	700.3	20 mg catalyst, TEOA
CdSe/WS ₂ /g-C ₃ N ₄	White LED		1290	5 mg catalyst, TEOA solution
CoSeO ₃ /g-C ₃ N ₄	300 W lamp	Xe	1459.2	20 mg catalyst, TEOA solution
CuInS ₂ /g-C ₃ N ₄	350 W lamp	Xe ($\lambda > 365 \text{ nm}$)	102.4	20 mg catalyst, TEOA solution
g-C ₃ N ₄ /W ₁₈ O ₄₉	300 W lamp	Xe ($\lambda > 400 \text{ nm}$)	5231	50 mg catalyst, TEOA solution, Pt cocatalyst

Dual functional catalytic tests

Integrating pollutant degradation with hydrogen production in a single process can reduce operational costs compared to treating pollutants and producing hydrogen separately. Based on our structural and mechanistic insights, it was obvious that our hybrids are suited for simultaneous RhB degradation and HER where RhB molecules adsorbed on the surface of the hybrid would quench the holes and maintain a higher availability of electrons by photoexcitation for H₂ generation. At the same time, the dye molecules will also act as the source of protons necessary for a sustained HER. All experiments were performed using aqueous RhB dye solutions along with 1wt% Pt photodeposited onto B_RT without any additional sacrificial agents. **Figure 3.23** shows that the hybrid B_RT is successfully able to produce H₂ while simultaneously oxidising RhB to CO₂ gas.

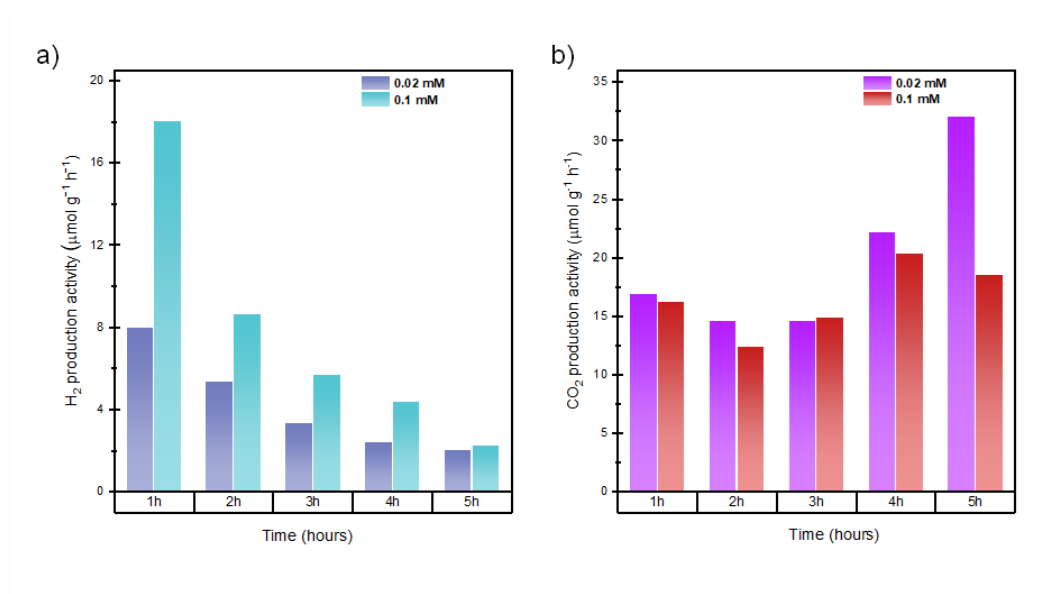


Figure 3.23 Simultaneous H₂ production a), and Rhodamine B dye degradation indicated by CO₂ evolution b) using PhCN/TiO₂ B_RT.

We observe an initial rate of 8 μmol h⁻¹ of H₂. Moreover, the H₂ production rate was further doubled when increasing the amount of RhB, with an optimal dye concentration of 0.04 mM for best HER results of 17.5 μmol h⁻¹, since further increasing the RhB concentration did not yield any improvement in the HER performance. As expected, the amount of H₂ produced using RhB as the sacrificial agent was much lower than when with TEOA because of the high basicity of TEOA and its small molecular size which helps it to diffuse better in the pores of the hybrid photocatalyst leading to a more effective electron donation process. Complementarily, the amount of evolved CO₂, as the product of RhB degradation, increased with time showing that more RhB molecules are being degraded. However, longer illumination reveals a sharp decrease in the H₂ production rate which is

first most likely due to the lack of sufficient amounts of RhB in the solution to consume the photogenerated holes, resulting in an increase in the number of charge-recombination, and secondly could be due to the agglomeration and deactivation of Pt NPs. Nonetheless, UV-Vis spectroscopic measurement confirmed the complete degradation of 0.02mM RhB after 5 h of illumination (**Figure 3.24b**), along with a cease in any H₂ production further demonstrating that RhB acts as the source of CO₂ and H₂. Similar is the case with 0.1mM RhB. It is important to note that the negligible amount of H₂ produced in the latter half of the illumination cycle could also be due to the lack of dissolution of the dissolved H₂ in the reaction solution. Therefore, the successful production of H₂ by the degradation of RhB dye showed that the PhCN/TiO₂ hybrid B_RT has a good redox capability i.e., electron reduction through HER and hole oxidation through RhB degradation.

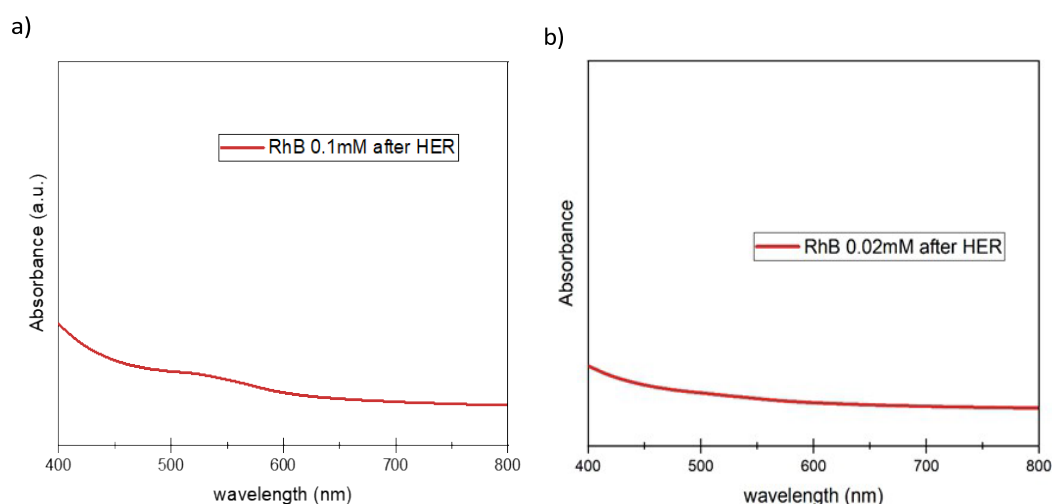


Figure 3.24 Vis absorption spectra of a) 0.1M and b) 0.02mM RhB after simultaneous HER and dye degradation test.

Based on the results above, coupled with XPS analysis, optoelectronic studies and mechanistic insights, a mechanism of dual photocatalytic behaviour of oxidative coupling of RhB degradation integrated with H₂ evolution over PhCN/TiO₂ can be proposed as follows:

- 1) When the PhCN/TiO₂ hybrid comes in contact with the RhB molecules in water under dark conditions, it starts to adsorb the dye molecules onto its surface which is highly facilitated by the high porosity of the sample
- 2) Once the adsorption-desorption equilibrium is achieved in 30 mins and the visible light is incident to the system, the PhCN, owing to its suitable bandgap, absorbs visible-light photons and forms photogenerated e⁻ - h⁺ pairs

- 3) The adsorbed RhB molecules also get photoexcited owing to its LUMO and HOMO band positions at -1.42 and 0.95 eV (vs NHE) respectively and Pt gets photodeposited on the surface of the hybrid via the reduction by the photoexcited electrons
- 4) The photogenerated electrons from RhB migrate to the conduction band of TiO_2 as well as the LUMO of PhCN whereas the excited electrons from the LUMO band (σ^* level) of PhCN are transferred to the conduction band of Ti due to the favourable alignment of their energy levels.
- 5) The deposited Pt acts as an electron acceptor due to the position of its fermi level which enhances the spatial charge separation and lowers the activation energy barrier to enhance the photocatalytic performance.
- 6) The holes accumulated at the HOMO of PhCN react directly with the RhB molecules to further oxidize them to CO_2 and other degraded products
- 7) Simultaneously the surface-adsorbed protons react with the localised trapped electrons on Pt to generate H_2 at the CB of TiO_2 .

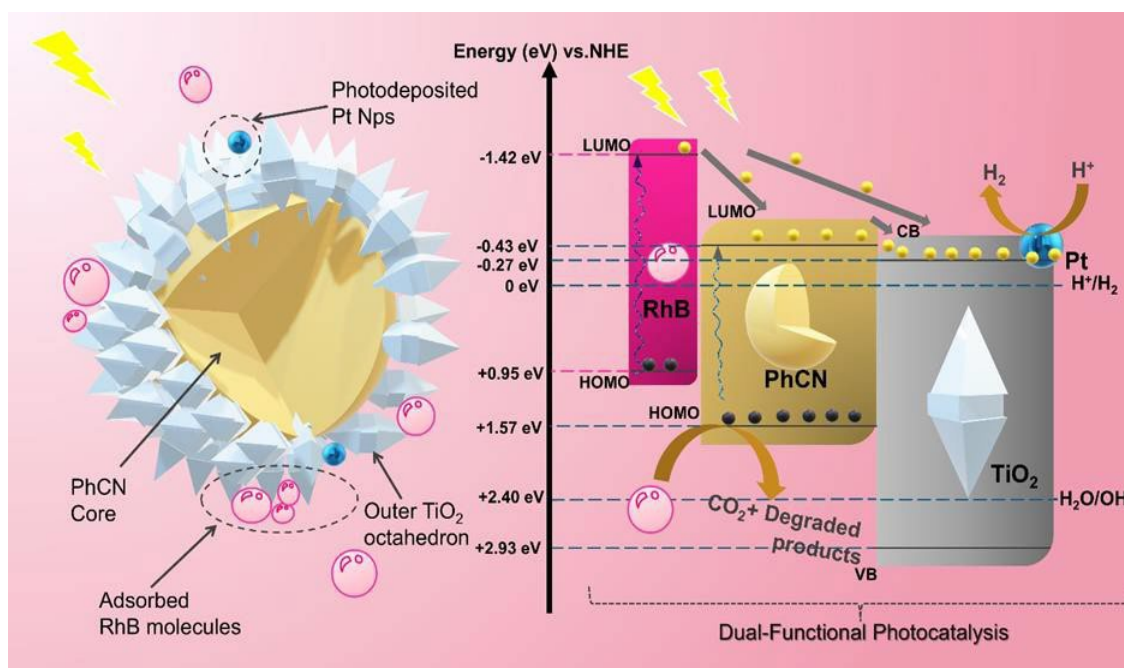


Figure 3.25 Type II charge transfer scheme of improved PhCN/ TiO_2 hybrid for simultaneous Rhodamine B degradation and H_2 production under 445nm LED illumination.

This is a type II charge transfer mechanism (**Figure 3.25**) where the photogenerated electrons and holes are utilised for H_2 production and oxidative degradation of Rhodamine B dye respectively, resulting in a dual-functional photocatalysis process. The irregular shape of the hybrid aids in the formation of maximum number of heterojunctions

and the porous surface ensures a high interaction between the adsorbed species and the photogenerated charge carriers. The intermeshed structure guarantees less time for $e^- h^+$ recombination and shorter electron travel path from the PhCN core to the surface of the hybrid. Through this efficient pathway, the gradient core-shell PhCN/TiO₂ hybrid exhibits a good redox performance under visible light irradiation for dual-functional photocatalysis.

3.3.2. Inactivation of H1N1 virus by PhCN/TiO₂ hybrid for indoor conditions.

From the previous section, it was established that the optimised PhCN/TiO₂ hybrid acts as a good photocatalyst under visible-light conditions. The successful degradation of the organic rhodamine B dye indicated probable good interactions with other organic species such as- microorganisms. The quenching tests performed previously, depicted that reactive oxygen species (ROS) such as hydroxyl radicals ($\bullet\text{OH}$), superoxide anions ($\text{O}_2^{\bullet-}$), and singlet oxygen ($^1\text{O}_2$) were evolved during the dye degradation process under environmental conditions and visible- light illumination. These ROS are highly reactive and can attack various organic molecules, breaking down their chemical bonds.

When a microorganism, such as a bacterium or virus, comes into contact with these ROS, the cell or viral envelope can be damaged, along with essential biomolecules like proteins, lipids, and nucleic acids.¹⁸² The ROS can disrupt the cell membrane, leading to cell lysis, or damage viral capsids, which are essential for virus survival and infectivity. Additionally, ROS can break down DNA or RNA, which stops replication and effectively inactivates the microorganism.¹⁸²

Therefore, we perform the following tests to establish whether our PhCN/TiO₂ system is an effective disinfectant for H1N1 virus:

Cytotoxicity tests

Before applying the hybrid system for the inactivation of viruses, its interaction with healthy MDCK cells were analysed to determine the extent of its cytotoxicity. Madin-Darby Canine Kidney (MDCK) cells are a line of epithelial cells originally isolated from the kidney tissue of a normal adult cocker spaniel dog. MDCK cells support the replication of many viruses, making them a standard choice for viral titration and plaque assays.¹⁸³ All the tests were performed with a white-LED lamp (11 W, 0.2 mW/cm²). The MTT colorimetric assay was used to check cell vitality. MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) is a yellow, water-soluble compound that is metabolically reduced by cellular enzymes in viable cells to form a water-insoluble purple formazan. This reduction process is used in the MTT assay to assess cell viability and proliferation. The intensity of the purple colour, which can be measured spectrophotometrically, correlates with the number of viable cells. For the control measurement, dimethyl sulfoxide (DMSO) and glycine buffer mixture was used as a reagent to dissolve the formazan crystals formed after the reduction of MTT by viable cells. It allows the formazan to be solubilized, enabling accurate measurement of its absorbance at 540 nm, which correlates with cell viability.

A non-viable cell is one that cannot reduce MTT to formazan due to a lack of metabolic activity. This means that the cell is either dead or has lost its functional viability, resulting in no or minimal formation of the purple formazan product. Consequently, non-viable cells do not contribute to the absorbance measured at 540 nm, indicating reduced or absent cell viability. The "% of control" for the MTT assay refers to the comparison of

the absorbance values of treated cells with the toxin to those of untreated control cells (with only DMSO). It is calculated as the percentage of the absorbance of treated cells relative to the absorbance of control cells, which are considered 100% viable. It is to quantify the extent of cell viability or cytotoxicity induced by a treatment with a certain chemical. For our tests, this chemical would be PhCN/TiO₂ photocatalyst.

Various photocatalyst concentrations, ranging from 10 mg/ml to 0.020 mg/ml with a 0.5 dilution factor, were made and tested. The results are shown in **Figure 3.26** with the cell viability vs the concentration of the photocatalyst used for the cytotoxicity test. The tests were repeated multiple times to generate the error bar. The cytotoxicity tests were carried out under lit as well as dark conditions to eliminate the function of light as a factor to kill cells. The cell vitality (% control) is calculated as – (Absorbance of treated cells/ absorbance of control cells) ×100. When no cells are harmed then the vitality remains at 100%. When cell vitality is more than 100%, it indicates that the treated cells have a higher metabolic activity or proliferation rate compared to the untreated control cells. This can happen if the treatment promotes cell growth, enhances metabolic activity, or increases the number of viable cells.

Figure 3.26 shows that the increasing concentration of the photocatalyst decreases cell vitality. From the concentration of 0.020 mg/ml to 1.25 mg/ml, a cell vitality of 100% or more was measured for at least one measurement. This implies that for these concentrations, the MDCK cells enhanced their metabolism or maintained it at a similar level. Following this, the highest permissible concentration (1.25 mg/mL) was used for plaque assays to allow for maximum observable photocatalytic activity.

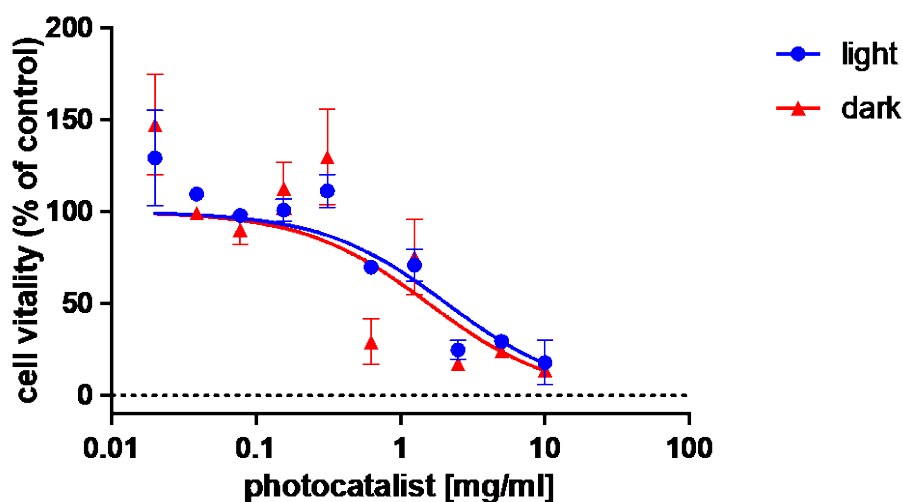


Figure 3.26 Direct cytotoxic effect of PhCN/TiO₂ on MDCK-2 cell line¹⁸⁴

H1N1 Virus Inactivation

A plaque assay was used for estimating the viral activity in the MDCK cells. This assay helps determine the concentration of viruses, typically in terms of plaque- forming units

(PFU), which reflect the number of infectious viral particles capable of forming visible plaques on a cell layer.¹⁸⁵ When cells are infected, they form a circular zone of white colour which is called a “plaque”. For our experiments we assumed that each plaque is caused by one viral particle.

Firstly, 600 PFU of Influenza Virus (H1N1) were combined with 1.25 mg of the photocatalyst. Since, it is important to establish the significance of light and utilization of photocatalysis, the mixture was divided in half: one portion was exposed to irradiation for 2 hours using a white LED lamp while the other half was kept in the dark.

Following irradiation, plaque assays were conducted by inoculating various dilutions of the virus solution (1:1, 1:10, 1:100) onto cell monolayers, both with and without the photocatalyst. The monolayers were incubated at 37°C in a 5% CO₂ atmosphere for 1 hour to allow viral attachment to the cells.

After incubation, the suspension was removed, and the monolayers were covered with an agar-containing immobilizing solution, forming a gel. This ensures that newly produced viruses only infect adjacent cells, forming localized infection sites called plaques. The monolayers were then incubated for an additional 72 hours, during which plaques were formed. To visualize the plaques, the cell monolayers were stained with 500 mL of crystal violet, followed by washing and drying before counting. The **Figure3.27** shows the overall experimental procedure for the tests.

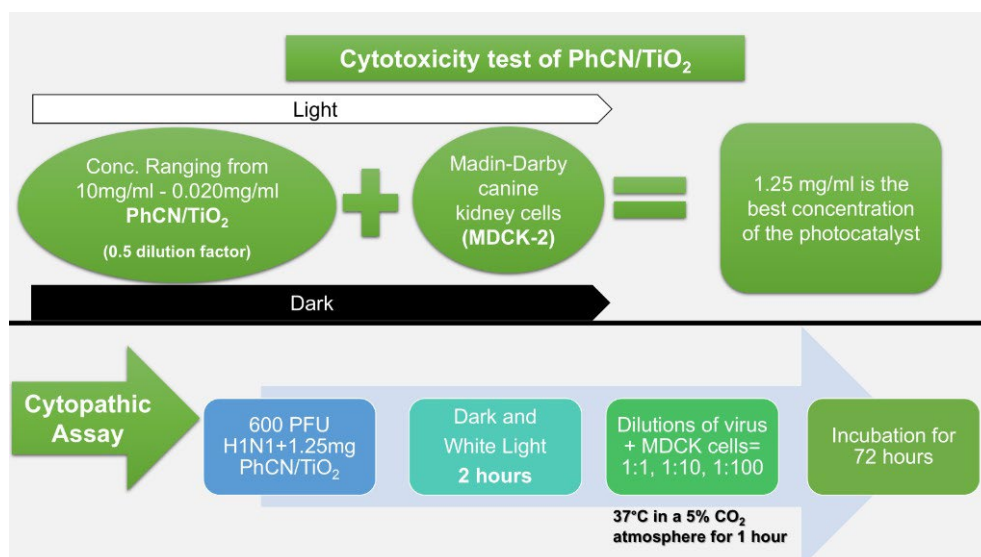


Figure 3.27 Schematic of the experiments done for the photocatalytic viral inactivation.

Additionally, two control solutions were tested: (i) virus without photocatalyst, and (ii) photocatalyst without virus. Both underwent light as well as dark reactions. Results were expressed in PFU/mL, indicating the number of infectious particles in the sample, with each plaque assumed to represent a single infectious virus particle.

The emission spectrum of the light source was measured as shown in **Figure 3.28** where it is compared with the absorption spectrum of the PhCN/TiO₂ hybrid. The **Figure 3.28** shows the experimental set up for this study. The experiment was performed with MDCK cells and the H1N1 virus, both standard models in influenza virus research.¹⁸⁶ There was no UV component in the emission spectra of the LED bulb used. Therefore, the assay results are in anyway not affected by any incident UV light which could lead to virucidal activity.

The virus titer was calculated by multiplying the observed plaque count by the dilution factor of the virus solution. **Figure 3.29** shows the results of the plaque assay where a] shows the assay grid with all the viral dilutions in increasing order from top to bottom; and the column show uninfected cell with photocatalyst, infected cell without photocatalyst and infected cell with photocatalyst from left to right.

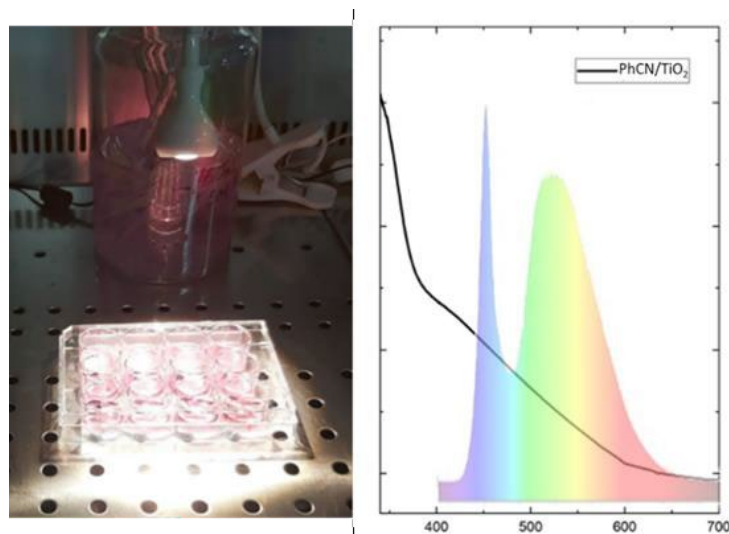


Figure 3.28 Photocatalytic virus disinfection experiment with an illustration of the absorption spectrum of the material compared to the emission spectrum of the LED.¹⁸⁴

The first column of the assay showed no plaques, indicating that the photocatalyst was not harmful towards the MDCK cells. The middle column in the data shows great deal of infections by the virus as its concentration increases. When compared to the right most column, we can observe a reduction in the infections due to the presence of the photocatalyst. This phenomenon was observed for all the dilutions of the virus which denied the possibility for it to be an artifact of the amount of photocatalyst used. Hence,

it could be concluded that the presence of PhCN/TiO₂ hampered the growth of H1N1 flu virus. It appeared to reduce the infectivity of the virus particles, likely by damaging the virus's genetic material or outer envelope, rendering them incapable of infecting cells.^{187,188,189}

To assess the statistical significance of these findings, a t-test was employed to compare plaque numbers under different conditions (**Table 3.4**). The t-test is a standard statistical method for determining whether observed differences between data sets are significant.¹⁸⁵ Here, the results revealed a significant difference across all test conditions. A p-value, which quantifies the likelihood that the observed differences arose by chance, was obtained.¹⁹⁰ Typically, a p-value below 0.05 is considered statistically significant, meaning there is less than a 5% probability that the observed differences occurred randomly.¹⁹⁰ In this case, a p-value below 0.05 indicated a statistically significant difference between the groups compared.

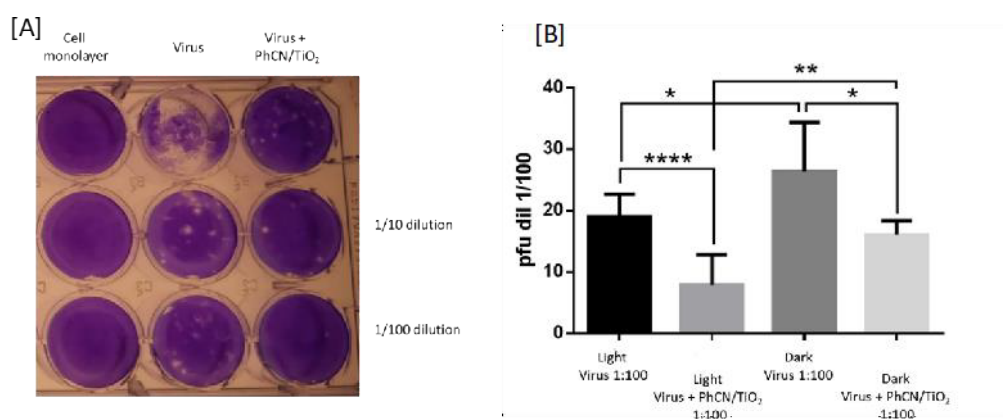


Figure 3.29 (A) Representative result of a plaque assay titrating the samples obtained after irradiation procedure. Column1 MDCK-2 control wells with PhCN/TiO₂, Column 2 Virus control dilution without photocatalyst, Column 3 Virus dilution treated with photocatalyst. (B) Result of a plaque assay titrating the samples obtained after irradiation procedure. Plaque-forming units were quantified by visual inspection. Statistical significance was determined with an unpaired-*t* test using Prism 9.01.¹⁸⁴

In this study, the significant p-values obtained from t-tests reveal substantial differences across the experimental conditions. For example, comparisons between virus exposure to light versus dark conditions and virus plus photocatalyst under light versus dark conditions showed statistically significant p-values, suggesting that light enhances the photocatalyst's virucidal effect. Notably, viral titers were reduced by over 50% after only 2 hours of treatment with both light and photocatalyst. Further, t-tests comparing conditions where the virus and photocatalyst were in darkness versus virus alone, as well as virus plus photocatalyst in light versus virus alone, also yielded statistically significant p-values. This confirms that the photocatalyst alone exerts a strong virucidal effect

against H1N1 in MDCK cells. These comparisons are graphically represented in **Figure 3.29 b** for the dilution 1/100 of the virus.

Overall, the statistically significant p-values from the t-tests provide strong evidence that the photocatalyst effectively reduces H1N1 viral plaques in MDCK cells, with its impact further enhanced by light. This study underscores the potential of PhCN/TiO₂ as virucidal agents and highlights the importance of investigating light's role in such antiviral processes.

Table 3.4 Results of the *t*-test *p*-values for the tested conditions.¹⁸⁴

Compared Tests (dil. = viral dilution)	Dark + 1:100 dil.	Dark + 1:100 dil. + photocatalyst	Dark + 1:100 dil. + photocatalyst	Light + 1:100 dil. + photocatalyst
	vs	vs	vs	vs
	Light + 1:100 dil.	Light + 1:100 dil. + photocatalyst	Dark + 1:100 dil.	Light + 1:100 dil.
	(Without Photocatalyst)	(With Photocatalyst)	(Dark)	(Light)
P Value	0.032	0.0051	0.0231	< 0.0001
P Value Summary	*	**	*	****
P < 0.05	Yes	Yes	Yes	Yes

3.4. Conclusion

This study successfully demonstrated the synthesis and application of a novel PhCN/TiO₂ hybrid photocatalyst with a gradient core-shell structure, designed for dual-functional photocatalysis and viral inactivation. The PhCN/TiO₂ hybrid was shown to efficiently utilize visible light for simultaneous hydrogen production and Rhodamine B (RhB) degradation, thus showcasing its potential in environmental remediation and sustainable energy generation.

Key findings highlight that the PhCN core, paired with a porous TiO₂ shell, promotes efficient charge separation and transfer, enabling high photocatalytic activity under visible light. Structural and optoelectronic analyses confirmed the formation of a Type II heterojunction within the hybrid, facilitating effective charge migration from PhCN to

TiO₂, enhancing the interaction with pollutants, and reducing electron-hole recombination rates. The tailored synthesis approach, including controlled TiO₂ crystallization and thermal treatment, allowed optimization of the hybrid's photocatalytic efficiency, balancing its surface area and active site accessibility.

The photocatalytic performance, validated through extensive dye degradation and hydrogen evolution tests, demonstrated the hybrid's effectiveness. The photogenerated holes were found to be the major reactive oxygen species (ROS). These ROS are also responsible for its virucidal activity under visible-light illumination. Statistical analysis indicated significant reductions in viral infectivity with the presence of light and photocatalyst, reinforcing the system's virucidal potential. The work further underscores the importance of light in optimizing the virucidal process, with over 50% reduction in viral titer observed under visible light irradiation.

This study not only contributes to the understanding of dual-functional photocatalysis mechanisms but also presents a scalable, environmentally friendly approach with implications for wastewater treatment and green energy production along with its indoor applications. Future research may focus on enhancing the stability and scalability of the PhCN/TiO₂ hybrid, including exploration of bio- friendly alternatives to platinum, for broader commercial applications. The mechanism of viral disinfection shall be investigated and the interaction between the photocatalyst and the H1N1 flu virus in dark shall be studied.

Chapter 4

Alterations in photocatalytic characteristics through Boron doping in Phenyl-grafted carbon nitride.

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Defect-state introduction in Phenyl modified Carbon Nitride through Boron doping for enhanced H₂ production. (Under preparation)

Abstract

Doping of boron in the carbon nitride framework has recently been explored to obtain visible-light active photocatalytic behaviour.^{191–193} These Boron doped materials are multifunctional and show an enhanced surface area and visible light absorption which translated to better usage of solar spectrum and higher number of surface active-sites for reactions to take place. Herein, we incorporate boron in the framework of our Phenyl-modified carbon nitride. This can also be considered as boron-phenyl co-doping of carbon nitride.

The aim of this chapter is to study the implications of boron doping in the Phenyl-containing structure of PhCN and to obtain an enhanced visible-light activity for photocatalytic environmental applications.

A one-step simple thermal polymerisation method was used to obtain the B-doped PhCN at 400°C using benzoguanamine and boric acid in the molar ratio 2:1. This resulted in the formation of a new polymer -BPhCN which showed novel structure and chemical properties. XRD, FTIR, Raman spectroscopy and XPS show a successful incorporation of B atoms into the structure of the carbon nitride through C atom substitution. The BET calculations show an increase in the surface area of the BPhCN material. Optical characterisations show a better charge separation ability through an increased bandgap and lower fluorescence. These properties translate to a better photocatalytic dye degradation activity of BPhCN than PhCN under visible light irradiation. The presence of defect states proved to be beneficial for providing high activity to degrade pollutant. This material is a promising photocatalyst for molecule/reaction targeted application under visible, as well as UV light.

4.1. Introduction

Doping is a well-established method in semiconductor science to modify and enhance material properties. The case of graphitic carbon nitride (g-C₃N₄), elemental doping is widely explored to overcome limitations such as low visible- light absorption and rapid electron-hole recombination.¹⁹⁴ Through doping, additional energy states can be introduced within the band structure of g-C₃N₄, enabling more efficient charge separation and light absorption across a broader spectrum.¹⁹⁵

Several elemental dopants have been studied to enhance the photocatalytic activity of g-C₃N₄, with metal ions being among the most common. Metal doping involves introduction of Fe, Cu, Ag, and Zn, etc. into the g-C₃N₄ framework.¹⁹⁵ These metals have partially filled d-orbitals that can interact with the electronic structure of g-C₃N₄, creating mid-gap states and narrowing the bandgap which enhances their photocatalytic ability to degrade pollutants in water.¹⁹⁵ Wang et al. reported enhancement in H₂ production and methylene blue dye degradation under visible light by Mn doping with g-C₃N₄.¹⁹⁶ Hu et al. showed high recyclability for refractory pollutant removal by Fe-doped g-C₃N₄.¹⁹⁶ Sudrajat and Hartuti used Zn doping in g-C₃N₄ to eliminated the need of a co-catalyst during H₂ production with a 8times faster rate.¹⁹⁷ Despite the enhanced photocatalytic activity achieved through metal doping, theh practical applications of the materials are limited due to low lifetime of activity. Metal-doped g-C₃N₄ can suffer from stability issues, as the incorporation of metal atoms may disrupt the intrinsic stability of the carbon nitride framework, particularly under photocatalytic conditions that involve reactive species.¹⁹⁵ This degradation can reduce the material's photocatalytic efficiency over time.

To tackle with the stability and introduction of excessive recombination sites in g-C₃N₄, researchers started exploring non-metal doping in g-C₃N₄ matrix in the hope of comparable enhancements without the problems. In contrast to metal doping, non-metal doping has emerged as an effective approach to enhance the photocatalytic properties of g-C₃N₄ while maintaining its inherent stability and metal-free structure. Non-metal elements, such as boron (B), phosphorus (P), sulfur (S), and nitrogen (N), have proven to be effective dopants in modifying g-C₃N₄'s electronic and optical properties.¹⁹⁸ Non-metal doping introduces defect sites and modifies the band structure, which can lead to improved visible-light absorption and more efficient charge carrier separation without significantly affecting the stability of the carbon nitride framework.¹⁹⁴ This metal-free approach is particularly attractive for sustainability goals as they do not possess reactive sites like metal atoms, would not lead to eutrophication and have higher stability when compared to metal-doped counterparts.

Among the non-metal dopants, boron (B) has shown promise in enhancing the photocatalytic performance of g-C₃N₄.^{192,199–201} Boron doping has attracted significant interest as a modification strategy for enhancing the photocatalytic efficiency of g-C₃N₄. As a non-metal, boron maintains the metal-free nature of g-C₃N₄, aligning with the need for environmentally friendly and sustainable materials in photocatalysis.

In recent years, many reports have arisen stating the benefit of Boron incorporation in g-C₃N₄ matrix utilizing it for all sorts of g-C₃N₄ applications like- CO₂ reduction¹⁹⁸, organic pollutant degradation^{120,202}, water splitting^{192,201}, photoluminescence²⁰³, electroluminescence²⁰³, H₂O₂ synthesis¹⁵², pharmaceutical degradation²⁰⁴ and more. **Table 4.1.** summarises some of the key discoveries related to B-doped g-C₃N₄ materials.

Boron has shown to be particularly effective in modifying the electronic structure and charge transport properties of g-C₃N₄, introducing defect sites that enhance charge carrier mobility and reduce recombination rates.¹⁹⁸ These characteristics make boron-doped g-C₃N₄ a promising candidate for applications in water purification, pollutant degradation, and renewable energy. Boron atoms, when incorporated into the g-C₃N₄ lattice, introduce p-type conductivity due to their electron-deficient nature. This creates an electric field that facilitates charge separation by drawing photoinduced electrons and holes apart, reducing the likelihood of recombination and enabling greater photocatalytic efficiency.²⁰⁵ Additionally, boron doping can introduce mid-gap states, which allow g-C₃N₄ to absorb light in the visible spectrum more effectively, thereby enhancing its utility under natural sunlight or other visible-light sources.²⁰⁶ By DFT calculations it was found that doped B atoms preferentially replace the C atom within the g-C₃N₄, leading to the formation of neighboring N species with unsaturated coordination.¹⁵²

Through a thorough literature review, we find that Boron doping in g-C₃N₄ leads to-

- i. Enhanced light absorption
- ii. Enhanced charge separations.
- iii. Improved charge carrier mobility
- iv. Improved visible-light absorption
- v. Defect site introduction
- vi. Electronic Structure Modification
- vii. Increased surface affinity for reactants

The recent developments of Boron doped carbon nitride compounds have provided useful insights on the possible mechanisms of enhancement of its photocatalytic efficacy.

Table 4.1. Advances in B-doped g-C₃N₄ structures.

Sample	Application	Activity enhancement	Key Finding	Ref
T/B-CN <i>B-doped g-C₃N₄ nanocomposite with TiO₂</i>	H ₂ evolution, CH ₄ production	29×high, 16×high	New B-induced surface states are created near VB	206
CNN/BDCNN <i>Heterostructure of 2D g-C₃N₄ and 2D B-doped g-C₃N₄</i>	Water Splitting	1.16% solar-to-hydrogen efficiency	Varying levels of B doping changes the HER/OER capacity	199
B@N-doped C ₂ N	4,5 dichloroguaiacol removal	--	B-doping leads to band narrowing and high adsorption	207
CNB <i>Chemically exfoliated Boron-doped g-C₃N₄</i>	H ₂ evolution	3× more H ₂ generation rate than g-C ₃ N ₄	B-doping enhanced photocurrent value and decreases charge transfer resistance of g-C ₃ N ₄	201
B-doped g-C ₃ N ₄	CO ₂ reduction	Elevated from 22.1 to 28.5 nmol/(ml _{H2O} ·g _C at.h)	Higher charge-separation efficiency and more charges generated due to B-doping	198
B-N@CS <i>Boron and nitrogen doped fluffy carbon</i>	MB, RhB, I ₂ removal	1.4×, 1.3× higher than CS	More active-sites generated through B-doping	208
B-g-C ₃ N ₄	H ₂ evolution	More than 12 times of g-C ₃ N ₄	B-doping increased the surface area	192
B-doped g-C ₃ N ₄ (BCN)	H ₂ evolution	2x higher than g-C ₃ N ₄	Nanosheets are transformed to nanotubes by B-doping	205

B-g-C₃N₄ Surface charge transfer B-doping of g-C ₃ N ₄ films	Photoelectrochemical water splitting	3x photocurrent density vs RHE with no sacrificial reagents as compared to g-C ₃ N ₄	B readily substituted the N atoms	209
CN-B-N_x <i>B-doped g-C₃N₄</i>	H ₂ O ₂ photosynthesis is	100% selectivity achieved	B-doping introduced a donor state below the CB of g-C ₃ N ₄	149

Due to these advantageous results reported by researchers in the recent times, we were motivated to dope the Phenyl-modified carbon nitride with boron as well. A high reactivity of B-doped g-C₃N₄ with organic contaminants in addition to the above-mentioned points make B-doping an attractive modification strategy to verify the enhancement in the photocatalytic efficacy of PhCN. Additionally, we aim to study the changes in the interactions of the system due to the presence of phenyl co-doping.

The objective of this study is to investigate the effects of doping phenyl-modified carbon nitride with boron on its photocatalytic performance. This study aims to build upon existing limited research on phenyl modification and boron doping by examining the synergistic impact of combining both modifications in a carbon nitride photocatalyst framework. By comprehensively characterizing the structural, electronic, and photocatalytic properties of phenyl-boron co-doped polymeric carbon nitride, this study seeks to understand the mechanisms through which these modifications affect the photocatalytic activity under visible light.

4.2. Materials and Methods

4.2.1. Materials

Boric acid (H₃BO₃) (source- Sigma Aldrich), benzoguanamine (6-Phenyl-1,3,5- triazine-2,4-diamine) from Sigma Aldrich.

4.2.2. Synthesis of photocatalysts

PhCN was prepared by the thermal polymerisation of benzoguanamine at 400°C for 2 hours. The sample BPhCN was prepared by co-polymerisation of benzoguanamine with boric acid in 2:1 molar ratio at identical conditions used for the preparation of the reference PhCN.

4.2.3. Photocatalytic Tests

The photocatalytic rhodamine B dye degradation tests were carried out by preparing 0.02mM solution of the dye in distilled water. Followed by addition of the photocatalyst with 1mg/ml concentration in the dye solution. The tests were carried out under a white light 11W commercial bulb. The solution was left in dark for 30minutes to establish adsorption-desorption equilibrium and then irradiated with light when 2ml aliquots were taken every hour.

The photocatalytic HER tests were done in a batch reactor with jacket cooling at a constant temperature of 15°C. 0.1M TEOA was used as a sacrificial agent and 1% wt% Pt was added before the reaction for photodeposition as a co-catalyst. The concentration of the photocatalyst was kept 1mg/ml in the sacrificial agent solution. 365nm and 445nm LED lamps were used for illumination. The reaction was carried out on the absence of oxygen. The concentration of H₂ produced by the reaction in 1 hour was measured by gas chromatography (Shimadzu) through a Dielectric-Barrier Discharge Ionization Detector (BID detector).

4.2.4. Characterization

X-ray diffraction patterns were collected at room temperature by using a Rigaku Miniflex II diffractometer with θ -2 θ Bragg-Brentano geometry with Cu K α ($\lambda = 1.5418 \text{ \AA}$), radiation at room temperature. The scan speed was kept at $0.4^\circ \text{min}^{-1}$ with a step size of 0.02° .

Spectrum Two **FT-IR** Spectrometer from Perkin Elmer was used to acquire the infrared spectra of all the hybrids and pristine samples (LiTaO₃ detector, scan range $4000\text{--}450\text{cm}^{-1}$). The resolution was 0.5 cm^{-1} . All the measurements were done in attenuated total reflectance mode with 10 spectra averaging.

Raman spectroscopy was conducted using BW-TEK: i-Raman® Plus , Fiber coupled Raman system at 1064 nm. No discernible heating effect on the samples was observed. The measurements were carried out at room temperature, with a spectral resolution of 1cm^{-1} . Acquisitions were taken for 8000ms with 20 % LASER intensity.

All measurements were carried out on a custom-built SPECS **XPS-spectrometer** equipped with a monochromatized Al-K α X-ray source (μ Focus 350) and a hemispherical WAL-150 analyser (acceptance angle: 60°). The received powder samples were placed onto the sample holder using double-sided carbon tape.

Pass energies of 100 eV and 30 eV and energy resolutions of 1 eV and 50 meV were employed for survey and detail spectra respectively (excitation energy: 1486.6 eV, beam energy and spot size: 70 W onto $400 \mu\text{m}$, angle: 51° to sample surface normal, base pressure: 3×10^{-10} mbar, pressure during measurements: 7×10^{-9} mbar).

Data analysis was performed using CASA XPS software, employing transmission corrections (as per the instrument vendor's specifications). For all elements Shirley backgrounds and the corresponding Scofield sensitivity factors were utilized. Charge correction was performed by shifting the adventitious carbon peak (C-C peak) to 284.8 eV binding energy (BE).

All content values shown are in units of relative atomic percent (at%), where the detection limit in survey measurements usually lies around 0.1-1 at%, depending on the element. The accuracy of XPS measurements is around 10-20% of the values shown.

A PerkinElmer **Thermogravimetric** analyser 8000 (Waltham, USA), was used to measure the mass loss with temperature in an aluminium oxide (Al_2O_3) crucible under air with a ramp rate of $10\text{ }^\circ\text{C min}^{-1}$.)

SEM was recorded on a FEI Quanta 250 Field-Emission-Gun-SEM, equipped with an Everhardt-Thornley secondary electron detector. The device was operated at an electron acceleration voltage of 10 kV at a working distance of about 5 mm. EDS was measured coupled to this SEM instrument. The powder samples were sprinkled on a carbon tape adhered to the aluminium sample stud and then extra powder was dusted off before the measurement.

N₂ physisorption characterization was performed using a Micrometrics ASAP 2020 Porosimeter at 77 K. Surface area and pore-size distribution were calculated by the Brunauer-Emmett-Teller and Barret-Joyner-Halenda methods, respectively. The measurements used in this research were acquired by Dr.rer.nat. Shaghayegh Naghdi from TU Wien, and their contribution is deeply appreciated.

Absorption measurements of solid samples were obtained by **diffuse reflectance spectroscopy** utilizing a UV-Vis-NIR Agilent Technologies Cary 5000 Spectrometer (Santa Clara, CA, USA). Measurements were performed by using a PbS solid-state photodetector. The reflection configuration measures the diffuse reflection of the sample with respect to a KBr reference that is considered to have 100% reflectivity. The Kubelka-Munk equation was applied to extract the absorption features.

The absorbance spectra of the dye solutions were obtained by the same instrument with a liquid sample holder and absorbance was calculated from transmission. The baseline was measured with water in reference as well as sample cuvettes.

Three-dimensional fluorescence mapping was performed using Horiba Jobin Yvon Fluoromax-3 with a 450 W xenon lamp as the excitation source (Horiba Ltd., Kyoto, Japan). The maps were collected with an excitation range of 300–600 nm and an emission range of 400–800 nm with a 2 nm spectral bandwidth for excitation and emission and a 10% filter at the excitation slit.

Time-resolved photoluminescence (TR-PL) measurements were performed by exciting the samples with 410nm by an optical parametric amplifier (Light Conversion TOPAS-C) pumped by a regenerative Ti:Sapphire amplifier (Coherent Libra-HE, Coherent Inc., Santa Clara, CA, USA). The repetition frequency was 1 kHz, and the PL signal was recovered by a streak camera (Hamamatsu C10910, Hamamatsu Photonics, Hamamatsu City, Shizuoka Pref., Japan) equipped with a grating spectrometer (Princeton Instruments Acton SpectraPro SP-2300, Teledyne Princeton Instruments, Trenton, NJ, USA).

4.3. Results and Discussion

The structural, chemical, and optical properties of BPhCN were studied and compared to those of PhCN to understand the effects of Boron doping in phenyl carbon nitride matrix.

XRD

The XRD spectra of PhCN (**Figure 4.1a**) shows a broad peak at 13-20° (attributed to the (100) plane) indicating in-plane structural packing of the heptazine units and around 27.4° (attributed to the (002) plane) corresponding to interlayer stacking of the conjugated aromatic system. In BPhCN, (**Figure 4.1b**) the peaks related to PhCN were not evident. Instead, the most crystalline peak was located at 4 degrees which could represent a larger periodicity, or an ordered structure introduced by the boron atoms. A number of amorphous peaks were observed from 10-30 deg which could be from boron-rich clusters. All of these peaks in BPhCN could not be matched to the precursors benzoguanamine or boric acid so, they were not remnants of those chemicals. In fact, these broad peaks are often associated with disordered structures or defective phases, which can arise when dopants like boron create defect sites or disrupt the regular stacking of g-C₃N₄ layers. To be sure about the presence of these B-induced phases, we washed the sample and again performed XRD which failed to remove the extra peaks. The persistence of these broad peaks even after washing suggests that the amorphous phases are not simply residual precursors but rather chemically integrated within the BPhCN matrix.

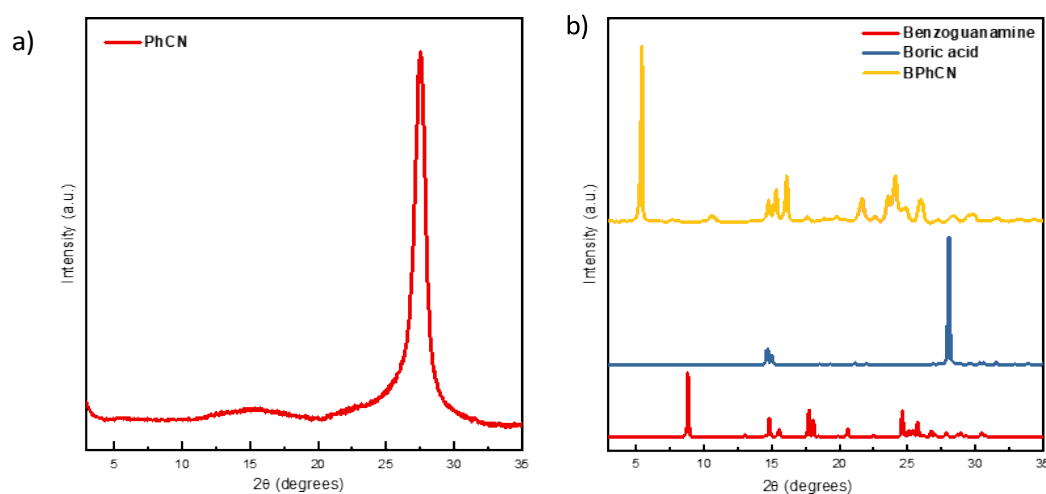


Figure 4.1 XRD of a) PhCN and b) BPhCN with the precursors used for its synthesis.

FTIR

(Figure 4.2a,b) The broad peak around 3200 cm^{-1} is typically attributed to N–H stretching vibrations of amine groups in PhCN. It was observed that the peak in that region became sharp in BPhCN. It suggests a more uniform N–H environment with reduced hydrogen bonding.

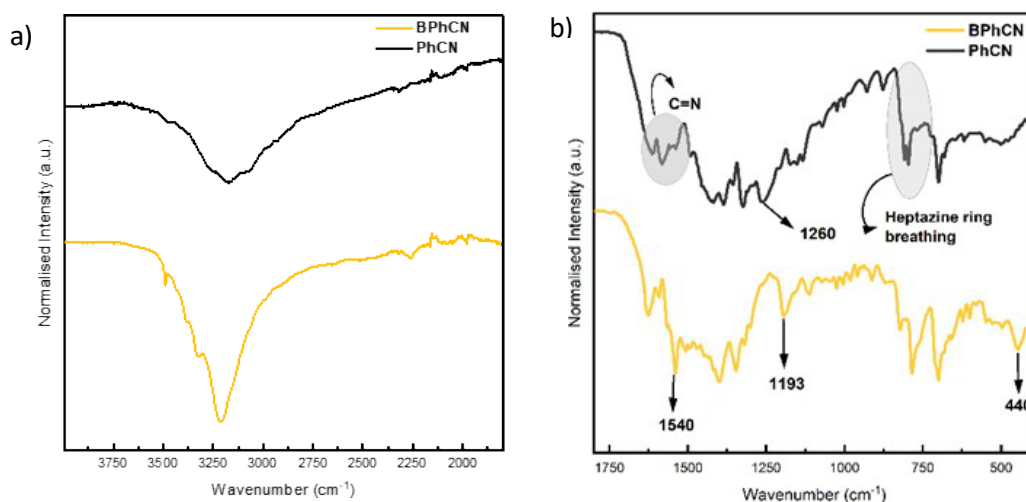


Figure 4.2 FTIR spectra of PhCN and BPhCN a) data from $4000\text{--}1800\text{cm}^{-1}$, and b) data from $1800\text{--}400\text{ cm}^{-1}$.

The region from $1600\text{--}1200\text{cm}^{-1}$ shows multiple peaks from C–N stretching and C–N heterocycles in PhCN which undergoes many shifts and profile changes in BPhCN. We observed shifts towards larger wavenumbers in the C–N stretching region of IR spectrum which could be due to boron atoms creating localized defect sites or changing the bond strength around nitrogen atoms, increasing the vibrational frequency slightly. This shift might also indicate changes in the delocalization of electrons within the carbon nitride structure due to boron-induced defects. The changes in the C=N stretch area around 1610 cm^{-1} suggests an alteration in the C=N bonding environment, possibly due to electron withdrawal by boron atoms nearby. Boron, being electron-deficient, may increase the double bond character of adjacent C=N bonds, slightly raising their vibrational frequency. This shift indicates stronger or modified C=N bonds, which is typical when boron creates defect states that alter the local electronic structure. The 1260 cm^{-1} peak in PhCN is typically associated with C–N stretching within the phenyl-modified carbon nitride structure which is missing in BPhCN. Boron doping could have changed the C–N bonding environment, particularly if boron substituted for carbon and formed B–N bonds. This

change can alter the vibrational energy of C–N bonds, resulting in a shift or disappearance of this peak. The shifted peak in BPhCN at 1193 cm^{-1} could indicate a modified C–N or B–N stretching vibration influenced by boron doping, as boron can introduce defect states that alter the bonding environment around nitrogen and carbon atoms in g- C_3N_4 .

The characteristic heptazine breathing mode at 810 cm^{-1} in PhCN does not appear similar in BPhCN, which suggests alteration of the vibrational energy of the tri-s- triazine rings by B-doping. PhCN framework, creating a slightly more constrained or modified structure around these rings, thus shifting the breathing mode frequency. A new peak at 440 cm^{-1} in BPhCN could correspond to B–N stretching modes or B–O–B bending vibrations.

RAMAN

The Raman spectra were collected by 1024 nm LASER excitation. (**Figure 4.3**) The Raman peaks in PhCN are- N=C-N bending and C-N stretching in the heptazine rings at 693 cm^{-1} , ring breathing mode I at 760 cm^{-1} , NH_2 mode at 1000 cm^{-1} , -CN stretch at 1150 cm^{-1} and 1493 cm^{-1} , C=N-C bending at 1256 cm^{-1} , conjugated stretching vibration (C–C) between the phenyl ring and the triazine ring at 1392 cm^{-1} , and phenyl group motion at 1601 cm^{-1} .

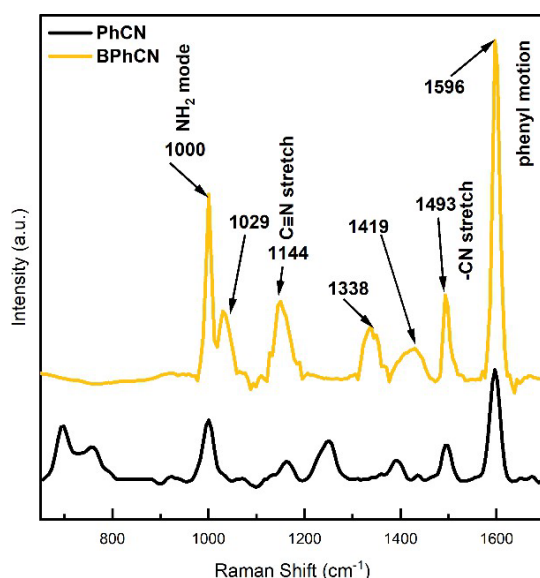


Figure 4.3 Raman spectra of PhCN and BPhCN.

The Raman intensities for BPhCN are significantly higher across all peaks compared to PhCN, indicating that boron doping enhances the Raman activity of the material. Enhanced Raman signals indicate a better crystallinity level which is also supported by the XRD results. On the other hand, newly introduced defect sites (if introduced) may act as Raman-active centres.

Table 4.2 The summary of Raman data of BPhCN and PhCN.

Peak in PhCN (cm ⁻¹)	Peak in BPhCN (cm ⁻¹)	Assignment	Explanation
693	--	Combined N=C–N Loss bending and C–N stretching	of symmetry in BPhCN
760	--	Ring breathing mode I of heptazine rings	due to structural disorder introduced by boron doping.
1000	1000	NH ₂ stretching	NH ₂ groups are retained
--	1029	New B induced perturbation in NH ₂ environment	boron might be altering the electronic environment around NH ₂ group
1150	1144	C–N stretch	
1256	--	C=N–C bending	Structural disordered due to B doping
--	1338	A new B-related species	Multiple bonding environments
1392	1419	Conjugated C–C stretching between phenyl and triazine rings	B close to C–C bonds which withdraws electrons and makes bonds strong
1493	1493	C–N stretch	C–N bonds associated with the phenyl group remain stable after doping.
1601	1597	Phenyl group motion	Phenyl groups are present with stronger bonds

In BPhCN Raman spectrum, we observe the absence of certain polarizations; introduction of new species and shifts of the other species. These observations are discussed in **Table 4.2**.

The Raman results showed that Boron was successfully incorporated in the polymer and a new organic polymer BPhCN is formed with Phenyl and Boron functionalization of polymeric carbon nitride. The absence of triazine breathing modes in FTIR and Raman indicate the perturbation of the rings by B atoms and formation of new states were evident with new peaks. The presence of a high amount of electron withdrawing group like B results in vibrational shifts

XPS

The chemical structure of BPhCN was further probed with X-ray photoelectron spectroscopy to determine the surface species as shown in **Figure 4.4**. The survey spectra shows the presence of B,C,N and O with atomic concentrations- 7.4%, 66.3%, 15% and 11.4% respectively. The band positions of the species found in PhCN and BPhCN are summarised in **Table 4.3**. During the preparation, the molar ratio used for B:N was 1:2 which is same as the atomic concentration ratio of B and N on the surface of BPhCN. This could be an indication towards a homogeneous sample.

Table 4.3 XPS data summary of PhCN and BPhCN.

Sample	Edge	Position (eV)	%At. Conc.
PhCN	O 1s	532.8	7.08
	C 1s	284.8	68.6
	N 1s	398.8	24.32
BPhCN	O 1s	532.3	11.4
	C 1s	284.8	66.31
	N 1s	398.8	14.95
	B 1s	191.8	7.35

The comparative survey spectra of BPhCN with PhCN and Boric acid can be observed in **Figure 4.5a**. The B1s spectra centered at 191.8 eV in BPhCN which is characteristic of

N-B-N coordination, confirms the introduction of B into C sites in the carbon nitride framework. The O1s spectra shows the increase in oxygen content in BPhCN suggesting possible surface oxidation or adsorbed oxygen, potentially due to increased defect sites introduced by boron doping. These sites may facilitate the adsorption of oxygen species. The shift towards lower binding energy in O1s is indicative of weak bonding of the O species with the organic framework due to B doping. A notable decrease in nitrogen concentration in BPhCN was observed which may result from boron substitution for nitrogen. Since the binding energy remains at 398.8 eV, it suggests that most nitrogen is still in a similar C=N bonding state. However, the reduction in concentration aligns with boron atoms potentially replacing some nitrogen sites in the PhCN framework, thereby lowering the relative nitrogen percentage. Figure 4.5b shows the detailed N2s edge of the XPS spectrum of BPhCN and PhCN. BPhCN shows a new bond N-B present at the binding energy of 399.2 eV.¹⁹¹ The bond C-NH is not present in BPhCN but the position for the bond C-N=C stayed the same. In addition, N-(C)³ shifts towards lower binding energy due to the rearrangement of the bonds in BPhCN

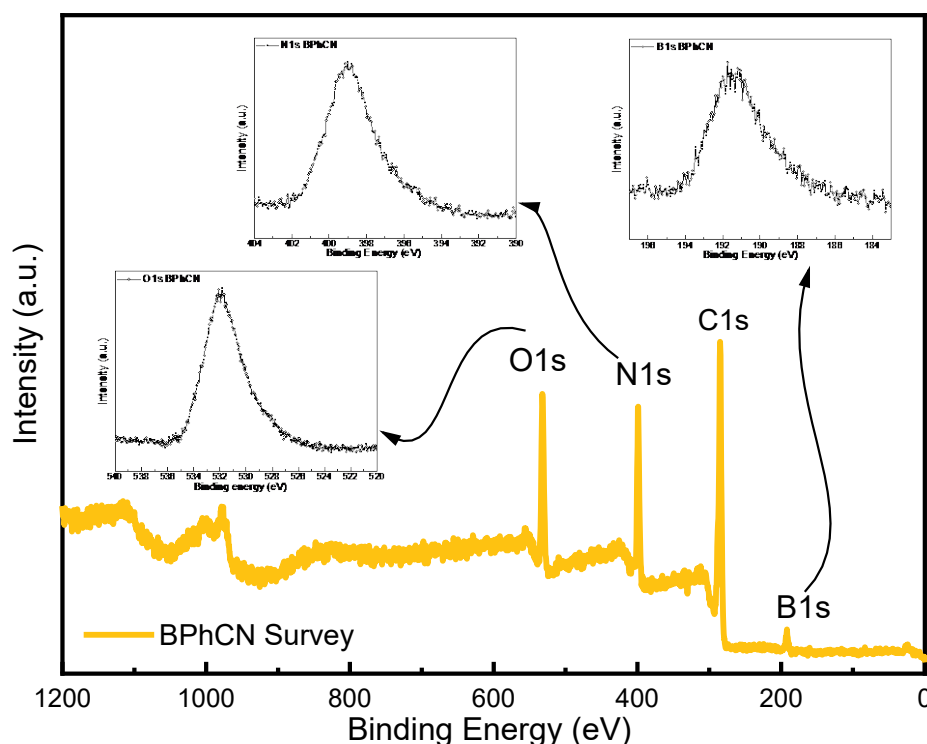


Figure 4.4 XPS survey spectra of BPhCN with individual band edges.

These changes support the conclusions from FTIR and Raman analysis, indicating that boron doping has successfully modified the structure and bonding environment in PhCN by substituting certain C positions in the PhCN matrix, potentially enhancing photocatalytic activity through defect formation and electronic alterations.

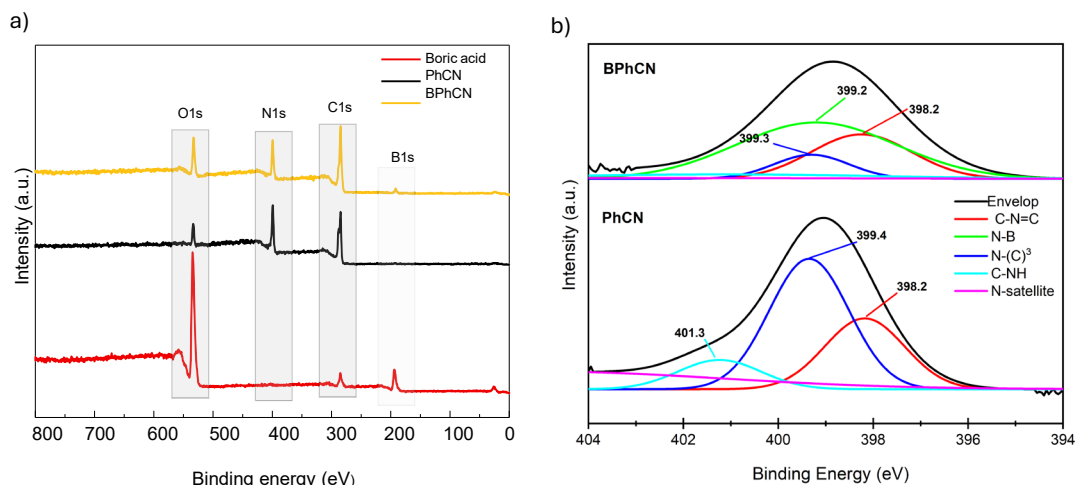


Figure 4.5 XPS a) survey spectra of BPhCN, PhCN and Boric acid and, b) N1s edge of BPhCN and PhCN.

TGA/DTG

To study the thermal stability of BPhCN, we performed thermogravimetric analysis. PhCN shows only 4% weight loss till 300°C but BPhCN showed more loss during the same heating profile (**Figure 4.6 a,b**). Almost 14% mass of BPhCN was lost at 420°C which happened in multiple steps. When heated further till 500°C, PhCN showed an additional loss of only 8% of the mass while BPhCN had lost more 27% mass since 420°C. From 500°C onwards we observed the characteristic thermal degradation of heptazine rings which is the thermal fingerprint of PhCN. This region is well observed also in BPhCN from 500°C. The TGA curve of PhCN shows complete mass loss at 700°C while, BPhCN was left at 20% of its initial mass at the same temperature.

The increased early-stage mass loss in BPhCN results from volatilization of surface adsorbed groups which were introduced by B-doping. The introduction of defect sites leads to a higher susceptibility to thermal decomposition below 300°C in BPhCN. The multi-step mass loss pattern in BPhCN indicates that boron doping introduces diverse bonding environments that decompose across a range of temperatures. As shown by FTIR and

XPS results, Boron incorporation in the framework reduced the bond strengths of many species which could then degrade thermally easily than in PhCN till 500°C. The conservation of the characteristic degradation curve of PhCN that the core carbon nitride structure remains largely intact in BPhCN. The remaining 20% mass in BPhCN points to stable boron- containing residues, such as boron nitride (BN) or boron oxides, which do not decompose fully even at 700°C. This residual mass underscores the enhanced thermal stability that boron introduces to certain regions of the structure.

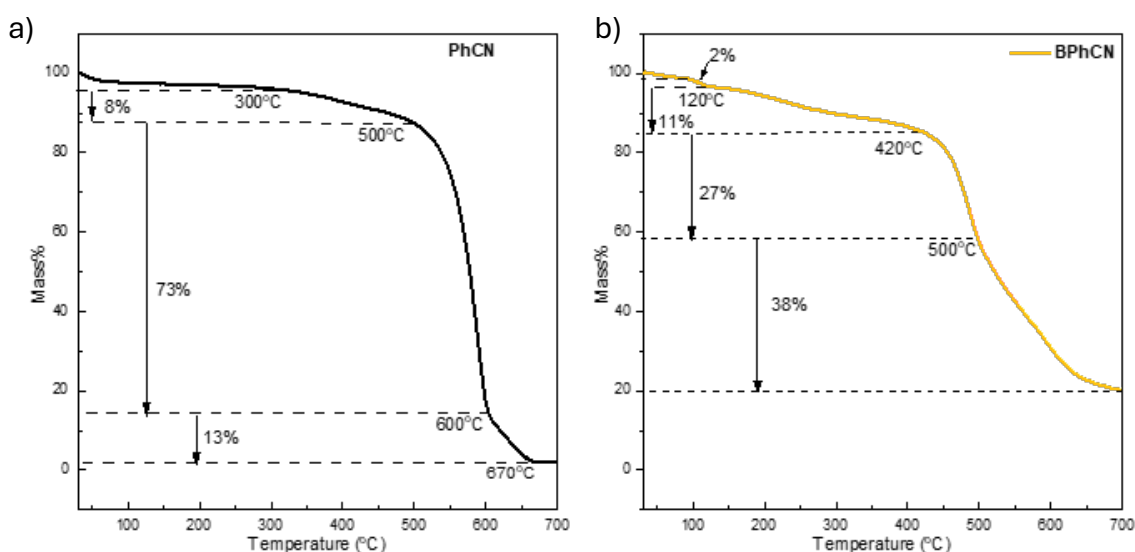


Figure 4.6 TGA data of a) PhCN and b) BPhCN.

When the differential thermogravimetry (DTG) was analysed (**Figure 4.7**), we observed that the PhCN shows a big peak of negative mass loss centered at 587°C which corresponds to the breaking of heptazine related bonds as established in Chapter 3 XPS analysis. This decomposition curve of PhCN is characteristic in nature. On the other hand, BPhCN did not show any high mass loss rates comparable to PhCN. The characteristic PhCN decomposition did not show up in BPhCN indicating that a new material with different chemical environment was formed. The BPhCN shows the decomposition of volatile components at 106°C which may include the oxides and precursors remnants. The chemical reaction at 485°C can be from the decomposition of defect states or newly formed B-N bonds.

TGA results suggest that while boron doping introduces some instability at lower temperatures, it also enhances the thermal stability of specific components within the carbon nitride structure, potentially providing improved performance in applications requiring thermal robustness.

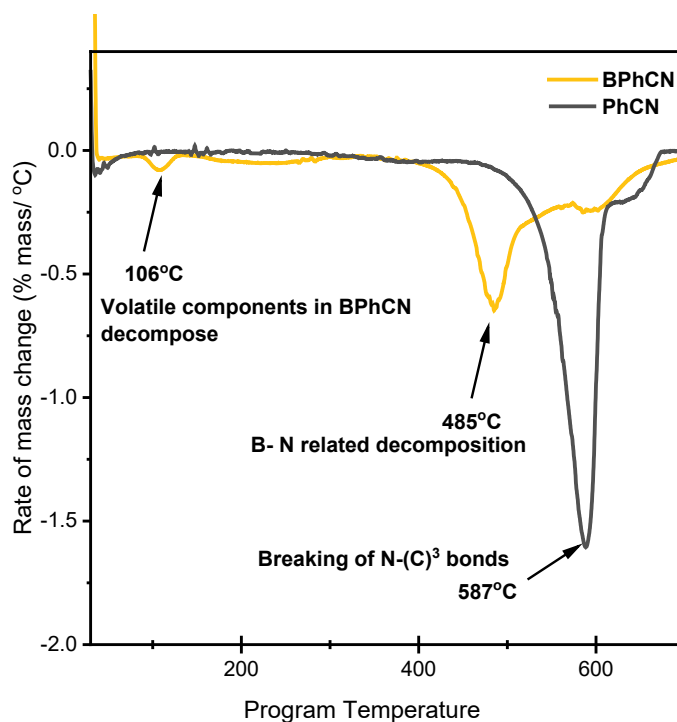


Figure 4.7 DTG data of PhCN and BPhCN

EDS

The EDS spectrum suggests successful boron doping in the BPhCN structure, as indicated by the prominent peaks representing carbon, nitrogen, oxygen and boron in **Figure 4.8**. The relative peak intensities suggest higher N content than B, which is terms with the doping %. A higher oxygen content is again observed in BPhCN compared to the B content. This is from the adsorbed oxygen at the defect states. This data aligns well with the XPS findings, where boron was confirmed as an incorporated element, potentially increasing defect density and thermal stability in the BPhCN framework.

Since EDS coupled with SEM is not suitable for detecting light elements, further conclusions are out of scope from this measurement.

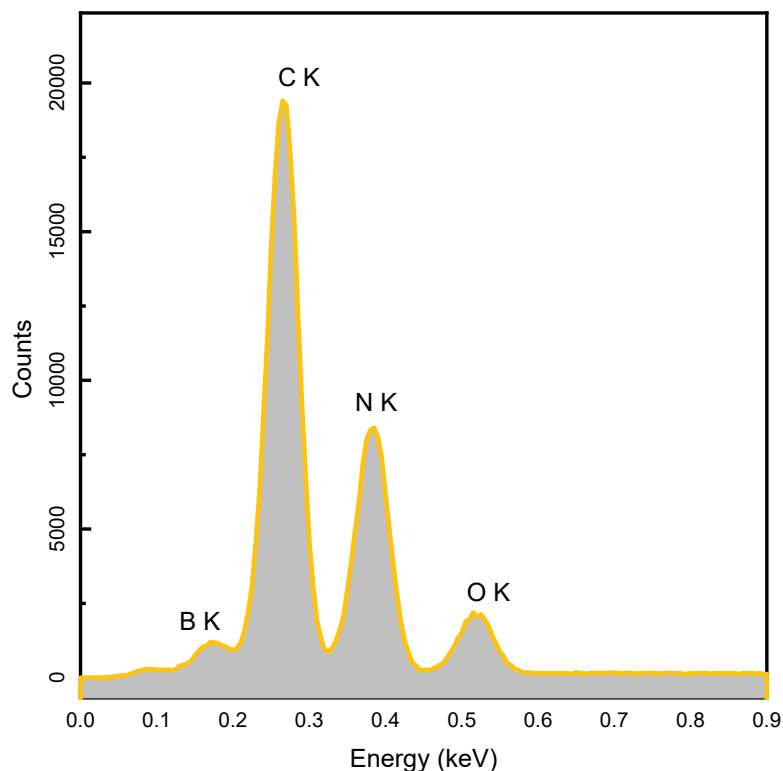


Figure 4.8 EDS spectra of BPhCN.

SEM

The structural characterizations suggest that a new material different to PhCN has been synthesised by B-doping. The structural reorganisations must alter the morphological appearance and texture which we study through SEM.

As shown in **Figure 4.9**, PhCN shows dahlia-like structures with a big particle size. The surface of PhCN appears to be petal-like layered and complex, which could provide high surface area and better light absorption. On the other hand, BPhCN shows no similarity to the morphology of PhCN. This indicated that boron incorporation affects the self-assembly or structural organization of the phenyl carbon nitride, resulting in a new morphology. In lower magnification, BPhCN does not show any layered petal structures

and showed more bulky appearance. Micrographs at higher magnification might indicate the small textures on the surface of BPhCN.

These morphological implications can change the surface area and porosity of the samples which are then studied by N₂ physisorption.

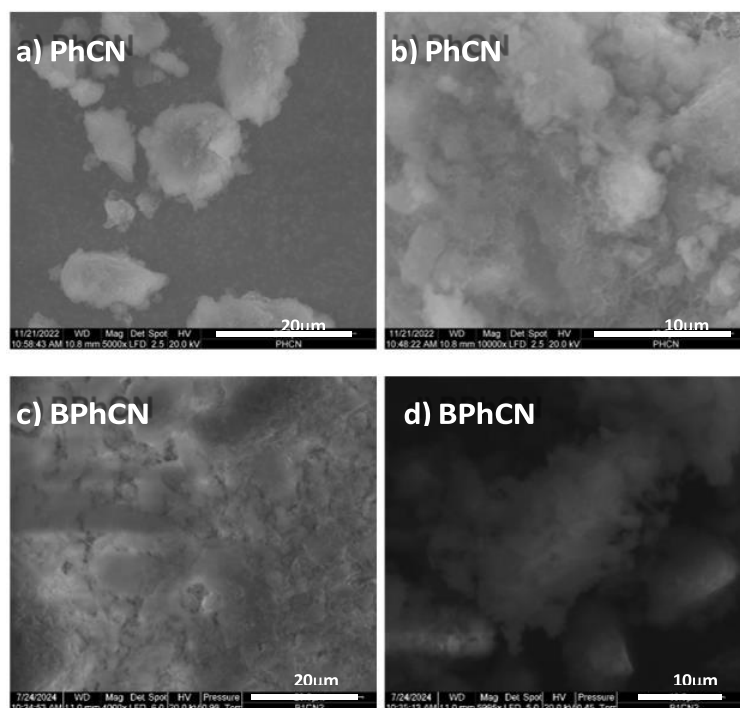


Figure 4.9 SEM images of PhCN and BPhCN.

N₂ sorption

Table 4.4 Summary of N₂sorption data of PhCN and BPhCN.

	PhCN	BPhCN
Surface Area (m ² /g)	14.3	21.1
Pore Volume Density (cm ³ /g)	0.056	0.137
Pore Size (nm)	15.6	26

The N₂ sorption measurements yielded surface area and porosity analysis through BET and BJT calculations respectively. These results for PhCN and BPhCN are summarised in **Table 4.4** and the hysteresis curve is shown in **Figure 4.10**.

Both PhCN and BPhCN showed hysteresis Loop (Type IV). PhCN appears is non- porous with a layered structure and low porosity. It does not have a well-developed internal pore network that significantly contributes to gas adsorption.

As the initial part of the adsorption were similar for both PhCN and BPhCN, we can comment that at low relative pressures (P/P_0), the adsorption mechanism is similar. This could imply surface adsorption or adsorption on external surfaces rather than within pores, which would be consistent with the layered but largely non-porous structure of PhCN. Therefore, both PhCN and BPhCN are comprised of big particles.

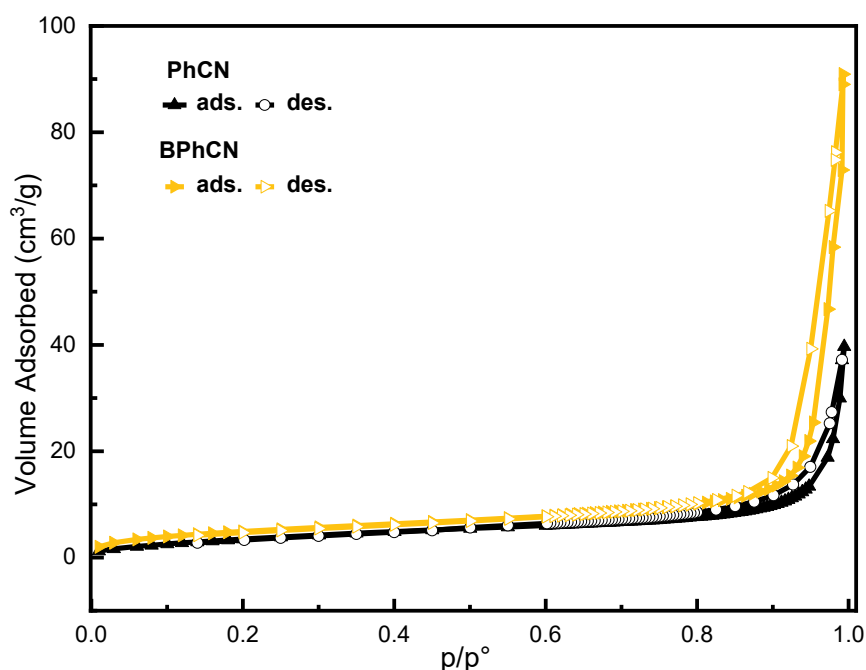


Figure 4.10 BET hysteresis curves of PhCN and BPhCN.

We observed a significant uptake at high relative pressure ($P/P_0 \approx 1$) in BPhCN, with an adsorption volume of ~ 90 cm³/g STP, indicating that BPhCN has a much greater capacity for gas adsorption compared to PhCN in this region.

The calculations show that surface area, pore density and pore size all were significantly enhanced after boron introduction. The increase in surface could be attributed to new defect sites in BPhCN. The pore volume density in BPhCN (0.137 cm³/g) is significantly

greater than in PhCN ($0.056 \text{ cm}^3/\text{g}$). The higher pore volume could improve adsorption capacity, beneficial for applications involving molecular interactions. Larger pores facilitate easier diffusion of molecules, which could be advantageous in adsorption applications, as it allows better access to the active sites within the material.

Boron doping not only increased the surface area but also significantly altered the pore structure, transforming PhCN from a non-porous material to a mesoporous structure with a high pore volume. This may be due to boron creating defects and disrupting the layer stacking in PhCN, leading to a more open structure. The increased pore indicates that boron doping contributes to an expanded internal structure, possibly creating additional mesopores.

DRS

Reflectance spectra of PhCN and BPhCN were measured by Diffuse reflectance spectroscopy method. Kubelka-munk function was used to obtain the absorbance spectra from the reflectance one (**Figure 4.11**) and tauc plots were utilised to estimate the band gap of the materials (**Insets Figure 4.11 a,b**). PhCN shows a broad absorption spectrum which extends to the visible light range. The band edge lies around $\sim 450\text{-}500\text{nm}$ which aligns well with other carbon nitrides. PhCN shows limited visible light absorption. Most of the absorption was in the UV to near-UV- visible range ($300\text{--}500 \text{ nm}$). The gap of PhCN was found to be at 2.62 eV .

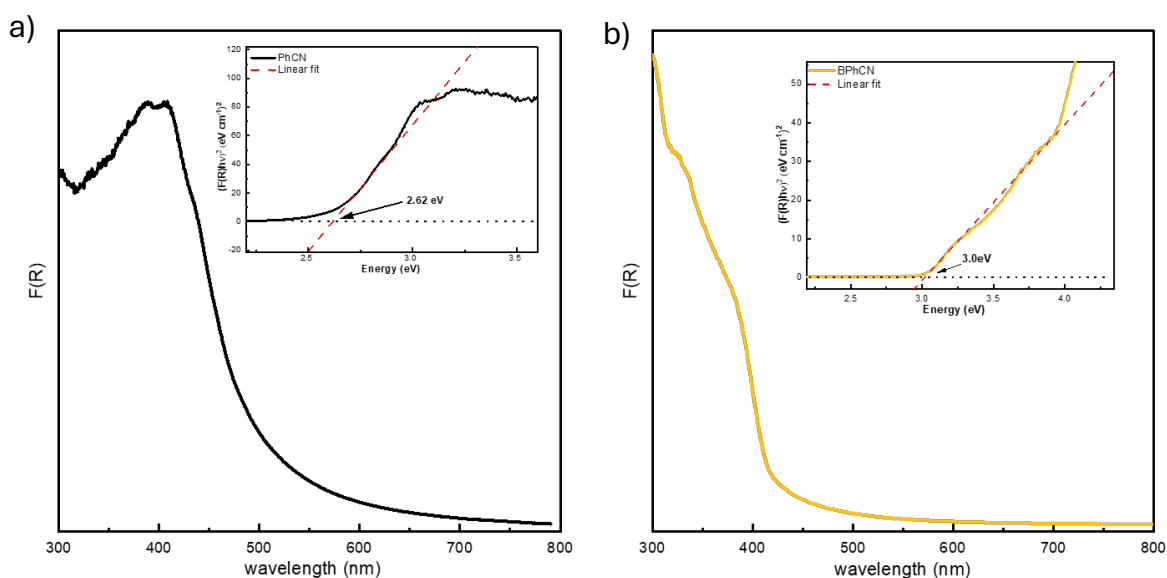


Figure 4.11 DRS spectra and tauc plots of a)PhCN and b) BPhCN.

BPhCN sample showed a blue shift of the absorbance characteristics. The band gap was found to be at 3.0 eV which indicated that BPhCN absorbs little to no visible- light. We find two shoulders at 320nm and 380 nm in the absorption spectrum of BPhCN which shows multiple allowed electronic transitions arising from the defect states introduced in the material through B-doping. It was observed that the absorption of the light kept on increasing with the energy. However, the absorption of low-energy UV light was also higher for PhCN than BPhCN.

The absorption spectra showed that PhCN has higher light-absorbing efficiency while BPhCN can be used for exclusive UV-light active applications with fine- tuning capabilities due to the presence of multiple electronic states.

Steady-state Photoluminescence

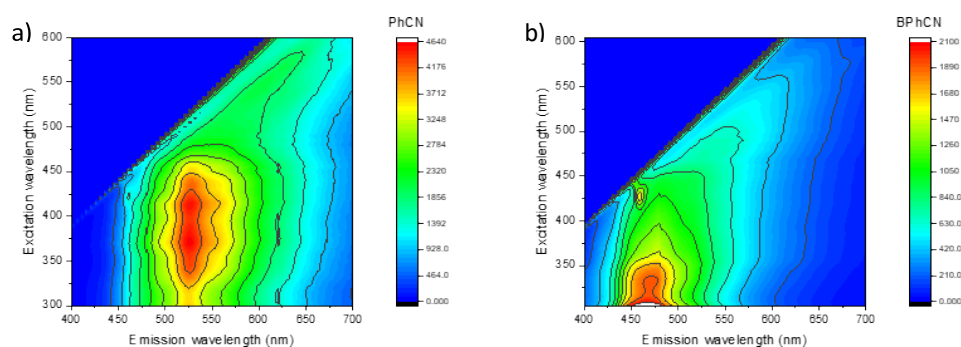


Figure 4.12 3D PL mapping of a) PhCN and b) BPhCN.

PL mapping of both PhCN and BPhCN was carried out with excitations from 300- 600nm as shown in **Figure 4.12**. The measurement of PhCN was carried out with a 10% filter at the excitation window of the spectrofluorimeter while no such filter was used for BPhCN's measurement.

From our previous studies, it was well established that PhCN is a fluorescent material with a broad luminescence spectrum centered at 525nm. It was observed that with B-doping, the PL spectra was blue-shifted significantly which ensures that the band gap was increased. Low emission was observed at visible-light excitations as the sample BPhCN is not responsive (does not absorb significantly) to those wavelengths. The PL counts in BPhCN was much lower than that of PhCN. This could be from the defect states introduced in the framework which also act as trap states for the charge-carriers and lowers the radiative recombination.

TRPL

It was observed in the steady-state photoluminescence study that higher energies result in radiative recombination in BPhCN, the higher the energy- more PL counts are generated. Hence, we performed time decay studies of PhCN and BPhCN using two excitation wavelengths- 440nm and 380nm as shown in **Figure 4.13 a,b**.

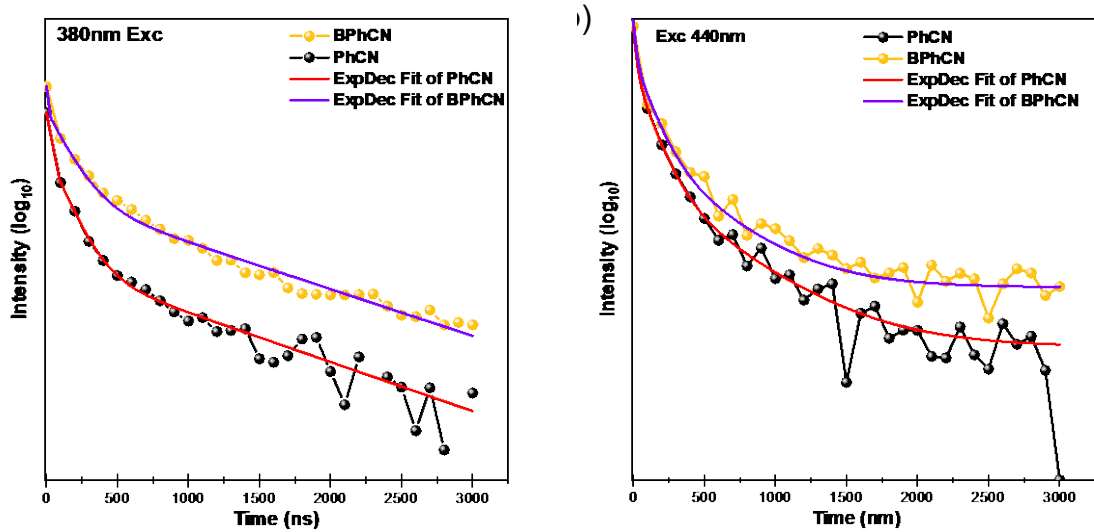


Figure 4.13 TRPL data of BPhCN and PhCN in a) 380nm excitation and b) 440nm excitation.

The fluorescence of carbon nitrides are easily observed phenomenon, with an average lifetime typically in the nanosecond range.³⁵ It is often determined through non-single exponential PL decays, suggesting that multiple factors contribute to the overall spectrum and that non-radiative pathways are present. We assumed the presence of three decays and used the exponential decay function-

$$y = A1 * \exp\left(-\frac{x}{t1}\right) + A2 * \exp\left(-\frac{x}{t2}\right) + A3 * \exp\left(-\frac{x}{t3}\right) + y0$$

to fit the TRPL data of the samples with both excitations. The average lifetime τ_{avg} under 380nm excitation of PhCN and BPhCN are 56.7ns and 106.8ns respectively. The average lifetime τ_{avg} under 440 nm excitation of PhCN and BPhCN are 82.5 ns and 73.1 ns respectively.

We observed a slower PL decay in BPhCN, which suggests that boron-doping introduced defect states or traps that extend the lifetime of photogenerated charge carriers. These defect states could temporarily trap electrons or holes, preventing immediate radiative recombination and thus prolonging the decay time. This longer decay indicates that charge carriers have an extended lifetime in BPhCN.

The difference in decay time between BPhCN and PhCN is more pronounced with 380 nm excitation than with 440 nm excitation, suggesting that 380 nm light is more effective at exciting defect states or specific transitions introduced by boron doping.

380 nm excitation corresponds to higher-energy photons that are closer to the UV absorption shoulders observed in BPhCN. This indicates that higher-energy excitation is more effective in populating the defect states or mid-gap states introduced by boron, which are not as accessible at lower excitation energies (440 nm).

Therefore, the PL studies indicate that defect states in BPhCN may be more active or involved in recombination processes when higher-energy UV light is used.

Photocatalytic Tests

The photocatalytic Rhodamine B degradation tests were performed under visible- light illumination with PhCN and BPhCN for 5 hours. **Figure 4.14 a,b** shows the UV-Vis absorption spectra of RhB degradation process under white light LED bulb with photocatalyst PhCN and photocatalyst BPhCN respectively. The absorption spectrum of the solution was measured before illumination (T0) and at every hour subsequently (T 1-5) after turning on the light. It was observed that BPhCN showed a better RhB degradation under visible light than PhCN. The % concentration of RhB degraded after 5 hours by PhCN was ~20%, while for BPhCN it was ~40%. Therefore, the efficiency of PhCN to degrade the organic dye RhB under visible light illumination increased by two-folds after Boron doping. The calculated rate constants of the photocatalytic dye degradation are $8.7 \times 10^{-4} \text{ min}^{-1}$ for PhCN and $1.8 \times 10^{-3} \text{ min}^{-1}$ which shows a considerable increase in the rate of RhB degradation by the new material with boron (**Figure 4.15a**).

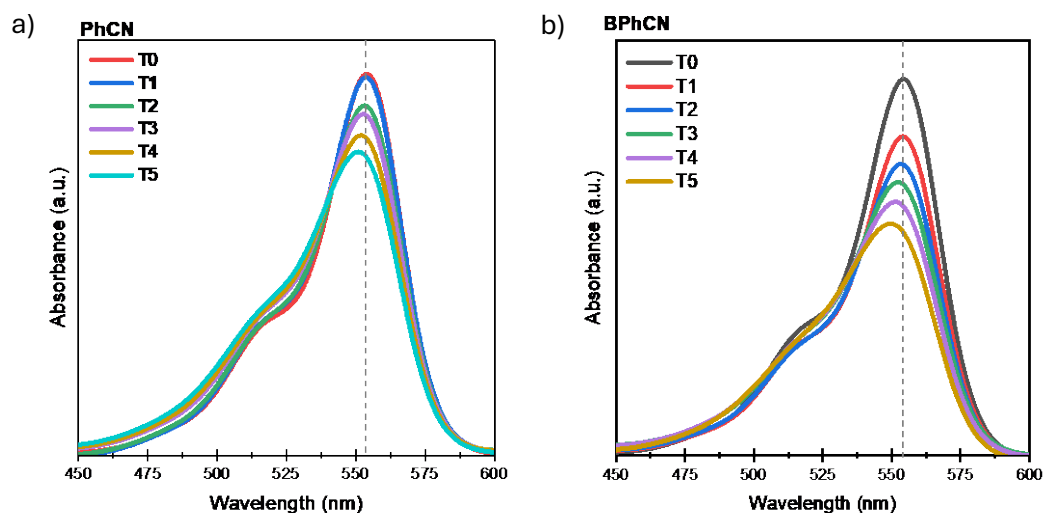


Figure 4.14 Photocatalytic Rhodamine B dye degradation under visible light with a) PhCN and b) BPhCN.

We also did HER tests with BPhCN under 365nm LED and 445nm LED as shown in **Figure 4.14b**. It was observed that BPhCN showed an increase in the H_2 activity when irradiated with UV light. This could be ascribed to its higher UV absorption. From our previous discussions, we came to know that the PhCN tends to lose its photocatalytic HER capability in UV light compared to visible light due to higher charge recombination.

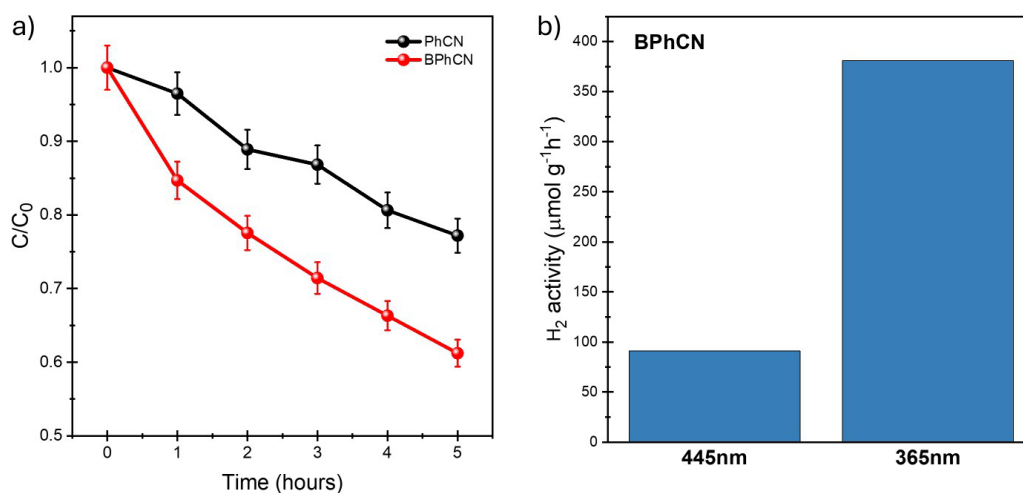


Figure 4.15 a) Photocatalytic Rhodamine B dye degradation, b) Photocatalytic HER

Therefore, it can be said that the doping of Boron pulls the photocatalytic activity of PhCN to the UV region due to the presence of defect states transitions which helps in PL quenching. However, when the H₂ activity of PhCN is compared to that of BPhCN, we observe a diminished performance for HER with Boron doping. This could arise from the presence of multiple band positions at different redox potentials which hamper the ROS generation necessary for the evolution of H₂ gas.

The HER tests of BPhCN show that it is more efficient working in UV irradiation and is not suitable for water splitting reactions due to presence of reactive defect states. On the other hand, this reactivity of the defect states prove beneficial for organic pollutant degradation under visible light.

4.4. Conclusion

By careful structural studies it can be concluded that we were able to synthesize a new Boron-doped PhCN with new chemical, morphological and optical properties. The FTIR, Raman and XPS analyses indicated that boron doping introduced significant modifications in the bonding environment and vibrational characteristics of PhCN. The shifts and new peaks associated with C–N and B–N stretching vibrations reflect boron-induced defect states, which alter electron density and bonding dynamics within the carbon nitride framework. Formation of B–N bonds were confirmed which changed the whole electronic configuration in the carbon nitride framework and introduced many defect levels as observed by the optical studies. This also changes the morphology of the material and increased the surface area and introduced new pores which could result in high adsorption. Due to the electron deficiency of B atoms, B doping into the carbon nitride matrix reduced the electron density of the p-state-conjugated system and lone pair (LP) state of PhCN. This resulted in alterations in the positions of valence states (LUMO) of PhCN and its antibonding orbitals. This redistribution of energy and electrons in the 2D layers of the material resulted in an enlarged bandgap and a blue-shift in the PL spectra

The lower PL intensity and slower PL decay in BPhCN indicated that boron doping effectively suppresses radiative recombination by introducing defect states. These defect states acted as trap sites for electrons and holes, reducing recombination and allowing for a longer lifetime of photogenerated charge carriers. This extended carrier lifetime means that more electrons and holes are available to participate in photocatalytic redox reactions, enhancing the photocatalytic efficiency of BPhCN compared to PhCN. **Table 4.5** summarises the reasons for a better performance of BPhCN from PhCN for photocatalytic dye degradation.

Table 4.5 Comparison of different characteristics of PhCN and BPhCN.

Characteristic	PhCN	BPhCN	Effect on photocatalysis
Charge Separation	Moderate separation, higher recombination	Enhanced separation, slower recombination	Improved efficiency for BPhCN
UV Absorption	Moderate, absorbs UV and some visible	Strong, focused on UV range	Better suited for UV- driven reactions in BPhCN
Surface Area	Lower	Higher	More active sites in BPhCN
Defect States	Fewer defects	Boron-induced defect states	Increased reactivity in BPhCN

BPhCN exhibits a superior photocatalytic activity compared to PhCN for RhB dye degradation under visible light. The combination of improved charge separation, enhanced UV absorption, higher surface area, and defect-driven reactivity makes BPhCN a more effective photocatalyst, especially in environments where UV light is the primary illumination source, and a high number of reactive sites are needed.

The slower PL decay in BPhCN, especially at 380 nm excitation, confirms that boron doping effectively introduces defect states that trap charge carriers, extending their lifetimes. This effect is more prominent with higher-energy UV excitation, suggesting that these defect states interact more with higher-energy photons. For photocatalytic applications, this longer carrier lifetime and the optimal excitation around 380 nm make BPhCN a potentially more efficient material for UV-driven processes, as it can utilize photogenerated carriers more effectively for surface reactions.

In photocatalytic materials, excitons (electron-hole pairs) play a crucial role in driving chemical reactions. When PhCN is exposed to light, it absorbs photons and generates excitons. For efficient photocatalysis, these excitons must dissociate into free electrons and holes, which then participate in redox reactions. However, in PhCN, excitons tend to recombine rapidly due to their strong binding energy, limiting the availability of free charge carriers and reducing overall photocatalytic efficiency.

Boron doping creates defects that significantly alter its electronic structure and charge distribution. By introducing boron atoms, defect levels are formed within the band structure, which disrupts the regular arrangement of electrons around the heptazine rings. This disruption weakens the excitonic effect by creating sites where excitons can dissociate into free charge carriers.

These boron-induced defect sites act as localized traps for electrons or holes, effectively extending the lifetime of these charge carriers and preventing rapid recombination. The presence of these defects enhances the separation of photoinduced electron-hole pairs,

which is critical for boosting photocatalytic efficiency. The increased availability of free electrons and holes at the surface allows for more efficient interaction with Rhodamine B molecules, improving reaction rates in photocatalytic RhB dye degradation.

Hence the novel Boron-doped Phenyl carbon nitride is a promising photocatalyst which can be used as a targeted pollutant remover under both UV and visible-light.

Chapter 5

Conclusion

This study extensively explored the development and application of phenyl- modified carbon nitride (PhCN) for environmental remediation and energy applications, addressing key challenges such as limited light absorption and high charge recombination. Each chapter presented targeted modifications to improve the photocatalytic performance of PhCN, yielding promising results.

In Chapter 2, the hybridization of exfoliated PhCN with 2D WS₂ demonstrated a 42-fold enhancement in hydrogen production under visible light than only using the exfoliated PhCN without any addition of co-catalyst. This success is attributed to effective charge separation facilitated by WS₂ as a co-catalyst, providing a sustainable alternative to expensive noble metals like platinum.

Chapter 3 highlighted the synthesis of PhCN/TiO₂ heterojunctions, which achieved dual photocatalytic applications, including Rhodamine B dye degradation and hydrogen generation, under visible light. Notably, this system also demonstrated the inactivation of H1N1 flu virus in indoor conditions, showcasing its potential for multifunctional environmental applications.

In Chapter 4, boron doping into the PhCN framework resulted in a novel BPhCN material with superior charge separation and enhanced photocatalytic activity for dye degradation under visible-light irradiation. Structural and optical characterizations confirmed the effectiveness of boron doping in improving photocatalyst performance through the abundance of defect states.

The collective findings of this research underscore the success of PhCN modifications in enhancing photocatalytic efficiency for varied purposes in environmental applications. These advancements not only pave the way for sustainable energy production and water remediation but also highlight the versatility of PhCN in environmental applications. Future work can focus on scaling up these systems, exploring other dopants or hybrid materials, and expanding applications to broader environmental challenges, including CO₂ reduction and advanced pollutant management. This study marks a significant step toward developing cost-effective, visible-light-active photocatalysts for global sustainability.

Appendix A – Supporting information for Chapter 2



Figure A.1 Image of PhCN dispersions after 8h sonication in different solvents for liquid phase exfoliation



Figure A.2 Image of WS₂ dispersions after a completed exfoliation in IPA followed by centrifugation.

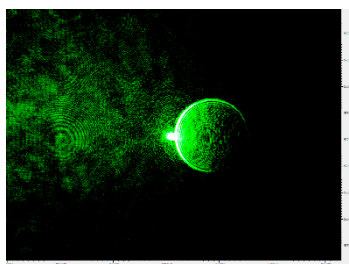


Figure A.3 Image of LASER 532nm focus on WS₂_1 dispersion for Raman spectroscopy.

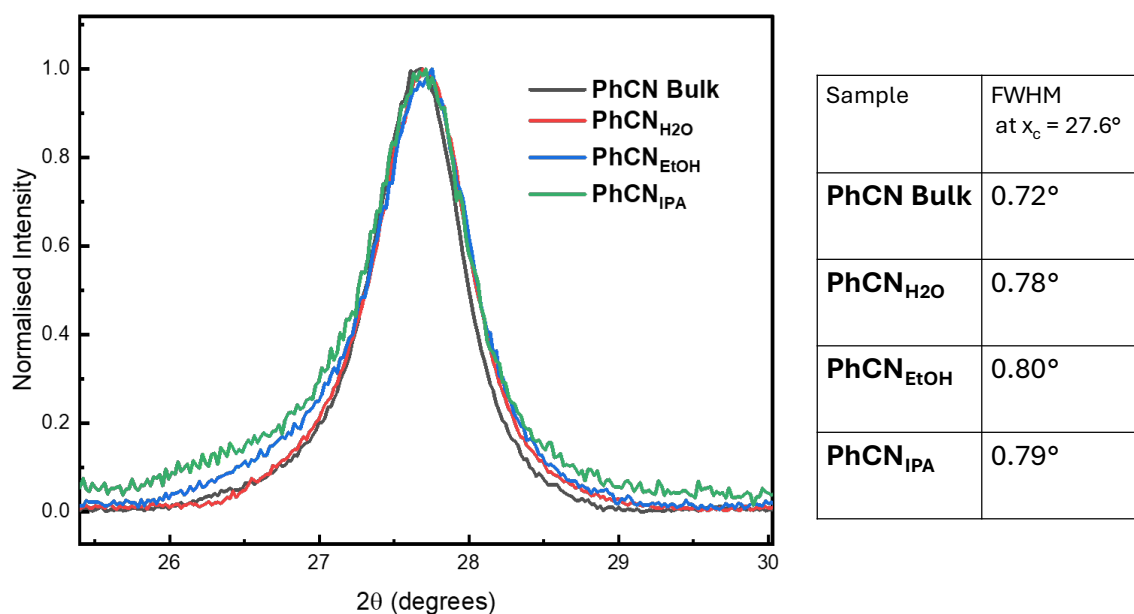


Figure A.4 XRD graph of PhCN Bulk compared to exfoliated PhCN samples with normalized intensity and calculated fwhm for the dominant peak at 27.6° .

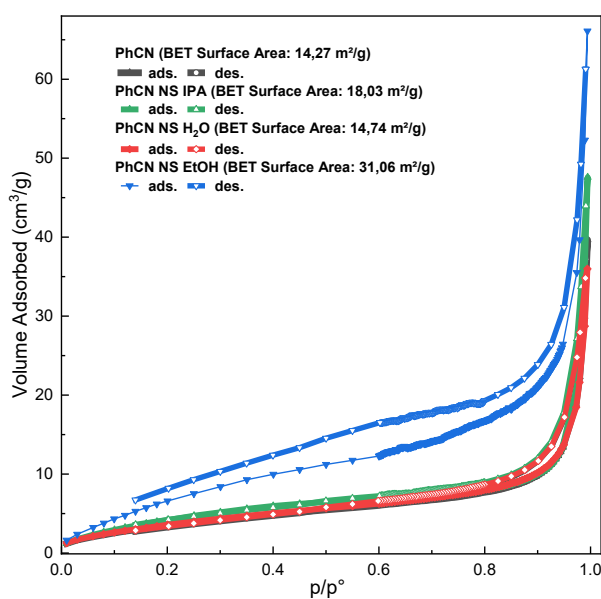


Figure A.5. N_2 adsorption isotherms of PhCN Bulk and the exfoliated versions.

Bulk PhCN shows non-porosity and a low surface area by the N₂ sorption measurements and shows a type H3 adsorption hysteresis curve.²⁰⁷ After the exfoliation procedure, the PhCN powders do not show an increase in surface area except for PhCN_{EtOH}. It is known that a porous structure can yield a high specific surface area and high light absorption.¹³¹ However, the PhCN_{EtOH} shows low porosity after an enhancement in the surface area. All the samples show type III hysteresis loops which hints towards a greater degree of agglomeration or a macroporous surface.²⁰⁷ It is concluded that the interparticular distances are very small for all the exfoliated samples due to agglomeration which may arise from the surface tension of the solvents. This aggregation of the nanosheets makes it difficult to accurately measure the porosity through N₂ sorption experiments.

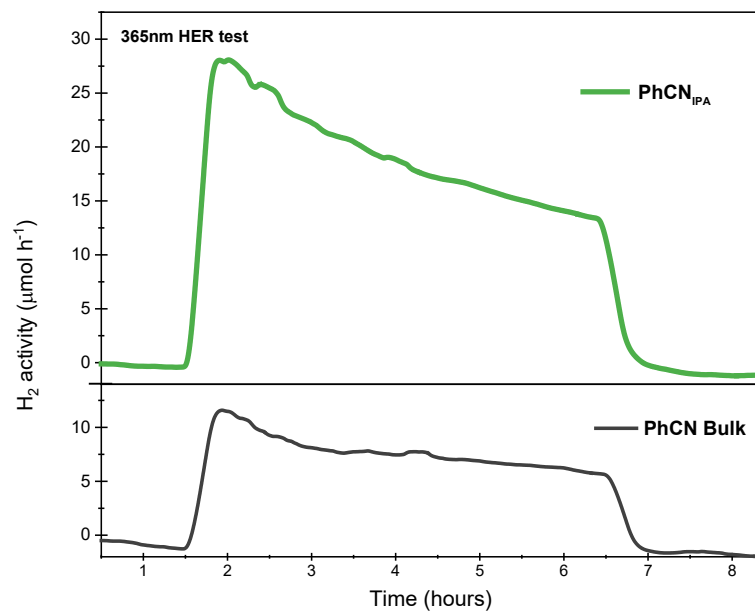


Figure A.6. Continuous HER flow test done with 365nm LED and the H₂ activity was measured for PhCN_{IPA} and PhCN Bulk.

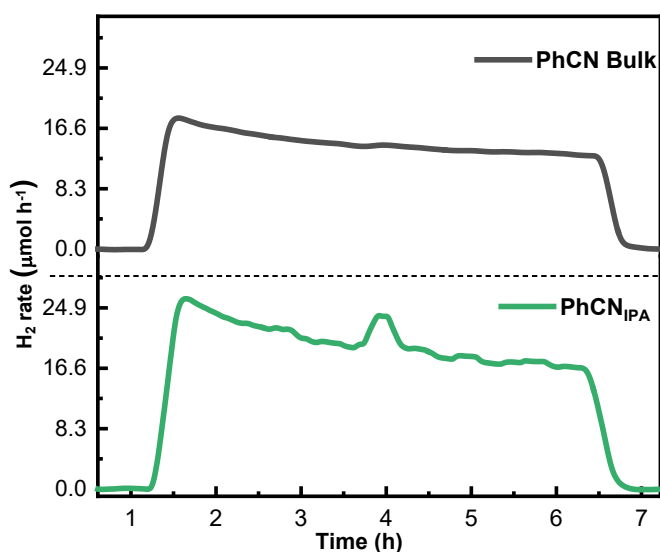


Figure A.7 Continuous HER flow test done with 445nm LED and the H₂ activity was measured for PhCN_{IPA} and PhCN Bulk.

The flow tests of PhCN_{IPA} and PhCN bulk under 365nm and 445nm yield a very important result. While we observe an increase in the H₂ activity with exfoliation under both UV and visible light for PhCN, we observe that PhCN Bulk loses some of the activity in UV but the exfoliated sample's activity was enhanced in UV.

This can be correlated with the PL spectra of the samples where PhCN Bulk shows higher radiative recombinations under UV light and the PhCN_{IPA} sample showed a higher recombination under 445nm.

Hence, we can say that charge carrier recombination is a major factor in the H₂ production activity of PhCN materials.

Appendix B – Supporting information for Chapter 3

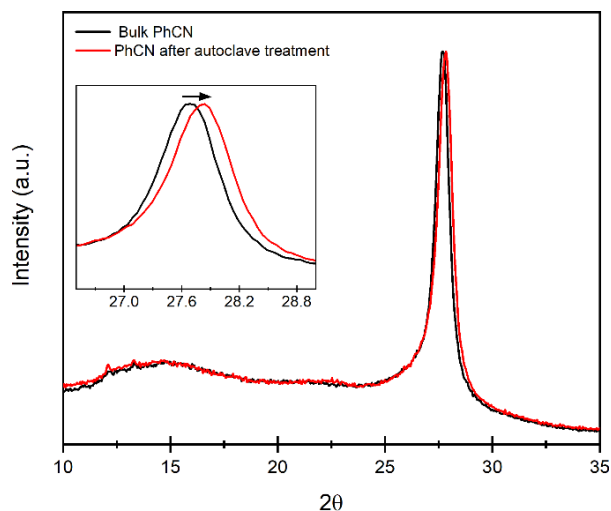


Figure B1 XRD of PhCN before and after the autoclave treatment at 180°C for 8 hours

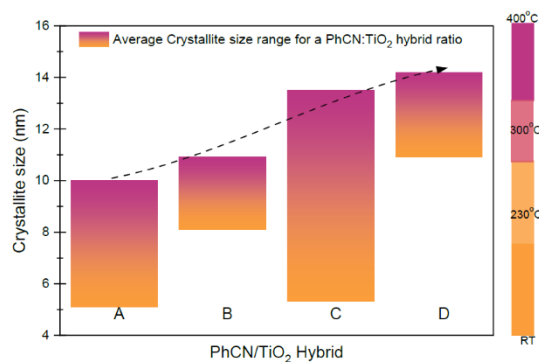


Figure B2 Average crystallite sizes of all the PhCN/TiO₂ hybrids calculated through Scherrer's formula.

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Where:

- D is the average crystallite size.
- K is the shape factor, typically around 0.9.
- λ is the X-ray wavelength.

- β is the full width at half maximum (FWHM) of the diffraction peak (in radians).
- θ is the Bragg angle.

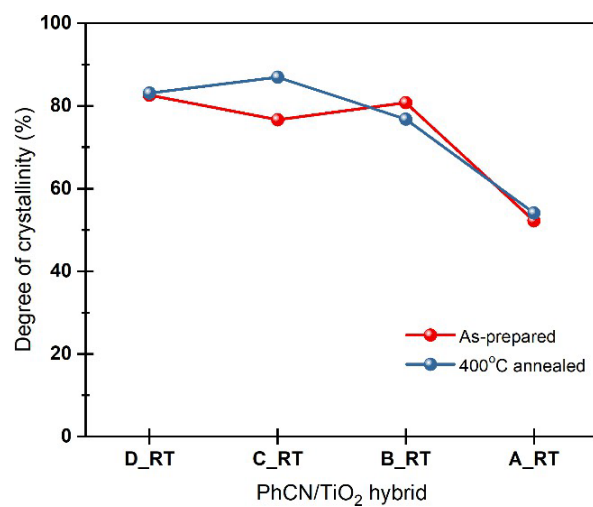


Figure B3 Degree of crystallinity calculated by XRD diffractograms of PhCN/TiO₂ hybrids

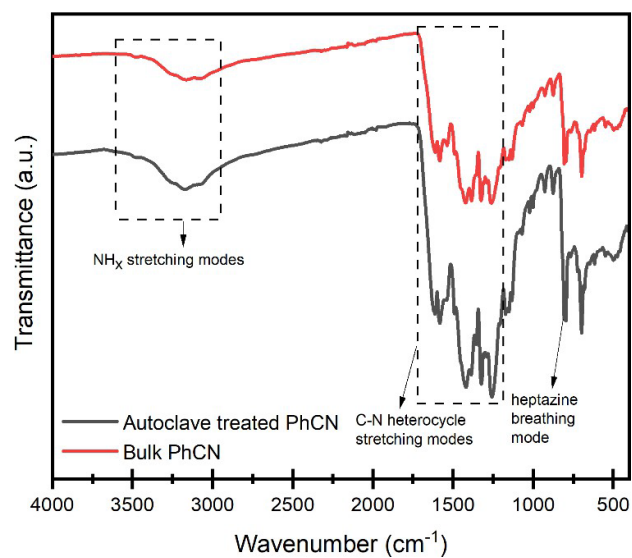


Figure B4 Comparison of FTIR spectra of PhCN pre and post autoclave treatment.

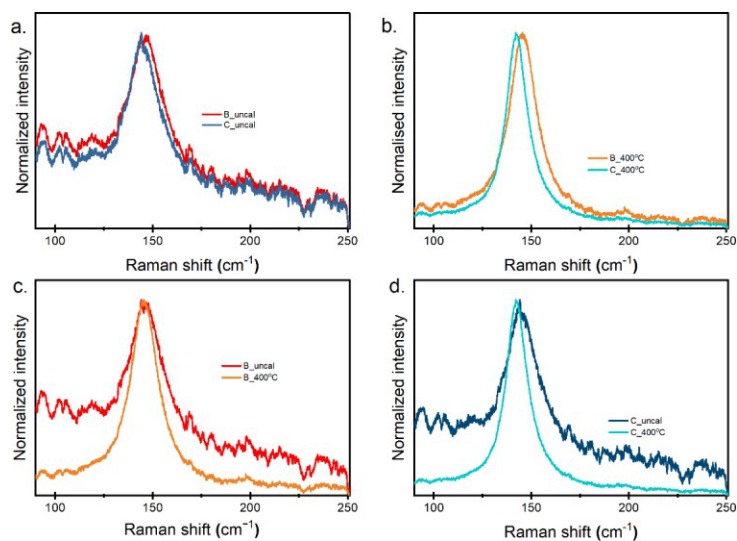


Figure B5 RAMAN spectra obtained by 785nm LASER of PhCN/TiO₂ hybrids

The Raman spectra of the hybrids show the characteristic TiO₂ anatase E_g mode of vibration (**Figure S5**). The shape and position of the TiO₂ Raman modes have been previously correlated with photocatalytic activity through the phonon confinement model which connects the linewidth and position of the Raman modes to the particle size and hence the number of surface-active sites.²⁰⁸ According to the phonon confinement model, the TiO₂ nanocrystals in the hybrid are confined in space with an interrupted lattice periodicity at the particle surface. Because of this, optical phonons present over all of the Brillouin zones contribute to the first-order scattering instead of only the phonons near the centre of the Brillouin zone. When crystal sizes are in the nanometre range, a larger portion of the BZ can participate in scattering processes due to the relaxation of the rule $q_0 \approx 0$.²⁰⁹ The extent of this region in the quasi-momentum space is determined by the confinement of the $q_0 = 0$ phonon wave function. This can be formally explained by considering the modulation of the phonon wave function in an infinite crystal with an appropriate ‘weighting’ function. By expanding this modulation using Fourier integrals, we can calculate the first-order Raman spectrum of nano-sized crystals.

$$I(\omega) = \int_{BZ} \frac{|C(\omega)|}{[\omega - \omega(q)]^2 + \left(\frac{\Gamma_0}{2}\right)^2} dq$$

where $C(q)$ stands for Fourier coefficients of the $q_0 = 0$ phonon wave function, $\omega(q)$ for the phonon dispersion curve and Γ_0 for the intrinsic Raman band linewidth. The equation can be simplified assuming an isotropic dispersion in a spherical BZ:²⁰⁹

$$I(\omega) = \int_0^{\pi/a} \frac{q^2 e^{\frac{-q^2 L^2}{16\pi^2}}}{[\omega - \omega(q)]^2 + \left(\frac{\Gamma_0}{2}\right)^2} dq$$

where ‘L’ stands for the particle size and ‘a’ for the lattice parameter. On this basis the confinement effect can be observed in the position and shape of the Raman E_g mode at 144 cm⁻¹. As the diameter of the particles decreases, the maxima of the Raman peak corresponding to the E_g vibration mode shift to higher wavelength values which is observed in the hybrids with increasing TiO₂ amounts.²¹⁰⁻²¹² Consequently, a broadening of this vibration mode and an increase in asymmetry toward higher wavelength values can also be observed. As expected, the heat treatment of hybrids progressively decreases the FWHM of the Raman mode and shifts it to lower frequencies indicating an increase in particle size which is consistent with the XRD measurements. Similar trend is observed in pristine TiO₂ nanoparticles when annealed (**Figure S6**) which guarantees that the shifts observed in the hybrids are the result of phonon confinement in TiO₂ nanocrystals.

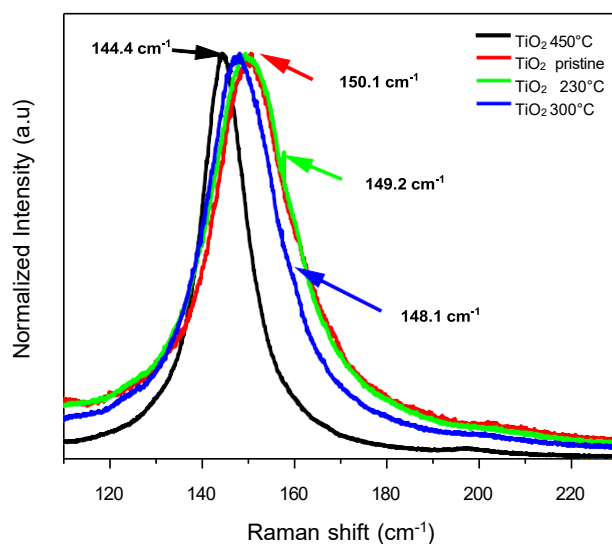


Figure B6 RAMAN E_g spectra of TiO₂ nanoparticles annealed at different temperatures.

Table B1 Comparison of %PhCN present in the as-prepared hybrids calculated from TGA and measured experimentally

S.No	Sample	% PhCN from TGA	%PhCN from weight measurement after synthesis
1	A_RT	40.8	66.7
2	B_RT	21.8	26.3
3	C_RT	8.9	13.3
4	D_RT	2.7	6.3

The TGA curves of autoclave treated PhCN does not show any distinction to the same of bulk PhCN. When a hybrid is annealed in the presence of oxygen, the O vacancies of TiO₂ are lessened leading to less adsorption of organic molecules on the surface with the nanocrystals' size. Growth. This rapid and prolonged growth of the small TiO₂ crystals is in all directions on the surface of PhCN nanosheets, which leads to their rupture and probable loss of chemical integrity. Hence, the characteristic PhCN mass loss dip between 500-650°C is very low in the hybrid B_400.

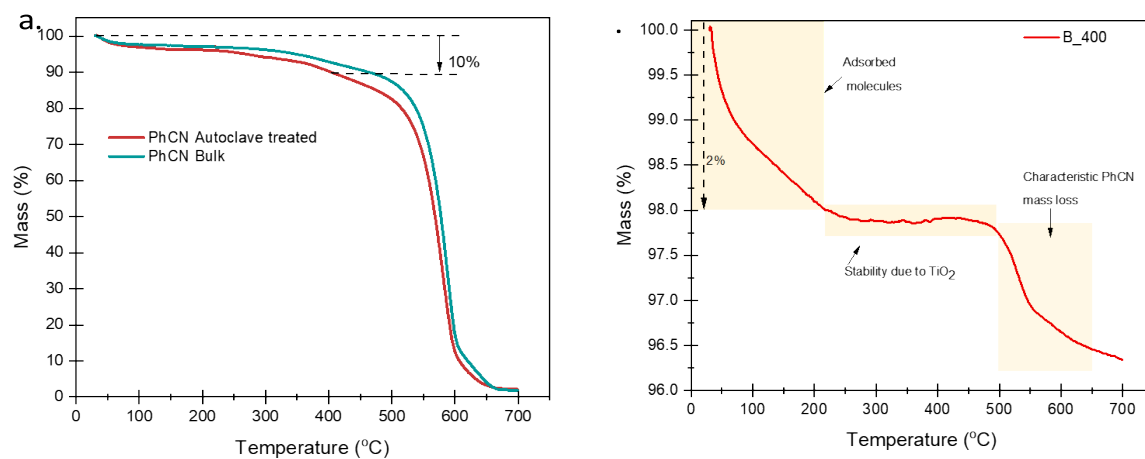


Figure B7 TGA Curves of a) PhCN Bulk and autoclave treated, b) Hybrid B_400

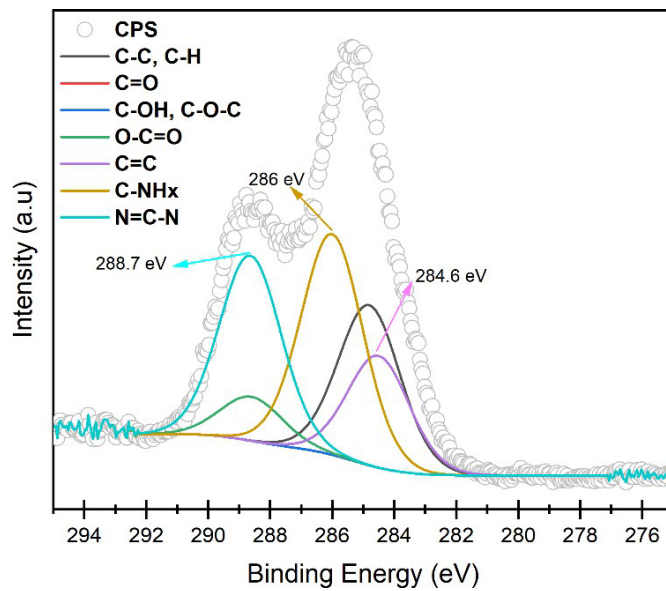


Figure B8 XPS N1s edge of pristine PhCN

The amount of N present on the surface of the hybrids decreases with increasing TiO₂ loadings. While barely little amounts of Ti are found on the surface of A_RT, the hybrid B_RT shows an equal distribution of N and Ti on its surface. Even with extremely high TiO₂ content in hybrid D_RT, N still shows up on the surface but is too small signal to have a trusting deconvolution.

Table B2 Atomic % of N and Ti found on the surface of the as-prepared hybrids through XPS measurements.

<i>Sample</i>	<i>N (atomic %)</i>	<i>Ti (atomic %)</i>
<i>PhCN</i>	32.89	0
<i>A_RT</i>	27.42	4.64
<i>B_RT</i>	14.85	14.53
<i>C_RT</i>	2.6	17.87
<i>D_RT</i>	3.5	24.8
<i>TiO₂</i>	0	21.96

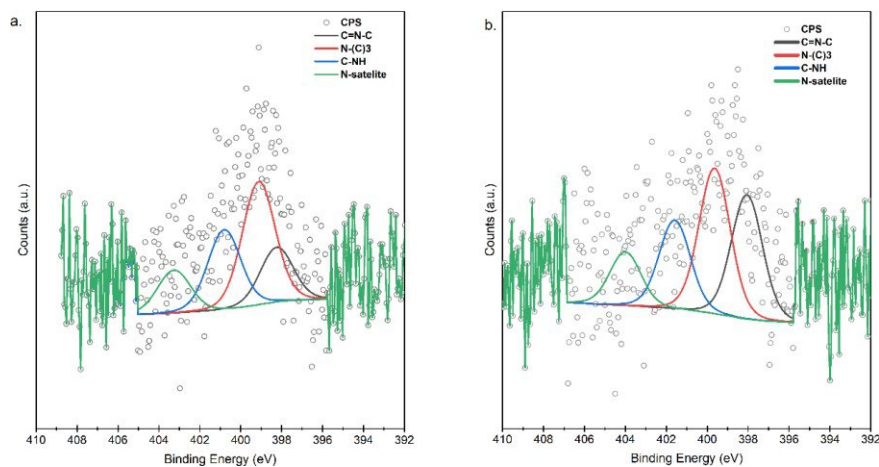


Figure B9 N1s edge spectra of a. C_RT and b. D_RT

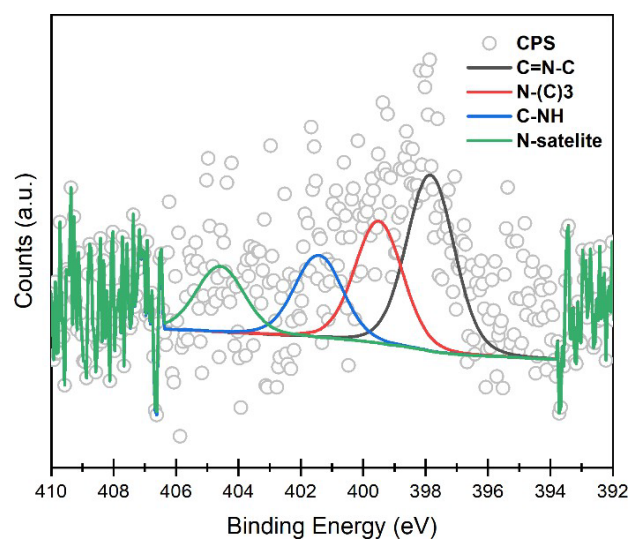


Figure B10 XPS N₂s edge of hybrid B₄₀₀

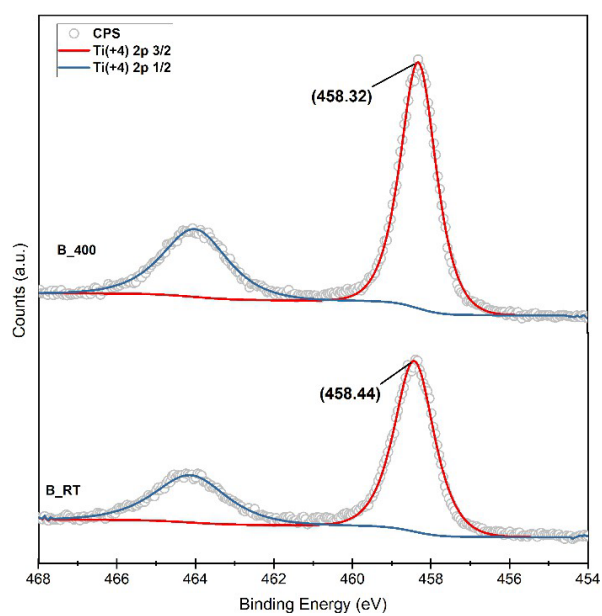


Figure B11 XPS Ti₂p edge of hybrid B₄₀₀ compared with B_{RT}

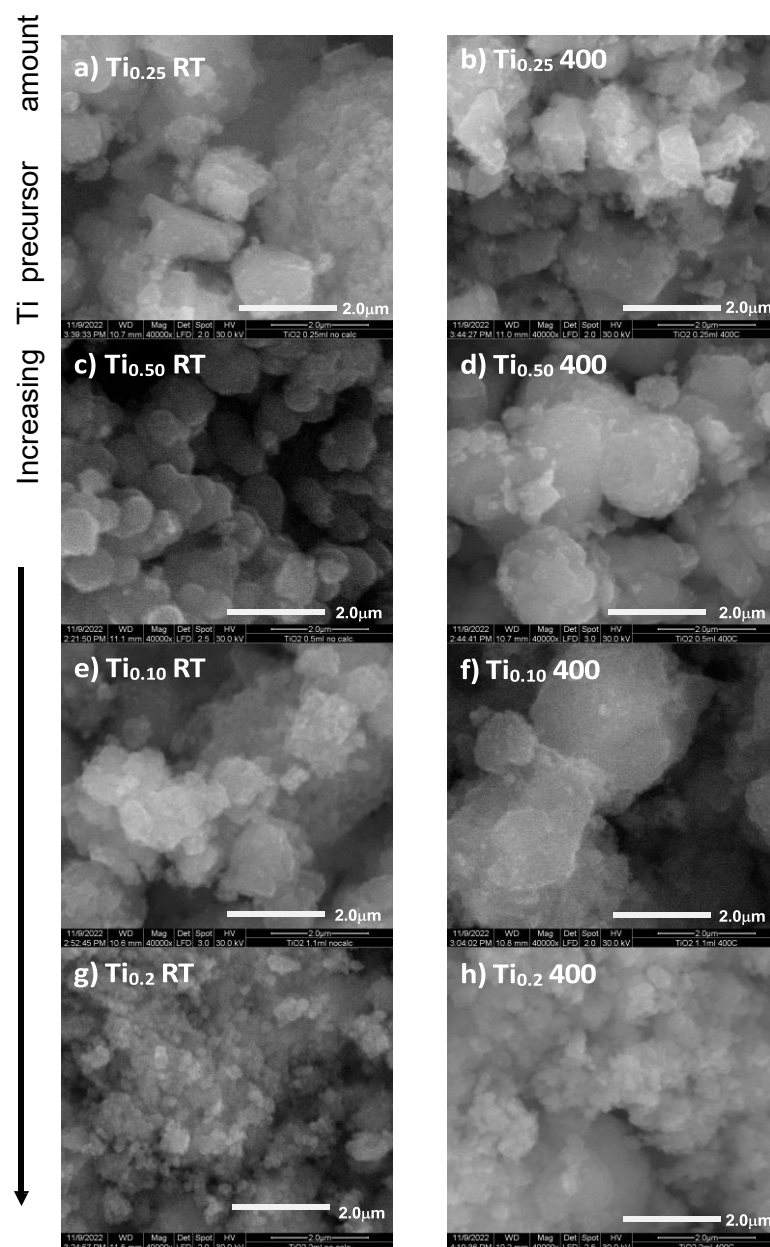


Figure B12 SEM images of TiO_2 nanoparticles prepared with different amounts of TiCl_4 precursor pristine and annealed at 400°C

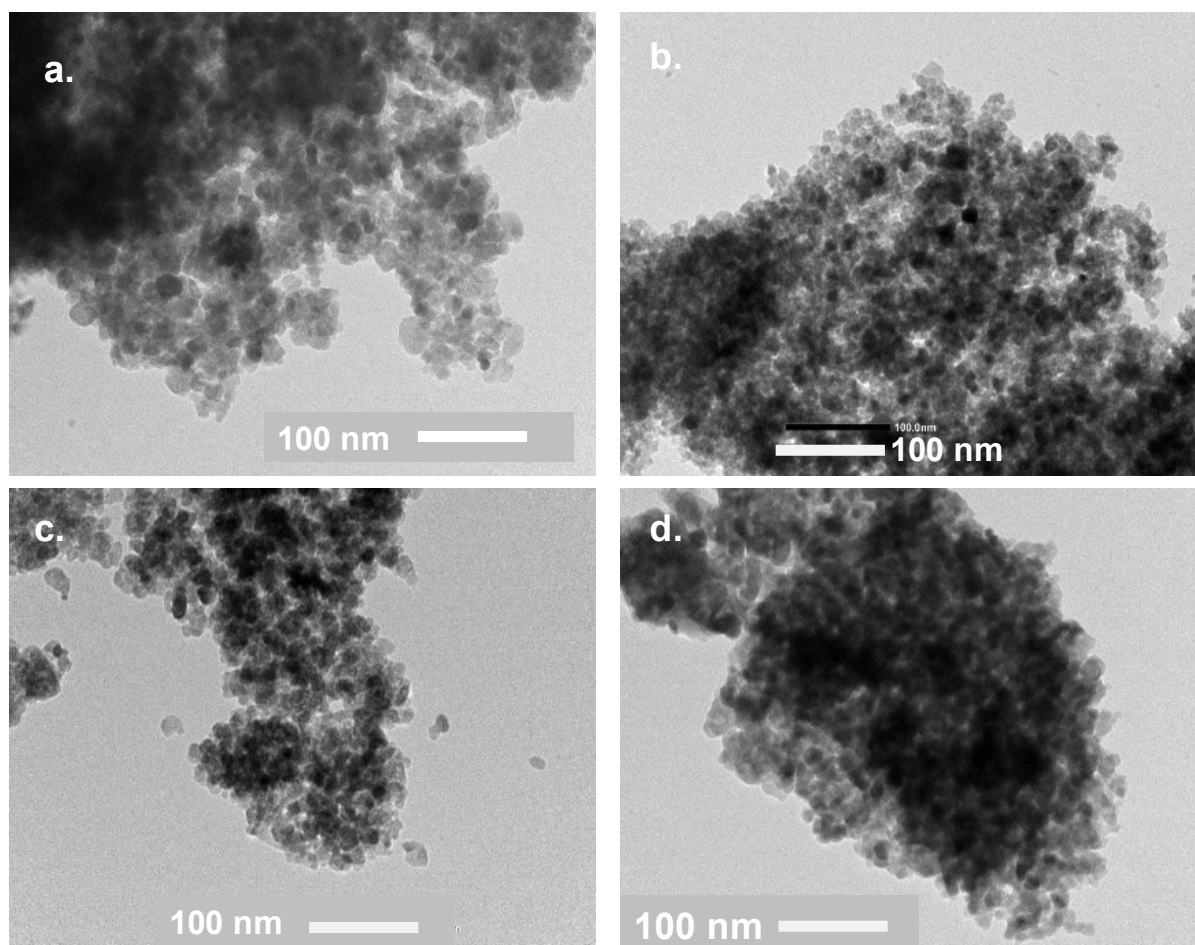


**Figure B13 TEM images of TiO₂ nanoparticles annealed at different temperatures
a) pristine, b)230 °C, c)300 °C, d)450 °C**

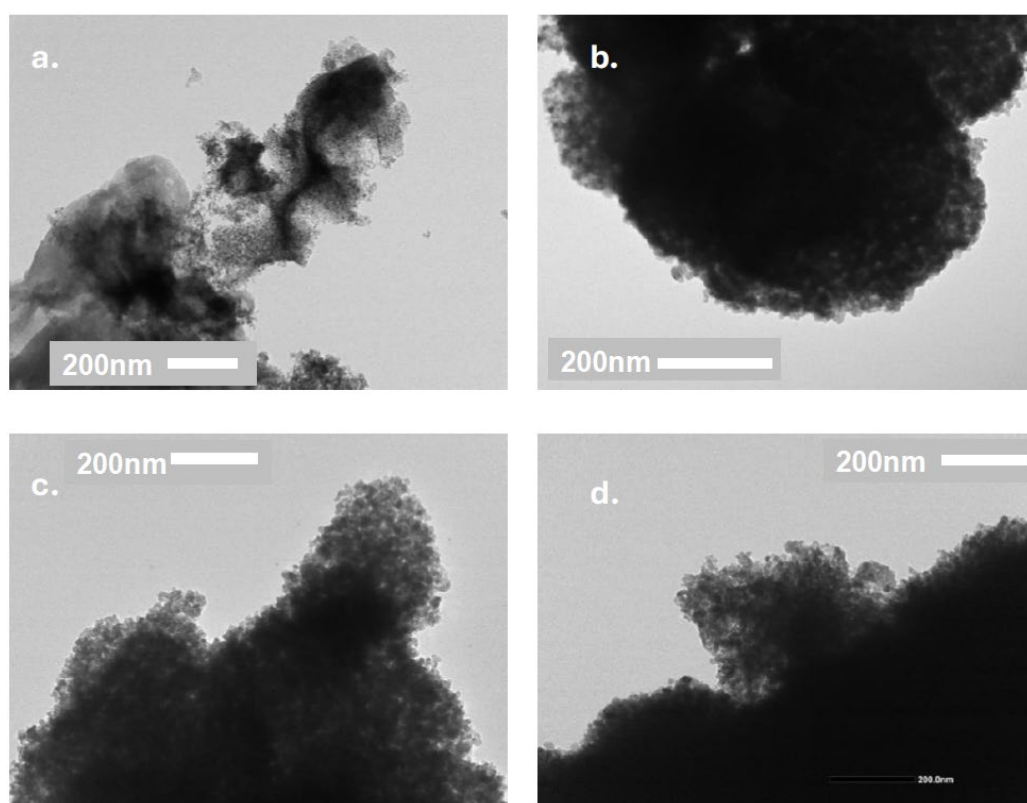


Figure B14 TEM images of PhCN/TiO₂ hybrids a. A_400, b.B_400, c.C_400, d.D_400

.D_4

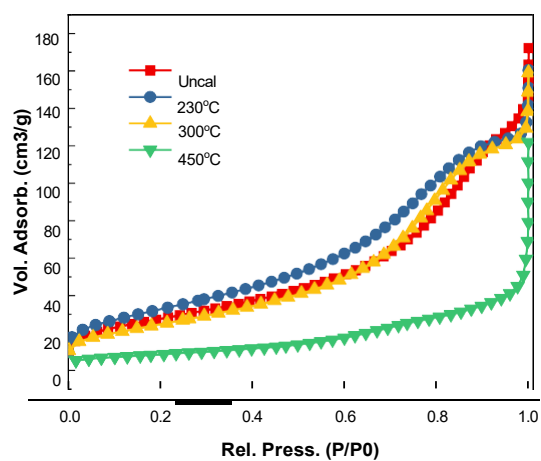


Figure B15 N₂ adsorption curve of TiO₂ nanoparticles annealed at different temperatures.

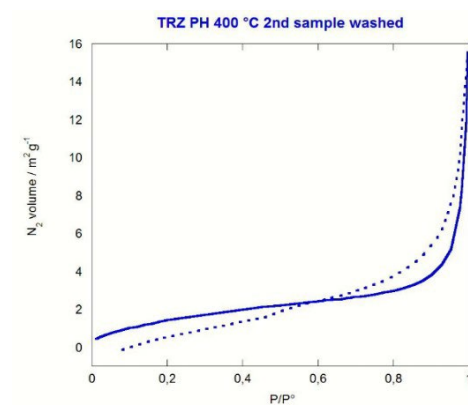


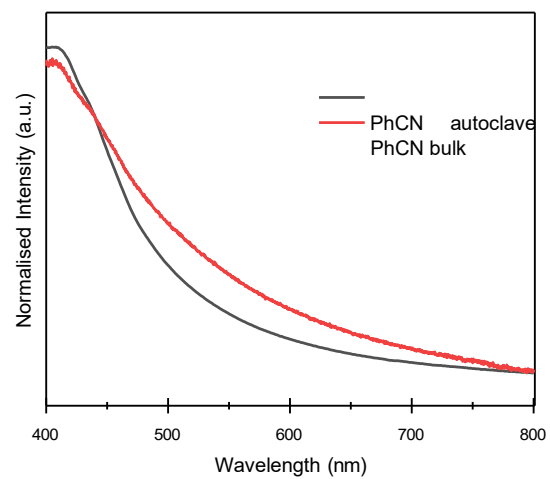
Figure B16 N₂ adsorption-desorption isotherm of PhCN bulk.

Table B3 BET and BJT calculated surface area and pore volume respectively for hybrid series C.

Sample	Pore volume (cm³g⁻¹)	Specific surface area (m²g⁻¹)
C_RT	0.29	212
C_230	0.29	108
C_300	0.29	85
C_400	0.39	29

Table B4 BET and BJT calculated surface area and pore volume

Sample	Surface area (m²g⁻¹)	Pore volume (cm³g⁻¹)
PhCN	5.9	---
A_RT	91	0.05
D_RT	119	0.22
TiO ₂	101.6	0.22



FigureB17 Absorbance spectra of autoclave treated PhCN and Bulk PhCN.

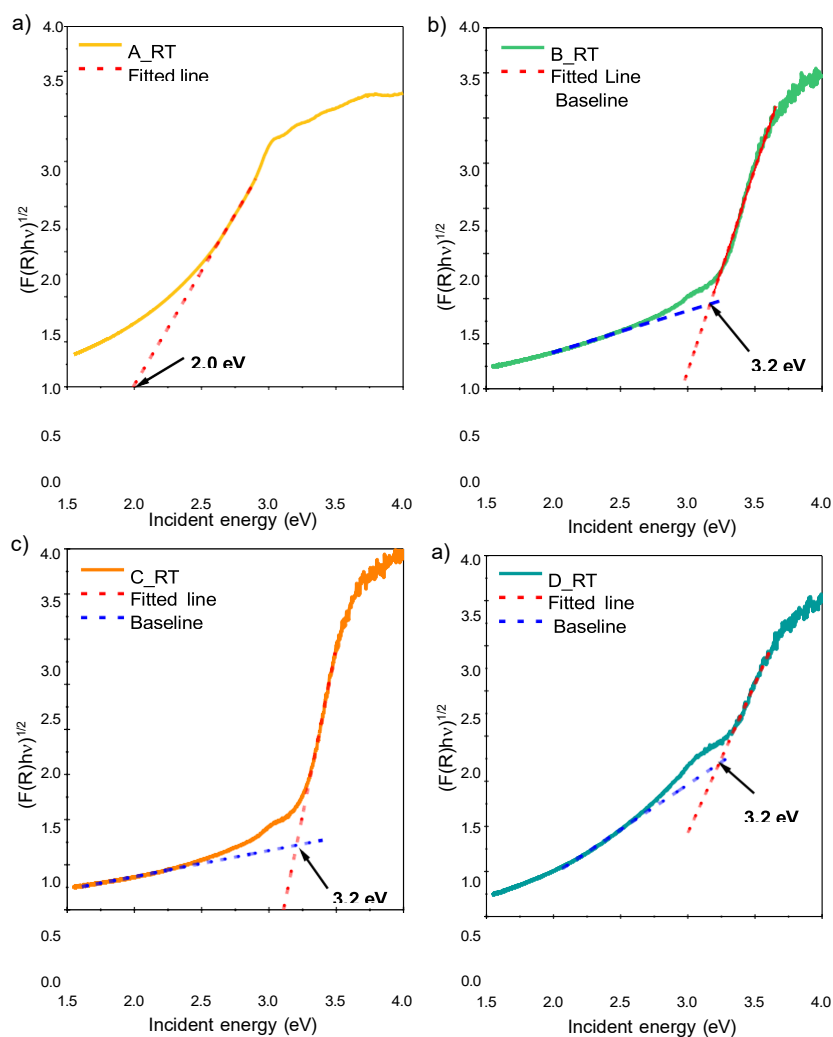


Figure B18 Tauc plots determining optical bandgaps of a) hybrid A_RT, b) hybrid B_RT, c) hybrid C_RT and d) hybrid D_RT.1

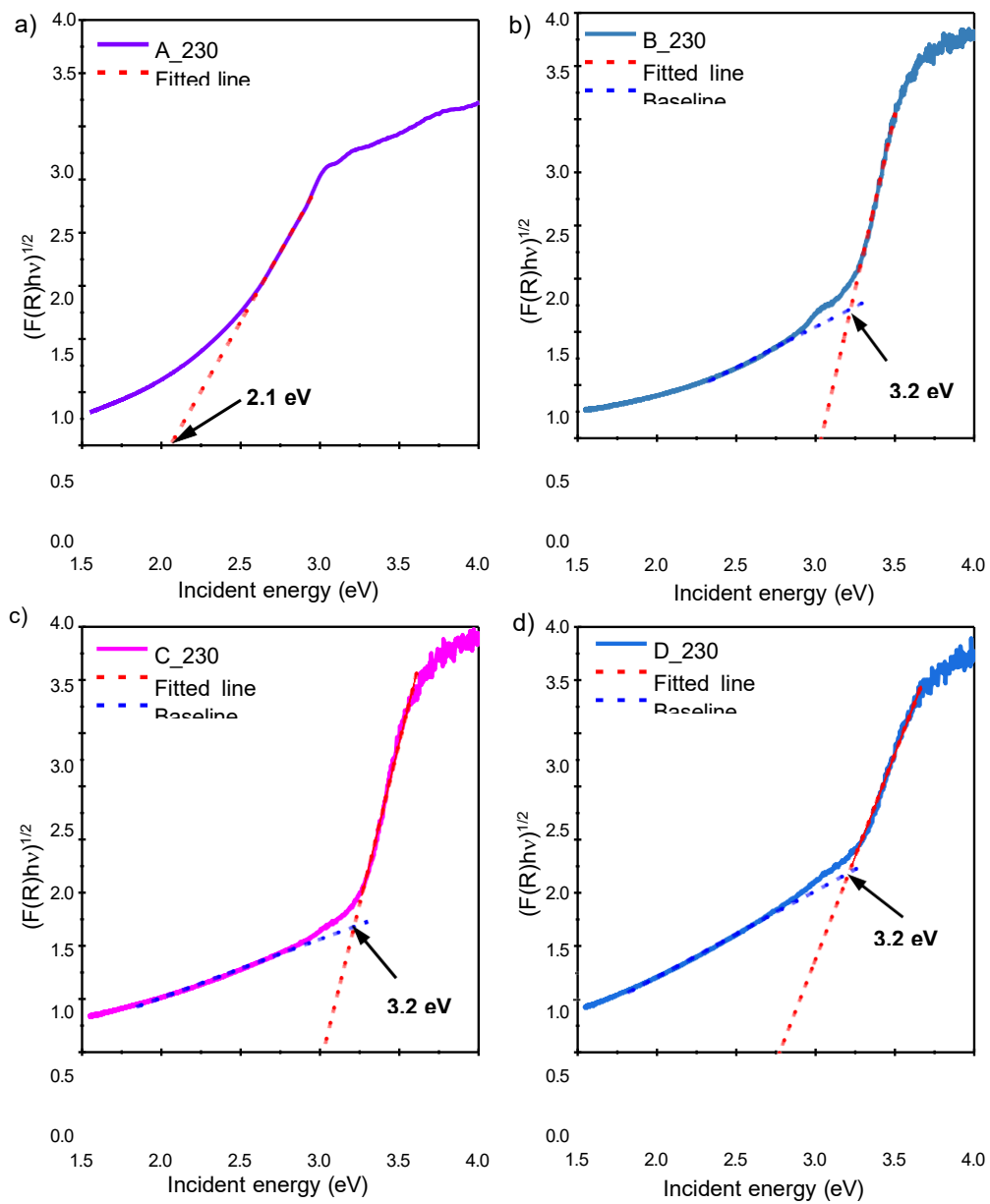


Figure B19 Tauc plots determining optical bandgaps of a) hybrid A_230, b) hybrid B_230, c) hybrid C_230 and d) hybrid D_230

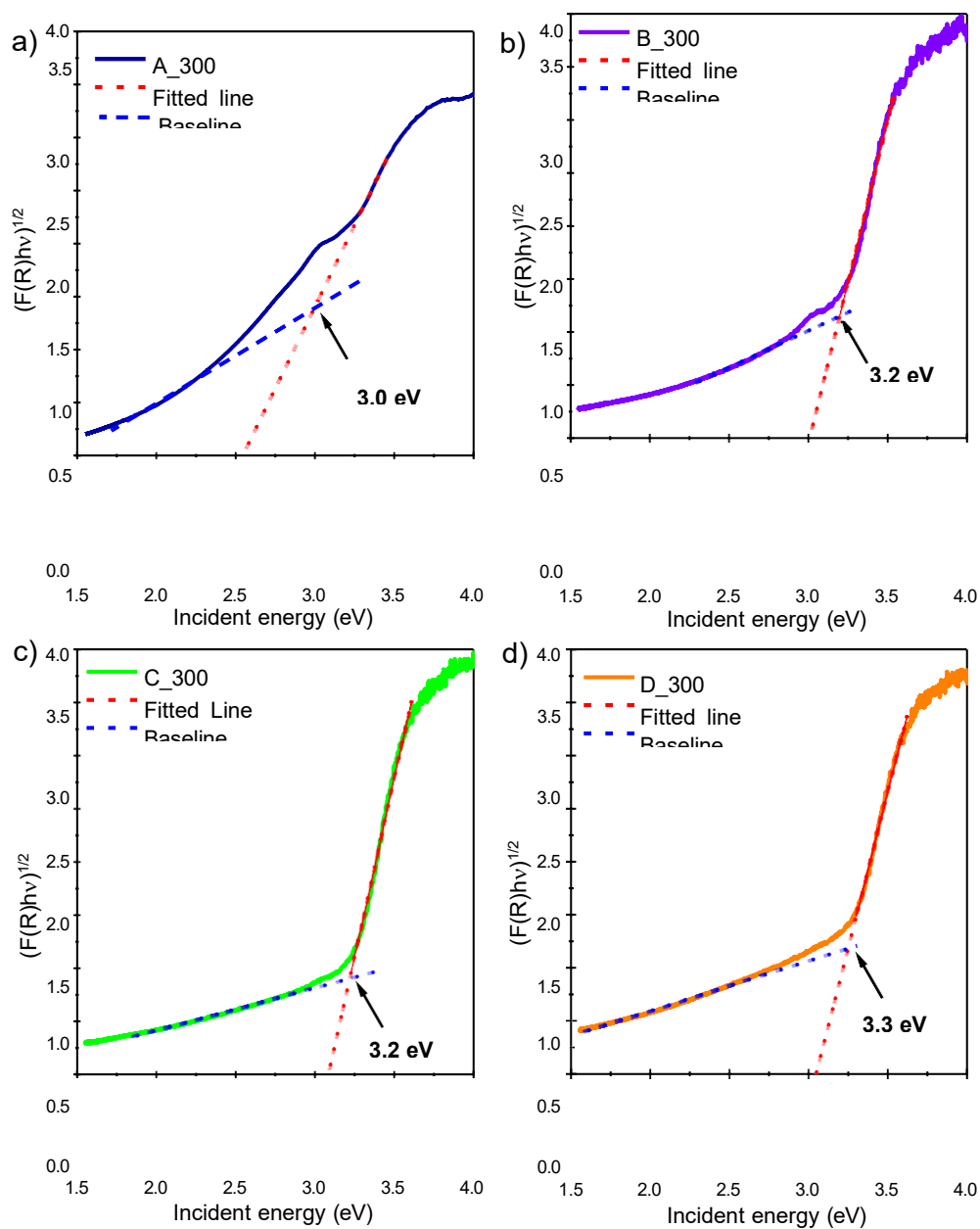


Figure B20 Tauc plots determining optical bandgaps of a) hybrid A_300, b) hybrid B_300, c) hybrid C_300 and d) hybrid D_300

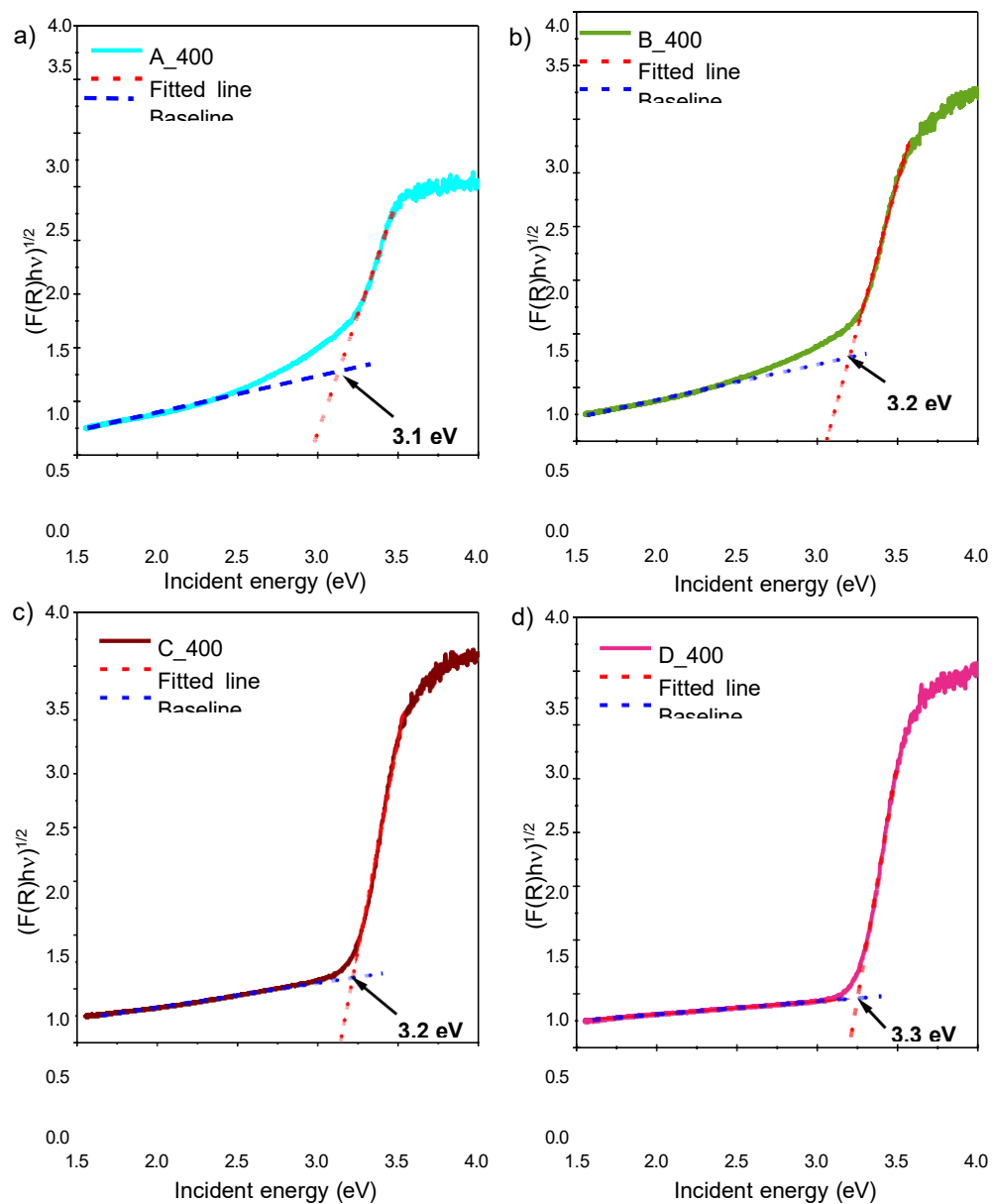


Figure B21 Tauc plots determining optical bandgaps of a) hybrid A_400, b) hybrid B_400, c) hybrid C_400 and d) hybrid D_400

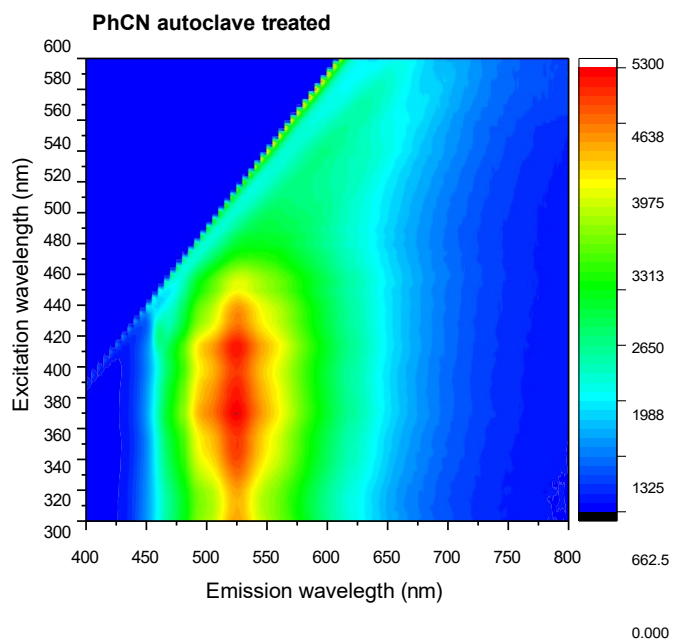


Figure B22 3D fluorescence map of autoclave treated PhCN

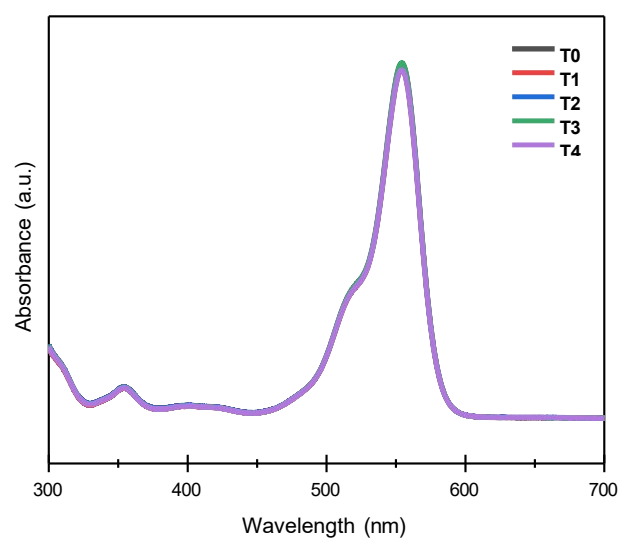


Figure B23 Uv-Vis absorption spectra of Rhodamine B dye kept under white light source for 4 hours.

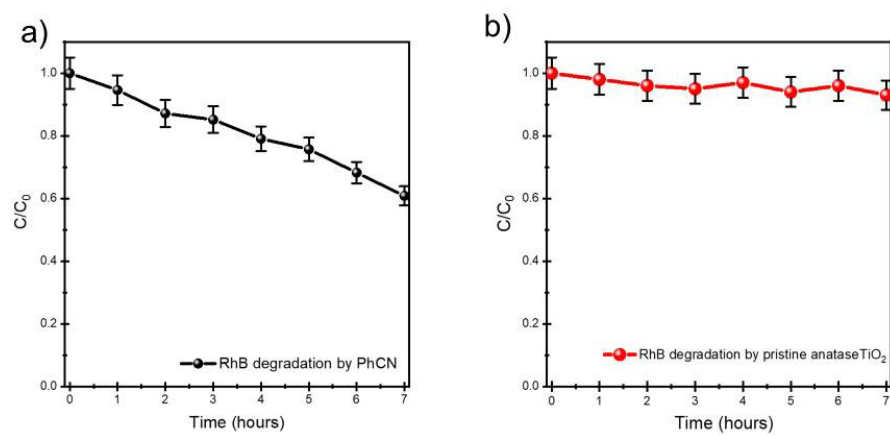


Figure B24 RhodamineB dye degradation tests under vis-light with a)pristine PhCN and b) pristine TiO_2

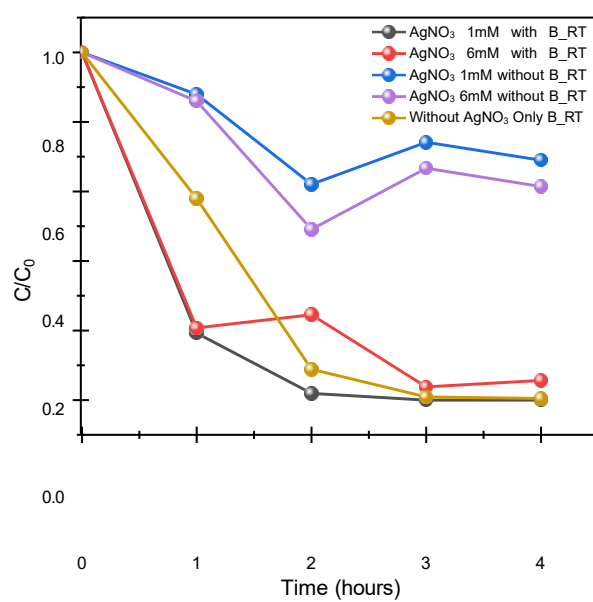


Figure B25 Rhodamine B degradation tests with AgNO_3

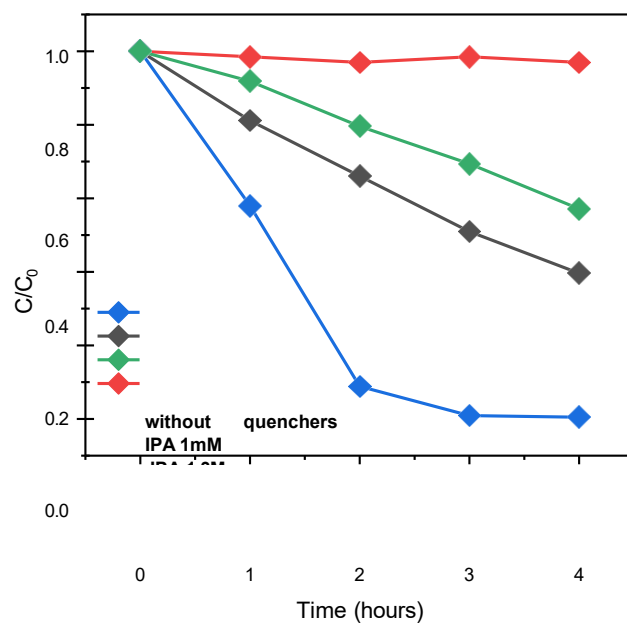


Figure B26 Quenching tests with IPA as a scavenger for OH[·] radicals, with different concentrations.

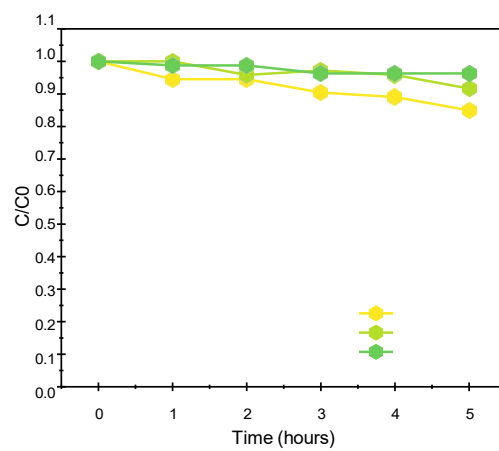


Figure B27 Quenching tests with TEOA

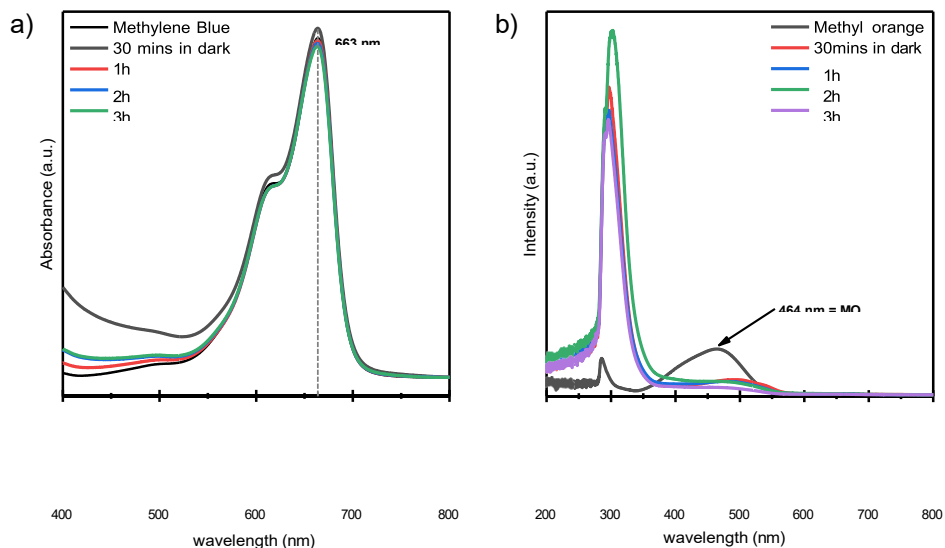


Figure B28 Methylene blue and b)Methyl orange dye degradation tests under white light with B_RT

Photocatalytic degradation performance of PhCN/TiO₂ hybrid B_RT has been done with Methylene blue (MB), Methyl orange (MO) and Rhodamine B (RhB) organic pollutants. The graphs for MB and MO have been added as Figure S36 in the supporting information file.

It was observed that the hybrid system was not able to degrade MB in 3 hours to any extent. It is to be noted that MB has absorption peaks at 664nm and 610nm and does not absorb at 445nm. We did not observe any adsorption of the MB dye on the surface of the photocatalyst. Therefore, the photocatalytic system showed barely any interaction with MB which is a cationic dye. On the other hand, tests with anionic MO showed a very high level of adsorption (over 60%) in 30 mins and got completely degraded in 3 hours. The MO dye absorbs at 464nm.

These results show that the surface of the hybrid B_RT is supposedly highly positive in nature as it could not adsorb MB molecules due to electrostatic repulsion and adsorbed MO readily due to high electrostatic attraction. The quenching tests also showed the dominance of holes in the RhB degradation pathway which can add to the positive charge of the surface of the photocatalyst.

The RhB dye absorbs at 554nm and does not absorb 445nm like MB. It is predominantly known as a cationic dye like MB but interacts very well with our photocatalyst. This is because at higher pH levels, RhB⁺ undergoes deprotonation and forms its zwitterionic state which prevents quenching of the active sites and

electrostatic repulsion with the photocatalyst. Basic pH conditions can facilitate the generation of $\bullet\text{OH}$ radicals, enabling degradation through an $\bullet\text{OH}$ radical oxidation mechanism. These factors collectively enhance the degradation of RhB and its reaction intermediates. The existence of zwitterionic RhB indicates that our reaction medium was basic which ultimately was useful for H_2 generation.

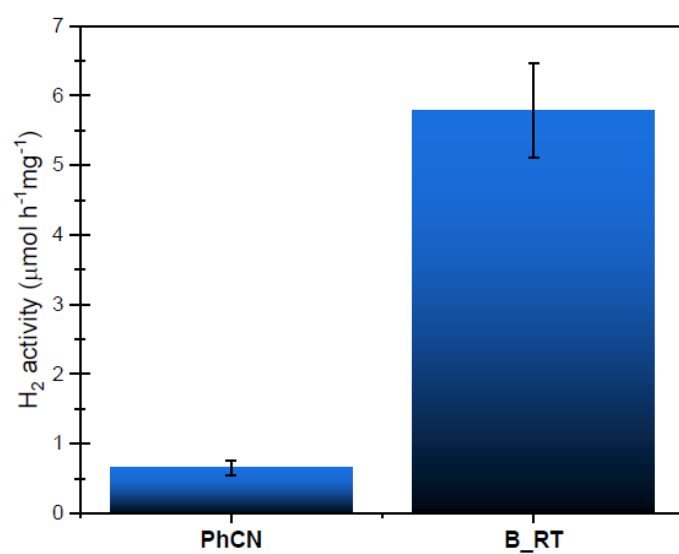


Figure B29 The HER activity of PhCN compared with hybrid B_RT under 445nm.

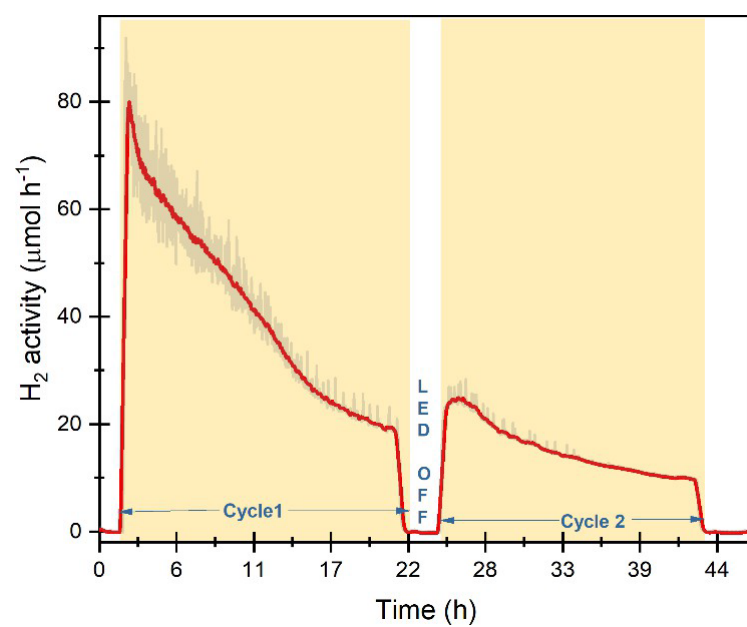


Figure B30 H₂ production test with hybrid B_RT for 44 hours continuously

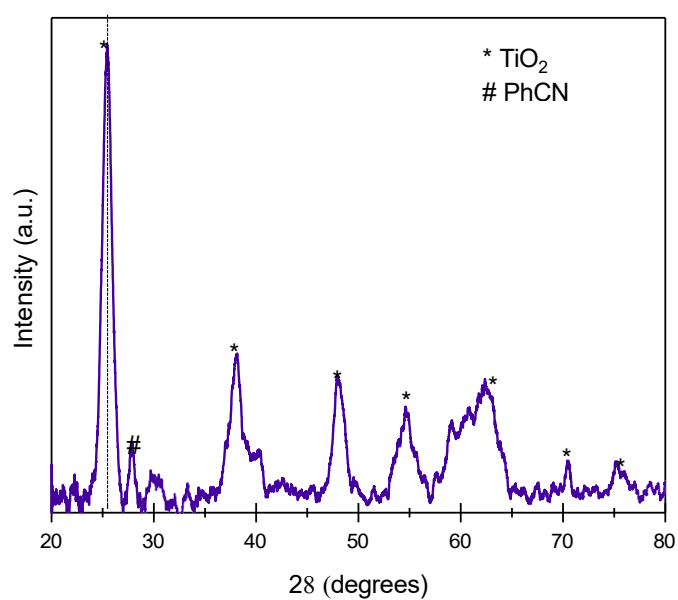


Figure B31 XRD of hybrid B_RT retained after 44 hours flow Her test.

Bibliography

1. Regional Office for Europe, W.; Health Organization, W. *Nature, Biodiversity and Health: AN OVERVIEW OF INTERCONNECTIONS WHO Collaborating Centre on Natural Environments and Health*; 2021.
2. UNESCO World Water Assessment Programme. *The United Nations World Water Development Report 2024: Water for Prosperity and Peace*; 2024.
3. Ren, G.; Han, H.; Wang, Y.; Liu, S.; Zhao, J.; Meng, X.; Li, Z. Recent Advances of Photocatalytic Application in Water Treatment: A Review. *Nanomaterials*. MDPI AG July 1, 2021. <https://doi.org/10.3390/nano11071804>.
4. - International Energy Agency, I. *Global Hydrogen Review 2023*; 2023. www.iea.org.
5. *Circular Economy Action Plan (CEAP) 2020 Summary for Business Implications and next Steps*.
6. PURE-H2O Project 2024. *Introduction of a drinking water treatment plant*.
7. History of Wp.
8. Sanjay K. Sharma, R. S. *Advances in Water Treatment and Pollution Prevention*, illustrated.; Springer Science & Business Media, 2012, 2012.
9. Bates, M. E.; Grieger, K. D.; Trump, B. D.; Keisler, J. M.; Plourde, K. J.; Linkov, I. Emerging Technologies for Environmental Remediation: Integrating Data and Judgment. *Environ Sci Technol* **2016**, 50 (1), 349–358. <https://doi.org/10.1021/acs.est.5b03005>.
10. Kalita, E.; Baruah, J. 16 - Environmental Remediation. In *Colloidal Metal Oxide Nanoparticles*; Thomas, S., Tresa Sunny, A., Velayudhan, P., Eds.; Elsevier, 2020; pp 525–576. <https://doi.org/https://doi.org/10.1016/B978-0-12-813357-6.00014-0>.
11. Comninellis, C.; Kapalka, A.; Malato, S.; Parsons, S. A.; Poullos, I.; Mantzavinos, D. Advanced Oxidation Processes for Water Treatment: Advances and Trends for R&D. *Journal of Chemical Technology and Biotechnology* **2008**, 83 (6), 769–776. <https://doi.org/10.1002/jctb.1873>.
12. Koyuncu, I.; Sengur, R.; Turken, T.; Guclu, S.; Pasaoglu, M. E. 3 - Advances in Water Treatment by Microfiltration, Ultrafiltration, and Nanofiltration. In *Advances in Membrane Technologies for Water Treatment*; Basile, A., Cassano, A., Rastogi, N. K., Eds.; Woodhead Publishing Series in Energy; Woodhead Publishing: Oxford, 2015; pp 83–128. <https://doi.org/https://doi.org/10.1016/B978-1-78242-121-4.00003-4>.
13. Chauke, N. M.; Mohlala, R. L.; Ngqoloda, S.; Raphulu, M. C. Harnessing Visible Light: Enhancing TiO₂ Photocatalysis with Photosensitizers for Sustainable and Efficient Environmental Solutions. *Frontiers in Chemical Engineering*. Frontiers Media SA 2024. <https://doi.org/10.3389/fceng.2024.1356021>.
14. Serpone, N.; Emeline, A. V. Semiconductor Photocatalysis - Past, Present, and Future Outlook. *Journal of Physical Chemistry Letters*. March 1, 2012, pp 673–677. <https://doi.org/10.1021/jz300071j>.
15. Photocatalysis. **2019**. <https://doi.org/doi:10.1351/goldbook.P04580>.
16. Banerjee, T.; Podjaski, F.; Kröger, J.; Biswal, B. P.; Lotsch, B. V. Polymer Photocatalysts for Solar-to-Chemical Energy Conversion. *Nature Reviews Materials*. Nature Research February 1, 2021, pp 168–190. <https://doi.org/10.1038/s41578-020-00254-z>.
17. Yang, X.; Wang, D. Photocatalysis: From Fundamental Principles to Materials and Applications. *ACS Applied Energy Materials*. American Chemical Society December 24, 2018, pp 6657–6693. <https://doi.org/10.1021/acsaem.8b01345>.
18. Marschall, R. Semiconductor Composites: Strategies for Enhancing Charge Carrier Separation to Improve Photocatalytic Activity. *Adv Funct Mater* **2014**, 24 (17), 2421–2440. <https://doi.org/10.1002/adfm.201303214>.
19. Wang, Q.; Domen, K. Particulate Photocatalysts for Light-Driven Water Splitting: Mechanisms, Challenges, and Design Strategies. *Chemical Reviews*. American Chemical Society January 22, 2020, pp 919–985. <https://doi.org/10.1021/acs.chemrev.9b00201>.
20. Song, W.; Chong, K. C.; Qi, G.; Xiao, Y.; Chen, G.; Li, B.; Tang, Y.; Zhang, X.; Yao, Y.; Lin, Z.; Zou, Z.; Liu, B. Unraveling the Transformation from Type-II to Z-Scheme in Perovskite-Based Heterostructures for Enhanced Photocatalytic CO₂ Reduction. *J Am Chem Soc* **2024**, 146 (5), 3303–3314. <https://doi.org/10.1021/jacs.3c12073>.

21. Guan, R.; Wang, D.; Zhang, Y.; Liu, C.; Xu, W.; Wang, J.; Zhao, Z.; Feng, M.; Shang, Q.; Sun, Z. Enhanced Photocatalytic N₂ Fixation via Defective and Fluoride Modified TiO₂ Surface. *Appl Catal B* **2021**, 282. <https://doi.org/10.1016/j.apcatb.2020.119580>.
22. Kiwaan, H. A.; Atwee, T. M.; Azab, E. A.; El-Bindary, A. A. Photocatalytic Degradation of Organic Dyes in the Presence of Nanostructured Titanium Dioxide. *J Mol Struct* **2020**, 1200. <https://doi.org/10.1016/j.molstruc.2019.127115>.
23. Borah, M. J.; Sarmah, H. J.; Bhuyan, N.; Mohanta, D.; Dekka, D. Application of Box-Behnken Design in Optimization of Biodiesel Yield Using WO₃/Graphene Quantum Dot (GQD) System and Its Kinetics Analysis. *Biomass Convers Biorefin* **2022**, 12 (2), 221–232. <https://doi.org/10.1007/s13399-020-00717-x>.
24. Hassaan, M. A.; El-Nemr, M. A.; Elkatory, M. R.; Ragab, S.; Niculescu, V. C.; El Nemr, A. Principles of Photocatalysts and Their Different Applications: A Review. *Topics in Current Chemistry*. Springer Science and Business Media Deutschland GmbH December 1, 2023. <https://doi.org/10.1007/s41061-023-00444-7>.
25. Djurišić, A. B.; He, Y.; Ng, A. M. C. Visible-Light Photocatalysts: Prospects and Challenges. *APL Materials*. American Institute of Physics Inc. March 1, 2020. <https://doi.org/10.1063/1.5140497>.
26. Mohamadpour, F.; Amani, A. M. Photocatalytic Systems: Reactions, Mechanism, and Applications. *RSC Advances*. Royal Society of Chemistry July 1, 2024, pp 20609–20645. <https://doi.org/10.1039/d4ra03259d>.
27. Niu, L.; Coleman, J. N.; Zhang, H.; Shin, H.; Chhowalla, M.; Zheng, Z. Production of Two-Dimensional Nanomaterials via Liquid-Based Direct Exfoliation. *Small* **2016**, 12 (3), 272–293. <https://doi.org/10.1002/sml.201502207>.
28. Rahmanian, E.; Malekfar, R.; Pumera, M. Nanohybrids of Two-Dimensional Transition-Metal Dichalcogenides and Titanium Dioxide for Photocatalytic Applications. *Chemistry - A European Journal*. Wiley-VCH Verlag January 2, 2018, pp 18–31. <https://doi.org/10.1002/chem.201703434>.
29. Zhang, C.; Ren, K.; Wang, S.; Luo, Y.; Tang, W.; Sun, M. Recent Progress on Two-Dimensional van Der Waals Heterostructures for Photocatalytic Water Splitting: A Selective Review. *Journal of Physics D: Applied Physics*. Institute of Physics November 30, 2023. <https://doi.org/10.1088/1361-6463/acf506>.
30. Lau, V. W. hei; Lotsch, B. V. A Tour-Guide through Carbon Nitride-Land: Structure- and Dimensionality-Dependent Properties for Photo(Electro)Chemical Energy Conversion and Storage. *Advanced Energy Materials*. John Wiley and Sons Inc January 1, 2022. <https://doi.org/10.1002/aenm.202101078>.
31. Fina, F. *METAL LOADED G-C₃N₄ FOR VISIBLE LIGHT-DRIVEN H₂ PRODUCTION*; 2014. <http://research-repository.st-andrews.ac.uk/>.
32. Yue, D.; Raj, S. N. M.; Kumar, J. V.; Alam, M. W.; Rosaiah, P.; Selvaraj, M.; Reddy, I. N.; Bai, C. History of Metal Free G-C₃N₄ Photocatalysts for Hydrogen Production: A Comprehensive Review. *Diamond and Related Materials*. Elsevier Ltd June 1, 2024. <https://doi.org/10.1016/j.diamond.2024.111228>.
33. Yan, L.; Zhong, S.; Xiao, C.; Chen, Y. Optimization of Hydrothermal Pretreatment to Prepare G-C₃N₄ with Enhanced Catalyst Yield and Photocatalytic Activity for Aqueous Contaminant Removal. *Materials Today Sustainability* **2023**, 22. <https://doi.org/10.1016/j.mtsust.2023.100374>.
34. Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M. A Metal-Free Polymeric Photocatalyst for Hydrogen Production from Water under Visible Light. *Nat Mater* **2009**, 8 (1), 76–80. <https://doi.org/10.1038/nmat2317>.
35. Supervisor, S. P.; Pier, P.; Ricci, C. *Carbon Nitride Compounds for Photonic and Photocatalytic Applications*.
36. Fina, F. *METAL LOADED G-C₃N₄ FOR VISIBLE LIGHT-DRIVEN H₂ PRODUCTION*. <http://research-repository.st-andrews.ac.uk/>.
37. Ghaffar Rana, A. *Modification of Graphitic Carbon Nitride (g-C₃N₄) for Photocatalytic Redox Reactions*.
38. Archana, B.; Kottam, N.; Nayak, S.; Chandrasekhar, K. B.; Sreedhara, M. B. Superior Photocatalytic Hydrogen Evolution Performances of WS₂over MoS₂Integrated with CdS Nanorods. *Journal of Physical Chemistry C* **2020**, 124 (27), 14485–14495. <https://doi.org/10.1021/acs.jpcc.0c03411>.
39. Li, J.; Shen, B.; Hong, Z.; Lin, B.; Gao, B.; Chen, Y. A Facile Approach to Synthesize Novel Oxygen-Doped g-C₃N₄ with Superior Visible-Light Photoreactivity. *Chemical Communications* **2012**, 48 (98), 12017–12019. <https://doi.org/10.1039/c2cc35862j>.
40. Dehkordi, A. B.; Badiei, A. Insight into the Activity of TiO₂@nitrogen-Doped Hollow Carbon Spheres Supported on g-C₃N₄ for Robust Photocatalytic Performance. *Chemosphere* **2022**, 288. <https://doi.org/10.1016/j.chemosphere.2021.132392>.

41. Mafa, P. J.; Malefane, M. E.; Idris, A. O.; Liu, D.; Gui, J.; Mamba, B. B.; Kuvarega, A. T. Multi-Elemental Doped g-C₃N₄ with Enhanced Visible Light Photocatalytic Activity: Insight into Naproxen Degradation, Kinetics, Effect of Electrolytes, and Mechanism. *Sep Purif Technol* **2022**, 282. <https://doi.org/10.1016/j.seppur.2021.120089>.
42. Gnanaguru, M. V. L.; Ghangrekar, M. M.; Chowdhury, S. 2D–2D g-C₃N₄/WS₂ Z-Scheme Heterojunction: Comparison of the Photocatalytic Degradation of Tetracycline and Sulfamethoxazole. *J Photochem Photobiol A Chem* **2024**, 456. <https://doi.org/10.1016/j.jphotochem.2024.115818>.
43. Song, T.; Xie, C.; Matras-Postolek, K.; Yang, P. 2D Layered G-C₃N₄/WO₃/WS₂S-Scheme Heterojunctions with Enhanced Photochemical Performance. *Journal of Physical Chemistry C* **2021**, 125 (35), 19382–19393. <https://doi.org/10.1021/acs.jpcc.1c06753>.
44. Jian, S.; Ran, L.; Zhu, Y.; Yang, W.; Liu, Y.; Yang, H.; Duan, G.; Jiang, S. Visible Light Responsive SiO₂/g-C₃N₄/BiOBr/Bi Heterojunction Photocatalyst for Degradation of Rhodamine B. *Composites Communications* **2024**, 49. <https://doi.org/10.1016/j.coco.2024.101977>.
45. Wang, W.; Fang, J.; Shao, S.; Lai, M.; Lu, C. Compact and Uniform TiO₂@g-C₃N₄ Core-Shell Quantum Heterojunction for Photocatalytic Degradation of Tetracycline Antibiotics. *Appl Catal B* **2017**, 217, 57–64. <https://doi.org/10.1016/j.apcatb.2017.05.037>.
46. Wang, Y.; Tan, G.; Dang, M.; Dong, S.; Liu, Y.; Liu, T.; Ren, H.; Xia, A.; Lv, L. Study on Surface Modification of G-C₃N₄ Photocatalyst. *J Alloys Compd* **2022**, 908. <https://doi.org/10.1016/j.jallcom.2022.164507>.
47. Lin, J.; Tian, W.; Zhang, H.; Sun, H.; Wang, S. Electronic Structure and Functions of Carbon Nitride in Frontier Green Catalysis. *Acc Chem Res* **2024**, 57 (16), 2303–2315. <https://doi.org/10.1021/acs.accounts.4c00266>.
48. Ma, Z.; Guo, W.; Zhang, K.; Wang, N.; Li, Z.; Li, J. Liquid Exfoliation of Bulk G-C₃N₅ to Nanosheets for Improved Photocatalytic Antibacterial Activity. *Environmental Science and Pollution Research* **2023**, 30 (26), 69486–69498. <https://doi.org/10.1007/s11356-023-27330-5>.
49. Stagi, L.; Chiriu, D.; Carbonaro, C. M.; Corpino, R.; Ricci, P. C. Structural and Optical Properties of Carbon Nitride Polymorphs. *Diam Relat Mater* **2016**, 68, 84–92. <https://doi.org/10.1016/j.diamond.2016.06.009>.
50. Tahir, M.; Sherryana, A.; Khan, A. A.; Madi, M.; Zerga, A. Y.; Tahir, B. Defect Engineering in Graphitic Carbon Nitride Nanotextures for Energy Efficient Solar Fuels Production: A Review. *Energy and Fuels*. American Chemical Society August 18, 2022, pp 8948–8977. <https://doi.org/10.1021/acs.energyfuels.2c01256>.
51. Tan, J.; Tian, N.; Li, Z.; Li, J.; Yao, X.; Vakili, M.; Lu, Y.; Zhang, T. Intrinsic Defect Engineering in Graphitic Carbon Nitride for Photocatalytic Environmental Purification: A Review to Fill Existing Knowledge Gaps. *Chemical Engineering Journal*. Elsevier B.V. October 1, 2021. <https://doi.org/10.1016/j.cej.2020.127729>.
52. Jiang, L.; Yang, J.; Yuan, X.; Guo, J.; Liang, J.; Tang, W.; Chen, Y.; Li, X.; Wang, H.; Chu, W. Defect Engineering in Polymeric Carbon Nitride Photocatalyst: Synthesis, Properties and Characterizations. *Advances in Colloid and Interface Science*. Elsevier B.V. October 1, 2021. <https://doi.org/10.1016/j.cis.2021.102523>.
53. Kalantari Bolaghi, Z.; Rodriguez-Seco, C.; Yurtsever, A.; Ma, D. Exploring the Remarkably High Photocatalytic Efficiency of Ultra-Thin Porous Graphitic Carbon Nitride Nanosheets. *Nanomaterials* **2024**, 14 (1). <https://doi.org/10.3390/nano14010103>.
54. Guo, M.; Ma, Y.; Liu, Z.; Wang, D.; Yang, Y.; Li, X.; Liu, E. Electron, Hole and Radical Competition Mechanism of Layered Porous g-C₃N₄ for Hydrogen Generation and Organic Pollutant Degradation. *J Catal* **2024**, 430. <https://doi.org/10.1016/j.jcat.2024.115332>.
55. Li, B.; Zhang, B.; Zhang, Y.; Zhang, M.; Huang, W.; Yu, C.; Sun, J.; Feng, J.; Dong, S.; Sun, J. Porous G-C₃N₄/TiO₂ S-Scheme Heterojunction Photocatalyst for Visible-Light Driven H₂-Production and Simultaneous Wastewater Purification. *Int J Hydrogen Energy* **2021**, 46 (64), 32413–32424. <https://doi.org/10.1016/j.ijhydene.2021.07.090>.
56. Tian, C.; Li, C.; Zhao, C.; Liu, D.; He, X. A Novel Synthetic 3D Interconnected Porous Carbon-Rich Graphitic Carbon Nitride for Boosting Visible Light Photocatalytic Hydrogen Production and Dye Contaminant Degradation. *Catalysts* **2023**, 13 (10). <https://doi.org/10.3390/catal13101345>.
57. Zou, X.; Zhao, Y.; Li, M.; Zhou, S.; Chen, C. Construction of Graphitic Carbon Nitride Nanosheets via an Improved Solvent Exfoliation Strategy and Interfacial Mechanics Insight from Molecular Dynamics Simulations. *Journal of Porous Materials* **2021**, 28 (3), 943–954. <https://doi.org/10.1007/s10934-021-01047-7>.
58. Ajmal, Z.; Tu, X.; Abbas, W.; Ibrahim, E. H.; Ali, H.; Hussain, I.; Al-Muhana, M. K.; Khered, M.; Iqbal, A.; Rahaman, S.; Wang, S.; Akkinapally, B.; Alshammari, A.; Qadeer, A. Recent Advances in Carbon-Nitride Based Advance Materials: Synthesis, Characterization and Photo-Electrochemical Energy Application: Key Challenges and Prospects. *Fuel*. Elsevier Ltd December 15, 2024. <https://doi.org/10.1016/j.fuel.2024.132903>.

59. Song, X.; Zhang, X.; Li, X.; Che, H.; Huo, P.; Ma, C.; Yan, Y.; Yang, G. Enhanced Light Utilization Efficiency and Fast Charge Transfer for Excellent CO₂ Photoreduction Activity by Constructing Defect Structures in Carbon Nitride. *J Colloid Interface Sci* **2020**, *578*, 574–583. <https://doi.org/10.1016/j.jcis.2020.06.035>.
60. Liu, E.; Lin, X.; Hong, Y.; Yang, L.; Luo, B.; Shi, W.; Shi, J. Rational Copolymerization Strategy Engineered C Self-Doped g-C₃N₄ for Efficient and Robust Solar Photocatalytic H₂ Evolution. *Renew Energy* **2021**, *178*, 757–765. <https://doi.org/10.1016/j.renene.2021.06.066>.
61. Ho, W.; Zhang, Z.; Lin, W.; Huang, S.; Zhang, X.; Wang, X.; Huang, Y. Copolymerization with 2,4,6-Triaminopyrimidine for the Rolling-up the Layer Structure, Tunable Electronic Properties, and Photocatalysis of g-C₃N₄. *ACS Appl Mater Interfaces* **2015**, *7* (9), 5497–5505. <https://doi.org/10.1021/am509213x>.
62. Wang, Y.; Zhang, M.; Wang, L.; Xing, J. Graphitic Carbon Nitride Emitter: From Structural Modification to Optoelectronics Applications. *Advanced Optical Materials*. John Wiley and Sons Inc December 4, 2023. <https://doi.org/10.1002/adom.202301547>.
63. Wang, Y.; Wang, K.; Dai, F.; Zhang, K.; Tang, H.; Wang, L.; Xing, J. A Warm-White Light-Emitting Diode Based on Single-Component Emitter Aromatic Carbon Nitride. *Nat Commun* **2022**, *13* (1). <https://doi.org/10.1038/s41467-022-34291-9>.
64. Porcu, S.; Roppolo, I.; Salaun, M.; Sarais, G.; Barbarossa, S.; Casula, M. F.; Carbonaro, C. M.; Ricci, P. C. Come to Light: Detailed Analysis of Thermally Treated Phenyl Modified Carbon Nitride Polymorphs for Bright Phosphors in Lighting Applications. *Appl Surf Sci* **2020**, *504*. <https://doi.org/10.1016/j.apsusc.2019.144330>.
65. Chen, T.; Chen, C.; Liu, Q.; Zhang, Z.; Fang, X. A One-Step Process for Preparing a Phenyl-Modified g-C₃N₄ Green Phosphor with a High Quantum Yield. *RSC Adv* **2017**, *7* (81), 51702–51710. <https://doi.org/10.1039/c7ra09873a>.
66. Chen, J.; Qiu, Y.; Liu, X.; Guo, L. Phenyl-Modified Carbon Nitride Based Multifunctional Gel for the Detection, Adsorption, Photocatalytic Reduction and Recycling of Chromium(VI) in Wastewater. *Appl Surf Sci* **2024**, *652*. <https://doi.org/10.1016/j.apsusc.2023.159278>.
67. Zhang, C.; Liu, J.; Huang, X.; Chen, D.; Xu, S. Multistage Polymerization Design for G-C₃N₄ Nanosheets with Enhanced Photocatalytic Activity by Modifying the Polymerization Process of Melamine. *ACS Omega* **2019**, *4* (17), 17148–17159. <https://doi.org/10.1021/acsomega.9b01510>.
68. Cui, Q.; Xu, J.; Wang, X.; Li, L.; Antonietti, M.; Shalom, M. Phenyl-Modified Carbon Nitride Quantum Dots with Distinct Photoluminescence Behavior. *Angewandte Chemie - International Edition* **2016**, *55* (11), 3672–3676. <https://doi.org/10.1002/anie.201511217>.
69. Porcu, S.; Secci, F.; Abdullah, Q. A.; Ricci, P. C. 4-nitrophenol Efficient Photoreduction from Exfoliated and Protonated Phenyl-doped Graphitic Carbon Nitride Nanosheets. *Polymers (Basel)* **2021**, *13* (21). <https://doi.org/10.3390/polym13213752>.
70. Dai, A.; Huang, Z.; Tian, L.; Zhang, Z.; Guan, X.; Guo, L. Phenyl-Incorporated Carbon Nitride Photocatalyst with Extended Visible-Light-Absorption for Enhanced Hydrogen Production from Water Splitting. *J Colloid Interface Sci* **2022**, *622*, 494–502. <https://doi.org/10.1016/j.jcis.2022.04.159>.
71. Supervisor, S. P.; Pier, P.; Ricci, C. *Carbon Nitride Compounds for Photonic and Photocatalytic Applications*.
72. Wang, B.; Huang, M.; Jiang, M.; Jia, Y.; Niu, Y.; Sun, W. Boosting Photocatalytic Performance of Polymeric Carbon Nitride by Adjusting Its Donor-Acceptor Structure via Functional Group Modification Strategy. *Chemosphere* **2024**, *364*. <https://doi.org/10.1016/j.chemosphere.2024.143137>.
73. Yu, M.; Shao, W.; Tai, G.; Han, J.; Wu, G.; Xing, W. Facilitating Charge Transport by Phenyl-Substitution and Sulfate-Intercalation on Carbon Nitride Tubes for Highly Efficient Photocatalytic Hydrogen Evolution. *Int J Hydrogen Energy* **2024**, *85*, 832–840. <https://doi.org/10.1016/j.ijhydene.2024.08.398>.
74. Chauhan, D. K.; Jain, S.; Battula, V. R.; Kailasam, K. Organic Motif's Functionalization via Covalent Linkage in Carbon Nitride: An Exemplification in Photocatalysis. *Carbon*. Elsevier Ltd November 1, 2019, pp 40–58. <https://doi.org/10.1016/j.carbon.2019.05.079>.
75. Barrio, J.; Shalom, M. Rational Design of Carbon Nitride Materials by Supramolecular Preorganization of Monomers. *ChemCatChem*. Wiley Blackwell December 21, 2018, pp 5573–5586. <https://doi.org/10.1002/cctc.201801410>.
76. Tang, W.; Tian, Y.; Chen, B.; Xu, Y.; Li, B.; Jing, X.; Zhang, J.; Xu, S. Supramolecular Copolymerization Strategy for Realizing the Broadband White Light Luminescence Based on N-Deficient Porous Graphitic Carbon Nitride (g-C₃N₄). *ACS Appl Mater Interfaces* **2020**, *12* (5), 6396–6406. <https://doi.org/10.1021/acsaami.9b19338>.
77. Porcu, S.; Castellino, M.; Roppolo, I.; Carbonaro, C. M.; Palmas, S.; Mais, L.; Casula, M. F.; Neretina, S.; Hughes, R. A.; Secci, F.; Ricci, P. C. Highly Efficient Visible Light Phenyl Modified Carbon Nitride/TiO₂ Photocatalyst for Environmental Applications. *Appl Surf Sci* **2020**, *531*. <https://doi.org/10.1016/j.apsusc.2020.147394>.

78. Xu, J.; Antonietti, M.; Shalom, M. Moving Graphitic Carbon Nitride from Electrocatalysis and Photocatalysis to a Potential Electrode Material for Photoelectric Devices. *Chemistry - An Asian Journal*. John Wiley and Sons Ltd September 20, 2016, pp 2499–2512. <https://doi.org/10.1002/asia.201600857>.
79. Vidyasagar, D.; Manwar, N.; Gupta, A.; Ghugal, S. G.; Umare, S. S.; Boukherroub, R. Phenyl-Grafted Carbon Nitride Semiconductor for Photocatalytic CO₂-Reduction and Rapid Degradation of Organic Dyes. *Catal Sci Technol* **2019**, 9 (3), 822–832. <https://doi.org/10.1039/c8cy02220h>.
80. Zhang, M.; Duan, Y.; Jia, H.; Wang, F.; Wang, L.; Su, Z.; Wang, C. Defective Graphitic Carbon Nitride Synthesized by Controllable Co-Polymerization with Enhanced Visible Light Photocatalytic Hydrogen Evolution. *Catal Sci Technol* **2017**, 7 (2), 452–458. <https://doi.org/10.1039/c6cy02318e>.
81. Ishida, Y.; Chabanne, L.; Antonietti, M.; Shalom, M. Morphology Control and Photocatalysis Enhancement by the One-Pot Synthesis of Carbon Nitride from Preorganized Hydrogen-Bonded Supramolecular Precursors. *Langmuir* **2014**, 30 (2), 447–451. <https://doi.org/10.1021/la404101h>.
82. Zhang, G.; Wang, X. A Facile Synthesis of Covalent Carbon Nitride Photocatalysts by Co-Polymerization of Urea and Phenylurea for Hydrogen Evolution. *J Catal* **2013**, 307, 246–253. <https://doi.org/10.1016/j.jcat.2013.07.026>.
83. Li, Y.; Jin, R.; Li, G.; Liu, X.; Yu, M.; Xing, Y.; Shi, Z. Preparation of Phenyl Group Functionalized G-C₃N₄ Nanosheets with Extended Electron Delocalization for Enhanced Visible-Light Photocatalytic Activity. *New Journal of Chemistry* **2018**, 42 (9), 6756–6762. <https://doi.org/10.1039/c8nj00298c>.
84. Gu, Q.; Jiang, P. P.; Zhang, K.; Leng, Y.; Zhang, P.; Thin wai, P.; Haryono, A.; Li, Z.; Li, Y.; Pan, L.; Pan, J. Phenyl-Doped Porous Carbon Nitride for Enhanced Visible Light-Driven Photocatalytic Oxidation of Aromatic Alcohols. *J Solid State Chem* **2023**, 317. <https://doi.org/10.1016/j.jssc.2022.123670>.
85. Zhang, M.; Yang, Y.; An, X.; Zhao, J.; Bao, Y.; Hou, L. an. Exfoliation Method Matters: The Microstructure-Dependent Photoactivity of g-C₃N₄ Nanosheets for Water Purification. *J Hazard Mater* **2022**, 424. <https://doi.org/10.1016/j.jhazmat.2021.127424>.
86. Fernandes, E.; Mazierski, P.; Miodyńska, M.; Klimczuk, T.; Pawlyta, M.; Zaleska-Medynska, A.; Martins, R. C.; Gomes, J. Carbon Nitride Exfoliation for Photocatalysis and Photocatalytic Ozonation over Emerging Contaminants Abatement. *J Environ Chem Eng* **2023**, 11 (5). <https://doi.org/10.1016/j.jece.2023.110554>.
87. Wang, Y.; Liu, L.; Ma, T.; Zhang, Y.; Huang, H. 2D Graphitic Carbon Nitride for Energy Conversion and Storage. *Advanced Functional Materials*. John Wiley and Sons Inc August 1, 2021. <https://doi.org/10.1002/adfm.202102540>.
88. Shen, J.; He, Y.; Wu, J.; Gao, C.; Keyshar, K.; Zhang, X.; Yang, Y.; Ye, M.; Vajtai, R.; Lou, J.; Ajayan, P. M. Liquid Phase Exfoliation of Two-Dimensional Materials by Directly Probing and Matching Surface Tension Components. *Nano Lett* **2015**, 15 (8), 5449–5454. <https://doi.org/10.1021/acs.nanolett.5b01842>.
89. Huang, J.; Klahn, M.; Tian, X.; Dai, X.; Rabeah, J.; Aladin, V.; Corzilius, B.; Bartling, S.; Lund, H.; Steinfeldt, N.; Peppel, T.; Logsdail, A. J.; Jiao, H.; Strunk, J. Exfoliated Polymeric Carbon Nitride Nanosheets for Photocatalytic Applications. *ACS Appl Nano Mater* **2024**, 7 (7), 7442–7452. <https://doi.org/10.1021/acsanm.4c00133>.
90. Mei, H.; Shu, H.; Lv, M.; Liu, W.; Wang, X. Fluorescent Assay Based on Phenyl-Modified g-C₃N₄ Nanosheets for Determination of Thiram. *Microchimica Acta* **2020**, 187 (3). <https://doi.org/10.1007/s00604-020-4135-9>.
91. Yang, S.; Gong, Y.; Zhang, J.; Zhan, L.; Ma, L.; Fang, Z.; Vajtai, R.; Wang, X.; Ajayan, P. M. Exfoliated Graphitic Carbon Nitride Nanosheets as Efficient Catalysts for Hydrogen Evolution under Visible Light. *Advanced Materials* **2013**, 25 (17), 2452–2456. <https://doi.org/10.1002/adma.201204453>.
92. Liu, X.; Zhang, H.; Cai, Z.; Guo, L. Fluorescent Graphitic Carbon Nitride with Photocatalytic Oxidase-like Activity for Anti-Counterfeiting Application. *Spectrochim Acta A Mol Biomol Spectrosc* **2022**, 268. <https://doi.org/10.1016/j.saa.2021.120685>.
93. Backes, C.; Higgins, T. M.; Kelly, A.; Boland, C.; Harvey, A.; Hanlon, D.; Coleman, J. N. Guidelines for Exfoliation, Characterization and Processing of Layered Materials Produced by Liquid Exfoliation. *Chemistry of Materials*. American Chemical Society January 10, 2017, pp 243–255. <https://doi.org/10.1021/acs.chemmater.6b03335>.
94. Ni, P.; Dieng, M.; Vanel, J. C.; Florea, I.; Bouanis, F. Z.; Yassar, A. Liquid Shear Exfoliation of MoS₂: Preparation, Characterization, and NO₂-Sensing Properties. *Nanomaterials* **2023**, 13 (18). <https://doi.org/10.3390/nano13182502>.
95. Luo, Y.; Liu, Z.; Liu, J.; Cai, W.; Liao, Z.; Feng, X.; Zheng, J.; Zhang, C.; Fang, Y. Adjustable N→π* Electronic Transition by Sulfonated Benzene Functionalized G-C₃N₄ for Enhanced Photocatalytic H₂ Generation. *Int J Hydrogen Energy* **2024**, 64, 558–568. <https://doi.org/10.1016/j.ijhydene.2024.03.262>.

96. Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M. A Metal-Free Polymeric Photocatalyst for Hydrogen Production from Water under Visible Light. *Nat Mater* **2009**, *8* (1), 76–80. <https://doi.org/10.1038/nmat2317>.
97. ZHENG, L. li; XIAO, X. yan; LI, Y.; ZHANG, W. ping. Enhanced Photocatalytic Activity of TiO₂ Nanoparticles Using WS₂/g-C₃N₄ Hybrid as Co-Catalyst. *Transactions of Nonferrous Metals Society of China (English Edition)* **2017**, *27* (5), 1117–1126. [https://doi.org/10.1016/S1003-6326\(17\)60130-4](https://doi.org/10.1016/S1003-6326(17)60130-4).
98. Yi, J.; She, X.; Song, Y.; Mao, M.; Xia, K.; Xu, Y.; Mo, Z.; Wu, J.; Xu, H.; Li, H. Solvothermal Synthesis of Metallic 1T-WS₂: A Supporting Co-Catalyst on Carbon Nitride Nanosheets toward Photocatalytic Hydrogen Evolution. *Chemical Engineering Journal* **2018**, *335*, 282–289. <https://doi.org/10.1016/j.cej.2017.10.125>.
99. Porcu, S.; Secci, F.; Ricci, P. C. Advances in Hybrid Composites for Photocatalytic Applications: A Review. *Molecules*. MDPI October 1, 2022. <https://doi.org/10.3390/molecules27206828>.
100. Shao, M.; Chen, W.; Ding, S.; Lo, K. H.; Zhong, X.; Yao, L.; Ip, W. F.; Xu, B.; Wang, X.; Pan, H. WXy/g-C₃N₄ (WXy=W₂C, WS₂, or W₂N) Composites for Highly Efficient Photocatalytic Water Splitting. *ChemSusChem* **2019**, *12* (14), 3355–3362. <https://doi.org/10.1002/cssc.201900844>.
101. Yan, T.; Yang, Q.; Feng, R.; Ren, X.; Zhao, Y.; Sun, M.; Yan, L.; Wei, Q. Highly Effective Visible-Photocatalytic Hydrogen Evolution and Simultaneous Organic Pollutant Degradation over an Urchin-like Oxygen-Doped MoS₂/ZnIn₂S₄ Composite. *Front Environ Sci Eng* **2022**, *16* (10). <https://doi.org/10.1007/s11783-022-1566-z>.
102. Yu, H.; Zhang, M.; Cai, Y.; Zhuang, Y.; Wang, L. The Advanced Progress of MoS₂ and WS₂ for Multi-Catalytic Hydrogen Evolution Reaction Systems. *Catalysts*. Multidisciplinary Digital Publishing Institute (MDPI) August 1, 2023. <https://doi.org/10.3390/catal13081148>.
103. Wang, J. C.; Cui, C. X.; Kong, Q. Q.; Ren, C. Y.; Li, Z.; Qu, L.; Zhang, Y.; Jiang, K. Mn-Doped g-C₃N₄ Nanoribbon for Efficient Visible-Light Photocatalytic Water Splitting Coupling with Methylene Blue Degradation. *ACS Sustain Chem Eng* **2018**, *6* (7), 8754–8761. <https://doi.org/10.1021/acssuschemeng.8b01093>.
104. Ye, S.; Wang, R.; Wu, M. Z.; Yuan, Y. P. A Review on G-C₃N₄ for Photocatalytic Water Splitting and CO₂ Reduction. In *Applied Surface Science*; Elsevier B.V., 2015; Vol. 358, pp 15–27. <https://doi.org/10.1016/j.apsusc.2015.08.173>.
105. Liu, J.; Liu, H.; Peng, W.; Li, Y.; Zhang, F.; Fan, X. High-Yield Exfoliation of MoS₂ (WS₂) Monolayers towards Efficient Photocatalytic Hydrogen Evolution. *Chemical Engineering Journal* **2022**, *431*. <https://doi.org/10.1016/j.cej.2021.133286>.
106. Lu, Q.; Yu, Y.; Ma, Q.; Chen, B.; Zhang, H. 2D Transition-Metal-Dichalcogenide-Nanosheet-Based Composites for Photocatalytic and Electrocatalytic Hydrogen Evolution Reactions. *Advanced Materials*. Wiley-VCH Verlag March 9, 2016, pp 1917–1933. <https://doi.org/10.1002/adma.201503270>.
107. Li, H.; Jia, X.; Zhang, Q.; Wang, X. Metallic Transition-Metal Dichalcogenide Nanocatalysts for Energy Conversion. *Chem*. Elsevier Inc July 12, 2018, pp 1510–1537. <https://doi.org/10.1016/j.chempr.2018.03.012>.
108. Xu, D.; Xu, P.; Zhu, Y.; Peng, W.; Li, Y.; Zhang, G.; Zhang, F.; Mallouk, T. E.; Fan, X. High Yield Exfoliation of WS₂ Crystals into 1-2 Layer Semiconducting Nanosheets and Efficient Photocatalytic Hydrogen Evolution from WS₂/CdS Nanorod Composites. *ACS Appl Mater Interfaces* **2018**, *10* (3), 2810–2818. <https://doi.org/10.1021/acsami.7b15614>.
109. Tran, H. H.; Truong, D. H.; Truong, T. T.; Xuan Dieu Nguyen, T.; Jin, Y. S.; Kim, S. J.; Vo, V. A Facile Synthesis of WS₂/g-C₃N₄ Composites with Improved Photocatalytic Activity. *Bull Korean Chem Soc* **2018**, *39* (8), 965–971. <https://doi.org/10.1002/bkcs.11536>.
110. Lin, B.; Chen, H.; Zhou, Y.; Luo, X.; Tian, D.; Yan, X.; Duan, R.; Di, J.; Kang, L.; Zhou, A.; Yang, G.; Li, Y.; Zhou, J.; Liu, Z.; Liu, F. 2D/2D Atomic Double-Layer WS₂/Nb₂O₅ Shell/Core Nanosheets with Ultrafast Interfacial Charge Transfer for Boosting Photocatalytic H₂ Evolution. *Chinese Chemical Letters* **2021**, *32* (10), 3128–3132. <https://doi.org/10.1016/j.ccl.2021.03.057>.
111. Li, X.; Yu, J.; Low, J.; Fang, Y.; Xiao, J.; Chen, X. Engineering Heterogeneous Semiconductors for Solar Water Splitting. *Journal of Materials Chemistry A*. Royal Society of Chemistry February 14, 2015, pp 2485–2534. <https://doi.org/10.1039/c4ta04461d>.
112. Liang, K.; Yin, M.; Ma, D.; Fan, Y.; Li, Z. Facile Preparation and Photocatalytic Hydrogen Production of WS₂ and Its Composites. *Int J Hydrogen Energy* **2022**, *47* (91), 38622–38634. <https://doi.org/10.1016/j.ijhydene.2022.09.058>.
113. Dahal, A. Enhanced Photocatalytic Activity of Liquid Phase Exfoliated WS₂ Nanosheets. *J Appl Phys* **2023**, *133* (23). <https://doi.org/10.1063/5.0152206>.
114. Yang, C.; Qin, J.; Rajendran, S.; Zhang, X.; Liu, R. WS₂ and C-TiO₂ Nanorods Acting as Effective Charge Separators on g-C₃N₄ to Boost Visible-Light Activated Hydrogen Production from Seawater. *ChemSusChem* **2018**, *11* (23), 4077–4085. <https://doi.org/10.1002/cssc.201801819>.

115. Hou, Y.; Zhu, Y.; Xu, Y.; Wang, X. Photocatalytic Hydrogen Production over Carbon Nitride Loaded with WS₂ as Cocatalyst under Visible Light. *Appl Catal B* **2014**, 156–157, 122–127. <https://doi.org/10.1016/j.apcatb.2014.03.002>.
116. Yousef, A.; Thiehmmed, Z.; Abdul Shakoar, R.; Altahtamouni, T. Recent Progress in WS₂-Based Nanomaterials Employed for Photocatalytic Water Treatment. *Catalysts*. MDPI October 1, 2022. <https://doi.org/10.3390/catal12101138>.
117. Li, C.; Zhang, X.; Song, T.; Tian, Y.; Wang, S.; Yang, P. Interface-Engineering Derived WS₂/S-g-C₃N₄ Nanosheet Z-Scheme Heterostructures towards Enhanced Photocatalytic Redox and H₂O₂ Generation. *J Environ Chem Eng* **2024**, 12 (5). <https://doi.org/10.1016/j.jece.2024.113396>.
118. Zhang, X.; Yang, P.; Jiang, S. P. Horizontally Growth of WS₂/WO₃ Heterostructures on Crystalline g-C₃N₄ Nanosheets towards Enhanced Photo/Electrochemical Performance. *J Nanostructure Chem* **2021**, 11 (3), 367–380. <https://doi.org/10.1007/s40097-020-00373-7>.
119. Zhou, Y.; Ye, X.; Lin, D. One-Pot Synthesis of Non-Noble Metal WS₂/g-C₃N₄ Photocatalysts with Enhanced Photocatalytic Hydrogen Production. *Int J Hydrogen Energy* **2019**, 44 (29), 14927–14937. <https://doi.org/10.1016/j.ijhydene.2019.04.091>.
120. Liang, Z.; Yang, S.; Wang, X.; Cui, H.; Wang, X.; Tian, J. The Metallic 1T-Phase WS₂ Nanosheets as Cocatalysts for Enhancing the Photocatalytic Hydrogen Evolution of g-C₃N₄ Nanotubes. *Appl Catal B* **2020**, 274. <https://doi.org/10.1016/j.apcatb.2020.119114>.
121. Ma, Y.; Li, J.; Liu, E.; Wan, J.; Hu, X.; Fan, J. High Efficiency for H₂ Evolution and NO Removal over the Ag Nanoparticles Bridged G-C₃N₄ and WS₂ Heterojunction Photocatalysts. *Appl Catal B* **2017**, 219, 467–478. <https://doi.org/10.1016/j.apcatb.2017.07.061>.
122. Lin, D.; Zhou, Y.; Ye, X.; Zhu, M. Construction of Sandwich Structured Photocatalyst Using Monolayer WS₂ Embedded G-C₃N₄ for Highly Efficient H₂ Production. *Ceram Int* **2020**, 46 (9), 12933–12941. <https://doi.org/10.1016/j.ceramint.2020.02.061>.
123. Cao, R.; Yuan, H.; Yang, N.; Lu, Q.; Xue, Y.; Zeng, X. Enhanced Photocatalytic Hydrogen Production Utilizing Few-Layered 1T-WS₂/g-C₃N₄ Heterostructures Prepared with One-Step Calcination Route. *Fuel* **2024**, 357. <https://doi.org/10.1016/j.fuel.2023.129808>.
124. Ma, Z. P.; Ma, X.; Zhang, L.; Cheng, H.; Shi, F. N. 1T-WS₂/NCN Photocatalyst with Unique Trion Behavior and Cyano-Defects: Photocatalytic Hydrogen Evolution and Mechanistic Insights. *Sep Purif Technol* **2023**, 325. <https://doi.org/10.1016/j.seppur.2023.124743>.
125. Akple, M. S.; Low, J.; Wageh, S.; Al-Ghamdi, A. A.; Yu, J.; Zhang, J. Enhanced Visible Light Photocatalytic H₂ - Production of g-C₃N₄/WS₂ Composite Heterostructures. In *Applied Surface Science*; Elsevier B.V., 2015; Vol. 358, pp 196–203. <https://doi.org/10.1016/j.apsusc.2015.08.250>.
126. Liu, W.; Zhang, D.; Wang, R.; Xie, H.; Zhang, Z.; Qiu, S. In-Situ Vulcanization Enhances the Two-Dimensional Interface Effect and Promotes Carrier Separation to Achieve Efficient Photocatalytic Hydrogen Evolution. *J Alloys Compd* **2023**, 961. <https://doi.org/10.1016/j.jallcom.2023.170957>.
127. Li, J.; Cao, W.; Li, Y.; Xu, X.; Jiang, Y.; Lin, K. In Situ Synthesis of Hybrid-Phase WS₂ with S Defects as a Cocatalyst for the g-C₃N₄-Based Photocatalytic Hydrogen Evolution Reaction. *ACS Appl Energy Mater* **2022**, 5 (8), 9463–9470. <https://doi.org/10.1021/acsaem.2c01013>.
128. Acar, E. G.; Yilmaz, S.; Eroglu, Z.; Aslan, E.; Metin, Ö.; Patir, I. H. Solar-Light-Driven Photocatalytic Hydrogen Evolution Activity of GCN/WS₂ Heterojunctions Incorporated with the First-Row Transition Metals. *J Alloys Compd* **2023**, 950. <https://doi.org/10.1016/j.jallcom.2023.169753>.
129. Huang, X.; Song, J.; Wu, G.; Miao, Z.; Song, Y.; Mo, Z. Recent Progress on the Photocatalytic Hydrogen Evolution Reaction over a Metal Sulfide Cocatalyst-Mediated Carbon Nitride System. *Inorganic Chemistry Frontiers*. Royal Society of Chemistry March 22, 2024, pp 2527–2552. <https://doi.org/10.1039/d4qi00255e>.
130. Liu, X.; Zhao, C.; Muhmood, T.; Yang, X. Regulating the Assembly of Precursors of Carbon Nitrides to Improve Photocatalytic Hydrogen Production. *Catalysts* **2022**, 12 (12). <https://doi.org/10.3390/catal12121634>.
131. Akhundi, A.; Zaker Moshfegh, A.; Habibi-Yangjeh, A.; Sillanpää, M. Simultaneous Dual-Functional Photocatalysis by g-C₃N₄-Based Nanostructures. *ACS ES and T Engineering*. American Chemical Society April 8, 2022, pp 564–585. <https://doi.org/10.1021/acsestengg.1c00346>.
132. Nemiwal, M.; Zhang, T. C.; Kumar, D. Recent Progress in G-C₃N₄, TiO₂ and ZnO Based Photocatalysts for Dye Degradation: Strategies to Improve Photocatalytic Activity. *Science of the Total Environment*. Elsevier B.V. May 1, 2021. <https://doi.org/10.1016/j.scitotenv.2020.144896>.

133. Haselmann, G. M.; Eder, D. Early-Stage Deactivation of Platinum-Loaded TiO₂ Using in Situ Photodeposition during Photocatalytic Hydrogen Evolution. *ACS Catal* **2017**, 7 (7), 4668–4675. <https://doi.org/10.1021/acscatal.7b00845>.
134. Yousefi, M.; Villar-Rodil, S.; Paredes, J. I.; Moshfegh, A. Z. Oxidized Graphitic Carbon Nitride Nanosheets as an Effective Adsorbent for Organic Dyes and Tetracycline for Water Remediation. *J Alloys Compd* **2019**, 809. <https://doi.org/10.1016/j.jallcom.2019.151783>.
135. Paton, K. R.; Coleman, J. N. Relating the Optical Absorption Coefficient of Nanosheet Dispersions to the Intrinsic Monolayer Absorption. *Carbon N Y* **2016**, 107, 733–738. <https://doi.org/10.1016/j.carbon.2016.06.043>.
136. Ott, S.; Lakmann, M.; Backes, C. Impact of Pretreatment of the Bulk Starting Material on the Efficiency of Liquid Phase Exfoliation of WS₂. *Nanomaterials* **2021**, 11 (5). <https://doi.org/10.3390/nano11051072>.
137. Backes, C.; Smith, R. J.; McEvoy, N.; Berner, N. C.; McCloskey, D.; Nerl, H. C.; O'Neill, A.; King, P. J.; Higgins, T.; Hanlon, D.; Scheuschner, N.; Maultzsch, J.; Houben, L.; Duesberg, G. S.; Donegan, J. F.; Nicolosi, V.; Coleman, J. N. Edge and Confinement Effects Allow in Situ Measurement of Size and Thickness of Liquid-Exfoliated Nanosheets. *Nat Commun* **2014**, 5. <https://doi.org/10.1038/ncomms5576>.
138. Backes, C.; Hanlon, D.; Szydłowska, B. M.; Harvey, A.; Smith, R. J.; Higgins, T. M.; Coleman, J. N. Preparation of Liquid-Exfoliated Transition Metal Dichalcogenide Nanosheets with Controlled Size and Thickness: A State of the Art Protocol. *Journal of Visualized Experiments* **2016**, 2016 (118). <https://doi.org/10.3791/54806>.
139. Lotya, M.; Rakovich, A.; Donegan, J. F.; Coleman, J. N. Measuring the Lateral Size of Liquid-Exfoliated Nanosheets with Dynamic Light Scattering. *Nanotechnology* **2013**, 24 (26). <https://doi.org/10.1088/0957-4484/24/26/265703>.
140. Ricci, P. C.; Salis, M.; Anedda, A. Phonon Characterization of Nano-Crystals by Raman Spectroscopy. *Chem Phys Lett* **2008**, 457 (1–3), 191–193. <https://doi.org/10.1016/j.cplett.2008.04.002>.
141. Gertych, A. P.; Czerniak-Łosiewicz, K.; Łapinska, A.; Świniarski, M.; Ojrzynska, M.; Judek, J.; Zdrojek, M. Phonon and Thermal Properties of Thin Films Made from WS₂ Mono- And Few-Layer Flakes. *Journal of Physical Chemistry C* **2021**, 125 (26), 14446–14452. <https://doi.org/10.1021/acs.jpcc.1c02842>.
142. McCreary, A.; Berkdemir, A.; Wang, J. *et al.* Distinct photoluminescence and Raman spectroscopy signatures for identifying highly crystalline WS₂ monolayers produced by different growth methods. *Journal of Materials Research* **31**, 931–944 (2016). <https://doi.org/10.1557/jmr.2016.47>
143. Li, Z.; Rashvand, F.; Bretscher, H.; Szydłowska, B. M.; Xiao, J.; Backes, C.; Rao, A. Understanding the Photoluminescence Quenching of Liquid Exfoliated WS₂ Monolayers. *Journal of Physical Chemistry C* **2022**, 126 (51), 21681–21688. <https://doi.org/10.1021/acs.jpcc.2c05284>.
144. Das, K. K.; Mohanty, U. A.; Mohanty, R.; Sarangi, P. P.; Sahoo, D. P.; Parida, K. Improving Charge Carrier Separation through S-Scheme-Based 2D-2D WS₂/Sulfur-Doped g-C₃N₄ Heterojunctions for a Superior Photocatalytic O₂ Reduction Reaction. *ACS Appl Energy Mater* **2024**. <https://doi.org/10.1021/acs.aem.4c01061>.
145. Xuejun Xu, Lihui Li, Xiaoli Li, Xiaowen Hu, Mingming Yang, Qinglin Guo, Ying Wang, Xiujuan Zhuang, Baolai Liang, Different optical characteristics between monolayer and bilayer WS₂ due to interlayer interaction, *Optik*, Volume 251, 2022, 168374, ISSN 0030-4026, <https://doi.org/10.1016/j.ijleo.2021.168374>.
146. Stagi Luigi. Optical and Structural Characterization of Metal Oxides and Carbon Nitride Compounds for the Development of Organic/Inorganic Hybrid Systems, 2014.
147. Reshak, A. H.; Khan, S. A.; Auluck, S. Linear and Nonlinear Optical Properties for AA and AB Stacking of Carbon Nitride Polymorph (C₃N₄). *RSC Adv* **2014**, 4 (23), 11967–11974. <https://doi.org/10.1039/c4ra00388h>.
148. Yu, J.; Wang, Y.; Zhou, Y.; Fang, W.; Liu, B.; Xing, J. Intrinsic Self-Trapped Excitons in Graphitic Carbon Nitride. *Nano Lett* **2024**, 24 (15), 4439–4446. <https://doi.org/10.1021/acs.nanolett.4c00238>.
149. Zheng, L.; Wang, Z.; Zhang, H.; Shi, Y.; Wang, F.; Wang, Z.; Lin, D.; Yue, J.; Wang, Q. Boosting Excitons Dissociation in Defective-Rich Graphitic Carbon Nitride for Efficient Hydrogen Peroxide Photosynthesis and on-Site Environmental Governance. *Appl Catal B* **2024**, 347. <https://doi.org/10.1016/j.apcatb.2024.123811>.
150. Xia, G.; Xiao, S.; Su, J.; Zhou, H.; Liu, Y.; Zhu, X. A Dual-Functional Catalyst: Wood-Templated BiVO₄-CdS for Wood Dye Wastewater. *RSC Adv* **2023**, 13 (3), 1823–1833. <https://doi.org/10.1039/d2ra06735h>.
151. Wang, Y.; Yu, J.; Peng, W.; Tian, J.; Yang, C. Novel Multilayer TiO₂ Heterojunction Decorated by Low G-C₃N₄ Content and Its Enhanced Photocatalytic Activity under UV, Visible and Solar Light Irradiation. *Sci Rep* **2019**, 9 (1). <https://doi.org/10.1038/s41598-019-42438-w>.

152. Tan, Y.; Shu, R.; Xu, H.; Song, L.; Zhang, R.; Ouyang, C.; Xia, M.; Hou, J.; Zhang, X.; Yuan, Y.; Zhang, R. Supercritical Carbon Dioxide-Assisted TiO₂/g-C₃N₄ Heterostructures Tuning for Efficient Interfacial Charge Transfer and Formaldehyde Photo-Degradation. *J Environ Chem Eng* **2023**, *11* (5). <https://doi.org/10.1016/j.jece.2023.110992>.
153. Ma, R.; He, Y.; Feng, J.; Hu, Z. Y.; Van Tendeloo, G.; Li, D. A Facile Synthesis of Ag@PdAg Core-Shell Architecture for Efficient Purification of Ethene Feedstock. *J Catal* **2019**, *369*, 440–449. <https://doi.org/10.1016/j.jcat.2018.11.037>.
154. Zhao, Z.; Sun, Y.; Luo, Q.; Dong, F.; Li, H.; Ho, W. K. Mass-Controlled Direct Synthesis of Graphene-like Carbon Nitride Nanosheets with Exceptional High Visible Light Activity. Less Is Better. *Sci Rep* **2015**, *5*. <https://doi.org/10.1038/srep14643>.
155. Kampouri, S.; Nguyen, T. N.; Spodaryk, M.; Palgrave, R. G.; Züttel, A.; Smit, B.; Stylianou, K. C. Concurrent Photocatalytic Hydrogen Generation and Dye Degradation Using MIL-125-NH₂ under Visible Light Irradiation. *Adv Funct Mater* **2018**, *28* (52). <https://doi.org/10.1002/adfm.201806368>.
156. Le, T. L. T.; Le, T. H. T.; Nguyen Van, K.; Van Bui, H.; Le, T. G.; Vo, V. Controlled Growth of TiO₂ Nanoparticles on Graphene by Hydrothermal Method for Visible-Light Photocatalysis. *Journal of Science: Advanced Materials and Devices* **2021**, *6* (4), 516–527. <https://doi.org/10.1016/j.jsamd.2021.07.003>.
157. Lu, L.; Wang, G.; Zou, M.; Wang, J.; Li, J. Effects of Calcining Temperature on Formation of Hierarchical TiO₂/g-C₃N₄ Hybrids as an Effective Z-Scheme Heterojunction Photocatalyst. *Appl Surf Sci* **2018**, *441*, 1012–1023. <https://doi.org/10.1016/j.apsusc.2018.02.080>.
158. Wang, H.; Wang, B.; Bian, Y.; Dai, L. Enhancing Photocatalytic Activity of Graphitic Carbon Nitride by Codoping with P and C for Efficient Hydrogen Generation. *ACS Appl Mater Interfaces* **2017**, *9* (26), 21730–21737. <https://doi.org/10.1021/acsami.7b02445>.
159. Musa, E. N.; Kaur, S.; Gallagher, T. C.; Anthony, T. M.; Stickle, W. F.; Árnadóttir, L.; Stylianou, K. C. Two Birds, One Stone: Coupling Hydrogen Production with Herbicide Degradation over Metal-Organic Framework-Derived Titanium Dioxide. *ACS Catal* **2023**, *13* (6), 3710–3722. <https://doi.org/10.1021/acscatal.3c00265>.
160. Singh, A. P.; Arora, P.; Basu, S.; Mehta, B. R. Graphitic Carbon Nitride Based Hydrogen Treated Disordered Titanium Dioxide Core-Shell Nanocatalyst for Enhanced Photocatalytic and Photoelectrochemical Performance. *Int J Hydrogen Energy* **2016**, *41* (13), 5617–5628. <https://doi.org/10.1016/j.ijhydene.2016.02.029>.
161. Roškaric, M.; Žerjav, G.; Zavašnik, J.; Pintar, A. The Influence of Synthesis Conditions on the Visible-Light Triggered Photocatalytic Activity of g-C₃N₄/TiO₂ composites Used in AOPs. *J Environ Chem Eng* **2022**, *10* (3). <https://doi.org/10.1016/j.jece.2022.107656>.
162. Wang, Y.; Yang, W.; Chen, X.; Wang, J.; Zhu, Y. Photocatalytic Activity Enhancement of Core-Shell Structure g-C₃N₄@TiO₂ via Controlled Ultrathin g-C₃N₄ Layer. *Appl Catal B* **2018**, *220*, 337–347. <https://doi.org/10.1016/j.apcatb.2017.08.004>.
163. Wang, J.; Yang, Z.; Gao, X.; Yao, W.; Wei, W.; Chen, X.; Zong, R.; Zhu, Y. Core-Shell g-C₃N₄@ZnO Composites as Photoanodes with Double Synergistic Effects for Enhanced Visible-Light Photoelectrocatalytic Activities. *Appl Catal B* **2017**, *217*, 169–180. <https://doi.org/10.1016/j.apcatb.2017.05.034>.
164. Zhang, J.; Sun, P.; Jiang, P.; Guo, Z.; Liu, W.; Lu, Q.; Cao, W. The Formation Mechanism of TiO₂ Polymorphs under Hydrothermal Conditions Based on the Structural Evolution of [Ti(OH)_h(H₂O)_{6-h}]_{4-h} Monomers. *J Mater Chem C Mater* **2019**, *7* (19), 5764–5771. <https://doi.org/10.1039/c9tc00662a>.
165. Li, G.; Li, L.; Boerio-Goates, J.; Woodfield, B. F. High Purity Anatase TiO₂ Nanocrystals: Near Room-Temperature Synthesis, Grain Growth Kinetics, and Surface Hydration Chemistry. *JACS Articles* **2005**, *127* (24), 8659–8666. <https://doi.org/10.1021/ja050517g>.
166. Dong, M.; Yu, J.; Wang, J.; Zhang, Q.; Lin, W. Construction of Phenyl-Grafted Carbon Nitride for Enhancing the Visible-Light Activity. *Chem Phys Lett* **2019**, *737*. <https://doi.org/10.1016/j.cplett.2019.136817>.
167. Mohamed, M. A.; Jaafar, J.; M. Zain, M. F.; Minggu, L. J.; Kassim, M. B.; Rosmi, M. S.; Alias, N. H.; Mohamad Nor, N. A.; W. Salleh, W. N.; Othman, M. H. D. In-Depth Understanding of Core-Shell Nanoarchitecture Evolution of g-C₃N₄@C, N Co-Doped Anatase/Rutile: Efficient Charge Separation and Enhanced Visible-Light Photocatalytic Performance. *Appl Surf Sci* **2018**, *436*, 302–318. <https://doi.org/10.1016/j.apsusc.2017.11.229>.

168. Liu, C.; Niu, H.; Wang, D.; Gao, C.; Said, A.; Liu, Y.; Wang, G.; Tung, C. H.; Wang, Y. S-Scheme Bi-Oxide/Ti-Oxide Molecular Hybrid for Photocatalytic Cycloaddition of Carbon Dioxide to Epoxides. *ACS Catal* **2022**, *12* (14), 8202–8213. <https://doi.org/10.1021/acscatal.2c02256>.
169. Yang, Y.; Wang, S.; Ji, W.; Li, T.; Li, S.; Zhao, Q.; Li, G. TiCl₄ Precursor Affecting the Performance of HTM-Free Carbon-Based Perovskite Solar Cell. *Nanotechnology* **2024**, *35* (7). <https://doi.org/10.1088/1361-6528/ad0d22>.
170. Wei, H.; McMaster, W. A.; Tan, J. Z. Y.; Cao, L.; Chen, D.; Caruso, R. A. Mesoporous TiO₂/g-C₃N₄ Microspheres with Enhanced Visible-Light Photocatalytic Activity. *Journal of Physical Chemistry C* **2017**, *121* (40), 22114–22122. <https://doi.org/10.1021/acs.jpcc.7b06493>.
171. Adel Hamza, M.; Abd El-Rahman, S. A.; Ramadan, S. K.; Ezz-Elregal, E. E. M.; Rizk, S. A.; Abou-Gamra, Z. M. The Enhanced Visible-Light-Driven Photocatalytic Performance of Nanocrystalline TiO₂ Decorated by Quinazolinone-Photosensitizer toward Photocatalytic Treatment of Simulated Wastewater. *J Photochem Photobiol A Chem* **2024**, *452*. <https://doi.org/10.1016/j.jphotochem.2024.115599>.
172. Valadez-Renteria, E.; Oliva, J.; Rodriguez-Gonzalez, V. A Sustainable and Green Chlorophyll/TiO₂:W Composite Supported on Recycled Plastic Bottle Caps for the Complete Removal of Rhodamine B Contaminant from Drinking Water. *J Environ Manage* **2022**, *315*. <https://doi.org/10.1016/j.jenvman.2022.115204>.
173. Phadtare, V. D.; Parale, V. G.; Kim, T.; Lee, K. Y.; Kadam, A. N.; Choi, H.; Kim, Y.; Dhavale, R. P.; Lee, S. W.; Park, H. H. Ultrasonically Dispersed Ultrathin G-C₃N₄ Nanosheet/BaBi₂Nb₂O₉ Heterojunction Photocatalysts for Efficient Photocatalytic Degradation of Organic Pollutant. *J Alloys Compd* **2021**, *884*. <https://doi.org/10.1016/j.jallcom.2021.161037>.
174. Zhao, K.; Zhang, Z.; Feng, Y.; Lin, S.; Li, H.; Gao, X. Surface Oxygen Vacancy Modified Bi₂MoO₆/MIL-88B(Fe) Heterostructure with Enhanced Spatial Charge Separation at the Bulk & Interface. *Appl Catal B* **2020**, *268*. <https://doi.org/10.1016/j.apcatb.2020.118740>.
175. Lu, C.; Wu, W.; Zhou, H. In Situ Fabrication of BiOBr/BiFeWO₆ Heterojunction with Excellent Photodegradation Activity under Visible Light. *J Solid State Chem* **2021**, *303*. <https://doi.org/10.1016/j.jssc.2021.122465>.
176. Babu, B.; Koutavarapu, R.; Shim, J.; Yoo, K. SnO₂ Quantum Dots Decorated NiFe₂O₄ Nanoplates: 0D/2D Heterojunction for Enhanced Visible-Light-Driven Photocatalysis. *Mater Sci Semicond Process* **2020**, *107*. <https://doi.org/10.1016/j.mssp.2019.104834>.
177. Kumaravel, V.; Imam, M. D.; Badreldin, A.; Chava, R. K.; Do, J. Y.; Kang, M.; Abdel-Wahab, A. Photocatalytic Hydrogen Production: Role of Sacrificial Reagents on the Activity of Oxide, Carbon, and Sulfide Catalysts. *Catalysts* **2019**, *9* (3). <https://doi.org/10.3390/catal9030276>.
178. Dai, D.; Qiu, J.; Xia, G.; Tang, Y.; Yao, J. Defect Engineering Promoted Photocatalysis for Lignin Depolymerization: Performance and Mechanism Insight. *ACS Catal* **2023**, *13* (22), 14987–14995. <https://doi.org/10.1021/acscatal.3c03462>.
179. Zhang, J.; Toe, C. Y.; Kumar, P.; Scott, J.; Amal, R. Engineering Defects in TiO₂ for the Simultaneous Production of Hydrogen and Organic Products. *Appl Catal B* **2023**, *333*. <https://doi.org/10.1016/j.apcatb.2023.122765>.
180. Shu, Z.; Cai, Y.; Ji, J.; Tang, C.; Yu, S.; Zou, W.; Dong, L. Pt Deposits on TiO₂ for Photocatalytic H₂ Evolution: Pt Is Not Only the Cocatalyst, but Also the Defect Repair Agent. *Catalysts* **2020**, *10* (9), 1–12. <https://doi.org/10.3390/catal10091047>.
181. Shao, M.; Shao, Y.; Pan, H. Progress on Enhancing the Charge Separation Efficiency of Carbon Nitride or Robust Photocatalytic H₂ Production. PCCP. Royal Society of Chemistry March 19, 2024, pp 11243–11262. <https://doi.org/10.1039/d3p06333j>.
182. Soni, V.; Khosla, A.; Singh, P.; Nguyen, V.-H.; Le, Q. Van; Selvasembian, R.; Hussain, C. M.; Thakur, S.; Raizada, P. Current Perspective in Metal Oxide Based Photocatalysts for Virus Disinfection: A Review. *J Environ Manage* **2022**, *308*, 114617. <https://doi.org/https://doi.org/10.1016/j.jenvman.2022.114617>.
183. Schiller, C. D.; Kainz, A.; Mynett, K.; Gescher, A. Assessment of Viability of Hepatocytes in Suspension Using the MTT Assay. *Toxicology in Vitro* **1992**, *6* (6), 575–578. [https://doi.org/https://doi.org/10.1016/0887-2333\(92\)90070-8](https://doi.org/https://doi.org/10.1016/0887-2333(92)90070-8).

184. Porcu, S.; Maloccu, S.; Corona, A.; Hazra, M.; David, T.C.; Chiriu, D.; Carbonaro, C.M.; Tramontano, E.; Ricci, P.C. Visible Light-Mediated Inactivation of H1N1 Virus Using Polymer-Based Heterojunction Photocatalyst. *Polymers* **2023**, *15*, 2536. <https://doi.org/10.3390/polym15112536>
185. Nakano, R.; Ishiguro, H.; Yao, Y.; Kajioka, J.; Fujishima, A.; Sunada, K.; Minoshima, M.; Hashimoto, K.; Kubota, Y. Photocatalytic Inactivation of Influenza Virus by Titanium Dioxide Thin Film. *Photochemical & Photobiological Sciences* **2012**, *11* (8), 1293–1298. <https://doi.org/10.1039/c2pp05414k>.
186. Cui, H.; Jiang, J.; Gu, W.; Sun, C.; Wu, D.; Yang, T.; Yang, G. Photocatalytic Inactivation Efficiency of Anatase Nano-TiO₂ Sol on the H₉N₂ Avian Influenza Virus. *Photochem Photobiol* **2010**, *86* (5), 1135–1139. <https://doi.org/10.1111/j.1751-1097.2010.00763.x>.
187. De Pasquale, I.; Lo Porto, C.; Dell'Edera, M.; Curri, M. L.; Comparelli, R. TiO₂-based nanomaterials assisted photocatalytic treatment for virus inactivation: perspectives and applications. *Current Opinion in Chemical Engineering* **2021**, *34*, 100716. <https://doi.org/10.1016/j.coche.2021.100716>.
188. Hasija, V.; Patial, S.; Singh, P.; Nguyen, V.-H.; Van Le, Q.; Thakur, V. K.; Hussain, C. M.; Selvasembian, R.; Huang, C.-W.; Thakur, S.; Raizada, P. Photocatalytic inactivation of viruses using graphitic Carbon Nitride-Based photocatalysts: virucidal performance and mechanism. *Catalysts* **2021**, *11* (12), 1448. <https://doi.org/10.3390/catal11121448>.
189. Zhang, C.; Li, Y.; Shuai, D.; Shen, Y.; Wang, D. Progress and challenges in photocatalytic disinfection of waterborne Viruses: A review to fill current knowledge gaps. *Chemical Engineering Journal* **2018**, *355*, 399–415. <https://doi.org/10.1016/j.cej.2018.08.158>.
190. Nandan, A.; Siddiqui, N. A.; Singh, C.; Aeri, A.; Gwenzi, W.; Ighalo, J. O.; de Carvalho Nagliate, P.; Meili, L.; Singh, P.; Chaukura, N.; Rangabhashiyam, S. COVID-19 Pandemic in Uttarakhand, India: Environmental Recovery or Degradation? *J Environ Chem Eng* **2021**, *9* (6), 106595. <https://doi.org/https://doi.org/10.1016/j.jece.2021.106595>.
191. Juan Du, Songmei Li, Zhiguo Du, Shiming Meng, Bin Li, Boron/oxygen-codoped graphitic carbon nitride nanomesh for efficient photocatalytic hydrogen evolution, *Chemical Engineering Journal*, Volume 407, 2021, 127114, ISSN 1385-8947, <https://doi.org/10.1016/j.cej.2020.127114>.
192. Thaweesak S, Wang S, Lyu M, Xiao M, Peerakiatkhajohn P, Wang L. Boron-doped graphitic carbon nitride nanosheets for enhanced visible light photocatalytic water splitting. *Dalton Trans.* **2017** Aug 15;46(32):10714-10720. doi: 10.1039/c7dt00933j. PMID: 28590476.
193. Lin, T., Song, Z., Wu, Y., Chen, L., Wang, S., Fu, F., & Guo, L. (2018). Boron- and phenyl-codoped graphitic carbon nitride with greatly enhanced light responsive range for photocatalytic disinfection. *Journal of Hazardous Materials*, *358*, 62–68. <https://doi.org/10.1016/j.jhazmat.2018.06.053>
194. Pattanayak, D. S.; Pal, D.; Mishra, J.; Thakur, C. Noble Metal-Free Doped Graphitic Carbon Nitride (g-C₃N₄) for Efficient Photodegradation of Antibiotics: Progress, Limitations, and Future Directions. *Environmental Science and Pollution Research*. Springer Science and Business Media Deutschland GmbH February 1, 2023, pp 25546–25558. <https://doi.org/10.1007/s11356-022-20170-9>.
195. Kalidasan, K.; Mallapur, S.; Munirathnam, K.; Nagarajaiah, H.; Reddy, M. B. M.; Kakarla, R. R.; Raghu, A. V. Transition Metals-Doped g-C₃N₄ Nanostructures as Advanced Photocatalysts for Energy and Environmental Applications. *Chemosphere* **2024**, *352*. <https://doi.org/10.1016/j.chemosphere.2024.141354>.
196. Hu, J.; Zhang, P.; An, W.; Liu, L.; Liang, Y.; Cui, W. In-Situ Fe-Doped g-C₃N₄ Heterogeneous Catalyst via Photocatalysis-Fenton Reaction with Enriched Photocatalytic Performance for Removal of Complex Wastewater. *Appl Catal B* **2019**, *245*, 130–142. <https://doi.org/10.1016/j.apcatb.2018.12.029>.
197. Sudrajat, H.; Hartuti, S. One-Pot, Solid-State Loading of Zn into g-C₃N₄ for Increasing the Population of Photoexcited Electrons and the Rate of Photocatalytic Hydrogen Evolution. *Optik (Stuttg)* **2019**, *181*, 1057–1065. <https://doi.org/10.1016/j.ijleo.2018.12.145>.

198. Arumugam, M.; Tahir, M.; Praserthdam, P. Effect of Nonmetals (B, O, P, and S) Doped with Porous g-C₃N₄ for Improved Electron Transfer towards Photocatalytic CO₂ Reduction with Water into CH₄. *Chemosphere* **2022**, *286*. <https://doi.org/10.1016/j.chemosphere.2021.131765>.
199. Zhao, D.; Wang, Y.; Dong, CL. *et al.* Boron-doped nitrogen-deficient carbon nitride-based Z-scheme heterostructures for photocatalytic overall water splitting. *Nat Energy* **6**, 388–397 (2021). <https://doi.org/10.1038/s41560-021-00795-9>
200. Warshagha, M. Z. A.; Muneer, M. Visible Light Active Boron Doped Phenyl-g-C₃N₄ Nanocomposites for Decomposition of Dyes. *Surfaces and Interfaces* **2021**, *26*. <https://doi.org/10.1016/j.surfin.2021.101394>.
201. Mishra, B. P.; Babu, P.; Parida, K. Phosphorous, Boron and Sulfur Doped g-C₃N₄ nanosheet: Synthesis, Characterization, and Comparative Study towards Photocatalytic Hydrogen Generation. In *Materials Today: Proceedings*; Elsevier Ltd, 2021; Vol. 35, pp 258–262. <https://doi.org/10.1016/j.matpr.2020.05.567>.
202. Chu, Y.; Zheng, X.; Fan, J. Preparation of Sodium and Boron Co-Doped Graphitic Carbon Nitride for the Enhanced Production of H₂O₂ via Two-Electron Oxygen Reduction and the Degradation of 2,4-DCP via Photocatalytic Oxidation Coupled with Fenton Oxidation. *Chemical Engineering Journal* **2022**, *431*. <https://doi.org/10.1016/j.cej.2021.134020>.
203. Zhang, K.; Song, R.; Wu, N.; Wang, Y.; Zhang, M.; Chen, X.; Wang, L.; Xing, J. Enhancing the Photoluminescence and Electroluminescence of Graphitic Carbon Nitride via Atomic and Molecular Co-Modification. *Journal of Physical Chemistry Letters* **2024**, *15* (4), 925–932. <https://doi.org/10.1021/acs.jpclett.3c03409>.
204. Chen, T.; Chen, P.; Zhang, Q.; Zheng, X.; Xie, Z.; Zeng, Y.; Chen, P.; Liu, H.; Liu, Y.; Lv, W.; Liu, G. Photocatalyst with a Metal-Free Electron-Hole Pair Double Transfer Mechanism for Pharmaceutical and Personal Care Product Degradation. *Environ Sci Nano* **2019**, *6* (11), 3292–3306. <https://doi.org/10.1039/c9en00756c>.
205. Wang, X.; Liu, B.; Xiao, X.; Wang, S.; Huang, W. Boron Dopant Simultaneously Achieving Nanostructure Control and Electronic Structure Tuning of Graphitic Carbon Nitride with Enhanced Photocatalytic Activity. *J Mater Chem C Mater* **2021**, *9* (41), 14876–14884. <https://doi.org/10.1039/d1tc04142h>.
206. Raziq, F.; Qu, Y.; Zhang, X.; Humayun, M.; Wu, J.; Zada, A.; Yu, H.; Sun, X.; Jing, L. Enhanced Cocatalyst-Free Visible-Light Activities for Photocatalytic Fuel Production of g-C₃N₄ by Trapping Holes and Transferring Electrons. *Journal of Physical Chemistry C* **2016**, *120* (1), 98–107.
207. Wei, B.; Niu, C.; Zhou, G.; Sun, J.; Mei, Q.; An, Z.; Li, M.; He, M. Nonmetal Doped Carbon Nitride Nanosheet as Photocatalyst for Degradation of 4, 5-Dichloroguaiacol. *Environ Res* **2022**, *20*. <https://doi.org/10.1016/j.envres.2021.112623>.
208. Bhakare, M. A.; Lokhande, K. D.; Dhumal, P. S.; Bondarde, M. P.; Some, S. Multifunctional Heteroatom Doped Sustainable Carbon Nanocomposite for Rapid Removal of Persistent Organic Pollutant and Iodine from Water. *Sep Purif Technol* **2022**, *278*. <https://doi.org/10.1016/j.seppur.2021.119490>.
209. Baqi, S.; Deng, B.; Guo, Y.; Zhang, R. Q. Novel Two-Step Surface Boron Decoration of Graphitic Carbon Nitride Photoelectrodes for Efficient Charge Transport and Separation. *Journal of Physical Chemistry C* **2021**, *125* (45), 25207–25216. <https://doi.org/10.1021/acs.jpcc.1c06864>.
210. Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure and Applied Chemistry* **2015**, *87* (9–10), 1051–1069. <https://doi.org/10.1515/pac-2014-1117>.
211. Sangeetha, P.; Jayapandi, & S.; Saranya, & C.; Ramakrishnan, V. Phonon Confinement and Size Effect in Raman Spectra of TiO₂ Nanocrystal towards Photocatalysis Application. <https://doi.org/10.1007/s41779-020-00555-0/Published>.
212. Campbell, I. H.; Fauchet, P. M. *THE EFFECTS OF MICROCRYSTAL SIZE AND SHAPE ON THE ONE PHONON RAMAN SPECTRA OF CRYSTALLINE SEMICONDUCTORS*; 1986; Vol. 58.

213. Cappelletti, G.; Ricci, C.; Ardizzone, S.; Parola, C.; Anedda, A. Aged Titania Nanoparticles: The Simultaneous Control of Local and Long-Range Properties. *Journal of Physical Chemistry B* **2005**, *109* (10), 4448–4454. <https://doi.org/10.1021/jp045192p>
214. Bersani, D.; Lottici, P. P.; Ding, X. Z. Phonon Confinement Effects in the Raman Scattering by TiO₂ Nanocrystals. *Appl Phys Lett* **1998**, *72* (1), 73–75. <https://doi.org/10.1063/1.120648>.
215. Zhang, W. F.; He, Y. L.; Zhang, S.; Yin, Z.; Chen, Q. *Raman Scattering Study on Anatase TiO₂ Nanocrystals*; 2000; Vol. 33.