



GDAAŃSK UNIVERSITY
OF TECHNOLOGY

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Scientific discipline: Chemical Sciences

DOCTORAL DISSERTATION

Title of doctoral dissertation: Hybrid g-C₃N₄-based photocatalysts for degradation of pharmaceutical micropollutants

Title of doctoral dissertation (in Polish): Hybrydowe fotokatalizatory na bazie g-C₃N₄ do degradacji zanieczyszczeń farmaceutycznych

Supervisor

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Prof. Anna Zielińska-Jurek, PhD, DSc, Eng

Gdańsk, 30 April 2026

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DESCRIPTION OF DOCTORAL DISSERTATION

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Title of doctoral dissertation in Polish: Hybrydowe fotokatalizatory na bazie g-C₃N₄ do degradacji zanieczyszczeń farmaceutycznych

Language of doctoral dissertation: English

Supervisor: prof. dr hab inż. Anna Zielińska-Jurek

Date of doctoral defense:

Keywords of doctoral dissertation in Polish: fotokataliza heterogeniczna, grafitowy azotek węgla, farmaceutyki, oczyszczanie wody, peroksymonosulfany, magnetyczne fotokatalizatory

Keywords of doctoral dissertation in English: heterogeneous photocatalysis, graphitic carbon nitride, pharmaceuticals, water treatment, peroxymonosulfate, magnetic photocatalysts

Summary of doctoral dissertation in Polish:

Celem pracy doktorskiej było opracowanie i zbadanie wielofunkcyjnych hybrydowych fotokatalizatorów na bazie g-C₃N₄ przeznaczonych do degradacji mikrozanieczyszczeń farmaceutycznych w środowisku wodnym. Jako związki modelowe wybrano karbamazepinę (CBZ), paracetamol (ACT) oraz ibuprofen (IBU), ze względu na ich powszechne stosowanie oraz częste występowanie zarówno w ściekach, jak i wodach powierzchniowych na całym świecie. Dodatkowo, produkty ich przemian mogą wykazywać zwiększoną toksyczność wobec organizmów wodnych, stanowiąc zagrożenie dla stabilności ekosystemów i bioróżnorodności. Grafitowy azotek węgla o przerwie energetycznej wynoszącej około 2,7 eV, jest relatywnie tanim półprzewodnikiem aktywnym w zakresie światła widzialnego otrzymywanym z ogólnodostępnych prekursorów, takich jak melamina, mocznik czy tiomocznik. Jednak jego ograniczenia, w tym wysoka szybkość rekombinacji nośników ładunku, wymagają zastosowania odpowiednich strategii modyfikacji w celu poprawy separacji nośników ładunku, stabilności oraz aktywności fotokatalitycznej.

W niniejszej pracy zastosowano domieszkowanie g-C₃N₄ pierwiastkami bloku p, takimi jak fosfor i siarka, prowadzące do powstania centrów bogatych w elektrony, sprzyjających delokalizacji ładunku i ograniczeniu rekombinacji nośników ładunku. Następnie domieszkowany grafitowy azotek węgla połączono z półprzewodnikiem o szerokiej przerwie energetycznej w postaci dwuwymiarowego cząstek TiO₂. Utworzone heterozłącze umożliwiło efektywniejszą separację par elektron-dziura oraz rozszerzenie zakresu absorpcji promieniowania elektromagnetycznego. Otrzymany heterokompozyt wykazywał efektywność w degradacji karbamazepiny i paracetamolu.

W kolejnym etapie badań skoncentrowano się na poprawie możliwości odzysku i ponownego wykorzystania fotokatalizatora. W tym celu do struktury kompozytu wprowadzono nanocząstki ferrytu spinelowego o właściwościach superparamagnetycznych, umożliwiające łatwą separację materiału fotokatalitycznego z fazy wodnej. Otrzymany trójskładnikowy heterokompozyt $\text{ZnFe}_2\text{O}_4/(\text{P}, \text{S})\text{-g-C}_3\text{N}_4/2\text{D TiO}_2$ wykazywał zwiększoną aktywność fotokatalityczną oraz stabilność w co najmniej sześciu kolejnych cyklach degradacji. Dodatkowo, integracja z procesem zaawansowanego utleniania opartym na aktywacji peroksosiarcznanu (PS-AOP) znacząco zwiększyła efektywność degradacji karbamazepiny i ibuprofenu.

Ponadto, właściwości magnetyczne materiału umożliwiły zbadanie wpływu zewnętrznego pola magnetycznego na przebieg procesu fotokatalitycznego. Wykazano, że obecność pola magnetycznego sprzyja separacji nośników ładunku poprzez mechanizmy takie jak siła Lorentza oraz polaryzacja spinowa, co prowadzi do zwiększenia efektywności degradacji zanieczyszczeń.

W dalszej części pracy zastosowano chemiczną funkcjonalizację $\text{g-C}_3\text{N}_4$ poprzez hydroksylację. Hydroksylowany grafitowy azotek węgla oraz zdefektowany modyfikowany hydroksylowany tlenek cynku połączono w celu utworzenia heterostruktury typu sfrustrowanej pary Lewisa (FLP). Otrzymany układ wykazał wysoką skuteczność w degradacji karbamazepiny, która ulegała dalszemu zwiększeniu w obecności peroksosiarcznanu (PS-AOP).

Podsumowując, zaproponowana strategia badawcza oparta na synergicznym połączeniu inżynierii materiałowej oraz intensyfikacji procesów utleniania wskazuje na duży potencjał opracowanych materiałów do zaawansowanego oczyszczania wód w ramach czwartego stopnia oczyszczania ścieków.

Summary of doctoral dissertation in English:

The aim of the doctoral dissertation was to develop and investigate multifunctional $\text{g-C}_3\text{N}_4$ -based hybrid photocatalysts for pharmaceutical micropollutants degradation in water. Carbamazepine (CBZ), acetaminophen (ACT), and ibuprofen (IBU) were selected as representative compounds due to their widespread use and frequent occurrence in both wastewater and surface waters worldwide. Moreover, their transformation products may exhibit increased toxicity toward aquatic organisms and pose a risk to ecosystem stability and biodiversity. Graphitic carbon nitride with a bandgap of about 2.7 eV is a visible light active semiconductor and represents an environmentally friendly and low-cost material, synthesised from abundant precursors such as melamine, urea and thiourea. However, its limitations, including a high recombination rate of photogenerated charge carriers require modification strategies to improve electron-hole separation, stability, and overall photocatalytic activity.

The first strategy employed in this doctoral dissertation was elemental doping of $\text{g-C}_3\text{N}_4$ with p-block elements, including phosphorus and sulphur, leading to the formation of electron-rich sites that enhance charge delocalisation and suppress electron-hole recombination. Subsequently, phosphorus- and sulphur-doped graphitic carbon nitride was combined with a wide band gap semiconductor in the form of 2D TiO_2 . This heterojunction enabled improved charge separation and extended light absorption into

the solar spectrum. The formation of heterocomposite enabled the efficient degradation of carbamazepine and acetaminophen.

Following the successful formation of the heterocomposite, subsequent work focused on the development of photocatalysts with improved post-treatment separability from the aqueous phase. Therefore, the next modification step involved the incorporation of magnetic functionality, enabling facile recovery and enhanced recyclability. The resulting ternary heterocomposite of $\text{ZnFe}_2\text{O}_4/(\text{P}, \text{S})\text{-g-C}_3\text{N}_4/2\text{D TiO}_2$ exhibited improved photocatalytic activity and could be recycled for up to six consecutive cycles. Additionally, the integration of the heterocomposite with the persulfate-based advanced oxidation process (PS-AOP) significantly improved degradation efficiency, leading to the complete removal of carbamazepine and ibuprofen within 30 min.

Furthermore, the magnetic properties of the system enabled the investigation of magnetic field-assisted photocatalysis, where the application of an external magnetic field enhanced charge carriers' separation through mechanisms such as the Lorentz force and spin polarisation.

As a further modification strategy, chemical functionalisation of g- C_3N_4 by hydroxylation was investigated. Hydroxylated graphitic carbon nitride and defect-engineered hydroxylated zinc oxide were combined to form a frustrated Lewis pair (FLP)-type heterocomposite. The resulting material demonstrated efficient carbamazepine degradation, which was further improved upon integration with a persulfate-assisted advanced oxidation process.

Overall, the proposed research strategy provided synergistic integration of material design and process intensification, highlighting strong potential for sustainable, efficient wastewater treatment.

ACKNOWLEDGMENT

The pursuit of the PhD has been an enlightening journey, fostering both wisdom and humbleness, and significantly influencing my academic and personal development.

I would like to express my sincere gratitude to my supervisor, **Professor Anna Zielińska-Jurek**, for giving me the opportunity to pursue my PhD. Her invaluable guidance, insightful feedback, and constant support has been the instrument in the completion of this work. Thank you for your patience, resilience and continuous encouragement throughout this journey.

I would also like to thank the **members of the Department of Process Engineering and Chemical Technology**, and the **Photocatalysis Team**, especially Anna Grzegórska, Marta Kowalkińska, and Szymon Dudziak.

Many thanks to all collaborators whose valuable contributions have supported the publications arising from this work.

Finally, I am deeply grateful to **my family**, my father Kujtim, my mother Liri, my brother Arnold, my sister-in-law Elsa, and my nephew Noah for their enduring support and unwavering belief in me. Their love and encouragement have been a constant source of strength and motivation. I would like to express my heartfelt thanks to **my friends**, Sara Sumbal and Justyna Gołabek, for standing by me during challenging and joyful moments.

I wish to honour the memory of Anila, whose pride in me continues to be a source of inspiration.



The research presented in the PhD dissertation was part of the project:

Development of multifunctional materials for thermo-photocatalytic reduction of carbon dioxide and photodegradation of persistent organic pollutants, Polish National Science Centre, UMO-2021/43/B/ST5/02983.

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Abbreviations

API- Active pharmaceutical ingredients

CBZ-Carbamazepine

ACT-Acetaminophen

IBU-Ibuprofen

AOP-Advanced oxidation processes

BOD-Biological oxygen demand

COD-Chemical oxygen demand

TOC-Total organic carbon

UV-Ultraviolet light (photon wavelength in the range of 100-400 nm)

Vis-Visible light (photon wavelength in the range of 400-780 nm)

IR-Infrared light (photon wavelength above 780 nm)

NIR-Near infrared light (photon wavelength from 780 nm to 22 000 nm)

ROS-Reactive oxygen species

SR-AOP-Persulfate based advanced oxidation processes

PS-AOP-Persulfate based advanced oxidation processes

PDS-Peroxydisulfate

PMS-Peroxymonosulfate

VB-Valence band

CB-Conduction band

LUMO-Lowest unoccupied molecular orbital

HOMO-Highest unoccupied molecular orbital

FLP-Frustrated Lewis Pair

LVRPA-Local volume rate of photon absorption

TRPA-Total rate of photon absorption

B3LYP-hybrid exchange correlation function (Becke, 3-parameter, Lee-Yang-Parr)

DFT-Density Functional Theory

LCAO-Linear combination of atomic orbitals

EDD-Electron difference density

EDP-Electron difference potential

DOS-Density of states

PLDOS-Projected local density of states

PZC-Point of zero charge

MF-Magnetic field

MFE-Magnetic field effect

XRD-X-ray diffraction

FTIR- Fourier transform infrared spectroscopy

UV-Vis (DRs)- Diffuse reflectance spectroscopy

PL- Photoluminescence

SEM-Scanning electron microscopy

EDS, EDX-Energy dispersive x-ray spectroscopy

TEM-Transmission electron microscopy

XPS-X-ray photoelectron spectroscopy

XRF-X-ray fluorometry

HPLC-High performance liquid chromatography

LC-MS-Liquid chromatography mass spectrometry

Chapter I. Introduction

1. Water contamination as a global environmental issue

Water is a renewable resource that is naturally replenished through the hydrological cycle, a process crucial for maintaining global water balance and ensuring the continuity of life and biodiversity. This essential element regulates the Earth's climate, dissolves important substances such as minerals, gases, salts, and organic compounds necessary for living organisms; provides habitats ranging from microorganisms to large marine species, participates in key chemical and biochemical reactions, and supplies water for drinking, agricultural irrigation, and industrial applications. Therefore, ensuring high-quality water and protecting it from contamination is a critical goal of sustainable development in the contemporary world.

However, rapid population growth and resource depletion have intensified urbanisation and industrialisation, increasing contaminant discharge into aquatic systems and driving global water pollution. In particular, effluents from industries such as petrochemical, textile, food processing, pharmaceutical, and personal care production contribute to the release of contaminants into natural water bodies [1-3]. Although conventional wastewater treatment technologies are widely implemented, they are not effective at removing micropollutants, particularly pesticides, dyes, personal care products, and pharmaceuticals that are poorly biodegradable and highly persistent.

As the pharmaceutical and biotechnology sector ranks among the leading industries in terms of investment-to-net sales ratio, its continued expansion is associated with a growing need for efficient wastewater treatment systems [4]. Approximately 100,000 tonnes of pharmaceuticals are produced globally each year, of which 24% is destined for the European market. More than 3,000 active pharmaceutical ingredients (APIs) are currently in use for human and veterinary purposes, and approximately 600 of them have been analysed in the environment as active substances [5]. Presence of active pharmaceutical ingredients has been detected in significantly high concentrations in pharmaceutical industry wastewater

effluents. This issue has been particularly pronounced in China and India, which together account for approximately 80–90% of global antibiotic production [5]. Numerous classes of pharmaceuticals, including analgesics and anti-inflammatory drugs, anticonvulsants, antibiotics, antidiabetics, beta-blockers, antidepressants, hormones, and anticancer agents, are frequently reported in wastewaters, surface waters, marine environments, and drinking waters at concentrations ranging from ng/L to $\mu\text{g/L}$ [6]. They are released into the environment through hospital and veterinary facilities, improper household disposal, ineffective wastewater treatment, landfill leachate, and drainage systems. Active pharmaceutical ingredients may persist in aquatic environments, undergo transformation into by-products, or be degraded through biotic processes involving microorganisms or abiotic processes such as oxidation, photolysis, or hydrolysis [7]. The active pharmaceutical ingredients, which remain resistant to biological degradation, infiltrate the hydrological cycle and may accumulate over time. This persistence poses risks to ecosystems, adversely affects aquatic organisms, and increases the potential for these pollutants to enter the food chain through bioaccumulation. The pathways of pharmaceutical emissions and their distribution within the hydrological cycle are illustrated in Figure 1, highlighting the complexity of micropollutants' transport and environmental fate.

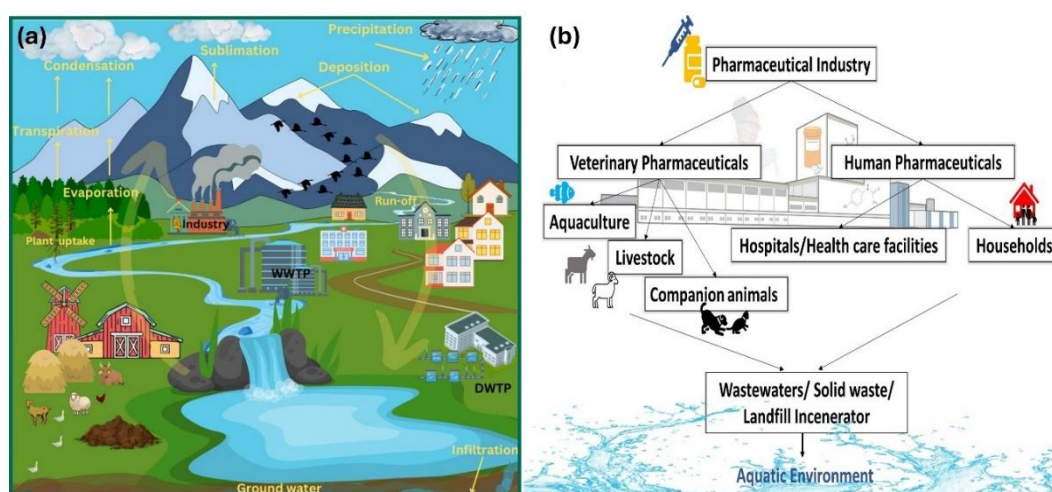
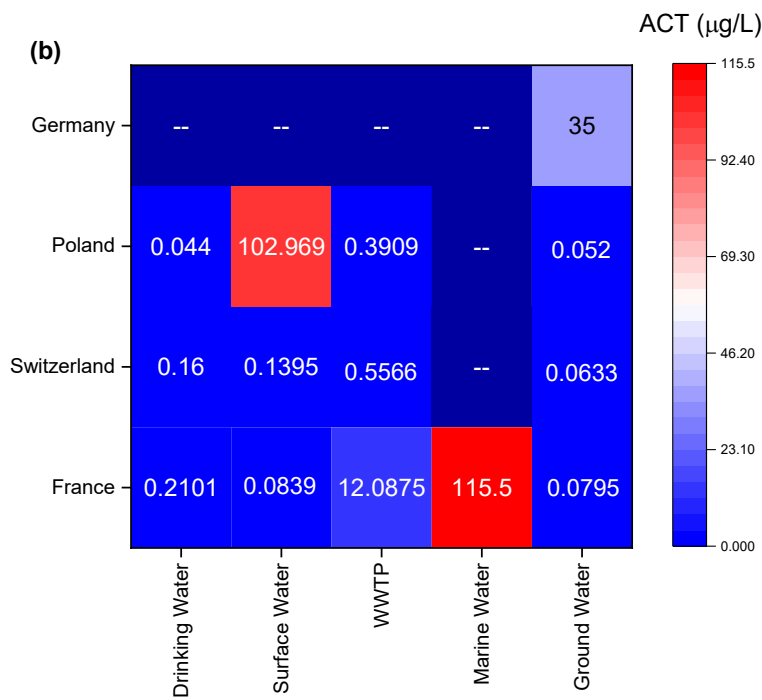
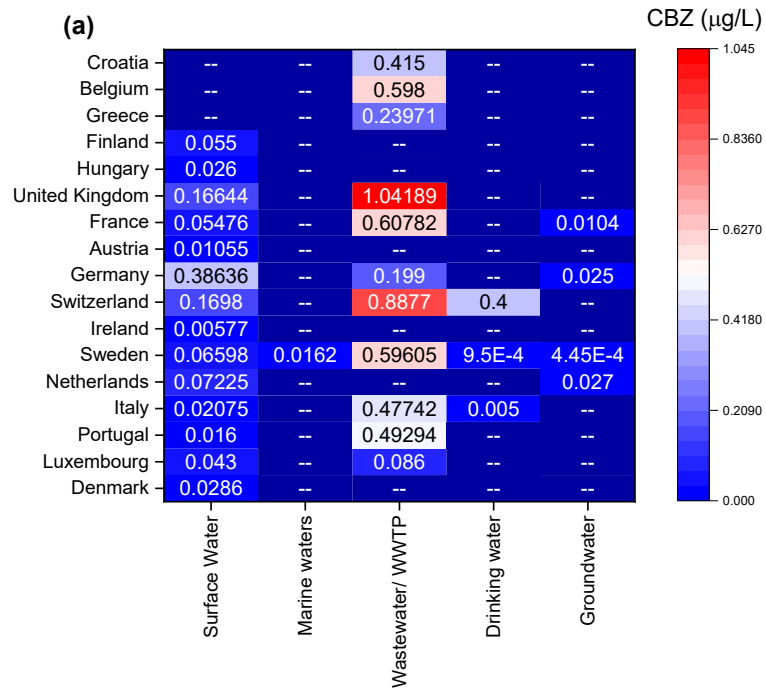


Figure 1: Water cycle (a) and active pharmaceutical ingredients (APIs) distribution in the environment (b). Based on the review article [Cako et al., Water Resources and Industry 31 (2024). 100242].

Carbamazepine is among the most frequently detected pharmaceuticals in aquatic environments and is therefore proposed as an anthropogenic marker of water contamination. Implementation of conventional biological wastewater treatment processes for the removal of carbamazepine has resulted in inefficient removal of the pollutant due to low sorption of its molecules onto activated sludge. Highly persistent pollutant of carbamazepine and its five metabolites, including 10,11-dihydro-10,11-dihydroxy-CBZ, 10,11-dihydro-10-hydroxy-CBZ, 10,11-epoxy-10,11-dihydro-CBZ, 2-hydroxy-CBZ, and 3-hydroxy-CBZ, were identified in 46 water samples measured in different sampling sites in Germany and Portugal [8]. Carbamazepine was also detected in wastewater from the United Kingdom and Switzerland, with concentrations of $1.04 \mu\text{g} \cdot \text{dm}^{-3}$ and $0.88 \mu\text{g} \cdot \text{dm}^{-3}$, respectively (Figure 2a). Additionally, carbamazepine frequently transforms into acridine, a highly toxic and persistent by-product [9].

Over the counter accessible drugs like ibuprofen and acetaminophen (paracetamol), classified as non-steroidal anti-inflammatory drugs, were frequently detected in European aqueous systems due to incomplete removal in conventional wastewater treatment methods. Collected samples from the Vistula river in Poland showed the presence of carbamazepine and ibuprofen at recorded concentrations of $0.104 \mu\text{g} \cdot \text{dm}^{-3}$ and $0.063 \mu\text{g} \cdot \text{dm}^{-3}$, respectively. High concentrations of acetaminophen have also been reported in other countries, including France ($115 \mu\text{g} \cdot \text{dm}^{-3}$ in marine waters) and Germany ($35 \mu\text{g} \cdot \text{dm}^{-3}$). Elevated concentrations of ibuprofen were also noticed at wastewater treatment plant sampling points in Denmark and Poland, reaching $17.6 \mu\text{g} \cdot \text{dm}^{-3}$ and $16.3 \mu\text{g} \cdot \text{dm}^{-3}$ (Figure 2c). Pharmaceuticals adversely affect the endocrine, locomotor, and reproductive systems of aquatic organisms. Reported concentrations of ibuprofen in aquatic species, including phytoplankton, zooplankton, and freshwater shrimps (*Macrobrachium nipponense* and *Exopalaemon modestus*), range from 28 ng/g in phytoplankton, 1–24 ng/g in zooplankton, 22 ng/g in *Macrobrachium nipponense*, and 4.0–26 ng/g in *Exopalaemon modestus* [10,11]. Acetaminophen concentration of $22.24 \text{ ng} \cdot \text{dm}^{-3}$ was found to pose a low ecological risk to crustaceans, while indicating a moderate risk to fish [11].



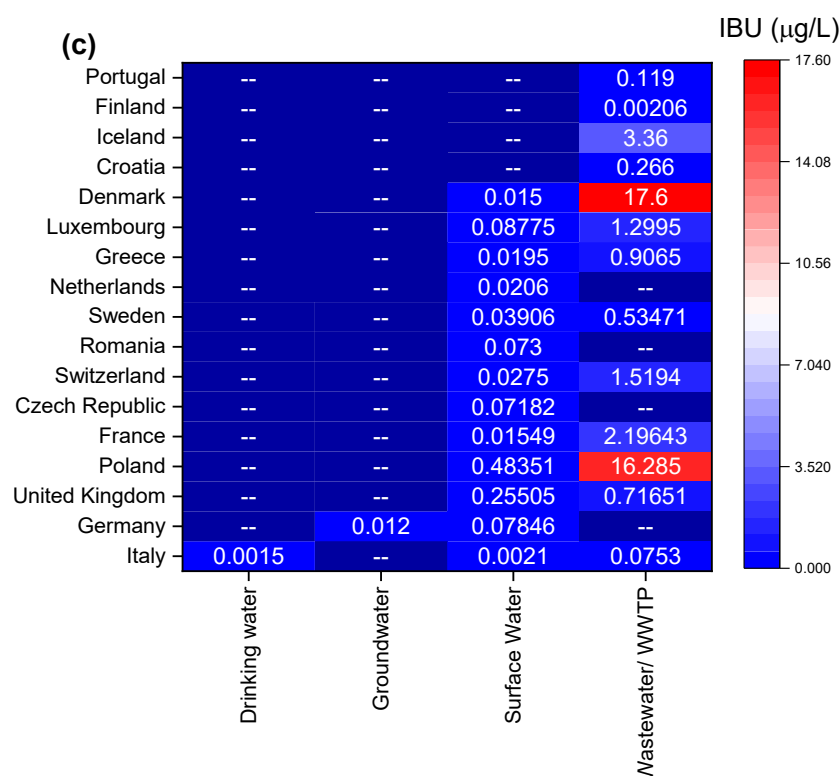


Figure 2. Monitoring data of carbamazepine (a), acetaminophen (b), and ibuprofen (c) detected in surface waters, marine waters, WWTP (after biological treatment), drinking water, and groundwater reported from different European countries [12].

The impact of chemicals and contaminants on the environment and living organisms can be estimated via 'Risk Quotient' (RQ). This dimensionless ratio suggests that for RQ values below 1, the contaminant poses minimal risk, and for values above 1, it poses potential risk to the environment and organisms [13]. Different pharmaceuticals, classified as antidepressants, are widely detected in water matrices and possess high potential risk to the aqueous environment due to their high risk quotients (RQs) of 4.88 for sertraline (SRT), 1.55 for citalopram (CTL), and 1.12 for bupropion (BUP) [14]. The toxicity of pharmaceuticals and their by-products can also be assessed using quantitative structure-activity relationship (QSAR) models, including the computer-based predictive tool Ecological Structure Activity Relationship Class Program (ECOSAR). The assessment of acute and chronic toxicity of different substances on fish, *Daphnia* and green algae is conducted through the analysis of lethal concentration (LC_{50}), effective concentration (EC_{50}), and chronic value (ChV). The effect of compounds can be classified as not harmful, harmful, toxic,

and very toxic, respectively, for determined ranges of $LC_{50}/EC_{50}/ChV > 10^2$, $10^2 \geq LC_{50}/EC_{50}/ChV > 10^1$, $10^1 \geq LC_{50}/EC_{50}/ChV > 10^0$, $LC_{50}/EC_{50}/ChV \leq 10^0$ [15]. ECOSAR toxicity prediction for carbamazepine showed moderate harmful effect in fish ($LC_{50, 96h}$), *Daphnia* ($LC_{50, 48h}$), and green algae ($EC_{50, 96h}$), whereas its intermediate, 9-carboxyaldehyde, showed high toxicity effect in aquatic organisms [16]. Acetaminophen exhibited high toxicity in *Daphnia* ($LC_{50, 48h}$) and green algae ($EC_{50, 96h}$), whereas moderate toxicity was observed for fish ($LC_{50, 96h}$) [17].

In view of this, carbamazepine, acetaminophen, and ibuprofen are of particular concern in Europe due to their frequent occurrence in municipal wastewater and surface waters, and their potential impact on aquatic organisms. Their environmental relevance extends beyond the scientific to the legislative, as reflected in European Union directives and monitoring frameworks (Figure 3). The revised Urban Wastewater Treatment Directive (EU) 2024/3019 broadens the scope of previous regulations regarding the removal of nitrogen and phosphorus for all large agglomerations and requires such treatment for discharges from agglomerations with a population equivalent (p.e.) of 10,000–100,000, where the receiving waters are sensitive to eutrophication [18].

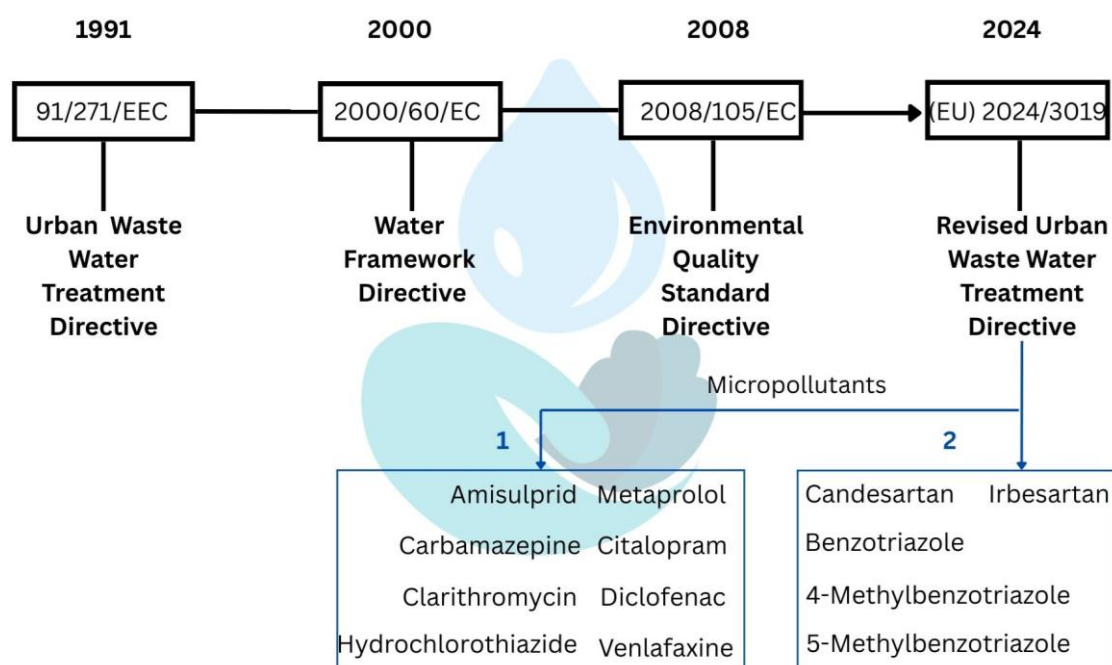


Figure 3. History of EU directives for remediation of aqueous systems.

Moreover, the new Directive, for the first time, requires the implementation of an advanced (quaternary) treatment step to degrade micropollutants, including pharmaceutical residues, achieving at least 80% removal efficiency for six selected substances (see Figure 3). Currently, carbamazepine and diclofenac are included among the micropollutants.

In this regard, there is a need to develop more advanced water treatment technologies to improve water quality and ensure the sustainability of water cycle management.

2. Advanced water treatment for micropollutants removal

The new mandatory EU Directive 2024/3019 requires the integration of quaternary treatment into existing wastewater treatment processes.

A proposed method for quaternary treatment involves the physical removal of contaminant molecules through adsorption with activated carbon, derived from carbon-rich materials such as biomass, wood, coal, and lignite [19]. Owing to its very high surface area and well-developed porous structure, it is widely used as an efficient adsorbent for the removal of a variety of pollutants from air and water. However, because adsorption is a physical process, activated carbon may become saturated over time, requiring periodic regeneration or replacement. Moreover, the presence of natural organic matter and coexisting ions in natural waters may inhibit the adsorption sites on activated carbon, whereas changes in environmental conditions can facilitate the desorption of pollutant molecules into the aqueous phase. Therefore, membrane filtration can be implemented to overcome the drawbacks of activated carbon. Membrane filtration offers improved operational stability and greater scalability in large wastewater applications. Membrane technologies such as microfiltration and ultrafiltration operate based on physical separation mechanisms, including size exclusion and electrostatic interactions, which facilitate consistent removal of contaminant molecules [20].

Furthermore, reverse osmosis, which uses a dense, non-porous membrane that operates via the solution-diffusion mechanism, is used to remove emerging contaminants efficiently. However, membrane technologies, including reverse

osmosis, are prone to disadvantages such as membrane fouling and high energy consumption [21].

Among the technologies considered for the fourth stage of wastewater treatment, ozonation is most commonly identified as a highly promising solution, enabling the efficient degradation of micropollutants. Ozonation is classified as an advanced oxidation process (AOP). Advanced oxidation processes are categorised by operational mechanisms for chemical and photochemical AOPs [22]. Advanced oxidation processes rely on the generation of reactive oxygen species, including hydroxyl radicals ($\text{HO}\cdot$), superoxide radicals ($\text{O}_2^{\cdot-}$), singlet oxygen ($^1\text{O}_2$), and sulfate radicals ($\text{SO}_4^{\cdot-}$), which efficiently degrade persistent contaminant molecules.

Ozone serves as a powerful oxidising agent with a redox potential of 2.07 V, targeting pollutant molecules via direct electrophilic reactions and indirect mechanisms involving ($\text{HO}\cdot$) radicals [23]. In 1840, Christian Friedrich Schönbein made the groundbreaking discovery of ozone, and 30 years later, Jacques-Louis Soret confirmed its chemical structure, establishing ozone as an allotrope of oxygen [24]. Ozone has been used as a germicide and bactericide since 1886, initially in France by de Meritens. Later in 1891, Frölich introduced ozone at a water treatment facility in Martinikenfield, West Germany. Ozone implementation was further expanded for viral inactivation, oxidation of organic molecules, removal of suspended solids, algae control, and microflocculation [25]. Ozone technologies are employed for their antimicrobial and disinfectant properties across a range of applications, including drinking water and wastewater treatment, aquaculture to maintain clean environments for aquatic organisms, the food industry, medical equipment sterilisation, and textile processing for antimicrobial and bleaching effects [26]. As a powerful advanced oxidation process, ozonation effectively breaks down complex pollutant molecules, increases biodegradability, diminishes colour and odour and serves as an on-site generation method, thus eliminating the necessity for hazardous chemical storage and transport [27]. Despite these advantages, ozone technologies have several limitations, including high energy and operational costs, low water solubility, and inefficient mass transfer. Furthermore, ozone is highly unstable,

requiring continuous generation and application, and may generate toxic by-products when treating persistent halogenated organic pollutants [27,28].

Another advanced wastewater treatment technology consists of Fenton-based AOPs, which is a pH-sensitive method that consists of the reaction of ferrous ions (Fe^{2+}) with hydrogen peroxide (H_2O_2), leading to the generation of ferric ions (Fe^{3+}), hydroxyl radicals, and hydroxyl ions under strong acidic conditions (pH of 2-3) [29]. At higher pH values, ferric ions tend to precipitate as ferric hydroxides, reducing iron availability in solution and consequently limiting the generation of hydroxyl radicals. The classical Fenton process employs iron(II) ions (Fe^{2+}). There are also modifications of this process, e.g., Fenton-like processes, which involve the use of ferric ions (Fe^{3+}) or other transition metal ions (M^{n+1}), which are reduced to their corresponding forms of (Fe^{2+}) or (M^n) and generate hydroperoxide ions ($E_o = 1.65 \text{ V}$) [30]. However, the main drawbacks of Fenton and Fenton-like processes in wastewater treatment are the generation of iron-containing sludge and the frequent need to maintain an acidic pH regime, which requires pH adjustment both before and after treatment.

Among advanced oxidation processes, heterogeneous photocatalysis is considered one of the most promising approaches, as it operates using a solid photoactive catalyst and solar irradiation, thereby reducing the need for continuous reagent input and potentially lowering the overall environmental impact.

Heterogeneous photocatalysis is a process in which a semiconductor absorbs light energy and initiates the chemical transformation of pollutant molecules [31]. Since the early development of heterogeneous photocatalysis, the most commonly utilized semiconductors in heterogeneous photocatalysis include titanium IV oxide (TiO_2), zinc (II) oxide (ZnO), cadmium (II) sulfide (CdS), copper (II) oxide (CuO), zinc (II) sulfide (ZnS), tungsten (VI) oxide (WO_3), molybdenum (IV) disulfide (MoS_2), bismuth orthovanadate (BiVO_4), tin (IV) oxide (SnO_2), copper (I) oxide (Cu_2O), bismuth (III) oxide (Bi_2O_3), strontium titanium (IV) oxide (SrTiO_3) [32].

Among semiconductor photocatalysts, titanium (IV) oxide and zinc (II) oxide are among the most widely investigated materials for the degradation of pollutants in the aqueous phase due to their strong oxidation potential [33,34]. However, their wide band gaps ($\sim 3.0\text{--}3.3 \text{ eV}$) limit photocatalytic activity predominantly to the UV

region. Moreover, both materials exhibit rapid recombination of photogenerated electron-hole pairs, further limiting their photocatalytic efficiency.

Developing and synthesising a highly active photocatalyst should meet the following requirements: a) the ability of light harvesting in a wide solar spectral range, b) the suitable energy band position of the semiconductor, c) the low recombination rate of electron-hole pairs (e^-h^+), d) high surface area and exposed active sites that facilitate the redox reactions [35]. The generated charge carriers migrate to the surface of the photocatalyst, initiating redox reactions in which holes (h^+) oxidise water molecules or hydroxide ions to generate hydroxyl radicals ($HO^\bullet$), while electrons (e^-) reduce oxygen molecules to form superoxide radicals ($O_2^{\bullet-}$). The reactive oxygen species (ROS) are essential for breaking down pollutant molecules, facilitating numerous chemical transformations, and achieving complete mineralisation [36].

In this regard, one of the main strategies for improving process efficiency is to accelerate the degradation kinetics of micropollutants through the rational design of photocatalytic materials and by exploiting synergistic interactions among integrated advanced water treatment processes.

2.1. Combination of heterogeneous photocatalysis with AOPs

Combining heterogeneous photocatalysis with different AOPs in hybrid processes can generate a high number of reactive oxygen species. For example, a hybrid process combining ozone (O_3) with TiO_2 -based photocatalysis increased the degradation and mineralisation rates of ibuprofen and diclofenac [37]. A Fenton-like process combined with a photocatalytic system using 3% Fe-MOF/g- C_3N_4 and H_2O_2 generated hydroxyl radicals, leading to complete degradation of tetracycline in 60 min [38]. Talwar et al. [39] reported that the dual effect of photocatalysis and photo-Fenton was a successful approach for treating industrial wastewater from a pharmaceutical effluent with 75% COD in 5 h, at a treatment cost of less than 0.1 $\$/dm^3$. Degradation of carbamazepine using Sb-doped Sn80%- $W_{20}\%$ -oxide coated anode in photoelectrocatalytic system resulted in complete removal of this drug within 60 minutes of treatment, and the system was estimated to be the most cost-effective process with energy consumption of less than 5 kWh/ m^3 , whereas the

photolysis and photocatalysis needed 32 and 24 kWh/m³ energy to remove 90% of CBZ [40]. This demonstrates that reaction kinetics and the selection of an appropriate photocatalytic material are crucial for reducing treatment costs in photocatalytic processes.

Another study revealed that the combination of sonolysis and photocatalysis synergistically increased the CBZ degradation, and the frequency of the sonoreactor was a very important parameter, since for high frequency, the bubbles collapsed rapidly, which increased the mass transfer of hydroxyl radicals into the bubble-liquid interface and the possibility to attack the CBZ molecules effectively [41]. However, from a technological perspective, sonolysis also increases the energy costs of the treatment process.

Furthermore, electrochemical advanced oxidation processes, such as electro-Fenton and photoelectro-Fenton, offer a viable method for in situ generation of highly reactive species. The electro-Fenton process consists of in-situ generation of hydrogen peroxide by the reduction of oxygen molecules in the cathode, and the produced H₂O₂ is later decomposed by ferrous ion (Fe²⁺) into hydroxyl radicals, whereas the anode is responsible for the oxidation of two water molecules to produce oxygen, hydrogen ions, and electrons [42]. Electro-Fenton can be considered an advanced oxidation process due to the in-situ generation of an oxidant; however, it requires an acidic pH medium and pH neutralisation after treatment [43]. The combination of electro-Fenton processes with irradiation (UV-vis or solar light) yields a hybrid photoelectro-Fenton system. The use of iron-based solid catalysts leads to the heterogeneous electro-Fenton process, which significantly reduces sludge generation compared to the conventional homogeneous Fenton process [44]. However, the relatively high operational costs and the dependence on reaction conditions in many AOP systems necessitate the development of treatment technologies that operate under mild conditions, within a near-neutral pH range, and require lower energy consumption.

Among homogeneous advanced oxidation processes, persulfates have recently attracted significant interest due to their ability to produce highly reactive sulfate radicals (SO₄•⁻) and hydroxyl radicals (HO•). These species exhibit high redox

potentials ($E_0 = 2.5\text{--}3.1\text{ V}$), making them among the strongest oxidants generated in situ in aqueous systems. During persulfate-based advanced oxidation processes (PS-AOPs), reactive species are produced through the activation of (PDS, $\text{S}_2\text{O}_8^{2-}$) or peroxymonosulfate (PMS, HSO_5^-). PS is highly soluble in water (about 556 g/dm^3 at $20\text{ }^\circ\text{C}$) and relatively stable due to the high bond energy of the persulfate bond (approximately 140 kJ/mol), which limits its direct reaction with organic compounds. Consequently, effective activation of PS is required to generate reactive radicals. This activation can be achieved using various approaches, including thermal treatment, irradiation with UV, visible, or solar light, sonochemical, and electrochemical methods. In addition, various catalytic materials can be used to improve the efficiency of persulfate activation [45-51]. Activation of PDS and PMS using carbon materials has also been studied. A broad range of carbon materials, including graphene, graphene oxide, reduced graphene oxide, activated carbon, biochar, carbon nanotubes, and graphitic carbon nitride, have been reported to promote surface interactions that play a key role in redox processes, electron transfer pathways, and the formation of reactive radical species [52,53]. The catalytic performance of carbon materials can be further improved by introducing surface defects and oxygen-containing functional groups, which act as active sites and enhance electron transfer, thereby facilitating redox reactions and improving the efficiency of persulfate activation. The subsequent approach to PS and PMS activation involves activation by transition metals such as Fe, Cu, and Co. They are introduced into the system as zero-valent metals, metal oxides, and metal-supported catalysts [54].

Reported studies have demonstrated that combining persulfate activation with other advanced oxidation processes can significantly enhance pollutant degradation and influence reaction kinetics. For example, UV-activated persulfate (UV/PS) has been shown to exhibit higher azathioprine degradation efficiency than the conventional UV/ H_2O_2 system [55]. Furthermore, the combination of visible light-active photocatalysts such as g- C_3N_4 with persulfate activation can increase the degradation efficiency of organic pollutants. Song et al. [56] investigated the interaction of g- C_3N_4 with peroxydisulfate (PDS) under simulated solar light and

found that this combination significantly improved the degradation of sulfamethoxazole. Similarly, oxygen- and phosphorus-doped g-C₃N₄, when combined with persulfate, synergistically degraded bisphenol A by almost 100% in 20 min, outperforming the standalone photocatalysis process, which achieved 99% degradation within 90 min of irradiation [57]. In addition, introducing defects in oxygen-doped 3D g-C₃N₄ proved to improve electron transfer and effectively improve peroxydisulfate activation under visible light irradiation, enabling the simultaneous pollutant degradation and hydrogen production [58]. A heterocomposite of TiO₂/g-C₃N₄ was used for acetaminophen degradation. The addition of 2 mM persulfate to the photocatalytic system resulted in 100% degradation and 82.5% mineralization of acetaminophen within 30 min [59]. The degradation rate of TiO₂/g-C₃N₄ combined with persulfate was 13 times greater than that of photocatalysis alone.

Overall, solar light-driven photocatalysis is an effective method for persulfate activation and enhanced pollutant degradation. The efficiency of this approach relies on effective material engineering to optimise light absorption, charge separation, and interfacial electron transfer.

2.2. Combination of heterogeneous photocatalysis with an external magnetic field

The application of an external magnetic field can enhance photocatalytic performance by suppressing the recombination of photogenerated charge carriers and influencing their transfer through spin polarisation effects in the photocatalyst. In recent years, significant research has focused on integrating photocatalysis with external magnetic-field activation to enhance photocatalytic efficiency and reduce charge recombination. The magnetic field promotes charge separation through spin polarisation and the Lorentz force. When a magnetic field is applied, the spin states of an electron become imbalanced, indicating that one spin orientation has a higher population than the other [60,61]. The magnetic field causes a slight reduction in energy for one spin direction and an increase in energy for the opposite direction. This phenomenon is also referred to as Zeeman splitting [61]. Spin polarisation leads to preferential alignment of charge carrier spins and inhibits the formation of singlet

states, which promotes rapid recombination [61]. Instead, it enhances the relative parallel spin (triplet like) configurations, which recombine slowly. Consequently, spin polarisation enhances charge separation by inhibiting the spin-allowed recombination pathways. The spin polarisation effect can be increased by modifying the photocatalyst structure and the magnetic field strength. Pan et al. [62] proved that by altering the content of metal vacancies in Ti-defected TiO_2 , it significantly improved the charge separation through parallel alignment of electron spin polarisations. Moreover, they observed that increasing the magnetic field strength from 0 Oe to 8000 Oe increased the degradation efficiency of the organic dyes Methyl orange, Rose Bengal, and Rhodamine B to approximately 20%, 45%, and 55%, respectively. The Sun et al. [63] investigated the photocatalytic degradation of Methylene blue using oxygen-vacancy graphene quantum dots (GQDs) and TiO_2 (GQDs/ TiO_2) under high magnetic fields ranging from 1000 mT to 5000 mT. The findings revealed that the magnetic field notably enhances spin polarisation, thereby promoting interactions between oxygen vacancies and electrons, while simultaneously suppressing charge recombination. Another study indicated that a combination of photocatalysis and an external magnetic field of 1500 Oe degraded 96.6% of Congo Red (CR) within 60 minutes, using a $\text{CoFe}_2\text{O}_4/\text{MoS}_2$ photocatalyst. The Lorentz force refers to the force that a charged particle encounters while moving through an electric or magnetic field, and it can influence the motion of photogenerated charge carriers [64]. The effectiveness of the magnetic field in the suppression of photogenerated charge carriers recombination was reported by Li et al. [65], who claimed that photocurrent density was increased when a magnetic field was applied in the system using $\alpha\text{-Fe}_2\text{O}_3/\text{rGO}$ photocatalyst. Overall, the reported studies indicate that magnetic-field-assisted photocatalysis is a viable approach for enhancing pollutant removal efficiency.

3. Carbon-related materials in advanced oxidation processes for the degradation of micropollutants

Carbon-related materials have attracted significant attention due to their unique structural and textural properties, superior thermal and mechanical stability, and

potential for a wide range of applications. In photocatalysis, carbon-based materials have been investigated to improve photocatalyst surface properties. As cocatalysts or functional components, they facilitate charge separation, enhance pollutant adsorption, improve photocatalyst stability, and provide additional active sites for photocatalytic reactions [66]. Carbon-related materials used in photocatalytic systems are typically categorised into five main groups: graphene-based materials, carbon nanotube-based materials, quantum dots, fullerenes, and other carbon-based materials. These materials can also be classified by dimensionality as zero-dimensional (fullerenes, carbon quantum dots), one-dimensional (carbon nanotubes), and two-dimensional (graphene-based materials and graphitic carbon nitride). Within these categories, graphene-based materials include graphene, graphene oxide, and reduced graphene oxide. Carbon nanotube-based materials comprise single-walled carbon nanotubes and multi-walled carbon nanotubes. The quantum dot family includes carbon quantum dots and graphene quantum dots, whereas the fullerene group consists primarily of C₆₀ and C₇₀ structures. Other carbon materials frequently used in photocatalytic systems include activated carbon and graphitic carbon nitride, as presented in Figure 4. Detailed information on the synthesis and applications of carbon-based materials can be found in our previously published review article [66].

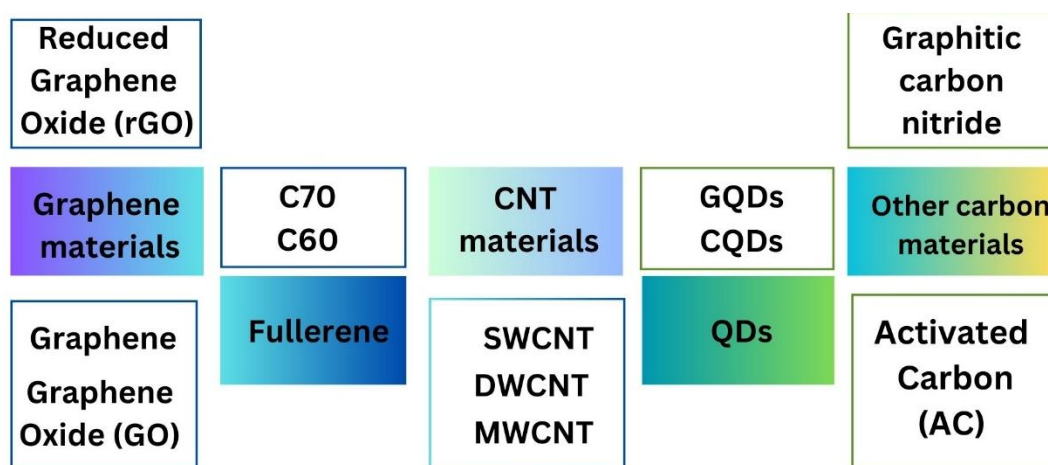


Figure 4. Types of carbon-related materials.

Among various carbon-based materials, graphitic carbon nitride (g-C₃N₄) has been extensively investigated for modification and hybridisation due to its

favourable band alignment with wide band gap semiconductors and ability to absorb visible light. Carbon nitride is an abundant, low cost, and non-toxic type of semiconductor. In 1834, Brezelius and Liebig synthesised a polymer of triazine units (C_3N_3) known as melon, which was derived from melem [67]. Carbon nitride can be produced via thermal condensation of nitrogen-rich precursors, such as melamine ($C_3H_6N_6$), dicyanamide (C_2HN_3), cyanamide (CH_2N_2), urea (CH_4N_2O), and thiourea (CH_4N_2S), which at 350°C form melem. Polycondensation of melem at temperatures above 500°C leads to the production of carbon nitride. The optimal temperature range for the thermal condensation of commonly used precursors is reported to be 500-580 °C for melamine, around 550 °C for cyanamide, dicyanamide, urea, and 450-650 °C for thiourea [68]. Different structures of carbon nitride materials, including α - C_3N_4 , β - C_3N_4 , c- C_3N_4 (cubic), p- C_3N_4 (pseudocubic), g- C_3N_4 (graphitic), g-h triazine, g-o-triazine, g-h-heptazine can be obtained through the thermal condensation of suitable precursors [69]. Graphitic carbon nitride (g- C_3N_4) demonstrates better stability and electronic properties as compared to other types of polymorphs. Graphitic carbon nitride consists of two-dimensional network layers of triazine (C_3N_3) or heptazine units (tri-s-triazine; C_6N_7), where one carbon atom forms covalent bonds to three nitrogen atoms, resulting in trigonal planar geometry (Figure 5) [70]. Among the various carbon nitride polymorphs, graphitic carbon nitride is regarded as the most thermodynamically stable and is therefore the most widely studied for photocatalytic applications. Control parameters of synthesis, including temperature, reaction time, precursor type, and precursor loading, strongly influence the crystallinity, specific surface area, and nanoscale structural features of carbon nitride materials.

Comparative studies have been conducted between bulk g- C_3N_4 and synthesised crystalline g- C_3N_4 regarding their efficacy in removing pharmaceutical pollutants [71]. The crystalline structure generally exhibits superior photocatalytic efficiency, as the condensed tri-s-triazine framework increases structural organisation, enhances electronic conductivity, and facilitates more effective charge-carrier movement, resulting in reduced recombination of electron-hole pairs and the production of reactive species. Higher efficiency was achieved for crystalline g- C_3N_4 ,

which resulted in complete degradation of indomethacin, carbamazepine and diclofenac, whereas lower degradation efficiency was achieved for naproxen, sulfamethoxazole, triclosan, ofloxacin and enrofloxacin with respective values of 79.5%, 79.4%, 97.2%, 84.2% and 95% within 150 min visible light irradiation treatment [71].

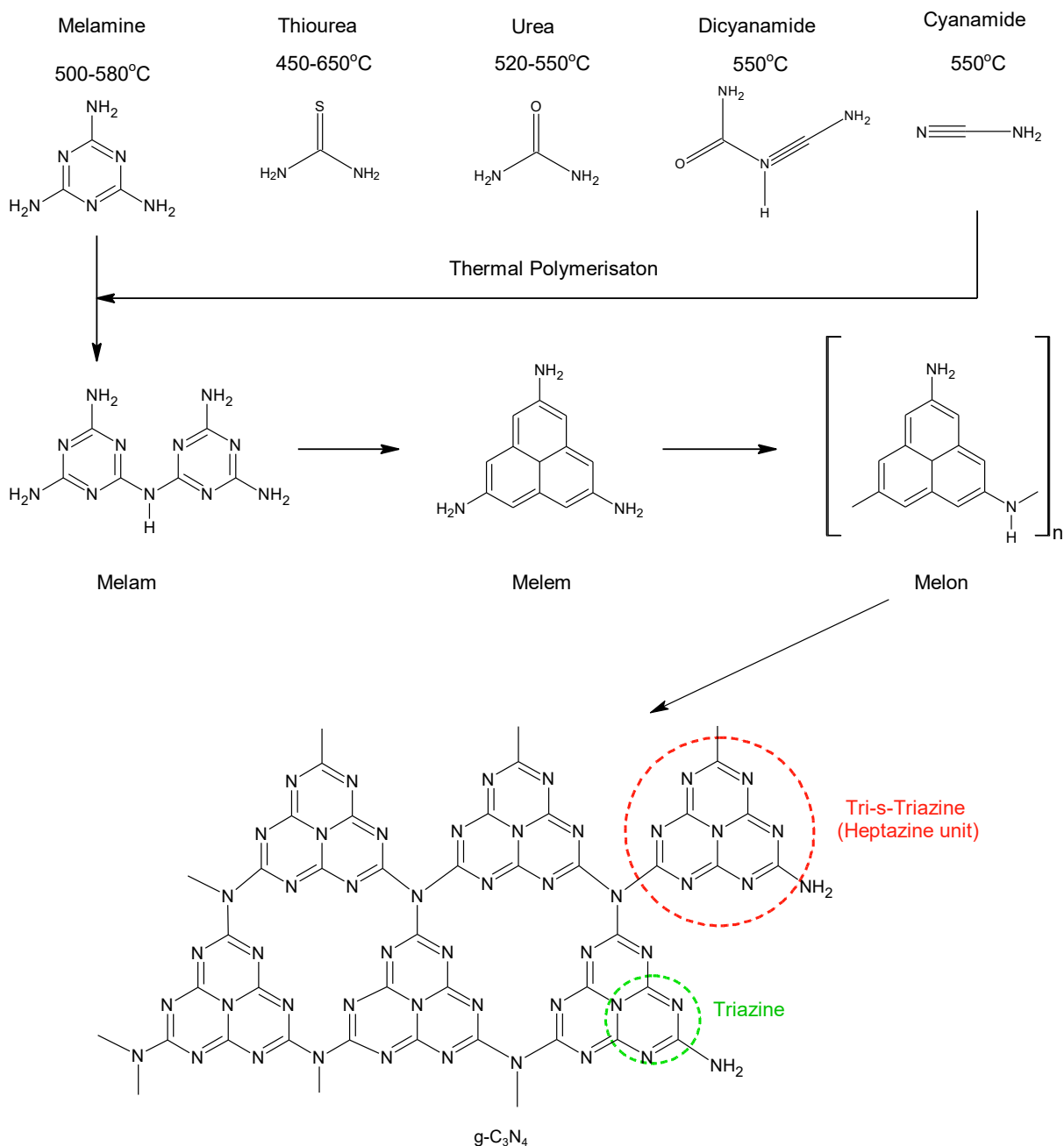


Figure 5. Synthesis of graphitic carbon nitride $g\text{-C}_3\text{N}_4$ [70].

Despite its intrinsic visible-light response, $g\text{-C}_3\text{N}_4$ suffers from several limitations, including rapid recombination of photogenerated charge carriers, a

relatively low specific surface area, and a limited light-harvesting efficiency. Several approaches and strategies are presented to improve the photocatalytic properties of g-C₃N₄, such as elemental doping, structural modification, surface functionalization, nanostructuring, heterojunction construction, and defect engineering (see Figure 6).

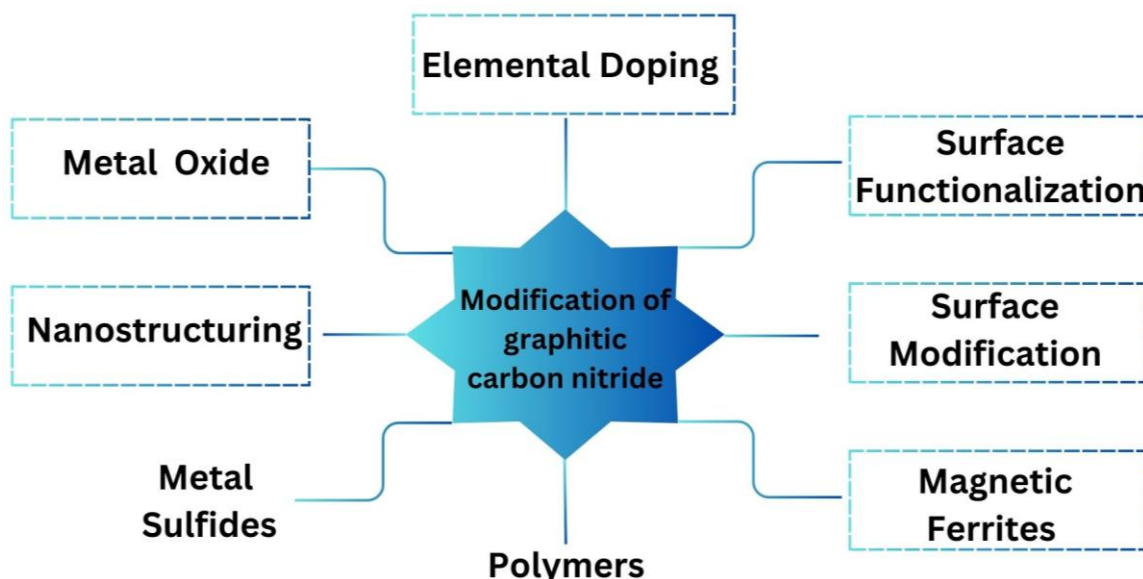


Figure 6. Modification strategies of graphitic carbon nitride.

The literature indicates that modification strategies for g-C₃N₄ primarily involve the formation of heterocomposites with various metal sulfides and metal oxides (WS₂, MoS₂, ZnS, CdS) [72-76], polymers (polyvinylidene fluoride PVDF, polyacrylonitrile PAN, polyaniline PANI) [77,79], elemental doping, metal oxides (TiO₂, ZnO, SrTiO₃, SnO₂, WO₃, BiVO₄, Cu₂O, Ag₂O, Co₃O₄), magnetic ferrites (Fe₃O₄, ZnFe₂O₄, CuFe₂O₄, CoFe₂O₄, NiFe₂O₄, MgFe₂O₄) and surface functionalization.

In this dissertation, particular emphasis is placed on modification strategies, such as elemental doping, combination with metal oxides, combination with magnetic ferrites, and surface functionalization, which are comprehensively described in the subsequent sections.

3.1. Elemental doping of graphitic carbon nitride

Elemental doping involves the incorporation of dopant atoms into the g-C₃N₄ framework, leading to modifications in its electronic and optical properties. The

incorporation of heteroatoms into the g-C₃N₄ framework can modify its band structure, introduce defect states, and enhance charge-carrier mobility, thereby improving light absorption and suppressing the recombination of photogenerated electron-hole pairs. Metal doping of carbon nitride has been achieved using alkaline earth, transition, and noble metals. For instance, Hu et al. [80] demonstrated that potassium incorporation into g-C₃N₄ resulted in reduced particle size, increased specific surface area, a narrowed band gap, and improved separation of photogenerated charge carriers. In another study, introducing magnesium into g-C₃N₄ decreased the band gap from 2.71 eV to 2.51 eV and reduced the recombination rate of electron-hole pairs, thereby enhancing the mineralisation of organic dyes in both model solutions and real textile effluents [81]. Precursor concentration is an important parameter that affects the electronic properties of semiconductors, and it has been reported that the conduction band (CB) and valence band (VB) potentials of Na-g-C₃N₄ can be tuned by controlling the sodium concentration [82].

Furthermore, transition metals can improve the electronic and optical properties of semiconductors. Fe-doped g-C₃N₄ resulted in increased RhB photodegradation efficiency since Fe³⁺ species were trapping photogenerated charged carriers (e⁻-h⁺), from which the electrons (e⁻) could reduce oxygen (O₂) to superoxide radical (O₂^{•-}) and holes (h⁺) could oxidise hydroxyl ions (OH⁻) or water molecules into hydroxyl radical (HO[•]) [83]. Pham et al. [84] reported that a narrow band gap photocatalyst Cu-g-C₃N₄ (2.54 eV) effectively removed 98.7% of caffeine from the aqueous phase and demonstrated good stability over five consecutive cycles. Introducing cobalt into graphitic carbon nitride significantly improved the separation efficiency of electrons (e⁻) and holes (h⁺), which resulted in high removal rates of paracetamol and volatile organic compounds [85].

Various noble metals, including platinum, silver, and gold, have been successfully deposited onto graphitic carbon nitride. For example, Liu et al. [86] demonstrated that anchoring Pt atoms onto carbon nitride nanosheets in the form of Pt-N₄ coordination sites significantly enhanced interfacial electron transfer, oxygen adsorption, and the generation of reactive oxygen species such as superoxide (O₂^{•-}) and hydroxyl radicals ([•]OH). In another study, Ag-modified g-C₃N₄ resulted in 96.8%

tetracycline degradation in hospital wastewater, compared with 68.3% removal using pristine g-C₃N₄ within 120 min of irradiation [87].

In addition to metal dopants, various non-metal elements, including sulfur [88], phosphorus [89], nitrogen [90], oxygen [91], carbon [92], and boron [93], have also been incorporated into the g-C₃N₄ structure. Halogen dopant elements (F, Cl, Br, I) can alter the structure and properties of graphitic carbon nitride. For example, Zhu et al. [94] demonstrated that halogen doping of graphitic carbon nitride affected the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), where the fluorine atoms alter the valence band (VB) and chlorine, bromine, and iodine alter the conduction band (CB). The inclusion of halogen atoms significantly decreased the band gap energy from 1.18 eV for g-C₃N₄ to 0.64 eV, 1.14 eV, 1.13 eV, and 0.95 eV for F and Cl. Br and I doped g-C₃N₄. Non-metal doping is particularly effective in modifying the π -conjugated structure of g-C₃N₄, thereby tuning the band gap, improving visible light absorption, and enhancing charge carriers' delocalisation. The addition of phosphorus in the structure of g-C₃N₄ leads to the formation of P-N/P=N bonds. Since phosphorus has a larger atomic radius than nitrogen, it disturbs the perfect heptazine network by creating interlayer spacing. The presence of phosphorus increases the separation efficiency of photogenerated electrons and holes and decreases the band gap energy [95]. Meanwhile, the addition of sulfur leads to the formation of C-S-C or C-S-N bonds, lattice distortion, and increased porosity [96].

3.2. Heterojunction formation

Furthermore, the construction of semiconductor heterojunctions is considered an effective strategy to enhance photocatalytic performance by promoting interfacial charge transfer, extending spectral response, and improving redox capability. Various wide and narrow band gap semiconductors, such as TiO₂, ZnO, WO₃, BiVO₄, and CdS, have been integrated with g-C₃N₄ to form type-II, Z-scheme, or S-scheme heterostructures. These hybrid systems facilitate spatial separation of photogenerated electrons and holes, thereby suppressing recombination and increasing the generation of reactive oxygen species involved in the degradation of emerging contaminants.

Titanium (IV) oxide is widely recognised as an efficient semiconductor due to its relatively low cost, natural abundance, and high chemical stability. However, its wide band gap (~ 3.2 eV) limits light absorption primarily to the UV region ($\lambda < 400$ nm), which constitutes only about 5 % of the solar spectrum [97]. The combination of TiO_2 and $\text{g-C}_3\text{N}_4$ enables the formation of heterostructures with extended photoresponse toward the visible region, and it addresses the main drawback of the high recombination rate of electron-hole pairs in $\text{g-C}_3\text{N}_4$.

Furthermore, the formation of a $\text{g-C}_3\text{N}_4/\text{TiO}_2$ heterojunction enhances interfacial contact and facilitates more efficient charge transfer across the interface [98]. For instance, enhanced photocatalytic performance has been reported for a type-II heterostructure composed of $\text{g-C}_3\text{N}_4$ nanowires and B-modified TiO_2 nanotubes, in which efficient interfacial charge transfer improved charge separation [99]. Z-scheme configurations have also been successfully developed for $\text{g-C}_3\text{N}_4/\text{TiO}_2$ systems. Zhou et al. [100] demonstrated that a heterostructure constructed from two-dimensional $\text{g-C}_3\text{N}_4$ nanosheets and TiO_2 nanotubes exhibited high activity toward the degradation of Rhodamine B and tetracycline under visible light irradiation. In addition, a three-dimensional $\text{g-C}_3\text{N}_4/\text{TiO}_2$ photocatalyst removed 87% of ibuprofen from aqueous solution within 60 min under visible light, indicating the potential of such hybrid systems for the treatment of persistent pharmaceutical compounds [101]. Overall, these findings highlight that the rational design of $\text{g-C}_3\text{N}_4/\text{TiO}_2$ heterojunctions can significantly improve charge carrier dynamics and photocatalytic degradation efficiency under solar light irradiation.

Zinc oxide is another commercial and widely investigated semiconductor for coupling with $\text{g-C}_3\text{N}_4$. As an n-type semiconductor with a wide band gap of about 3.2 eV, ZnO exhibits favourable physicochemical stability together with notable photocatalytic properties. Zhang et al. [102] investigated a ternary $\text{ZnO/g-C}_3\text{N}_4/\text{graphene oxide}$ nanocomposite for the photocatalytic degradation of Rhodamine B. The combination of ZnO with $\text{g-C}_3\text{N}_4$ exhibited photoactivity under UV-vis irradiation, while the addition of graphene oxide decreased the recombination rate of electron-hole pairs and improved the photocatalytic activity in the visible light range. These results demonstrate that ZnO -based heterostructures

with g-C₃N₄ can effectively improve charge separation and broaden the spectral response, leading to enhanced degradation of organic pollutants, while also offering favourable prospects for process scalability due to the wide availability and low cost of the constituent materials and the simplicity of the synthesis routes. However, another major challenge hindering the large scale implementation of photocatalytic technologies is the limited recoverability and reusability of suspended photocatalyst, which constrains their long-term operational application.

To overcome this limitation, magnetic spinel ferrite nanoparticles exhibiting superparamagnetic behaviour can be integrated into the g-C₃N₄ matrix, enabling efficient magnetic separation of the photocatalyst from treated water and thereby significantly improving its recyclability.

3.3. Modification of g-C₃N₄ with spinel ferrites

In photocatalytic systems, photocatalysts are commonly used as fine powders to optimise surface active sites; however, substantial challenges in photocatalyst recovery hinder their extensive industrial applications [103]. The recovery of the photocatalyst from the treated media is usually performed using traditional separation methods, such as filtration and centrifugation, which are time- and energy-intensive and present scalability issues that limit their applications.

Therefore, introducing magnetic properties into photocatalysts is a promising approach to improve the recovery and recyclability of photocatalytic materials. The combination of g-C₃N₄ with magnetic ferrites enables magnetic separation, allowing effective retrieval of the photocatalyst from aqueous media and providing a viable route to photocatalyst recyclability. Among different ferrite structures, spinel ferrites (MeFe₂O₄, where Me = Co, Zn, Cu, Ni, Mn, Mg) are most frequently employed for the modification of g-C₃N₄ owing to their suitable electronic structure, magnetic separability, and relatively simple and cost-effective synthesis routes. Besides magnetic recovery of photocatalysts, magnetic ferrites can alter the physicochemical properties of g-C₃N₄ in formed heterocomposites, thereby promoting charge carriers' separation. Introducing iron (II, III) oxide Fe₂O₃ into g-C₃N₄ led to the successful formation of a heterocomposite with enhanced visible light absorption, improved

charge carrier separation, and increased recyclability up to six consecutive cycles [104].

In addition, the introduction of magnetic properties opens the possibility of exploring photocatalytic processes assisted by an external magnetic field, which has recently emerged as a novel and relatively underexplored research area. Introducing a magnetic field into the photocatalytic system can enhance photocatalytic efficiency by improving charge carriers' separation [105,106]. Even though the mechanisms underlying the processes are not yet thoroughly investigated, magnetically modified photocatalysts extend their role beyond recyclability, contributing to the efficiency of the photocatalytic process. Nevertheless, careful consideration should be given when introducing magnetic material into a composite, since excess material may obstruct available active sites or form recombination centres, ultimately reducing the composite's photocatalytic activity. Therefore, the design of a photocatalyst that exhibits good recyclability, photocatalytic efficiency, and responsiveness to an external magnetic field remains a significant challenge. S-scheme heterojunction of $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ improved charge carriers separation and enhanced visible light absorption, successfully removing more than 90% of uranium (VI). Moreover, the photocatalyst could be used for up to 5 consecutive cycles [107].

A different approach in interfacial engineering involves core-shell heterocomposites, which ensure continuous contact between the magnetic material and the photocatalyst and facilitate efficient charge transfer. Yao et al. [108] reported that a well-defined interface between the outer shell of $\text{g-C}_3\text{N}_4$ and the magnetic core of copper ferrite (CuFe_2O_4) led to the successful formation of a highly active photocatalytic material with suppressed charge recombination. However, shell thickness and interfacial compatibility are two important factors that should be considered when designing core-shell heterocomposites since an excessive addition of magnetic material may hinder light absorption or reduce the availability of reactive sites, potentially mitigating the advantages of improved charge separation. The study revealed that the optimum mass ratio to form the core-shell structure of $\text{CuFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ consisted of (2:1) with 90% Orange (II) degradation in 180 min, and good stability of up to five consecutive cycles.

Considering the facts, it is important to design a magnetically recoverable g-C₃N₄ heterocomposite in which the spinel magnetic ferrite is introduced in a controlled manner that preserves surface accessibility and maintains efficient light absorption. By optimising the interfacial interactions between g-C₃N₄ and magnetic materials, the aim of this thesis was to develop stable, magnetically recoverable, and recyclable photocatalysts with sustained performance.

3.4. Surface functionalization of g-C₃N₄

Even though heterojunction modification has proven to effectively improve the stability and photocatalytic properties of graphitic carbon nitride, the inert surface of pristine g-C₃N₄ and the limited number of functional groups hinder its ability to react with contaminant molecules in water systems. To improve charge transfer and increase the number of active sites, it is necessary to modify the surface chemistry of g-C₃N₄ via surface functionalization [109].

Modifying the g-C₃N₄ surface with chemicals is known as covalent functionalization, as it involves the formation of covalent bonds between g-C₃N₄ and the introduced chemical reactant. In contrast, noncovalent functionalization refers to the modification of g-C₃N₄ through electrostatic interactions, hydrogen bonding, π - π bonding, and van der Waals forces [66,110]. Covalent functionalization can be achieved by oxidation, hydroxylation, sulfonation, amidation, and surface defects, whereas noncovalent functionalization is an example of heterojunction formation of g-C₃N₄ and other semiconductors or metal oxides [66,110]. Surface functionalization may increase surface polarity, leading to stronger interactions between polar or charged molecules and the generation of reactive species. Amine (-NH₂) functionalized graphitic carbon nitride was reported to effectively remove anionic pollutant molecules by introducing positive sites in the structure that can bind negatively charged molecules, leading to enhanced photocatalytic removal of pollutants [111]. The role of functional groups in g-C₃N₄ is to enhance the photocatalytic properties of the material by suppressing the recombination of electron-hole pairs, since functional groups act as charge carrier traps. For instance, the addition of a benzenesulfonic acid functional group in g-C₃N₄ led to improved separation of charge carriers since the sulfonic acid group (-SO₃H) serves as an

electron-withdrawing group [112]. Moreover, π - π stacking interactions occur between the benzene ring of the benzenesulfonic acid group and the conjugated structure of g-C₃N₄, thereby enhancing interfacial compatibility. Unlike aromatic functional groups, hydroxyl (-OH) functional groups improve the surface properties of g-C₃N₄ through hydrogen bonding and increased polarity, enhancing the adsorption of polar species and promoting the generation of hydroxyl radicals, which increases the photocatalytic activity [113].

Introducing surface defects in g-C₃N₄ is another way to implement surface functionalization, thereby significantly altering its electronic structure and facilitating the transfer of charge carriers. Defect engineering of g-C₃N₄ through carbon and nitrogen vacancies leads to localised electronic states that decrease the recombination rate of electron-hole pairs and improve surface reactivity. For example, the introduction of nitrogen vacancies into synthesised g-C₃N₄ significantly suppressed the recombination of photogenerated electrons and holes, as evidenced by fluorescence emission spectroscopy [114]. Nitrogen-vacancy g-C₃N₄ led to 97% degradation of carbamazepine, compared with 56% for bulk g-C₃N₄ within 120 min of treatment. Surface modification of g-C₃N₄ through the introduction of carbon vacancies increased the porosity of the material and significantly enhanced the photocatalytic degradation of lidocaine, mepivacaine, and ropivacaine [115]. The rate constant of reaction was increased from $2.09 \cdot 10^{-2} \text{ min}^{-1}$ for pure g-C₃N₄ to $5.05 \cdot 10^{-2} \text{ min}^{-1}$ for pore-structured carbon vacancy g-C₃N₄. Along with carbon and nitrogen vacancies, oxygen vacancies in metal oxides are another way to surface modification. In contrast to carbon and nitrogen vacancies, oxygen vacancies in metal oxides provide coordinatively unsaturated metal sites, thereby enhancing the activation of reactant molecules. Oxygen vacancies serve as electron donors, which cause the Fermi level to shift upward, and more electrons are concentrated in the conduction band [116]. The increase in electron density in the conduction band enhances mobility and promotes rapid transfer of photogenerated electrons to reactive sites, thereby suppressing electron-hole recombination. Hezam et al. [117] observed that the morphology of ZnO, especially nanoflowers with high surface area and exposed edge sites, facilitated the formation of oxygen vacancies by reducing atomic coordination. The presence of these

vacancies increased the charge-carrier density, enhanced visible-light absorption, and facilitated charge separation, thereby improving ZnO photocatalytic activity. At the same time, excess oxygen vacancies were reported to induce lattice distortion and to promote the transformation of the anatase phase to the less active rutile phase [118].

Improving semiconductor nanostructures requires a morphology design that effectively balances three key characteristics, such as large specific area, high charge carrier mobility, and low electron-hole recombination rate.

Two-dimensional nanostructures, particularly nanosheets, unlike low-dimensional counterparts (0D and 1D) or three-dimensional (3D) nanostructures, possess atomic-scale thickness that contributes to a high surface to volume ratio and abundant active sites that improve surface redox reactions. Additionally, short diffusion pathways significantly suppress the recombination of photogenerated electrons (e^-) and holes (h^+), and more photogenerated charges reach the photocatalyst surface, leading to improved photocatalytic efficiency. In contrast, one-dimensional (1D) and three-dimensional (3D) semiconductor architectures suffer from long radial diffusion pathways and inefficient photon absorption, with most absorption occurring near the surface. Considering the facts, two-dimensional (2D) semiconductor nanosheets are pivotal in research due to their ultrathin architecture, which enhances charge transfer, surface reactivity, and photocatalytic efficacy.

Ultrathin 2D TiO_2 is a promising photocatalyst due to its numerous active sites, which facilitate the binding of pollutant molecules, thereby enhancing overall photocatalytic efficiency [119]. Typically, 2D TiO_2 is synthesised by directional crystal growth, exposing highly reactive facets, via hydrothermal or solvothermal synthesis using titanium precursors in the presence of fluoride-containing agents [120]. Fluoride ions preferentially adsorb to the high-energy facets of anatase TiO_2 , which lowers surface energy and stabilises the facets, consequently encouraging the development of sheet-like structures [121]. However, introducing fluoride chemical reactants increases health and environmental concerns owing to their toxicity and safety hazards associated with handling during reactions. To mitigate these risks, freeze-drying and lyophilisation techniques may be utilised to eliminate the need for fluoride ions while maintaining the nanomaterial's morphology.

Lastly, it should be emphasised that excessive functionalization and uncontrolled defects may lead to undesired effects such as increased recombination centres and decreased photocatalytic activity. Therefore, mild functionalization approaches such as introducing hydroxyl groups do not destroy the characteristic features of the material and improve surface hydrophilicity and adsorption of g-C₃N₄. Similarly, regulating oxygen vacancies in metal oxides is crucial since excessive defects can negatively affect charge separation and surface reactivity. This thesis emphasises the development of a controlled modification strategy that optimises surface interactions and electronic properties to improve photocatalytic performance while preserving structural characteristics.

4. Summary

The occurrence of pharmaceutical contaminants in aquatic environments represents a significant challenge for water resource management and environmental protection. The development of the pharmaceutical industry, coupled with increased drug demand and their partial removal through metabolic processes, led to the widespread detection of pharmaceutical residues and their transformation products in treated effluents, surface waters, and groundwater.

Conventional wastewater treatment technologies employ processes and unit operations to purify water to acceptable levels. However, these processes were not specifically designed to eliminate pharmaceutical micropollutants. As a result, removal efficiencies vary significantly depending on the physicochemical properties of the compounds, often leading to incomplete elimination and ongoing discharge into receiving water bodies, and raising concerns about long-term ecological risks. These challenges prompted increased research regarding advanced treatment technologies for the degradation of persistent organic pollutants. Advanced oxidation processes (AOPs) have shown particular promise due to their ability to generate reactive oxygen species, such as hydroxyl radicals (HO•) and superoxide radicals (O₂•⁻), which are responsible for the degradation of a wide range of micropollutants. Within AOPs, heterogeneous photocatalysis has emerged as one of the most promising methods for efficient degradation of organic compounds in aqueous environments.

The performance of photocatalytic systems is strongly governed by intrinsic material properties, including band structure, light absorption characteristics, charge carrier dynamics, surface reactivity, and adsorption capacity. Widely studied semiconductors such as TiO_2 and ZnO offer advantages in terms of chemical stability, abundance, and cost-effectiveness. However, their practical application remains constrained by limited solar-light utilisation and rapid recombination of photogenerated charge carriers. To overcome these challenges, recent research has increasingly focused on heterostructure engineering and surface modification strategies aimed at improving light harvesting and charge separation.

Recently, 2D graphene-based materials have attracted significant attention as additive photocatalysts for solar light-driven photodegradation of organic pollutants. For example, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) has great potential as an efficient, multifunctional material with a medium bandgap of 2.7 eV, high stability, and visible light photocatalytic activity. Nevertheless, despite the reported improvements in photocatalytic activity, several critical limitations remain insufficiently addressed. In particular, the scalability and operational feasibility of photocatalytic systems are still hindered by difficulties in photocatalyst recovery, gradual deactivation, and reduced reusability. Furthermore, although hybridisation and doping strategies have been extensively explored, the synergistic integration of photocatalysis with complementary oxidation pathways, such as persulfate-based advanced oxidation processes, remains comparatively underdeveloped. The potential role of transition metal-containing phases in simultaneously promoting charge transfer, persulfate activation, and magnetic separation has not been systematically investigated.

Another emerging research direction concerns the design of two-dimensional semiconductor architectures, which offer enhanced surface accessibility and shorter diffusion pathways for photogenerated carriers. However, the combined effects of nanoscale structural engineering, magnetic functionality, and radical-based oxidation mechanisms on the degradation of pharmaceutical contaminants have not yet been comprehensively elucidated. These knowledge gaps highlight the need for the development of multifunctional photocatalytic systems that integrate improved

light utilisation, efficient photocatalyst recovery, and intensified oxidative degradation pathways. These approaches present significant opportunities for creating sustainable and efficient technologies aimed at safeguarding water resources and mitigating the effects of micropollutants on the environment.

5. References

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Chapter II. Scope, objectives and methodology

1. Scope of the dissertation and research objectives

The present research focuses on the design and synthesis of modified g-C₃N₄-based heterostructures incorporating wide band gap semiconductors and magnetic spinel ferrite phases, coupled with persulfate activation strategies. Such integrated systems are expected to enhance charge carrier dynamics, facilitate photocatalyst separation, and improve overall treatment efficiency for the removal of pharmaceutical pollutants from aqueous environments.

The main objective of this PhD dissertation was to develop g-C₃N₄-based photocatalytic materials with enhanced photocatalytic performance for the degradation of pharmaceutical contaminants from aqueous environments. Particular emphasis was placed on the selection of graphitic carbon nitride as a photocatalyst due to its facile one-step synthesis from inexpensive, readily available precursors, such as melamine and urea, making this material highly attractive for scalable photocatalytic applications. To enhance the photocatalytic properties of graphitic carbon nitride, three modification strategies doping, heterocomposite formation, and chemical functionalisation, were selected and investigated.

To address the identified research gaps and achieve the objectives of the PhD dissertation, the following research hypotheses were formulated:

1. Elemental doping of graphitic carbon nitride with non-metal heteroatoms of phosphorus and sulfur will enhance light absorption and improve photocatalytic degradation of micropollutants.
2. Coupling (P,S)-doped g-C₃N₄ with a wide-band-gap semiconductor, such as two-dimensional TiO₂, will result in the formation of an efficient heterojunction that promotes interfacial charge separation and enhances the photocatalytic degradation of selected pharmaceutical contaminants.
3. Incorporation of spinel zinc ferrite into the photocatalytic heterocomposite will enhance photocatalyst stability and recyclability through magnetic separability, while integration with persulfate-based advanced oxidation process will further intensify micropollutant degradation.

4. Application of an external magnetic field can influence charge carrier behaviour in magnetic photocatalytic systems, leading to improved photocatalytic efficiency in addition to enhanced photocatalyst recovery.
5. Chemical functionalization of g-C₃N₄ combined with a modified wide-band-gap semiconductor will enable the formation of a frustrated Lewis pair (FLP)-type heterocomposite, enhancing micropollutants degradation efficiency.
6. Surface functionalization and defect engineering in FLP-type heterostructures will promote charge separation and reactive species formation, while coupling with persulfate activation will further enhance radical-driven degradation pathways and facilitate more efficient removal of pharmaceutical pollutants.

Following clarification of the research goals, a structured workplan was developed to systematically investigate the proposed material and process modifications, as presented schematically in Figure 9. The key research questions addressed in this PhD dissertation were examined through a series of studies that resulted in three closely related publications (R1–R3), which are briefly summarised in the following sections. Finally, chapter 6 describes unpublished results (currently under review), which are a direct continuation of the research on g-C₃N₄ modification, therefore completing the work associated with the research goals.

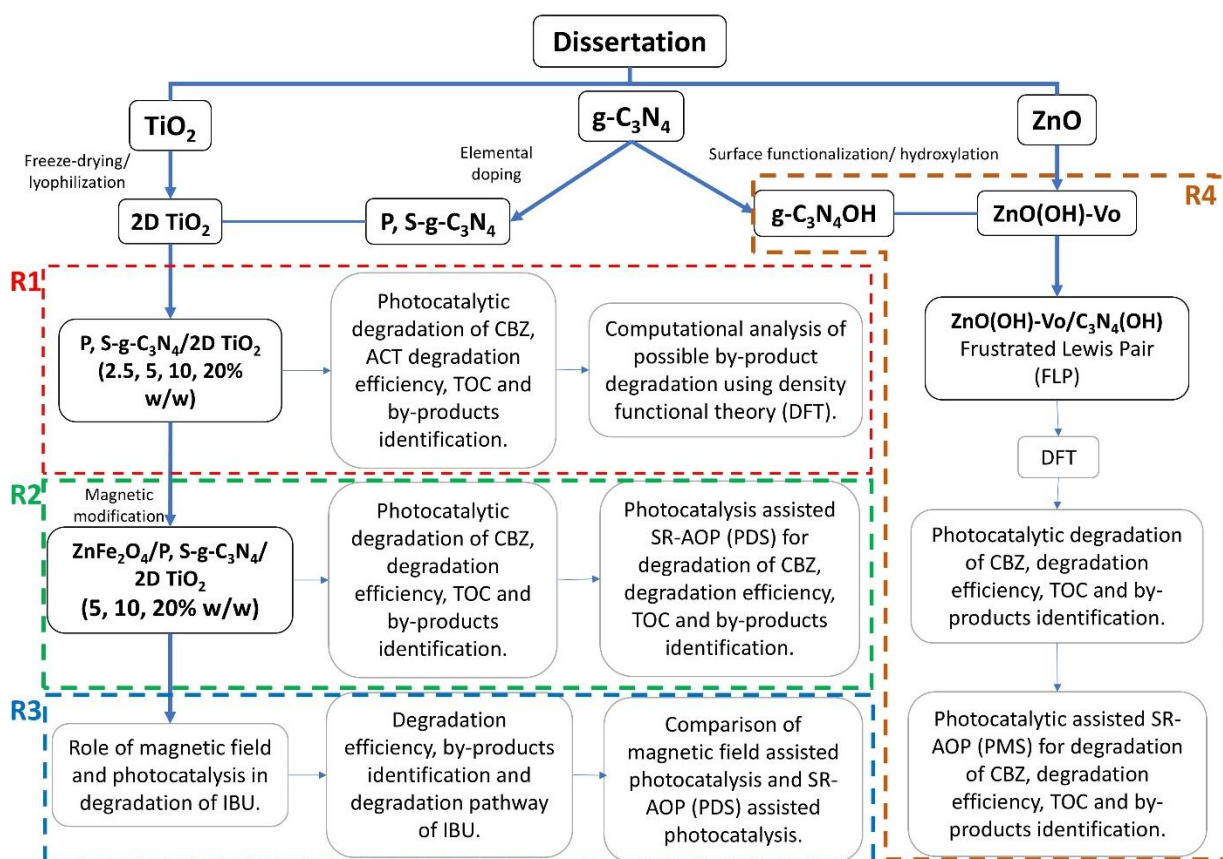


Figure 9. Scheme of the performed works and problems investigated within the presented PhD thesis, according to the research manuscripts R1 - R4.

2. Research methodology

Table 1 summarises the chemical reagents employed in the synthesis of photocatalytic materials, preparation of model pollutant solutions, and mechanistic investigations. All chemicals were used as received without further purification unless otherwise stated. Detailed synthesis procedures and experimental conditions are described in the following sections.

Table 1. Chemicals used for the implementation of research studies.

Compound	Producer	Purity	CAS Number	Usage
Melamine	Alfa Aesar	99%	108-78-1	Synthesis of g-C ₃ N ₄
Thiourea	Merck	99%	62-56-6	Synthesis of g-C ₃ N ₄
Ammonium phosphate dibasic	Merck	99%	7783-28-0	Synthesis of g-C ₃ N ₄

Titanium oxysulfate hydrate	Merck	technical grade	123334-00-9	Synthesis of 2D TiO ₂
Ammonia solution	POCH	25% wt.	1336-21-6	Synthesis of 2D TiO ₂
Hydrogen peroxide	POCH	30% wt.	7722-84-1	Synthesis of 2D TiO ₂ ; synthesis of ZnO(OH)
Sodium dodecyl sulfate	Acros organic	85%	151-21-3	Synthesis of (P, S)-g-C ₃ N ₄ / 2D TiO ₂
Methanol	POCH	pure p.a	67-56-1	Synthesis of (P, S)-g-C ₃ N ₄ / 2D TiO ₂
Iron nitrate nonahydrate	Alfa Aesar	98%	7782-61-8	Synthesis of ZnFe ₂ O ₄
Zinc nitrate hexahydrate	Merck	99%	13778-30-8	Synthesis of ZnFe ₂ O ₄
Ethylene glycol	CHEMPUR	≥ 99%	107-21-1	Synthesis of ZnFe ₂ O ₄
Sodium acetate anhydrous	POCH	99%	127-09-3	Synthesis of ZnFe ₂ O ₄
Zinc acetate dihydrate	AppliChem	for analysis	5970-45-6	Synthesis of ZnO(OH)
Carbamazepine	Merck	≥ 98%	298-46-4	Contaminant
Acetaminophen	Merck	≥ 99%	103-90-2	Contaminant
Ibuprofen	Merck	≥ 98%	15687-27-1	Contaminant
Para benzoquinone (P-BQ)	Sigma-Aldrich	≥ 98%	106-51-4	Scavenger (O ₂ ^{•-})
Isopropanol	POCH	pure p.a	67-63-0	Synthesis of ZnFe ₂ O ₄ / (P, S)-g-C ₃ N ₄ / 2D TiO ₂ ; Scavenger (HO [•] , SO ₄ ^{•-})
-Ammonium oxalate monohydrate	Merck	99.5%	6009-70-7	Scavenger (h ⁺)
Tert-butyl alcohol	Sigma-Aldrich	≥ 99.5	75-65-0	Scavenger (HO [•])
AgNO ₃	POCH	pure p.a	7761-88-8	Scavenger (e ⁻)
NaN ₃	Sigma-Aldrich	≥ 99%	266628-22-8	Scavenger (¹ O ₂)
Coumarin	Merck	>95%	91-64-5	Probe molecule for (HO [•]) identification
Nitric acid	Merck	65%	7697-37-2	pH correction

Sodium hydroxide	CHEMPUR	pure p.a	1310-73-2	pH correction
Orthophosphoric acid	POCH	85%	7664-38-2	HPLC phase
Formic acid	Merck	98-100%	64-18-6	HPLC phase
Acetonitrile	Supelco	HPLC grade	75-05-8	HPLC phase
Sodium nitrate	Merck	99.5%	7631-99-4	Role of anions
Sodium chloride	Merck	99.5%	7647-14-5	Role of anions
Sodium carbonate anhydrous	POCH	97.5%	497-19-8	Role of anions
Sodium sulfate anhydrous	Merck	99%	7757-82-6	Role of anions
Sodium persulfate	Sigma Aldrich	≥ 98%	7775-27-1	Oxidant in PS-AOP
Oxone (Monopersulfate compound)	Acros Organics	99%	70693-62-8	Oxidant in PS-AOP

2.1. Synthesis of photocatalysts and heterocomposite

Synthesis of g-C₃N₄ and (P, S)-g-C₃N₄ [research work R1, R2, R3]

Graphitic carbon nitride (g-C₃N₄) was prepared via calcination of melamine precursor at 550°C for 4 hours with a rate of 2°C/min. The obtained solid material was ground into a powder, heated at 500°C/min for 3 hours, and then heated at 5°C/min for 3 hours. Light yellow powder of g-C₃N₄ was prepared. Furthermore, the photocatalytic properties of g-C₃N₄ were improved via elemental doping of g-C₃N₄.

To prepare non-metal doped g-C₃N₄, three different precursors, like thiourea, melamine, and diammonium phosphate (NH₄)₂HPO₄ in the respective masses of 7.5 g, 7.5 g, and 1.36 g, were mixed and subjected to the same experimental conditions as for the preparation of g-C₃N₄. The final product was noted as phosphorus and sulfur codoped graphitic carbon nitride (P, S)-g-C₃N₄.

Synthesis of 2D TiO₂ [research works R1, R2, R3]

The freeze-drying method was used to prepare 2D TiO₂. An amount of 10 g titanium (IV) oxysulfate (TiOSO₄) was dissolved in warm water (300 cm³, 40°C). The prepared solution was placed on an ice bath to reach 5°C, and ammonia solution was

added dropwise until the pH reached 9 and a white precipitate formed. The precipitate was washed several times to remove residual ammonia and to reach neutral pH. The washed precipitate was resuspended in deionised water, and hydrogen peroxide (H_2O_2 , 30%) was added to a volume of 60 cm^3 until the pH reached 2, at which point the suspension turned yellow. The solution was aged at 5°C until a gel formed. The formed gel was introduced dropwise into liquid nitrogen to freeze it, and the resulting frozen sample was mounted in a freeze-dryer and lyophilised until a yellow, dry powder formed. The prepared powder was calcined at 700°C to produce the final 2D TiO_2 material.

Synthesis of (P, S) co-doped g- C_3N_4 / 2D TiO_2 composite [research works R1, R2, R3]

2D TiO_2 was introduced into a mixture of 50 cm^3 methanol and anionic surfactant of SDS (sodium dodecyl sulfate salt, 2% w/w) and mixed for 5 minutes. After a uniform suspension was observed, the (P, S) co-doped g- C_3N_4 was introduced to be coupled to 2D TiO_2 in four different mass ratios of 2.5 %w/w, 5% w/w, 10% w/w, and 20% w/w of (P, S)-g- C_3N_4 to 2D TiO_2 mass ratios. Afterwards, the mixture was introduced into an ultrasonic bath for 30 minutes, washed, and finally placed in a drying oven for 4h at 100°C .

Modification of (P, S)-g- C_3N_4 with spinel ferrite of ZnFe_2O_4 [research works R2, R3]

The next part of the research methodology consisted of the modification of (P, S)-g- C_3N_4 and 2D TiO_2 heterocomposite. Zinc ferrite (ZnFe_2O_4) was selected to introduce magnetic properties into the formed heterocomposite. Zinc ferrite nanoparticles were synthesised via hydrothermal and calcination routes. Iron nitrate nonahydrate $\text{Fe}(\text{NO}_3)_3 \cdot 9(\text{H}_2\text{O})$ (4 mmol) and zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2 mmol) were dissolved in 60 cm^3 ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$). Sodium acetate (CH_3COONa ; 20 mmol) was added, and the suspension was kept stirring until it was homogeneously dispersed. After stirring, the suspension was ultrasonicated for 30 min, then transferred to a teflon-lined autoclave at 180°C for 12 hours. Once the solvothermal reaction was complete, the precipitate was collected

and washed several times with anhydrous ethanol and water. The obtained sample was dried at 120°C for 6 h, powdered, and calcined at 500°C for 2 hours at a rate of 5°C/min. A fine, dark-brown powder with magnetic properties was obtained and used for subsequent steps. The next step involves modifying the ZnFe₂O₄ and (P, S)-g-C₃N₄ photocatalysts, denoted as (50:50 % w/w) and (70:30 % w/w) of the ZnFe₂O₄/P, S-g-C₃N₄ heterocomposite. A defined amount of zinc ferrite and doped carbon nitride was dissolved in 50 cm³ of deionised water (DI) and ultrasonicated for 3h. After ultrasonication, the suspension was placed in a teflon-lined reactor, where a hydrothermal reaction was performed at 150°C for 5 hours at a rate of 5°C/min. The collected sample was dried at 80°C for 4 hours.

Synthesis of ZnFe₂O₄/ (P, S)-g-C₃N₄/ 2D TiO₂ (5, 10, 20% w/w) [research works R2, R3]

Firstly, ZnFe₂O₄/P, S-g-C₃N₄ was incorporated into 2D TiO₂. Different loadings of ZnFe₂O₄/P and S-g-C₃N₄ (5, 10, and 20% w/w) were mixed with 2D TiO₂ in 50 cm³ of isopropanol. The mixture was ultrasonicated for 3 hours. After sonication, isopropanol was removed, and the sample was resuspended in 50 cm³ water and placed into a hydrothermal reactor at 150°C for 5 hours and at a rate of 5°C/min. The collected sample was dried at 100°C for 4 hours. Obtained powders were described as ZnFe₂O₄/P, S-g-C₃N₄/2D TiO₂ (5, 10, and 20% w/w).

Chemical functionalisation of g-C₃N₄ [research work R4]

A crucible contained a certain amount of melamine and was calcined at 550°C for 4 hours at a rate of 2°C/minute. The solid sample was pulverised and calcined at 500°C for 3 hours at a heating rate of 5°C/min. The alkaline etching was introduced as a means to introduce defects in the g-C₃N₄ structure. The prepared sample was ground into a powder, then introduced into 50 cm³ of 0.5 M sodium hydroxide (NaOH) and stirred for 60 min. After stirring, the solution was placed into a stainless steel, teflon-lined reactor and heated to 100°C for 5 h. After the hydrothermal reaction, the sample was centrifuged, washed to neutral pH, and dried to form the g-C₃N₄(OH) sample.

Synthesis of ZnO(OH)-V_q/g-C₃N₄(OH) frustrated Lewis pair (FLP) [research work R4]

Zinc acetate $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ was dissolved in 50 cm³ of deionised water (DI). Sodium hydroxide (NaOH; 4 M) was added to the salt solution until a white precipitate formed, and the solution was stirred for 30 min. The formed precipitate was centrifuged and collected, then washed to neutral pH. The precipitate was resuspended in 50 cm³ H_2O_2 (97 mM), and the suspension was stirred at room temperature for 24 hours. After the reaction, the sample was dried at 80 °C for 5 h under an argon (Ar) atmosphere. The final sample was described as zinc oxide hydroxide with oxygen vacancies $\text{ZnO}(\text{OH})\text{-V}_\text{o}$ was obtained.

A heterocomposite of $\text{ZnO}(\text{OH})\text{-V}_\text{o}/\text{g-C}_3\text{N}_4(\text{OH})$ was prepared via ultrasonication and the hydrothermal method. Hydroxylated carbon nitride and metal oxide hydroxide were mixed in methanol at a 1:1 ratio and ultrasonicated for 2 hours. After ultrasonication, the samples were placed in hydrothermal reactors and heated to 120 °C for 5 h. After the reaction, the samples were dried at 60 °C for 5 h.

2.2. Physicochemical properties of nanomaterials

X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) was conducted to analyse the phase composition of the photocatalysts. A Rigaku MiniFlex 600 X-ray diffractometer with Cu K α radiation was employed to analyse the samples. The measurement parameters were set to a 2θ range of 5-80°, a scan speed of 1°/min, and a scan step of 0.01°. The crystallite size of the photocatalysts was calculated using Debye-Scherrer's equation, described with the following formula: $D = K\lambda / \beta \cos\theta$, where K represents the Scherrer constant, λ represents the wavelength of the X-ray beam, β stands for the full width at half maximum of the peak, and lastly, the Bragg angle is represented by θ .

Brunauer-Emmett-Teller (BET) analysis

The surface area, pore size, and pore volume of photocatalysts were measured using multi-point Brunauer-Emmett-Teller (BET) analysis. The photocatalysts were analysed using Micromeritics Gemini V (model 2365) (Norcross, GA, USA). Before nitrogen adsorption analysis, the samples were degassed at 200°C for 2 hours.

UV-Vis diffuse reflectance spectroscopic analysis

Optical properties and diffuse reflectance (DR) spectra of samples were measured using a DR/UV-Vis spectroscopy. The measurements were performed

using a ThermoScientific Evolution 220 Spectrophotometer (Waltham, MA, USA). Absorption spectra were registered, and bandgap energy was calculated according to the Kubelka-Munk function of $\alpha h\nu = A(h\nu - E_g)^n$, where α stands for absorption coefficient, $h\nu$ stands for photon energy (eV), h is Planck's constant, ν is the frequency in s^{-1} , A is a constant, and n is equal to 0.5. Information on the recombination rate and the average lifetime of photogenerated charges was obtained from photoluminescence spectra combined with time-resolved PL-decay curves.

Photoluminescence spectroscopic analysis

PL measurements for (P, S)-g-C₃N₄/2D TiO₂ (2.5, 5, 10, 20% w/w) were performed using a grafting spectrograph (Princeton Instr. Model Acton 2500i) equipped with a streak camera (Hamamatsu Model C5680) with a temporal resolution of 20 ps. Additionally, an excitation source using a femtosecond laser (Coherent Model 'Libra') equipped with an optical parametric amplifier (Light Conversion Model 'OPerA') was used to record the emissions and to analyse the decay times. Emission spectras of ZnFe₂O₄, (P, S)-g-C₃N₄, 2D TiO₂, ZnFe₂O₄/ (P, S)-g-C₃N₄/2D TiO₂ (5, 10, 20 % w/w), ZnO(OH), ZnO(OH)-Vo, g-C₃N₄(OH), ZnO(OH)-Vo/g-C₃N₄(OH) were recorded using spectrofluorophotometer (RF 6000, SHIMADZU).

X-ray fluorescence spectroscopy

The sulfur content in the sample of (P, S)-g-C₃N₄ was measured using X-ray fluorescence spectroscopy (XRF) with a WDXRF S8 Tiger analyser (Bruker, S8 TIGER, Bruker, Karlsruhe, Germany), and the measurements were performed according to the standard PN-EN 15308:2010.

Fourier transform infrared spectroscopy (FTIR)

The functional groups of the photocatalyst before and after irradiation were investigated using Fourier transform infrared (FTIR) spectroscopy. Measurements were carried out using a Nicolet iS10 spectrometer (Thermo Fisher Scientific, Waltham) at room temperature. The spectra were recorded over the wavenumber range of 400-4000 cm⁻¹ with a resolution of 2 cm⁻¹.

Raman spectroscopy

A Raman spectrometer (Renishaw InVia) coupled with an IR laser diode and a CCD camera was used to record the Raman spectra of samples in a single scan with

a 30s exposure time and a 20× LWD objective. The IR diode laser emitting at 830 nm (1 mW) was used as the excitation source.

Microscopic measurements

Structural information and the morphology of selected photocatalysts were obtained using a Transmission Electron Microscope (TEM) model and a Scanning Electron Microscope (SEM). The TEM microscope model Tecnai F20 X-Twin, equipped with spectroscopic techniques (EDS, EELS), was used for the imaging of samples, which were measured using a dark field (DF) detector, whereas the STEM mode was realised using a high-angle annular dark field (HAADF) detector with an energy dispersive spectrometer (EDS) RTEM SN9577+ (EDAX, Pleasanton, USA) and parallel electron energy loss spectroscopy (PEELS) provided by Gatan (Plesanton, USA) was incorporated to determine the elements. The SEM images were recorded using Quanta 3D FEG, FEI Europe, with an Everhart-Thornley detector known as a secondary detector (SE).

X-ray photoelectron spectroscopy analysis (XPS)

The surface chemistry of the samples was analysed by X-ray photoelectron spectroscopy (XPS) using a PHI 5000 VersaProbe (ULVAC-PHI) spectrometer with monochromatic Al K α radiation ($h\nu=1486.6$ eV) from an X-ray source operating at 100 μm spot size, 25 W, and 15 kV was employed to record the spectra of powder samples. The high-resolution (HR) XPS spectra were analysed using a hemispherical analyser at a pass energy of 117.4 and an energy step size of 0.1 eV. The X-ray beam was positioned on the surface of the sample at an angle of 45° to the normal surface, and the analyser axis was positioned at 45° with respect to the surface. The XPS data were studied using the CasaXPS software, and a Shirley background and a Gaussian peak shape with 30% Lorentzian character were used for the deconvolution of all HR XPS.

Electrochemical measurements

Electrochemical impedance spectroscopy (EIS), Mott-Schottky analysis, and photocurrent response were performed using a Potentiostat/Galvanostat (Metrohm Autolab PGSTAT204) and an electrolyte of Na₂SO₄ (0.5 M). Carbon screen-printed electrodes with an Ag/AgCl reference electrode were used to place the sample in paste form, and the electrode was dried for a few minutes prior to use.

Zeta potential analysis

Zeta potential measurements were performed for the sample of (P, S)-g-C₃N₄/2D TiO₂ using a Nano ZS Zetasizer (Malvern Instruments, UK) equipped with a dynamic light scattering detector and a 4.0 mW internal laser.

Magnetic properties

Magnetic characterisation of photocatalysts was performed using a SQUID magnetometer (Quantum Design MPMS XL7) with temperature-dependent measurements up to 300 K and a ± 60 kOe measurement range.

2.3. Photocatalytic activity studies

The prepared photocatalysts were employed in the photocatalytic degradation of carbamazepine (CBZ; 14 mg·dm⁻³), acetaminophen (ACT; 20 mg·dm⁻³), and ibuprofen (IBU; 20 mg·dm⁻³). The pharmaceutical solution was added to a 25 dm³ quartz reactor. The reactor was placed in a black-box photocatalytic setup and connected to cooling water; the magnetic stirrer was turned on to ensure solution homogeneity, as shown in Figure 10. The solution was stirred for 30 min in the dark to reach adsorption-desorption equilibrium. After 30 min, the reaction was initiated by irradiation of the solution with UV-vis irradiation, using a xenon lamp with a flux of 30 mW·cm⁻². The samples were collected at time intervals of -30, 0, 15, 30, 60, and 120 minutes. However, if the reaction proceeded rapidly, the sampling frequency increased to every 5 minutes until the 20 minute mark.

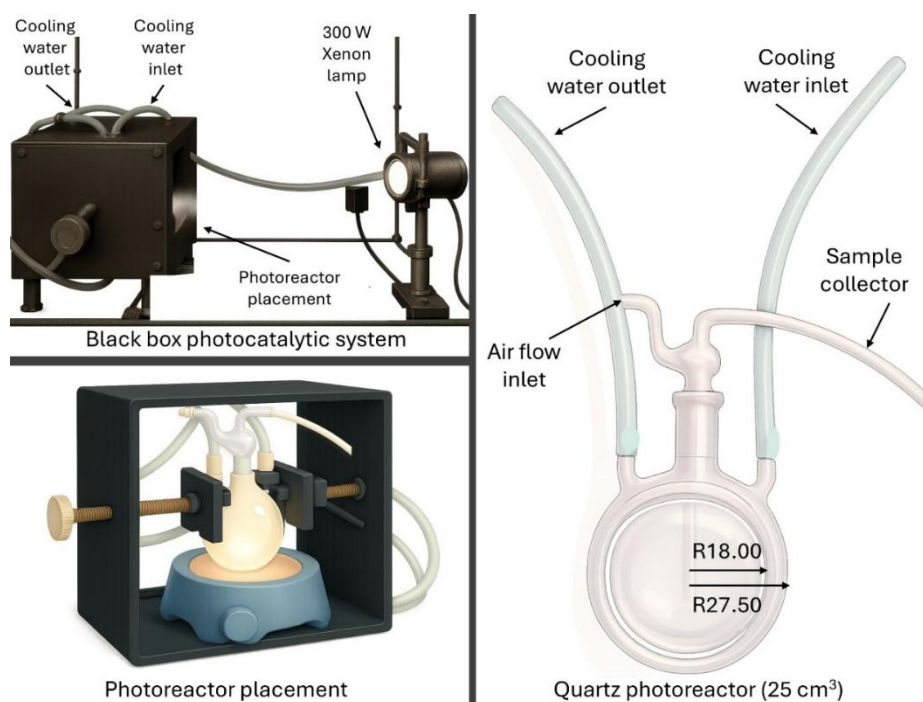


Figure 10. Scheme of photocatalytic set-up. The scheme of photocatalytic set-up was created using Illustrae (scientific illustration software).

To determine the reactive oxygen species produced during the photocatalytic reaction, the scavenging experiments were conducted. The trapping agents such as isopropanol ($\text{HO}^\bullet$, $\text{SO}_4^{\bullet-}$), tert-butyl alcohol (TBA; $\text{HO}^\bullet$), ammonium oxalate ($\text{NH}_4)_2\text{C}_2\text{O}_4$ (h^+), benzoquinone (BQ; $\text{O}_2^{\bullet-}$), sodium azide (NaN_3 ; $^1\text{O}_2$), and silver nitrate (AgNO_3 ; e^-) were added in the model solution to inhibit the respective ROS. The concentration of scavengers was 1 mM. Additionally, hydroxyl radical detection was performed using a spectrofluorophotometer by measuring the photoluminescence of hydroxycoumarin. Coumarin (0.5 mM) in reaction with hydroxyl radicals ($\text{HO}^\bullet$), produces 7-hydroxycoumarine, a fluorescent compound that emits at 450 nm.

The effects of water matrices and pH were investigated. Sodium chloride (NaCl), sodium carbonate (Na_2CO_3), sodium sulfite (Na_2SO_3), sodium sulfate (Na_2SO_4), and sodium nitrate (NaNO_3) in the concentration of 0.1 mM were added, and their influence on the photocatalytic reaction was described. The alkaline pH adjustment was made by sodium hydroxide (NaOH ; 0.5 M), and the acidic pH adjustment was made by chlorohydric acid (HCl , 0.5 mM).

The effect of persulfate (PS-AOP) in photocatalysis was studied by the addition of peroxydisulfate PDS (3mM) for the research study of ZnFe_2O_4 /(P, S)-g- C_3N_4 /2D TiO_2 (10% w/w) and the addition of peroxymonosulfate PMS (1 mM) for the research study of $\text{ZnO(OH)-Vo/g-C}_3\text{N}_4\text{(OH)}$.

The magnetic field effect (MFE) and photocatalysis were studied by incorporating an external magnet with a field strength of 60 mT into the system. The photocatalytic degradation of ibuprofen was conducted as described.

Determination of pharmaceutical concentrations and by-product identification were conducted using a high-performance liquid chromatography system (HPLC, Shimadzu LC-6A) coupled with a photodiode array detector (SPD-M20A) and a C18 column (Phenomenex Gemini 5 μm ; 150 $\times$ 4.6 mm) operating at 45°C. Different mobile phases were used for each pharmaceutical. For CBZ, the mobile phase consisted of (v/v) 60% H_2O , 0.5% orthophosphoric acid (85% w/w solution), and 39.5% acetonitrile, and was pumped through the HPLC system at a flow rate of 1.5 $\text{cm}^3\cdot\text{min}^{-1}$. Concerning ACT, the mobile phase consisted of (v/v) 30% methanol (MeOH), 69.9 % H_2O , and 0.1% formic acid (HCOOH) with a flow rate of 0.8 $\text{cm}^3\cdot\text{min}^{-1}$. Lastly, the mobile phase of IBU consisted of (v/v) 70% acetonitrile, 29.5% H_2O , and 0.5% orthophosphoric acid (85% w/w solution) at a flow rate of 0.5 $\text{cm}^3\cdot\text{min}^{-1}$.

Identification of intermediates was studied using high-performance liquid chromatography mass spectroscopy (LC-MS). The apparatus consisted of an HCT Ultra spectrometer (Bruker Daltonics, Billerica, Massachusetts, US) with an ESI source, and an Agilent 1200 liquid chromatograph (Agilent Technologies, Santa Clara, California, US). An Agilent column known as Eclipse XDB-C8, 4.6 $\times$ 150 mm, 5 μm , was used for chromatographic separation. The column oven temperature was set to 25°C, whereas the mobile phase consisted of two phases: mobile phase A (H_2O with 0.1% formic acid) and mobile phase B (acetonitrile with 0.1% formic acid). The flow rate was set to 0.4 $\text{cm}^3\cdot\text{min}^{-1}$ and the injection volume was 50 μL . The gradient program parameters were registered as follows: 0 min – 1%B, 5 min – 1%B, 25 min - 90%B, 30 min - 90% B, 35 min - 1%B, and the chromatograms were recorded at 220, 246, and 254 nm, and they were acquired in positive and negative ESI mode. The

capillary voltage was set at 113V, and the scanned mass range was 50-850 m/z with an accumulation time of 200 000 ms. Other parameters such as capillary voltage, drying gas flow, nebulising gas, and source temperature were set at 4.0 kV, 10 L.min⁻¹, 30 psi, and 350°C, respectively. Helium with a purity of 99.999% was employed as a collision gas in the ion trap. The mass spectrometer was operated in full scan and single ion monitoring modes (SIM).

The mineralisation efficiency of CBZ, ACT, and IBU was determined as total organic carbon (TOC) removal. The samples were analysed using a Shimadzu TOC-L equipment.

The rate constant of pollutants was calculated according to the pseudo-first-order kinetic model with the following equation:

$$\ln \frac{C_0}{C} = kt \quad (1)$$

The synergy index was calculated to evaluate the efficiency of heterocomposite formation, or to evaluate the combination of processes, by the following formula:

$$S = \frac{k(\text{heterocomposite})}{k(\text{semiconductor1}) + k(\text{semiconductor2})} \quad (2)$$

To assess catalyst stability, the extent of iron leaching after the photocatalytic experiment was measured by a DR 5000 spectrophotometer (Hach) and an LCK 521 cuvette test with a Hach pre-dosed reagent kit. Firstly, the zero sample is measured in which 5 cm³ of deionised water is added to the testing kit and inserted into the spectrophotometer to set the baseline absorbance to 0.000. After zeroing, 5 cm³ of sample is added into the kit, and is shaken according to the instructions in order for iron to react with ferrozine [3-(2-pyridyl)-5,6-bis(4-sulfophenyl)-1,2,4-triazine] and form a complex that exhibits a light brown to dark reddish colour depending on iron concentration. The sample is measured in the spectrophotometer, and the result is automatically displayed in mg/L Fe.

2.4. Numerical modelling and computational analysis

- Numerical modelling for (P, S)-g-C₃N₄/2D TiO₂ (5% w/w).

The ability of photon absorption for the best performing composite of P, S-g-C₃N₄/ 2D TiO₂ (5% w/w) and 2D TiO₂ was studied to evaluate the optical properties of photocatalyst suspensions. Different powder concentrations were used to measure direct/scattered transmittance from which the absorbance values were obtained [122]. Measurements were conducted within the wavelength range of 300-400 nm, and the final values were calculated as an average within this specific region. The optical properties were used to numerically model the local volume rate of photon absorption (LVRPA) using the six-flux model [123]. Calculations were conducted in accordance with the procedure outlined by Acosta-Herazo et al. [124]. Following the Henyey-Greenstein phase function as suggested for TiO₂ materials, the applied scattering probabilities in the forward, backward, and side directions were 0.754, 0.133, and 0.028. The total rate of photon absorption (TRPA) for a unit length of the reactor was calculated by integrating the LVRPA over the cross-section of the reactor [125]. The total number of absorbed UVA photons during the process for both materials was estimated by comparing the TRPA value with the incident photon flux.

- Density Functional Theory (DFT) for degradation of pharmaceuticals using (P, S)-g-C₃N₄/2D TiO₂ (5% w/w).

Computational analysis using density functional theory (DFT) was performed to anticipate the potential formation of by-products [126]. The calculations were performed using Orca 5.0.3, while structure modelling was conducted using B3LYP functionals, supplemented with the aug-cc-PVDZ basis set and incorporating the conductor-like polarizable continuum model (CPCM) to address the water matrix effect [127]. The geometry of each pharmaceutical was optimised to the default convergence thresholds of energy, gradient, and displacement. The energy effect of the possible reaction was calculated as the products-substrates energy difference, using O₂ and H₂O molecules to balance the stoichiometry during the photocatalytic process, since they are both primary substrates and final regenerated products in the ambient conditions after the process. For the selected compounds, additional time-dependent DFT calculations were performed at the optimised geometry to stimulate expected absorption spectra. Moreover, in the case of two carbamazepine structures, possible rearrangements of the molecule were studied using the nudged elastic band

method to determine the energy barrier and transition state for such processes. Finally, calculations of Fukui functions were performed based on the electron density maps for neutral, $N + 1$, and $N - 1$ electron states (N is the number of electrons) of the acetaminophen dimer to possibly suggest positions of the further reactive species attack.

- Density functional theory (DFT) for the determination of Lewis acid-Lewis base interaction in the case of $\text{ZnO(OH)-Vo/g-C}_3\text{N}_4\text{(OH)}$.

Density functional theory (DFT) simulations were performed to predict the Lewis acid and Lewis base interactions in the synthesised materials of $\text{ZnO(OH)-Vo/g-C}_3\text{N}_4\text{(OH)}$ to confirm the frustrated Lewis Pair (FLP) type of heterocomposite. QuantumATK v2024.09 software package from Synopsis was used to perform all DFT simulations. The molecular and slab structures were generated using the Builder tool in the ATK package [128]. The GGA-PBE theoretical framework was employed throughout the entire manuscript. The Linear Combination of Atomic Orbitals (LCAO) method was employed with the PseudoDojo scalar-relativistic basis set [129]. Grimme's D3 dispersion correction was utilised to enhance the characterisation of van der Waals forces. K-point density for standard simulations utilised a $4 \times 4 \times 4$ mesh, with energy values ranging from 75 to 150 Ha based on the arrangement. The Fermi-Dirac distribution was utilised. Boundary conditions are three-dimensional periodic unless stated otherwise. Electron difference density (EDD) and electrostatic difference potential (EDP) profiles were computed from the Hartree potential using the ATK package. The L-BFGS (Limited-memory Broyden-Fletcher-Goldfarb-Shanno) algorithm was employed for geometry optimisations with an energy cutoff of $0.05 \text{ eV}/\text{\AA}$ [130,131]. Density of states (DOS) analysis was conducted using a $7 \times 7 \times 7$ k-point mesh. To address the convergence issue, the mesh was refined to a resolution of $12 \times 12 \times 12$. DOS spectra were generated utilising a Gaussian broadening of 100 meV and were projected based on atoms, orbitals, or real space, referred to as Projected Local Density of States (PLDOS).

The first stage of DFT simulations consisted of the studies on the effect of hydroxylation on the electronic properties (DOS, PLDOS) and Lewis acid-base characteristics (EDD, EDP) of the hydroxylated graphitic carbon nitride $\text{g-C}_3\text{N}_4\text{(OH)}$.

The Quantum ATK building tool was used to make a two-layered model of g-C₃N₄ with melamine units that look like 2D graphene. The bulk version was obtained from the Materials Project database, and the P-6m2 symmetry was kept. Then, it was used to make a two-layered sheet with 20 Angstroms of vacuum above and primitive vectors $v1=[13.04, 0.00]$ and $v2=[6.52, 11.28]$. There were a total of 98 atoms in the model of pure g-C₃N₄. Hydroxyl groups were randomly added to C atoms to make the g-C₃N₄(OH) model work. It was possible to find the best settings for models with 1, 2, 3, or 4 surface OH groups. For all of these setups, EDD, EDP, DOS, and PLDOS profiles were found. The usual equation Eq (3) was used to figure out the hydroxylation energies:

$$E_{ads} = E_{gCN-OH} - E_{g-CN} - E_{OH} \quad (3)$$

The second stage of DFT calculations consisted of estimating the effects of hydroxyl groups (OH) and oxygen vacancies on the surface of zinc oxide (ZnO). The impact of hydroxylation on the electronic structure (EDD, EDP) and Lewis acid-base characteristics (DOS, PLDOS) was studied. The ZnO slab was designed from the tetragonal crystal structure of ZnO, as reported in the Materials Project database. The symmetry of the structure was identified as P42/mmm. The XRD results indicated that the slab was oriented along the (101) plane, comprising a total of 100 atoms. To model surface hydroxylation, OH groups were added to the highest Zn atoms (with saturated valencies). The grafting density was determined to be 8 OH groups per 100 atoms or 5.5 molecules per nm². Three categories of oxygen vacancies have been examined based on their proximity to the surface: deep, middle, and shallow, as illustrated in Fig S11-S12 (Supporting materials). In the scenario involving ZnOOH slabs, surface vacancies were excluded because of the surface's instability. The volumetric defect density was calculated to be 1 vacancy for every 100 atoms, converting to 0.8 vacancies per nm³ or $8 \times 10^{20} \text{ cm}^{-3}$. In the context of experimental measurements, the carrier concentration of n-type ZnO semiconductors can be regarded as reaching the high-doping limit [132].

The last stage of DFT calculations consisted of the estimation of different hydroxylation states of g-C₃N₄ and ZnO on the electronic properties of the formed junction. Four types of interfaces, like g-C₃N₄ + ZnO, g-C₃N₄(OH) + ZnO, g-C₃N₄ + ZnOOH, g-C₃N₄(OH) + ZnOOH, were created using an interface builder implemented in the ATK, where the strain was applied to atoms of the ZnO(OH) slab. Cells were chosen to ensure that in every instance, the strain remained below 3%. The final interfaces comprised approximately 250 atoms, varying with the number of OH groups present.

3. Thesis content

In the experimental part of the dissertation, the results of the conducted research are presented in the form of a series of three original research papers addressing the outlined scientific problems. These papers were published in journals indexed in the JCR database, with a cumulative impact factor of 17.2. A brief description of the individual works is provided below. In addition, one further study described in Chapter 6 is currently under review and constitutes a continuation and completion of the research on graphitic carbon nitride-based materials for the degradation of pharmaceutical contaminants in aqueous environments.

Chapter III. Heterojunction of (P, S) co-doped g-C₃N₄ and 2D TiO₂ for improved carbamazepine and acetaminophen photocatalytic degradation.

The research results presented in this chapter are described in the published article entitled:

E. Cako, S. Dudziak, P. Głuchowski, G. Trykowski, M. Pisarek, A. F. Borzyszkowska, & A. Zielińska-Jurek, (2023). Heterojunction of (P, S) co-doped g-C₃N₄ and 2D TiO₂ for improved carbamazepine and acetaminophen photocatalytic degradation. Separation and Purification Technology, 311, 123320. <https://doi.org/10.1016/j.seppur.2023.123320>. [IF = 9, CS = 15.1, MNI_{SW} = 140]. (Published).

In this study, hybrid photocatalytic materials based on phosphorus and sulfur co-doped graphitic carbon nitride integrated with TiO₂ nanosheets were successfully synthesised and applied for solar-driven degradation of selected pharmaceutical contaminants resistant to conventional biodegradation processes. The main

motivation of this research was to develop scalable multifunctional photocatalytic systems that combine electronic structure modification, heterojunction engineering, and structural design to improve light harvesting, enhance interfacial charge transfer, increase surface accessibility, and enhance overall photocatalytic degradation performance toward carbamazepine and acetaminophen under simulated solar irradiation. TiO_2 was employed as a wide bandgap photocatalytic component owing to its chemical stability, low cost, and well-established applicability in photocatalytic processes.

In order to enhance its photocatalytic activity under solar irradiation, TiO_2 was engineered into two-dimensional nanosheet architectures, providing increased specific surface area and shorter charge-diffusion pathways. These nanosheets were subsequently hybridised with multi-anion co-doped (P, S)-g- C_3N_4 to construct an efficient heterojunction system. Phosphorus incorporation was expected to improve charge carrier separation and modify the band structure, while sulfur substitution was associated with increased surface reactivity. Although individual doping with phosphorus or sulfur has been reported in carbon nitride-based systems, the synergistic effect of their simultaneous incorporation, combined with 2D TiO_2 heterostructure engineering, has not been previously investigated.

Structural characterisation confirmed the successful formation of the hybrid heterostructured photocatalyst. XRD analysis revealed the characteristic diffraction peak of (P, S)-g- C_3N_4 at 27.71° 2θ , corresponding to the diffraction plane of (0 0 2), whereas the presence of TiO_2 nanosheets was evidenced by the distinct peak at 25.53° 2θ assigned to the (1 0 1) plane. FTIR spectra further confirmed the coexistence of both components, showing typical N-H stretching vibrations at 3248 cm^{-1} , C-N and C=N stretching and rotational vibration in the region from 1250 cm^{-1} to 1625 cm^{-1} , whereas tri-s-triazine ring vibrations were noticed at 806 cm^{-1} . The presence of TiO_2 was confirmed with the stretching vibration of the Ti-O-Ti bridge between 500 cm^{-1} and 750 cm^{-1} . Morphological analysis revealed platelet-like structures of (P, S)-g- C_3N_4 and a 2D planar nanosheet of TiO_2 . High-resolution TEM confirmed the nanosheet architecture, revealing lattice fringes corresponding to the anatase (1 0 1) plane with an interplanar spacing of 0.349 nm . Doping of g- C_3N_4 enhanced visible light

absorption, lowered the bandgap energy, and inhibited charge carrier's recombination. The photoluminescence spectra and carrier's lifetime calculations showed better separation of charge carriers in UV light for 2D TiO₂ and under 405 nm excitation (the absorption maximum of (P, S)-g-C₃N₄ and the sideband of (P, S)-g-C₃N₄/TiO₂ for the composite material. Furthermore, electrochemical impedance spectroscopy analysis indicated reduced charge transfer resistance and suppressed recombination of photogenerated electron-hole pairs in the optimal (P,S)-g-C₃N₄/2D TiO₂ (5 wt%) composite. Local volume rate of photon absorption (LVRPA) and total rate of photon absorption (TRPA) were estimated following the six-flux model approach and the Henyey-Greenstein phase function. The acquired data disclosed that the main effect responsible for the improvement of photocatalytic activity of heterocomposite was electronic interaction between materials, rather than UVA light absorption. The optimum dosage of photocatalyst at which 90% of photons were absorbed was found to be 1 g·dm⁻³. Therefore, this dosage was maintained throughout the experiments.

Photocatalytic experiments demonstrated complete degradation of carbamazepine and acetaminophen within 30 and 60 minutes, respectively, following pseudo-first-order kinetics with rate constants of 0.203 min⁻¹ for carbamazepine and 0.074 min⁻¹ for acetaminophen. The effect of operational parameters showed that inorganic anions, such as chloride, nitrate, and carbonate, inhibit degradation efficiency through radical scavenging and competitive adsorption. The degradation behaviour was also strongly dependent on pH, which influenced electrostatic interactions between the photocatalyst surface and pollutant molecules. Optimal degradation conditions were observed near neutral pH. For carbamazepine, the lowest rate constants were observed at pH 3 and 5, with values of 0.140 and 0.141 min⁻¹, respectively. Although carbamazepine (pK_a = 13.9) remains neutral across this pH range, the heterocomposite surface becomes positively charged under acidic conditions, resulting in weak electrostatic attraction and reduced adsorption. For acetaminophen, the lowest degradation rates were observed at pH 3 and 9, with calculated values of 0.044 and 0.043 min⁻¹, respectively. Given its pK_a of 9.5, acetaminophen exists as a neutral/protonated form at low pH and as an anionic form

at high pH. Since the isoelectric point of the photocatalyst particles was determined to be pH 5.45, the surface was positively charged below this pH and negatively charged above it. At pH 3, weak interaction occurs due to a neutral drug and a positively charged surface, while at pH 9, electrostatic repulsion between a negatively charged surface and anionic acetaminophen reduces adsorption. Consequently, the most efficient acetaminophen degradation occurred between pH 5 and 7.

Scavenging tests confirmed that reactive oxygen species, primarily superoxide radicals ($O_2^{\bullet-}$) and hydroxyl radicals ($HO^{\bullet}$), were responsible for pollutant transformation. LC-MS analysis combined with density functional theory calculations enabled the identification of key degradation intermediates and proposed transformation pathways for both pharmaceuticals. CBZ was transformed into primary intermediates, including hydroxycarbamazepine (m/z 271.1) and dioxocarbamazepine (m/z 266.6). These results are in agreement with the performed DFT calculations, which indicated higher stability of dioxocarbamazepine compared with the parent compound. Subsequent oxidation and ring-opening reactions of acridone can result in the formation of short-chain carboxylic acids, which may ultimately be mineralised to CO_2 , H_2O , and NH_4^+ . For the most efficient composite sample of (P,S)-g- C_3N_4 /2D TiO_2 (5%), the mineralisation, measured as TOC removal efficiency, was about 76% after 60 min of irradiation.

The photocatalytic degradation of ACT proceeded through two main transformation pathways, including coupling reactions and hydroxylation/oxidation processes. The primary intermediates identified were the dimeric product (m/z 300.7) and hydroxylated and oxidised derivatives (m/z 167.5 and m/z 167.5). The hydroxylation/oxidation pathway involves electrophilic substitution of hydroxyl groups on the aromatic ring, a characteristic of the photocatalytic degradation of aromatic pharmaceuticals. Additionally, cleavage of the acetamide moiety (m/z 59.04) from the ACT molecule led to the formation of hydroquinone (m/z 110.04) and benzoquinone (m/z 108.09) as secondary intermediates. These transformation products are expected to undergo further oxidative degradation and ring-opening reactions, resulting in the formation of

short-chain organic compounds that can ultimately be mineralised to CO_2 , H_2O , and NH_4^+ . Moreover, the formation of the dimeric intermediate represents a less typical degradation route. Density functional theory calculations combined with Fukui function analysis indicated that the most reactive sites in this molecule are predominantly located on the aromatic rings, suggesting that further degradation may proceed through radical and electrophilic attack mechanisms analogous to those observed for the parent compound. Preferential electrophilic attack at the acetamide moiety was also identified as a possible pathway leading to the formation of an additional intermediate (m/z 258.6), consistent with mass spectrometry observations. Hydroxyl radicals are likely to initiate these transformations due to their strong electrophilic character and their confirmed involvement in the ACT degradation process. Furthermore, Fukui function analysis (f^+) indicated that the preferred site of nucleophilic attack is located at the dimer-forming bond (C4 and C20), suggesting that the dimeric intermediate may undergo cleavage into smaller molecules through nucleophilic pathways. Superoxide radicals ($\text{O}_2^{\bullet-}$) may contribute to such transformations, potentially leading to the formation of intermediates analogous to the (m/z 167.5) species. This interpretation is consistent with the experimentally observed role of superoxide radicals in the degradation process. However, it should be noted that the reactivity of superoxide radicals is generally slower than that of other reactive species. Therefore, this transformation might not be favoured. Regarding acetaminophen decomposition, the TOC removal efficiency was lower, reaching 40% after 60 min of irradiation. Overall, the results confirmed that the formation of the heterostructured (P,S)-g- C_3N_4 /2D TiO_2 system significantly improved photocatalytic activity compared with individual components, primarily due to enhanced interfacial charge transfer and radical-driven oxidation pathways. Regarding reusability, the photocatalytic activity of (P,S)-g- C_3N_4 /2D TiO_2 (5%) remained stable after subsequent cycles of carbamazepine and acetaminophen degradation.

Chapter IV. Dual approach for effective photodegradation and mineralization of carbamazepine using a ternary ZnFe_2O_4 /(P,S)-g- C_3N_4 /two dimensional TiO_2 composite.

The research results presented in this chapter are described in the published article entitled:

E. ako, C. Gomez-Polo, G. Trykowski, M. Pisarek, K. Sikora, A. Zielińska-Jurek. Dual approach for effective photodegradation and mineralization of carbamazepine using a ternary ZnFe₂O₄/(P, S)-g-C₃N₄/Two-Dimensional TiO₂ composite. ACS Omega, 11 (5) (2026) 7486-7500. <https://doi.org/10.1021/acsomega.5c08594>. [IF = 4.3, CS = 7.1, MNI_{SW} = 70]. (Published).

In this study, a magnetically recoverable ternary heterostructure based on ZnFe₂O₄, (P, S)-g-C₃N₄, and 2D TiO₂ was developed for efficient photocatalytic degradation and mineralisation of carbamazepine (CBZ). The main motivation of this work was to overcome key limitations of conventional photocatalysis in terms of recyclability and recovery of photocatalysts. Integration of magnetic zinc ferrite (ZnFe₂O₄) enables the formation of a magnetically recovered photocatalyst with increased reactivity towards pollutant degradation. Introducing ZnFe₂O₄ with (P, S)-g-C₃N₄ led to the formation of a heterojunction that promotes effective separation of photogenerated charges, suppressing the recombination and allowing the charged carriers to participate in redox reactions. Heterojunction formation enhances the visible light absorption, which leads to improved solar energy utilisation. Additionally, the magnetic nature of ZnFe₂O₄ facilitates easy recovery of the photocatalyst using an external magnet, making the system reusable and cost-effective.

Initially, binary ZnFe₂O₄/(P, S)-g-C₃N₄ magnetic composites were synthesised at different weight ratios (50:50 and 70:30% w/w). Photocatalytic experiments demonstrated that the 70:30% w/w ratio displayed enhanced activity relative to the 50:50% w/w ratio. The 70:30% w/w magnetic composite, designated as ZF/CN, was subsequently combined with 2D TiO₂ at loading percentages of 5, 10, and 20% w/w, yielding ternary heterocomposites denoted as ZF/CN/2D TiO₂ (5, 10, 20% w/w). Combination of ZF/CN with 2D TiO₂ enhances the photocatalytic performance through the formation of heterojunction that exhibits improved charge separation, broader light utilisation, and higher stability. In ternary heterocomposite (P, S)-g-C₃N₄ contributes with visible light absorption, whereas the ZnFe₂O₄ further extends

the visible light absorption while contributing to the magnetic recovery of the material. Presence of 2D TiO₂ contributes to utilisation of light in the ultraviolet UV region, enabling the entire ternary heterocomposite to absorb across the solar spectrum, including both UV and visible light (UV-Vis). The two-dimensional (2D) structure itself, consisting of ultrathin nanosheets, improves charge separation due to a short diffusion pathway that enables better charge mobility and suppresses recombination of electron-hole pairs.

Confirmation of the formed heterocomposite was achieved using different characterisation techniques. XRD analysis confirmed the coexistence of all phases, with a characteristic diffraction peak for ZnFe₂O₄ at $2\theta = 35.27^\circ$, corresponding to the (311) plane, in accordance with JCPDS card no. 82-1042, and anatase peak at $2\theta = 25.53^\circ$, corresponding to the (101) crystal plane, according to JCPDS card no. 21-1272. A peak at $2\theta = 13.2^\circ$, associated with the (100) plane of (P, S)-g-C₃N₄, was detected exclusively in the pure phase sample and was absent in the ZnFe₂O₄/(P, S)-g-C₃N₄ composite. Characteristic peak of (P, S)-g-C₃N₄ was measured at diffraction signal $2\theta = 27.7^\circ$ for the respective diffraction plane (002) assigned at the interlayer stacking of conjugated aromatic system. TEM observations revealed cubic ZnFe₂O₄ nanoparticles (~20 nm), platelet-like shaped (P, S)-g-C₃N₄, and well-developed TiO₂ nanosheets, confirming successful heterostructure formation. Optical properties were investigated through UV-vis diffuse reflectance spectroscopy (DRS), revealing that the synthesised heterocomposite effectively absorbs light in the UV-vis range, making it suitable for solar-driven photocatalytic applications. The determined optical band gaps were found to be 1.74 eV, 2.42 eV and 3.15 eV for ZnFe₂O₄, (P, S)-g-C₃N₄ and 2D TiO₂, respectively. Electrochemical impedance spectroscopy and photocurrent measurements demonstrated enhanced charge carrier separation and faster electron transport in the ternary system, particularly for ZF/CN/2D TiO₂ (10% w/w), which exhibited the lowest charge transfer resistance, faster electron transport and consequently better photocatalytic activity. Magnetic hysteresis loop showed that high field magnetisation for ZnFe₂O₄ was 26.8 emu·g⁻¹, and the anhysteretic loop of ZnFe₂O₄ demonstrated superparamagnetic properties, while the ternary composites retained sufficient magnetic response to enable efficient separation from

aqueous solutions despite reduced magnetisation due to the presence of diamagnetic components. Magnetic properties of heterocomposite demonstrate the capability of photocatalysts to be easily recovered from reaction media, highlighting its practical advantages in applications.

The performance of synthesised photocatalysts was evaluated through the photocatalytic degradation of carbamazepine (CBZ). Photocatalytic experiments showed that ZnFe_2O_4 alone exhibited negligible activity ($k = 0.001 \text{ min}^{-1}$), while coupling with (P, S)-g- C_3N_4 increased activity ($k = 0.004 \text{ min}^{-1}$). A significant enhancement was achieved upon incorporation of ZF/CN (70:30) with 2D TiO_2 in the loadings of (5%, 10%, 20% w/w). The apparent rate constants measured in the presence of three heterocomposites of ZnFe_2O_4 /(P,S)-g- C_3N_4 /2D TiO_2 (5%, 10%, 20% w/w) were found to be 0.071 min^{-1} , 0.176 min^{-1} and 0.042 min^{-1} after 30 min treatment time, whereas for the same amount of time, in the presence of 2D TiO_2 the apparent rate constant was found to be 0.121 min^{-1} . This improvement was attributed to the synergistic effects of enhanced visible-light absorption, improved interfacial charge transfer, and increased surface area provided by TiO_2 nanosheets.

A combination of ternary heterocomposite with persulfate (PS), offers significant advantages in a photocatalytic system by improving photocatalytic efficiency and reaction kinetics. Persulfate as an effective electron acceptor will be converted to sulfate radicals ($\text{SO}_4^{\bullet-}$), which have stronger activation potential and longer lifetime as compared to hydroxyl radicals ($\text{HO}^{\bullet}$). Three concentrations of persulfate (PS), specifically 0.5 mM, 1.5 mM and 3 mM, were assessed for their effectiveness in the degradation of carbamazepine (CBZ). The experiments revealed that a concentration of 3 mM PS resulted in the highest degradation rate, achieving 85% degradation in 120 min. Moreover, the findings confirmed that persulfate is efficiently activated under light irradiation, leading to the rapid conversion of CBZ into oxidation products, with total organic carbon (TOC) revealing 41% mineralization rate. However, when photocatalysis is combined with persulfate, significantly higher degradation efficiency of CBZ was achieved in the first 15 min of the process with a value of 99.5%. The apparent rate constant was found to be 0.370 min^{-1} , revealing that the combination of photocatalysis with persulfate increased the

rate constant by 2-fold as compared to the photocatalytic process only. The persulfate-assisted photocatalysis proved to be faster and more efficient because it combines rapid charge generation, efficient charge separation and intensified reactive radical generation. Utilising the coumarin fluorescence probe method, it was confirmed that persulfate-assisted photocatalysis led to an increase in 7-hydroxycoumarin concentration to 1807 nM in the first 5 min of reaction, highlighting the increased number of hydroxyl radicals due to fast conversion of sulfate radicals. Moreover, an improvement in TOC removal was also observed with a value of 74% for persulfate-assisted photocatalysis, as compared to 68% for photocatalysis only. Identification of reactive radicals tests indicated that photocatalytic degradation of carbamazepine was promoted by hydroxyl radicals ($\text{HO}^\bullet$), sulfate radicals ($\text{SO}_4^{\bullet-}$) and superoxide radicals ($\text{O}_2^{\bullet-}$). The degradation process produced intermediates such as epoxycarbamazepine and hydroxycarbamazepine, which subsequently decomposed into the smaller molecules, ultimately resulting in the mineralisation to carbon dioxide and water.

The presence of magnetic material of ZnFe_2O_4 in the formed heterocomposite of ZF/CN/2D TiO_2 (10%) contributed to the increased recyclability of the photocatalyst. The recyclability tests showed that the heterocomposite could be easily recovered and reused up to six consecutive cycles. The stability test of the heterocomposite revealed that iron leaching in the reaction media was negligible since the iron concentration was recorded to be below the detection limit.

Overall, the results demonstrate that the integration of magnetic ferrite, heterojunction engineering, and persulfate activation provides a highly efficient and scalable strategy for the degradation and mineralisation of persistent pharmaceutical contaminants. The developed ternary system combines enhanced photocatalytic performance with facile recovery and reusability, highlighting its strong potential for practical water treatment applications.

Chapter V. Comparison of ibuprofen photodegradation by persulfate-assisted and magnetic-field-assisted photocatalysis process.

The research results presented in this chapter are described in the published article entitled:

E. Çako, C. Gomez-Polo, M. Kowalkińska, M. Pisarek, A. Zielińska-Jurek, Comparison of ibuprofen photodegradation by persulfate-assisted and magnetic field-assisted photocatalysis processes. *Chemical Engineering and Processing-Process Intensification*, 222, (2026), 110740. <https://doi.org/10.1016/j.cep.2026.110740>. [IF = 3.9, CS = 7.9, MNI_{SW} = 140]. (Published).

This approach addresses the research gap related to the limited understanding of how different external activation strategies influence charge carrier dynamics, reactive species generation, and overall degradation efficiency in multifunctional photocatalytic systems. For this reason, the degradation of ibuprofen was studied using persulfate-assisted photocatalysis and magnetic field-assisted magnetic field. For the first time, the effect of two different methods coupled with photocatalysis was studied and compared. A synergistic combination of photocatalysis with persulfate-based advanced oxidation processes leads to a highly efficient treatment process. Upon exposure to light of the photocatalyst, the photogenerated electron-hole pairs facilitate the activation of persulfate to form sulfate radicals ($\text{SO}_4^{\bullet-}$). Since persulfate is an electron acceptor, it reduces electron-hole recombination and improves charge separation. This dual functionality ensures a consistent and improved generation of reactive species, including sulfate radicals ($\text{SO}_4^{\bullet-}$), hydroxyl radicals ($\text{HO}^{\bullet}$) and superoxide radicals ($\text{O}_2^{\bullet-}$), resulting in a markedly more efficient system compared to the use of photocatalysis or persulfate alone. Introducing magnetic field-assisted photocatalysis in our research is highly favourable due to the presence of magnetic material of zinc ferrite (ZnFe_2O_4) in the formed heterocomposite of ZnFe_2O_4 / (P, S)-g- C_3N_4 (ZF/CN) and ZF/CN/ 2D TiO_2 (10%). Introducing a magnetic field can improve photocatalytic efficiency by reducing the recombination of photogenerated charges and enhancing their mobility. This process is aided by mechanisms such as spin polarisation and the Lorentz force. Additionally, ZnFe_2O_4 contributes to increased recovery and recyclability of heterocomposite without significant loss of activity or structural degradation.

Persulfate-assisted photocatalysis (PS-AOP) and magnetic field-assisted photocatalysis were studied in the presence of ZnFe_2O_4 , (P, S)-g- C_3N_4 , ZF/CN and ZF/CN/ 2D TiO_2 (10%). X-ray diffraction (XRD) analysis revealed the phase

composition of materials. The characteristic peaks for ZnFe_2O_4 , (P, S)-g- C_3N_4 and 2D TiO_2 were recorded at 2θ 36.12° , 27.71° and 25.53° with respective indexed planes of (220), (002) and (101), identified as spinel ferrite phase, graphitic carbon nitride phase and anatase phase. Presence of anatase phase and spinel ferrite phase was confirmed by fast Fourier transform (FFT) with reciprocal distances of $d_1 = 0.296$ nm and $d_2 = 0.328$ nm for respective indexed planes of (220) and (101). The morphology analysis showed that platelet structures of graphitic carbon nitride were distributed over the anatase phase, along with cubic and various shapes of ZnFe_2O_4 . Brunauer-Emmet-Teller (BET) analysis was implemented to determine specific surface area, pore volume, and pore size. The specific surface area of 2D TiO_2 was measured to be 11.9 m^2/g , with a pore volume of 0.038 cm^3/g and a pore size of 17.36 nm. Bigger surface area, pore volume and pore size were observed in the case of ZF/CN/2D TiO_2 with respective values of 13.6 m^2/g , 0.059 cm^3/g , and 17.36 nm. Additionally, Type (IV) isotherms confirmed mesoporous structures of materials. X-ray photoelectron spectroscopy (XPS) analysis confirmed the successful integration of ZnFe_2O_4 , (P, S)-g- C_3N_4 , and 2D TiO_2 . The survey spectrum exhibited the presence of Zn, Fe, O, P, C, N, and Ti elements. Zn 2p spectrum assigned to Zn-O (Zn^{2+}) was recorded at 1022 eV and 1045 eV. The Fe 2p spectrum was recorded at 709.8 eV and 711.5 eV, attributed to Fe-O (Fe^{2+}) and Fe-O (Fe^{3+}). In the case of O 1s, three characteristic peaks assigned to the metal-oxygen bond (Me-O), P-O bond, and C=O bond were observed at 529.9 eV, 531.2 eV, and 532.1 eV. Presence of (P, S)-g- C_3N_4 was confirmed by observed spectra of P 2p, C 1s, and N 1s. The P 2p spectra were identified as P $2p_{3/2}$ and P $2p_{1/2}$ at 133.3 eV and 134.3 eV, corresponding to the phosphate bond (P-O). Moreover, an additional spectrum of Zn 3s was observed at 140.1 eV. In the case of the C 1s spectrum, three peaks were recorded at 284.8 eV, 287 eV, and 288.7 eV, assigned to aromatic and aliphatic bonds (C-C), C=O, and C-N bonds. N 1s spectrum confirmed at 398.9 eV and 400.6 eV were ascribed to sp^3 hybridisation of pyridinic (C-N) and surface amino groups (C-N-H). Presence of titanium (IV) oxide was confirmed by measured spectra of Ti 2p and O 1s. Ti 2p was recorded as Ti $2p_{3/2}$ and Ti $2p_{1/2}$ with binding energies of 458.7 eV and 464.3 eV assigned to Ti^{4+} in the TiO_2 lattice. Functional groups and chemical bonds in the heterocomposite were identified using

Fourier transform infrared spectroscopy (FTIR). Zn-O and Fe-O bonds were recorded at 565 cm^{-1} , which are attributed to symmetric and stretching vibrations of bonds. Stretching modes of C-N were obtained in the range of $1200\text{--}1700\text{ cm}^{-1}$, whereas triazine ring modes were identified at 801 cm^{-1} and 1470 cm^{-1} . Vibrations of absorbed water molecules and stretching mode of N-H bonds were recorded between $3000\text{--}3300\text{ cm}^{-1}$. The identified peaks in the frequency range of $800\text{--}400\text{ cm}^{-1}$ correspond to bending vibrations of Ti-O-Ti and Ti-O functional groups. To improve the charge separation and reduce the recombination of electrons and holes, it is essential to combine 2D TiO_2 with ZF/CN. A combination of materials led to a heterocomposite that exhibited decreased photoluminescence intensity as compared to 2D TiO_2 , suggesting suppressed charge carrier recombination and improved physicochemical properties of the heterocomposite. Regarding the magnetic properties of heterocomposite introduced by ZnFe_2O_4 , it was observed that the highest field magnetisation of $27\text{ emu}\cdot\text{g}^{-1}$ was obtained for ZnFe_2O_4 , which was significantly decreased to $1.40\text{ emu}\cdot\text{g}^{-1}$ when ZnFe_2O_4 was combined with (P, S)-g- C_3N_4 and 2D TiO_2 due to the negligible magnetisation of diamagnetic materials. From magnetic measurements, it was shown that bulk ZnFe_2O_4 is an antiferromagnetic material that, at the nanoscale, due to the distribution of cations between octahedral and tetrahedral sites, displays ferrimagnetic behaviour and superparamagnetic characteristics. Even though the ternary heterocomposite exhibited a low magnetisation, it has demonstrated potential for easy recovery and recyclability.

Photocatalytic experiments confirmed that the ternary heterostructure exhibited improved photocatalytic activity compared with individual components, achieving complete ibuprofen degradation within 60 min of irradiation. In contrast, significantly lower degradation efficiencies were observed for ZnFe_2O_4 (19%), (P,S)-g- C_3N_4 (47.96%), and 2D TiO_2 (83.5%), demonstrating the key role of heterojunction formation. Mineralisation studies revealed TOC removal efficiencies of 49% for the heterocomposite, exceeding that of pristine TiO_2 (41%). This improvement in photocatalytic activity was attributed to reduced recombination of photogenerated charge carriers, as confirmed by photoluminescence analysis, and improved light absorption across the UV-vis spectrum. Toxicity assessment using ECOSAR

modelling demonstrated that ibuprofen and its transformation products may pose environmental risks, particularly to aquatic organisms such as fish and *Daphnia*. In particular, the oxidation of monohydroxylated and quadric hydroxylated by-products increases LC50/EC50 and chronic toxicity values. However, after 60 min of treatment, the by-products disappeared, indicating that this process is critical for breaking the aromatic ring and facilitating further degradation toward less harmful, more biodegradable compounds.

To further intensify the process, persulfate-assisted photocatalysis was implemented. The combined system achieved complete ibuprofen degradation within 30 min, with a rate constant of 0.1586 min^{-1} , significantly higher than those obtained for standalone photocatalysis (0.0521 min^{-1}) and persulfate oxidation (0.0336 min^{-1}). Mineralisation efficiency was also enhanced, reaching 66% TOC removal within 30 min. The reactive species responsible for the degradation of ibuprofen consisted of sulfate radicals ($\text{SO}_4^{\bullet-}$), superoxide radicals ($\text{O}_2^{\bullet-}$), and hydroxyl radicals ($\text{HO}^{\bullet}$). Moreover, the presence of hydroxyl radicals ($\text{HO}^{\bullet}$) was further confirmed using the fluorescence probe method, in which coumarin was converted to 7-hydroxycoumarin (7-OHC). Additionally, the photocatalyst dosage was studied, and it was observed that the highest degradation efficiency could be achieved at the optimum dosage of $1 \text{ g}\cdot\text{cm}^{-3}$. Regarding the role of inorganic anions and natural organic matter (NOM), it was observed that the degradation efficiency of ibuprofen decreased to 48% and 75% in 120 min, respectively, for carbonate (CO_3^{2-}) and chloride anions (Cl^-). The reduced efficiency is related to the conversion of anions into their less reactive radical forms, such as $\text{CO}_3^{\bullet-}$, $\text{Cl}^{\bullet-}$ and $\text{Cl}_2^{\bullet-}$ which inhibit the reactivity of identified reactive species such as sulfate radicals ($\text{SO}_4^{\bullet-}$), hydroxyl radicals ($\text{HO}^{\bullet}$), and superoxide radicals ($\text{O}_2^{\bullet-}$).

In parallel, magnetic field-assisted photocatalysis was investigated using an external magnetic field (60 mT) generated by an NdFeB magnet, placed perpendicular to the reactor base. The application of the magnetic field improved degradation efficiency and reaction kinetics, with the highest rate constant (0.078 min^{-1}) observed in the presence of a ternary heterostructure. This enhancement is

primarily attributed to improved charge carrier separation induced by Lorentz forces, as well as possible contributions from spin polarisation and magnetohydrodynamic effects. The magnetic field effect (MFE) index was calculated for the degradation of ibuprofen. A positive value of the MFE index confirmed that the magnetic field improved the overall photocatalytic process. The highest magnetic field index was calculated for ZnFe_2O_4 with a value of 0.39 attributed to the highest field magnetisation of ZnFe_2O_4 ($27 \text{ emu}\cdot\text{g}^{-1}$). As magnetisation properties decreased for ZF/CN and ZF/CN/ 2D TiO_2 , the same effect was observed for the MFE index, which decreased to 0.14 and 0.04, respectively, due to the combination with diamagnetic materials of (P, S)-g- C_3N_4 and 2D TiO_2 . The same effect was observed in the degradation of methyl orange (MO) by magnetic field-assisted photocatalysis, confirming that magnetic field synergistically improves the photocatalytic activity of materials.

Comparative analysis of both activation strategies demonstrated that although both systems exhibit synergistic behaviour, persulfate-assisted photocatalysis showed a higher synergy index (1.85) compared with magnetic field-assisted photocatalysis (1.36). This indicates that persulfate activation is more effective in accelerating reaction kinetics due to additional radical generation, whereas the magnetic field primarily enhances charge separation without introducing new oxidising species.

Despite its lower kinetic enhancement, magnetic field-assisted photocatalysis offers important advantages, including the elimination of chemical additives and reduced risk of secondary pollution. In contrast, persulfate-based systems, while highly efficient, require careful control of oxidant dosage and may lead to sulfate accumulation. Therefore, each approach presents distinct advantages and limitations in the context of sustainable water treatment. Overall, the ZF/CN/2D TiO_2 (10%) heterostructure demonstrated high efficiency in both activation systems, confirming its potential as a multifunctional, magnetically recoverable photocatalyst. The results highlight that combining advanced material design with process intensification strategies provides a powerful approach for the efficient removal of persistent pharmaceutical contaminants in water.

Chapter III. Heterojunction of (P, S) co-doped g-C₃N₄ and 2D TiO₂ for improved carbamazepine and acetaminophen photocatalytic degradation.

Chapter IV. Dual approach for effective photodegradation and mineralization of carbamazepine using a ternary $\text{ZnFe}_2\text{O}_4/(\text{P},\text{S})\text{-g-C}_3\text{N}_4/\text{Two dimensional TiO}_2$ composite.

Chapter V. Comparison of ibuprofen photodegradation by persulfate-assisted and magnetic-field assisted photocatalysis process.

Chapter VI: Surface functionalisation and defect engineering in frustrated Lewis pairs type heterostructure of hydroxylated graphitic carbon nitride g-C₃N₄ (OH) and oxygen vacant zinc oxide hydroxide ZnO(OH)-Vo.

As discussed in the first chapter (section 3. 4), the surface functionalisation of graphitic carbon nitride (g-C₃N₄) represents an effective strategy to tailor its electronic structure. Surface functionalisation of graphitic carbon nitride involves the formation of covalent bonds between g-C₃N₄ and chemical reactants, enabling modifications such as oxidation, hydroxylation, sulfonation, amidation, and the introduction of surface defects [1]. In contrast, surface functionalisation via noncovalent functionalisation relies on weaker interactions, including electrostatic forces, π - π bonding, hydrogen bonding, and van der Waals forces [1]. This approach often leads to the formation of heterojunctions between g-C₃N₄ and various semiconductors or metal oxides.

The main motivation of this work was to explore an alternative mechanism of charge separation based on acid-base electrostatic interactions rather than conventional band alignment. The incorporation of functional groups and defects enables the formation of localised Lewis acidic and basic centres, which can be exploited in the design of frustrated Lewis pair (FLP)-type systems. In g-C₃N₄-based systems, defect sites such as vacancies can alter charge distribution and contribute to the formation of reactive surface sites. Some of the Lewis acid molecules used are B, Al, Ga, In, and Sn, while the Lewis base molecules are represented by C, N, O, S, P, and terminal hydroxyl groups (-OH) [2]. Surface defects of carbon nitride and exposed nitrogen sites served as a Lewis base platform when forming B-N/FLP and Al-N/FLP, where boron (B) and aluminium (Al) served as Lewis acids [3]. Defective boron carbon nitride (BN/FLP) was efficiently used in the organic synthesis of ammonia production [4]. Graphitic carbon nitride and planar carbon nitrides can serve as Lewis bases due to their active carbon and nitrogen sites, or as platforms for hosting FLPs. This can be achieved by introducing defects into the structure and

doping with external elements such as non-metals and metals, which serve as Lewis acids [2][175]. Despite growing interest in FLP chemistry, its application in photocatalysis, particularly for pharmaceutical degradation, remains largely unexplored, representing a clear research gap.

In this regard, a novel FLP-type heterostructure was developed by combining hydroxylated g-C₃N₄ (gCN-OH), acting as a Lewis base, with oxygen-deficient ZnO(OH) (ZnOH-V_o), which provides Lewis acid sites. This configuration introduces spatially separated yet electronically interacting acid-base pairs, preventing their mutual neutralisation and enabling unique interfacial charge transfer behaviour.

Results

The physicochemical properties of the synthesised photocatalysts were systematically investigated to evaluate the effect of surface functionalisation and defect engineering on structural, electronic, and optical properties.

The crystalline structure and phase composition of hydroxylated graphitic carbon nitride g-C₃N₄(OH), hydroxylated and oxygen vacant zinc oxide ZnO(OH)-V_o, and frustrated Lewis pair (FLP) type heterostructure ZnO(OH)-V_o/g-C₃N₄(OH) were studied using X-ray diffraction analysis (Figure 6.1a). To simplify the discussion, the photocatalysts are referred to as follows: gCN-OH, ZnOH-V_o, and ZnO(OH)-V_o/g-C₃N₄(OH), referred to as FLP.

The XRD signals for characteristic peaks of ZnOH-V_o were noticed at $2\theta = 31.7^\circ$, 34.4° , 36.2° , 47.5° , 56.5° , 62.7° , 66.3° , 67.8° , 69° , 72.4° , 76.8° indexed as diffraction planes of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2), (2 0 1), (0 0 4), (2 0 2) in agreement with wurtzite hexagonal structure. The observation of peak broadening and a slight displacement relative to stoichiometric ZnO indicates the presence of oxygen vacancies, which cause local lattice distortions. The distinctive peaks of gCN and gCN-OH were observed at $2\theta = 13.1^\circ$ and 27.7° for respective diffraction planes of (1 0 0) and (0 0 2). The diffraction pattern of the FLP heterocomposite revealed all characteristic signals of both materials, which indicate the successful formation of the heterocomposite. The presence of characteristic functional groups and bonding

interactions among the components indicated the successful formation of a heterocomposite.

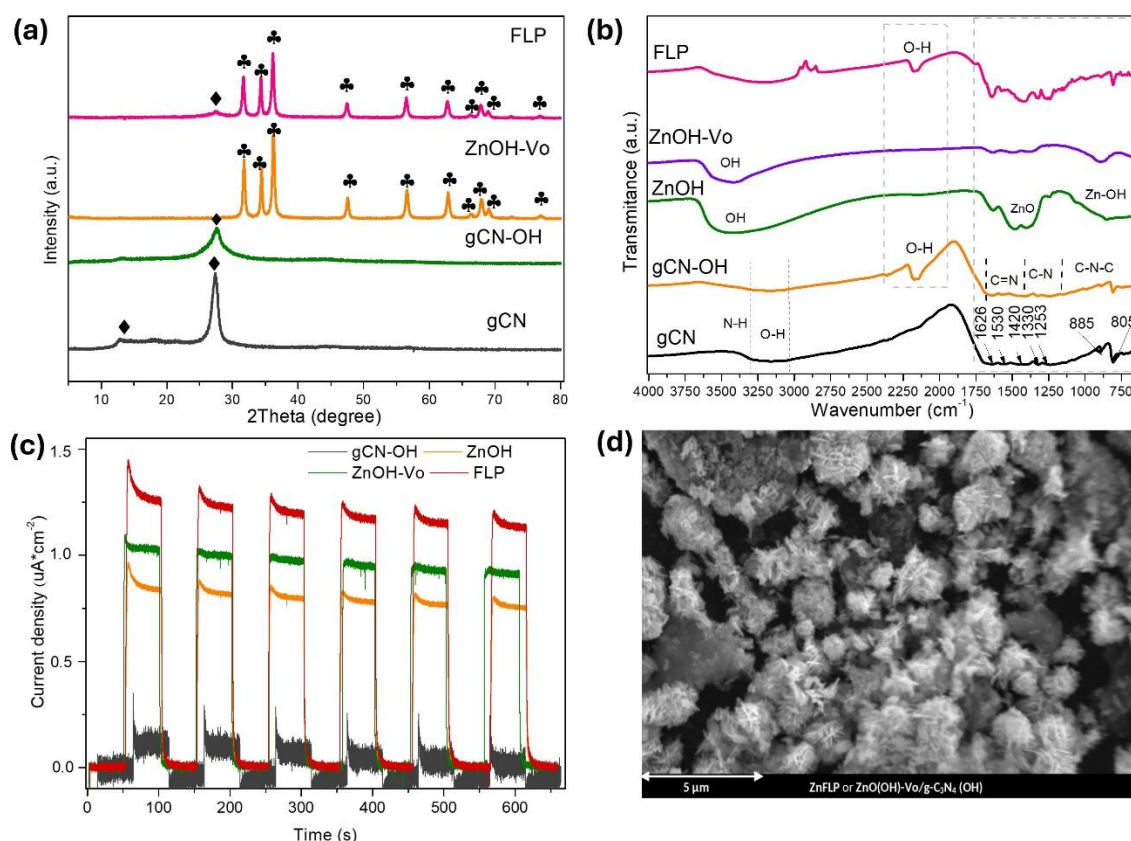


Figure 6.1. XRD patterns of gCN, gCN-OH, ZnOH-Vo, and the FLP heterocomposite (a), Fourier transform infrared spectroscopy (FTIR) patterns of gCN, gCN-OH, ZnOH, ZnOH-Vo, and the FLP heterocomposite, FESEM image of FLP in magnification of 5 μm (c), the transient photocurrent response of gCN-OH, ZnOH, ZnOH-Vo, and FLP.

The FTIR spectra provide additional support for the structural assignments and elucidate the surface chemistry relevant to FLP formation, as shown in Figure 6.1b. Three characteristic regions in the FTIR spectrum for gCN were observed in the first region of 895 cm^{-1} to 805 cm^{-1} , the second region from 1750 cm^{-1} to 1250 cm^{-1} , and the third region from 3250 cm^{-1} to 3000 cm^{-1} , which corresponded to the bending vibration of tri-s-triazine units, stretching vibration of C-N, C=N, and stretching vibrations of primary and secondary amine bond N-H. The peak at 2140 cm^{-1} confirmed the presence of a hydroxyl group (HO) in gCN-OH. In ZnOH and ZnOH-

V_o , the vibrational features at 3600 - 3400 cm^{-1} correspond to surface hydroxyl groups, while those at 1600 - 1300 cm^{-1} are due to Zn-O stretching modes. The band near 902 cm^{-1} indicates Zn-OH coordination. The presence of oxygen vacancies in ZnOH- V_o results in undercoordinated Zn^{2+} centres that act as Lewis acid sites. In contrast, the Lewis basic sites in hydroxylated graphitic carbon nitride gCN(OH) are formed due to the nitrogen lone pairs and surface hydroxyl groups. The integration of these materials imposes steric constraints and lattice mismatch, which impede full acid-base neutralisation, leading to FLP sites at the junction.

The pristine g- C_3N_4 absorbs visible light. Hydroxylation of g- C_3N_4 led to a slight redshift and a broader absorption tail, indicating improved visible-light harvesting due to surface-state modification. In contrast, ZnOH absorbed mainly in the UV region, whereas ZnOH- V_o displayed an extended absorption edge toward the visible range. This effect arises from vacancy-induced electronic states that modify the band structure, reducing the optical band gap from 3.35 eV to 3.19 eV. The absorption spectra of ZnOH- V_o /gCN-OH showed that the FLP material can be photocatalytically active in both UV and visible light ranges, highlighting the synergistic effect of surface hydroxyl groups and vacancy states at the interface. FESEM analysis indicated that gCN-OH possesses a porous morphology, whereas ZnOH- V_o forms flower-like assemblies composed of needle-shaped structures. In the composite, ZnOH- V_o nanostructures are homogeneously distributed on the gCN-OH surface, resulting in a hierarchical, well-interconnected architecture (Figure 6.1 c).

As shown in Figure 6.1 d, the transient photocurrent response confirms improved charge carrier dynamics in the modified system. The FLP heterostructure delivers the highest and most stable photocurrent signal, demonstrating efficient charge separation and migration under periodic illumination. ZnOH- V_o exhibits moderate performance, while gCN-OH shows the weakest response due to rapid recombination. The superior behaviour of the FLP composite can be attributed to the combined effects of interfacial interactions and vacancy-induced electronic states, which together enhance carrier mobility and suppress recombination.

To obtain detailed information on surface composition, oxidation states, and interfacial electronic interactions in the FLP heterostructure, high-resolution XPS analysis was conducted. Figure 6.2 presents the high-resolution spectra of the N 1s, C 1s, Zn 2p_{3/2}, and O 1s regions.

The N 1s spectra of g-C₃N₄(OH) and the FLP system were fitted with multiple components centred at ~398.4, 399.8, 400.9, 403.9, and 405.9 eV, corresponding to pyridinic, pyrrolic, and graphitic nitrogen species, along with oxidised nitrogen functionalities. These binding energy features confirm the preservation of the tri-s-triazine-based polymeric structure of carbon nitride.

The C 1s spectra can be deconvoluted into four main components located at approximately 284.5 eV (sp² C=C), 286.2 eV (C-O/C-N), 287.9 eV (N-C=N within the triazine framework), and a weak contribution near 293 eV attributed to C=O species. The prominent N-C=N peak confirms that the heptazine-based structure of g-C₃N₄ remains intact after composite formation.

All Zn-containing samples display a Zn 2p spin-orbit doublet characteristic of Zn²⁺ species, with the Zn 2p_{3/2} peak positioned at 1022.6-1022.9 eV, consistent with Zn-O bonding environments. In the FLP heterostructure, a noticeable positive shift (about 0.1-0.2 eV) of the Zn 2p_{3/2} peak is observed relative to ZnOH-V_o, indicating electron depletion at Zn sites. This behaviour reflects interfacial charge transfer toward the gCN-OH component, confirming strong electronic coupling and the establishment of an internal electric field that promotes efficient charge separation. Deconvolution of the O 1s spectra reveals three distinct contributions located at ~530.2, 531.3, and 532.4 eV, attributed to lattice oxygen, oxygen vacancy-associated species, and surface hydroxyl/adsorbed oxygen, respectively. The peak intensity of O 1s for V_o was slightly increased in the sample of ZnO(OH)-V_o. The proportions of oxygen lattice (O_{Lattice}) in Zn-O bond, oxygen vacancy (O_{Vacancy}), and adsorbed oxygen (O_{Ads}) were measured to be 32.8% at, 6.3% at, 4.78% at for ZnO(OH), whereas the values were increased to 34.26% at (O_{Lattice}), 7.76% at (O_{Vacancy}) for ZnO(OH)-V_o. The ratio of O_{Vacancy}/O_{Lattice} was increased from 0.19 to 0.22 when ZnO(OH) was calcined under an argon atmosphere to form oxygen vacancies in the structure of the obtained catalyst of ZnO(OH)-V_o. A similar observation was reported by Ranjibary

et al. [28], where the ratio of $O_{\text{Vacancy}}/O_{\text{Lattice}}$ was increased from 0.44 to 0.57 when oxygen vacancies were introduced in the zinc oxide (ZnO) structure. The proportion of adsorbed oxygen in the case of ZnO(OH)-V_o was decreased to 4.39% as compared to 4.78% for ZnO(OH), since the presence of argon can displace the adsorbed oxygen molecules on the surface of the sample during the calcination process. Consequently, the oxygen atoms could not be promptly restored, leading to an increase in oxygen vacancies [5]. Notably, the O 1s spectrum of the FLP heterostructure shows a slight shift toward lower binding energy, indicating increased electron density around surface oxygen atoms. This effect is attributed to interfacial charge transfer from ZnOH-V_o toward gCN-OH, accompanied by local charge compensation. The simultaneous upward shift of Zn 2p and the downward shift of O 1s confirm bidirectional charge redistribution and Fermi-level equilibration across the interface. Similar behaviour has been reported for defect-engineered ZnO systems subjected to reductive treatment [6,7].

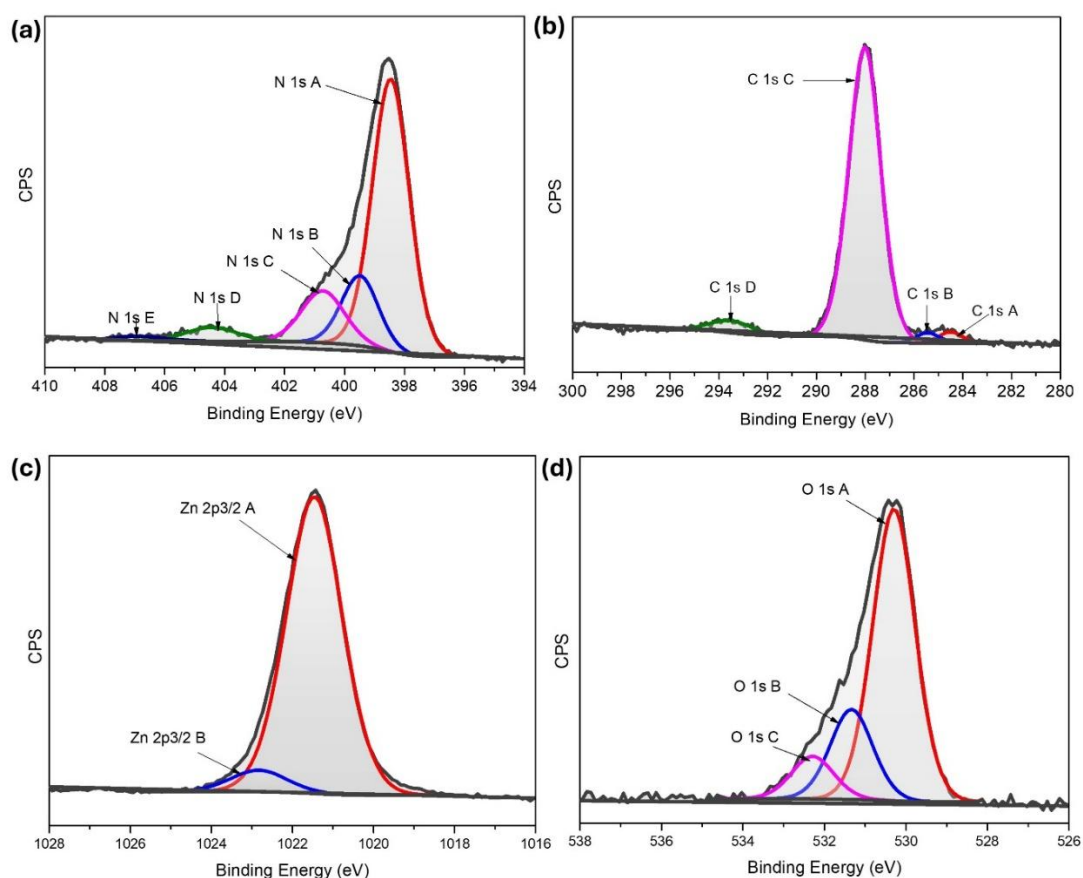


Figure 6.2. X-ray photoelectron spectroscopy(XPS) spectra of N 1s (a), C 1s (b), Zn 2p (c) and O 1s (d) elements in FLP heterocomposite.

The ZnOH-V_o/gCN-OH heterostructure was analysed to understand the role of surface hydroxylation and oxygen vacancies in shaping electronic properties and interfacial interactions. Comparative DFT studies were performed for pristine and modified systems (gCN vs gCN-OH, ZnO vs ZnOH, and ZnOH-V_o), enabling identification of structure-property relationships.

Hydroxylation of gCN was studied using an optimised two-layered model on the PBE-D3 level, which revealed that the distances between layers of gCN were 0.33 nm and are in line with prior reported experimental values of 0.34-0.35 nm and computational results of 0.31-0.34 nm (based on the type of XC functional and dispersion correction) [6,8]. The calculation of electron difference densities (EDD) and their maps was performed using DFT-optimized geometries (Figure 6.3). Negative EDD profiles showed the electrophilic nature of gCN (strong Lewis acid), which changed to positive EDD profiles when introducing hydroxyl groups (OH) on the surface of gCN and made the material slightly nucleophilic (weak Lewis base). This observation was further supported by electrostatic potential difference profiles, which exhibited a negative shoulder peak in the region corresponding to the -OH group, indicating its negative charge. Importantly, this behaviour is preserved across different hydroxylation levels.

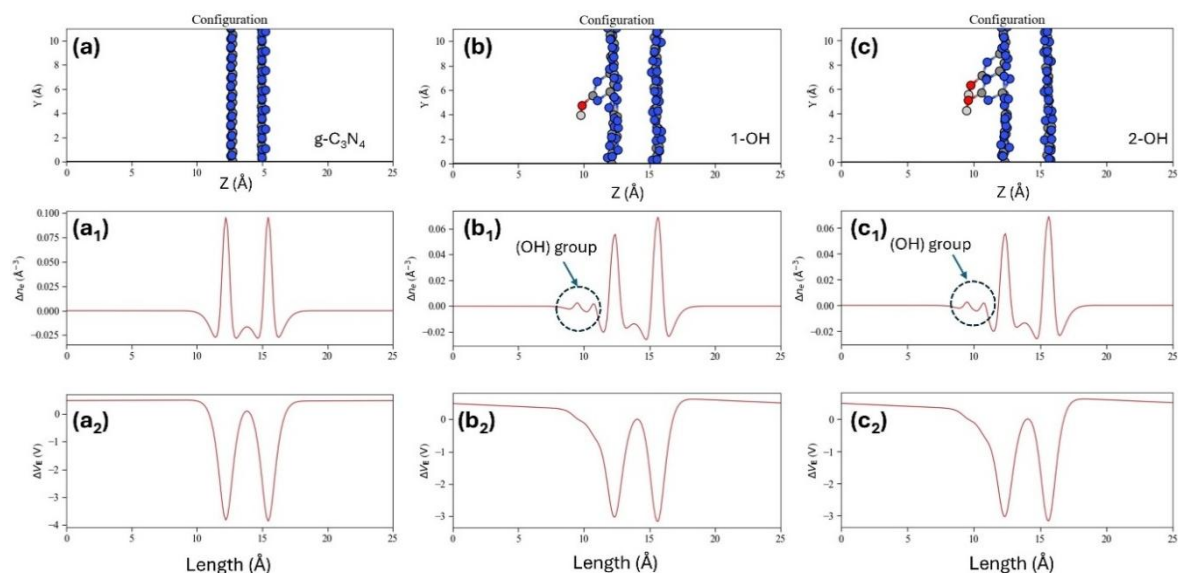


Figure 6.3. Optimised DFT geometries of pure g-C₃N₄, and hydroxylated g-C₃N₄(OH) (a, b, c) and corresponding electron difference density profiles (a₁, b₁, c₁) and electrostatic difference potential profiles (a₂, b₂, c₂).

In contrast, ZnO-based systems retain their electron-deficient (Lewis acidic) character even after hydroxylation and defect formation. ZnOH remains structurally stable, while the introduction of oxygen vacancies leads to the formation of surface electronic states and an upward shift of the Fermi level, characteristic of n-type behaviour. Notably, hydroxylated structures exhibit an increased tendency to form surface vacancies compared with pristine ZnO. Among the different types of defects, surface vacancies play a dominant role, as they significantly influence the electronic structure by introducing donor-like states and enhancing charge carrier mobility, whereas bulk and subsurface defects have only a minor effect (Figure 6.4).

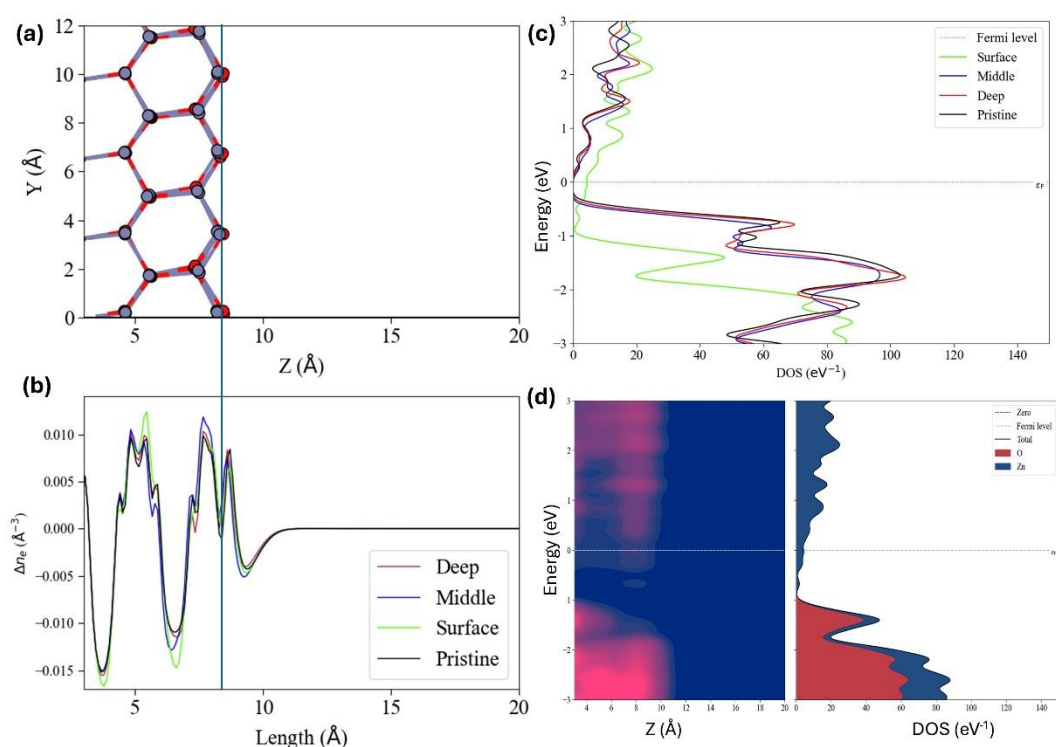


Figure 6.4. EDD profile of ZnO (a, b), EDP profile of ZnO(OH)-Vo (c), PLDOS plots of ZnO (d).

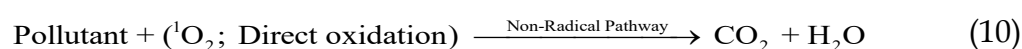
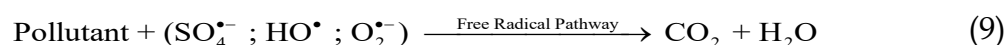
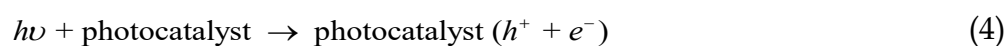
The combination of both components results in strong interfacial interaction, as confirmed by high binding energies of the modelled interfaces. Notably, the ZnOH-Vo/gCN-OH system exhibits significantly stronger interfacial adhesion compared with non-functionalised systems, indicating thermodynamic stability and effective coupling. At the interface, hydroxyl groups are not clearly associated with a single component but rather form a shared interfacial region. This leads to an unconventional interaction mechanism that deviates from classical semiconductor

heterojunction behaviour. Instead of forming a typical p-n junction with a space-charge region, the system develops an electrostatically driven interface governed by Lewis acid-base interactions. In this configuration, ZnOH-V_o acts as a Lewis acid, while gCN-OH behaves as a Lewis base. The interfacial -OH groups function as a dielectric spacer, preventing neutralisation and enabling the formation of a frustrated Lewis pair. This arrangement creates an internal electric field analogous to a nanoscale capacitor, in which charge separation is driven by electrostatic interactions rather than by band alignment. This FLP-type mechanism represents a fundamental shift from conventional heterojunction design, providing an alternative pathway for charge separation and offering new opportunities for photocatalytic system engineering.

Photocatalytic degradation of carbamazepine was studied in the presence of gCN, gCN.OH, ZnOH, ZnOH-V_o, and FLP heterocomposite of ZnOH-V_o/gCN-OH single photocatalysts and FLP heterocomposite. An efficient photocatalyst is defined by its capacity to absorb a wide spectrum of light, preferably within the visible range for solar applications, ability for low recombination of electron-hole pairs, improved mobility of charges, chemical stability, and recyclability. Hydroxylation of gCN improved the efficiency of the pristine gCN. Degradation efficiency of carbamazepine increased from 28.8 % to 83.1 % in 60 min, with respective rate constants of 0.0059 min⁻¹ and 0.0296 min⁻¹. Introducing oxygen vacancies in the structure of ZnOH, increased the degradation efficiency from 56.1% to 84.9% in 60 min, while calculated rate constants were found to be 0.0132 min⁻¹ and 0.0298 min⁻¹, respectively. Complete degradation of carbamazepine was observed for the FLP heterocomposite of ZnOH-V_o/gCN.OH in 60 min, confirming the successful formation of the heterocomposite with improved photocatalytic properties. The rate constant of carbamazepine degradation in the presence of FLP was increased by two-fold as compared to standalone components, with corresponding values of 0.0543 min⁻¹, 0.0296 min⁻¹, and 0.0298 min⁻¹ for FLP, gCN-OH, and ZnOH-V_o, respectively. Along with photocatalytic degradation efficiencies, it is essential to study total organic carbon removal. TOC analysis assesses the conversion of the parent molecule to intermediates and end products like CO₂ and H₂O. The difference between

photocatalytic degradation efficiency and mineralisation efficiency is attributed to the formation of partially oxidised intermediates during reactions. The mineralisation, measured as TOC removal efficiency, for gCN, gCN-OH, ZnOH, ZnOH-Vo, and FLP was 12%, 38%, 31%, 46%, and 53%, respectively.

The combination of photocatalysis with persulfate-assisted advanced oxidation process (PS-AOP) represents a method to enhance pollutant degradation. To improve the degradation of carbamazepine, FLP heterocomposite was combined with PMS activation, since in the presence of gCN-OH and ZnOH-Vo, the peroxymonosulfate can self-decompose to generate sulfate radicals ($\text{SO}_4^{\bullet-}$), followed by formation of other reactive species like hydroxyl radicals ($\text{HO}^{\bullet}$) and superoxide radicals ($\text{O}_2^{\bullet-}$). The reactions are described in Eqs (1-10) [9,10].



A combination of FLP with PMS resulted in a synergistic system that led to 100% degradation of carbamazepine in 30 min of treatment. The calculated rate constant was 0.1291 min^{-1} , significantly higher than the standalone processes of photocatalysis and PMS photolysis, as presented in Figure 6.5. These results demonstrate that PMS activation is predominantly catalysed by the FLP heterostructure rather than driven by direct photolysis, as reflected by 50% degradation of carbamazepine in the PMS/light system within 60 min.

Consequently, light irradiation plays a supportive role by accelerating the process, while the primary mechanism is governed by catalyst-mediated PMS activation.

The effect of pH was investigated for both photocatalysis and PMS-assisted photocatalysis under acidic (pH 3.0), neutral (pH 6.5), and alkaline (pH 10.0) conditions (Figure 6.5c,d). The pH of the reaction medium influences both the ionisation state of the pollutant and the generation, stability, and reactivity of radical species, thereby affecting overall degradation and mineralisation efficiency.

For the FLP-based photocatalytic system, variations in pH below neutral had only a minor impact on carbamazepine degradation (Figure 6.5c). Slightly reduced activity was observed under alkaline conditions, where degradation efficiency decreased from 100% (pH 6.5) to 95.7% (pH 3.0) and 94.9% (pH 10.0) after 60 min.

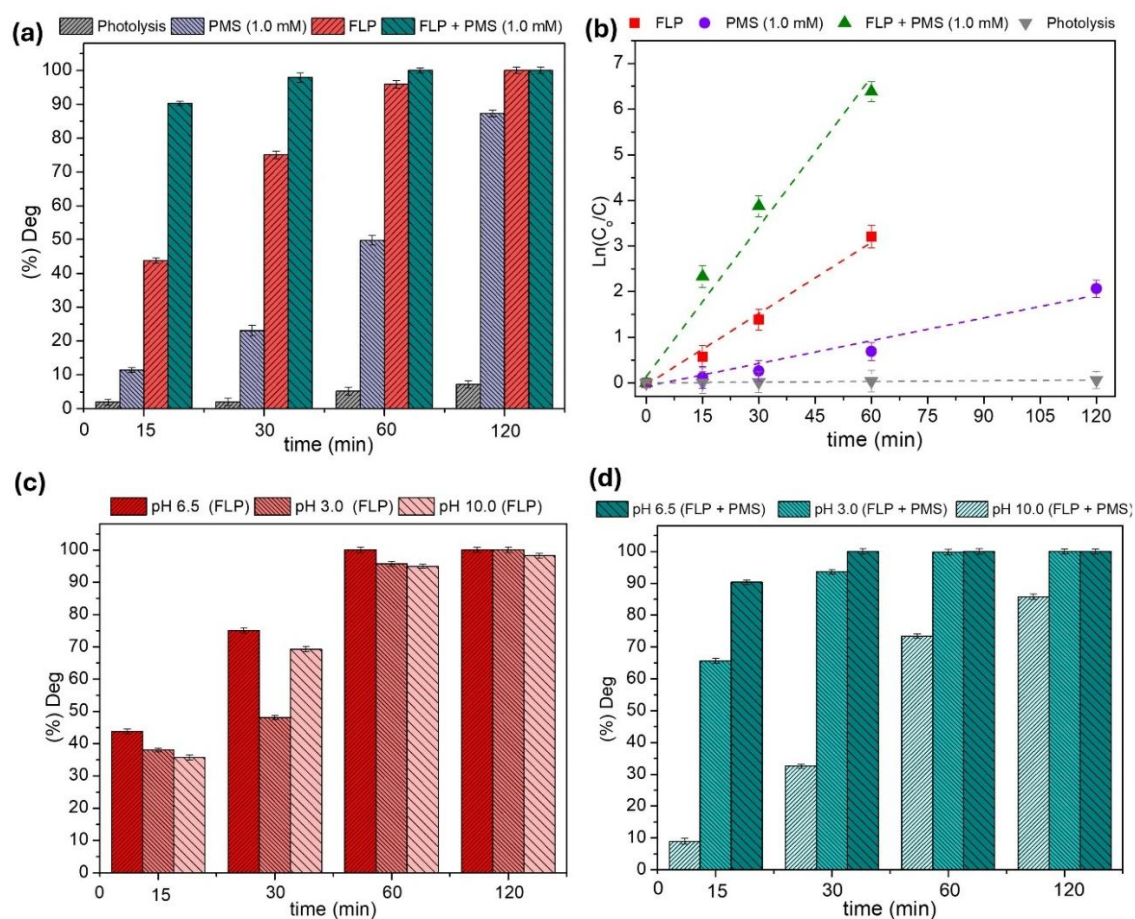
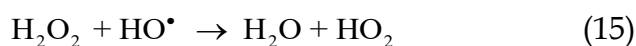
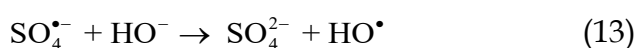
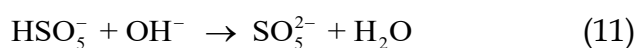


Figure 6.5. Photocatalytic activity of ZnO(OH)-V_o/g-C₃N₄(OH) FLP, PMS (1.0 mM), and PMS-activated FLP (FLP + PMS). Photodegradation efficiency of carbamazepine (CBZ) (a); Kinetics of CBZ degradation (b); Effect of pH during photocatalysis (c); Effect of pH during photocatalysis assisted PMS (d).

The corresponding rate constants were 0.0543 min⁻¹ (pH 6.5), 0.0541 min⁻¹ (pH 3.0), and 0.0338 min⁻¹ (pH 10.0), indicating that the FLP system is relatively insensitive to pH changes in the absence of additional oxidants.

In contrast, the PMS-assisted system showed a strong dependence on pH (Figure 6.5d). Under alkaline conditions (pH 10.0), the degradation efficiency decreased significantly from 100% (30 min at pH 6.5) to 69.4% after 60 min, with the rate constant dropping from 0.129 min⁻¹ to 0.0169 min⁻¹. This behaviour is related to the speciation of PMS, which exists predominantly as HSO₅⁻ under neutral and mildly acidic conditions, but shifts to the less reactive SO₅²⁻ form at higher pH values (pK_a ≈ 9.4) [11,12].

In strongly alkaline pH environments, sulphate radicals are transformed into sulphate ions and hydroxyl radicals. When in excess, hydroxyl radicals interact to produce hydrogen peroxide, a weaker oxidant, which can subsequently re-engage in reactions with hydroxyl radicals to generate hydroxy peroxide radicals (HO₂[•]), as illustrated in equations (14) and (15) [13,14]. Less hydroxyl radicals will be accessible in the system, hence lowering the degradation efficiency of CBZ, as shown in Eqs (11-15).



Under acidic conditions, a slight decrease in reaction rate was observed (k = 0.1054 min⁻¹), with nearly complete degradation achieved after 60 min. This behaviour is consistent with literature reports indicating enhanced degradation in acidic environments and suppressed activity under alkaline conditions [15]. The slightly lower activity observed under acidic conditions can be attributed to the increased stability of PMS and partial suppression of radical generation, as well as surface protonation effects that may limit interfacial charge transfer [16]. These

results indicate that near-neutral conditions favour more efficient generation of ROS and yield the best photocatalytic activity in the FLP/PMS system.

To identify the dominant reactive oxygen species involved in carbamazepine degradation, a series of scavenging experiments was performed using selective quenching agents, as presented in Figure 6.6.

In the photocatalysis process, the lowest degradation efficiency of carbamazepine was observed in the presence of para-benzoquinone (P-BQ) and tert-butyl alcohol (TBA), which are the scavenging agents of superoxide radicals ($O_2^{\bullet-}$) and hydroxyl radicals ($HO^{\bullet}$). The degradation efficiency in the presence of P-BQ decreased from 100% in 60 min to 47.7% in 120 min, whereas in the presence of TBA the degradation efficiency decreased to 92.3%. In the case of photocatalysis combined with PMS activation (FLP + PMS), the lowest degradation efficiency was observed in the presence of isopropanol (i-Pr), TBA, and P-BQ. Isopropanol (i-Pr) is a trapping agent of sulfate radicals ($SO_4^{\bullet-}$) and hydroxyl radicals ($HO^{\bullet}$). The degradation efficiency of carbamazepine decreased from 100% in 30 min treatment time to 56.2%, 75.4% and 86.4% in the presence of i-Pr, TBA, and P-BQ, which are responsible scavengers for sulfate radicals ($SO_4^{\bullet-}$) and hydroxyl radicals ($HO^{\bullet}$), hydroxyl radicals ($HO^{\bullet}$) and superoxide radicals ($O_2^{\bullet-}$). Therefore, the main ROS species responsible for degradation of carbamazepine in the photocatalytic system consists of superoxide radicals and hydroxyl radicals, whereas the main ROS species responsible for degradation of CBZ in PMS-assisted photocatalysis consists of sulfate radicals, hydroxyl radicals, and superoxide anion radicals.

Based on Mott-Schottky analysis, the flat-band potentials were determined as -0.82 V vs. NHE for gCN-OH and -0.37 V vs NHE for ZnOH-V_o. Considering their optical band gap positions of 2.69 eV for gCN-OH and 3.19 eV for ZnOH-V_o, the corresponding valence band positions were calculated to be 1.77 V and 2.72 V vs NHE. In the formed heterojunction, the dissolved oxygen is reduced to superoxide radicals ($O_2^{\bullet-}$) in the negatively positioned conduction band of gCN-OH, whereas the hydroxyl radicals are generated in the valence band of ZnOH-V_o. When PMS (HSO_5^-) is added to the photocatalytic system, the HSO_5^- is reduced into sulfate radicals

($\text{SO}_4^{\bullet-}$) and hydroxyl ions (OH^-). Hydroxyl ions (OH^-) interact with holes (h^+) to produce hydroxyl radicals ($\text{HO}^\bullet$).

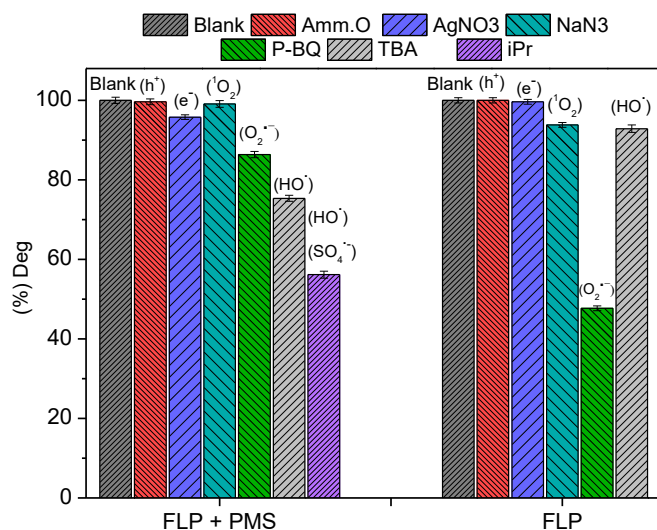


Figure 6.6. Role of scavengers in the degradation efficiency of CBZ in the photocatalytic system and PMS-assisted photocatalysis. Experimental conditions of $20 \pm 2^\circ\text{C}$, catalyst dosage of $1 \text{ g}\cdot\text{dm}^{-3}$, CBZ ($14 \text{ mg}\cdot\text{dm}^{-3}$), PMS (1.0 mM).

The stability tests were conducted over 4 cycles in both photocatalysis and PMS-assisted photocatalysis systems. The FLP photocatalyst was found to be recyclable up to five cycles and demonstrated exceptional cyclic stability in the degradation of CBZ, with comparable degradation efficiency to the first cycle. The stable performance demonstrates the resilience of the surface-active sites and the significant interfacial interaction between ZnOH-V_o and gCN-OH within the heterocomposite, thus inhibiting photocorrosion and promoting constant charge separation. A minor reduction in degradation was noted after the fifth cycle of PMS-assisted photocatalysis, due to an approximate 5% loss of photocatalyst during the recovery phase. The stability studies verified that FLP exhibits remarkable structural stability and chemical durability in both photocatalysis and PMS-assisted photocatalysis processes.

Summarising, in this study, a novel frustrated Lewis pair heterostructure based on $\text{ZnOH-V}_\text{o}/\text{gCN-OH}$ was successfully developed, introducing an alternative strategy for interfacial charge separation beyond conventional band alignment approaches. The designed system integrates a hydroxylated carbon nitride acting as

a Lewis base with a defect-engineered ZnOH phase exhibiting Lewis acidic properties. DFT analysis confirmed that surface hydroxylation induces nucleophilic behaviour in gCN-OH, while ZnOH remains electron-deficient, with its acidity further enhanced by hydroxyl groups. Surface oxygen vacancies were identified as key contributors to electronic modulation, promoting n-type behaviour through Fermi level shifts and facilitating charge transport.

The FLP heterostructure exhibited high photocatalytic efficiency for the degradation of carbamazepine, achieving complete removal within 60 min. The introduction of peroxymonosulfate significantly enhanced the process, leading to complete degradation within 30 min. This improvement is attributed to the dual functionality of the FLP system, which enables both efficient charge separation and catalytic activation of PMS, thereby enhancing the generation of reactive oxygen species. Importantly, the system demonstrated stability under varying reaction conditions, with negligible pH fluctuations during PMS activation and sustained performance over five consecutive cycles. These findings highlight the potential of FLP-based heterostructures as scalable and efficient photocatalytic systems, offering a new direction for the design of hybrid materials combining photocatalysis with an advanced oxidation process.

Overall, the results confirm the hypothesis of this work that rational surface functionalisation combined with defect engineering enables the formation of FLP-type heterostructures, in which interfacial electrostatic interactions govern charge separation and enhance photocatalytic performance.

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Conclusions

The doctoral dissertation presents a systematic investigation into the design, synthesis, and application of multifunctional photocatalytic systems for the degradation of pharmaceutical micropollutants in water. Graphitic carbon nitride has been proven to be an effective visible-light-active platform, although its intrinsic limitations, including rapid charge-carrier recombination, necessitate targeted modification strategies. Elemental doping of g-C₃N₄ with phosphorus and sulfur enhanced light absorption and promoted charge carriers' separation, leading to an increase from 48.7% to 92.6% degradation efficiency for carbamazepine and from 66.7% to 100% for acetaminophen within the same time frame for pure g-C₃N₄ compared to (P, S)-g-C₃N₄.

Further enhancement of photocatalytic activity was achieved by heterojunction formation with TiO₂ nanosheets. The heterojunction facilitated charge separation via the internal electric field generated at the interface, enhanced light absorption in UV-vis light, and improved stability. The resulting heterostructure enabled rapid and complete degradation of carbamazepine and acetaminophen in reduced treatment times of 30 minutes and 60 minutes, respectively, while modelling of photon distribution confirmed the importance of both optical and electronic effects in determining photocatalytic efficiency. Incorporation in the structure of photocatalytic material spinel zinc ferrite (ZnFe₂O₄) nanoparticles with magnetic properties, enabling efficient photocatalyst recovery and improved recyclability. The ternary heterocomposite ZnFe₂O₄/(P,S)-g-C₃N₄/2D TiO₂ exhibited enhanced activity across the UV-vis spectrum. The integration with a persulfate-based advanced oxidation process (PS-AOP) further intensified the degradation kinetics, leading to rapid, near-complete pollutant removal through the generation of highly reactive oxidation species. Furthermore, the application of an external magnetic field enhanced charge carrier's separation, resulting in improved photocatalytic efficiency and demonstrating an additional pathway for process intensification.

Chemical functionalisation and defect engineering lead to the formation of a frustrated Lewis pair (FLP)-type heterostructure. DFT analysis confirmed the formation of Lewis acid-base active sites, where hydroxylated g-C₃N₄ acts as a Lewis

base and defect-engineered ZnOH-V_o as a Lewis acid. The FLP heterostructure exhibited high photocatalytic activity, which was further enhanced upon persulfate activation, confirming the role of radical-driven degradation pathways. Overall, the results demonstrate that the rational integration of material engineering strategies, including doping, heterojunction formation, magnetic modification, and surface functionalisation, with advanced oxidation processes provides a highly effective approach for the degradation of persistent pharmaceutical micropollutants. The outcomes of this dissertation not only confirm the proposed research hypotheses but also establish FLP-based heterostructures as a novel and promising direction in photocatalyst design, offering strong potential for sustainable water treatment applications.

Contributors Declarations

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I confirm that I have contributed to the publications listed below, which constitutes part of the PhD thesis of Msc. Elvana Çako:

1. E. Çako, C. Gomez-Polo, G. Trykowski, M. Pisarek, K. Sikora, A. Zielińska-Jurek. Dual Approach for Effective Photodegradation and Mineralization of Carbamazepine Using a Ternary $\text{ZnFe}_2\text{O}_4/(\text{P}, \text{S})\text{-g-C}_3\text{N}_4/\text{Two-Dimensional TiO}_2$ Composite. ACS Omega. 11 (2026) 7486-7500.
2. E. Çako, C. Gomez-Polo, M. Kowalkińska, M. Pisarek, A. Zielińska-Jurek. Comparison of ibuprofen photodegradation by persulfate-assisted and magnetic field-assisted photocatalysis processes. Chemical Engineering and Processing-Process Intensification, 222 (2026) 110740.

In the above studies, I supervised the measurements of the magnetic properties of the photocatalysts, and photocatalytic experiments combined with magnetic field. I contributed to interpretation of data, reviewing and revising the manuscripts.



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I confirm that I have contributed to the publication listed below, which constitutes part of the PhD thesis of Msc. Elvana Çako:

I. E. Cako, S. Dudziak, P. Głuchowski, G. Trykowski, M. Pisarek, A. F. Borzyszkowska, K. Sikora, A. Zielińska-Jurek. Heterojunction of (P, S) co-doped g-C₃N₄ and 2D TiO₂ for improved carbamazepine and acetaminophen photocatalytic degradation. Separation and Purification Technology, 311 (2023) 123320.

In the above study, I contributed with analysis and description part of photoluminescence measurements.



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2. E. Çako, C. Gomez-Polo, G. Trykowski, M. Pisarek, K. Sikora, A. Zielińska-Jurek. Dual Approach for Effective Photodegradation and Mineralization of Carbamazepine Using a Ternary ZnFe₂O₄/(P, S)-g-C₃N₄/Two-Dimensional TiO₂ Composite. *ACS Omega*. 11 (2026) 7486-7500.

In the above studies, I contributed with analysis and description part of transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

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2. E. Çako, C. Gomez-Polo, G. Trykowski, M. Pisarek, K. Sikora, A. Zielińska-Jurek. Dual Approach for Effective Photodegradation and Mineralization of Carbamazepine Using a Ternary ZnFe₂O₄/(P, S)-g-C₃N₄/Two-Dimensional TiO₂ Composite. *ACS Omega*. 11 (2026) 7486-7500.
3. E. Çako, C. Gomez-Polo, M. Kowalkińska, M. Pisarek, A. Zielińska-Jurek. Comparison of ibuprofen photodegradation by persulfate-assisted and magnetic field-assisted photocatalysis processes. *Chemical Engineering and Processing-Process Intensification*, 222 (2026) 110740.

In the above studies, I contributed with analysis, interpretation and description of X-ray photoelectron spectroscopy (XPS) measurements.



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Çako, E., Gunasekaran, K. D., Rajendran, S., & Zielińska-Jurek, A. (2024). Recent advances on magnetic carbon-related materials in advanced oxidation processes of emerging pollutants degradation. *Water Resources and Industry*, 31, 100241.

I contributed to the preparation of the manuscript, including writing sections of the paper, as well as reviewing and editing the manuscript prior to submission. I confirm that the work presented in the thesis accurately reflects my contribution to this publication.



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1. E. Çako, C. Gomez-Polo, M. Kowalkińska, M. Pisarek, A. Zielińska-Jurek. Comparison of ibuprofen photodegradation by persulfate-assisted and magnetic field-assisted photocatalysis processes. *Chemical Engineering and Processing-Process Intensification*, 222 (2026) 110740.

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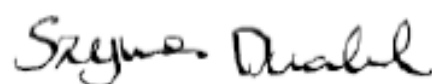
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1. E. Cako, S. Dudziak, P. Gluchowski, G. Trykowski, M. Pisarek, A. F. Borzyszkowska, K. Sikora, A. Zielińska-Jurek. Heterojunction of (P, S) co-doped g-C₃N₄ and 2D TiO₂ for improved carbamazepine and acetaminophen photocatalytic degradation. Separation and Purification Technology, 311 (2023) 123320.

In the above study, I modelled local volume rate of photon absorption (LVRPA) distributions, performed density functional theory (DFT) calculations and analysed Fukui functions. I participated in the interpretation and presentation of these results.



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1. E. Cako, S. Dudziak, P. Głuchowski, G. Trykowski, M. Pisarek, A. F. Borzyszkowska, K. Sikora, A. Zielińska-Jurek. Heterojunction of (P, S) co-doped g-C₃N₄ and 2D TiO₂ for improved carbamazepine and acetaminophen photocatalytic degradation. Separation and Purification Technology, 311 (2023) 123320.

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1. E. Çako, K. D. Gunasekaran, S. Rajendran, A. Zielińska-Jurek. Recent advances on magnetic carbon-related materials in advanced oxidation processes of emerging pollutants degradation. *Water Resources and Industry*, 31 (2024) 100241.

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2. E. Çako, C. Gomez-Polo, G. Trykowski, M. Pisarek, K. Sikora, A. Zielińska-Jurek. Dual Approach for Effective Photodegradation and Mineralization of Carbamazepine Using a Ternary ZnFe₂O₄/(P, S)-g-C₃N₄/Two-Dimensional TiO₂ Composite. ACS Omega. 11 (2026) 7486-7500.

In the above studies, I contributed with: LC-MS analysis, identification of by-products, curation of data of proposed by-products.

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1. E. Çako, K. D. Gunasekaran, S. Rajendran, A. Zielińska-Jurek. Recent advances on magnetic carbon-related materials in advanced oxidation processes of emerging pollutants degradation. *Water Resources and Industry*, 31 (2024) 100241.
2. E. Çako, S. Dudziak, P. Głuchowski, G. Trykowski, M. Pisarek, A. F. Borzyszkowska, K. Sikora, A. Zielińska-Jurek. Heterojunction of (P, S) co-doped g-C₃N₄ and 2D TiO₂ for improved carbamazepine and acetaminophen photocatalytic degradation. *Separation and Purification Technology*, 311 (2023) 123320.
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4. E. Çako, C. Gomez-Polo, M. Kowalkińska, M. Pisarek, A. Zielińska-Jurek. Comparison of ibuprofen photodegradation by persulfate-assisted and magnetic field-assisted photocatalysis processes. *Chemical Engineering and Processing-Process Intensification*, 222 (2026) 110740.

In the above studies, I contributed with: Literature review on the research topic, synthesis and characterisation of photocatalysis, analytical measurements of photocatalytic activity of photocatalysts, interpretation of obtained results, writing the original draft of manuscripts, revision of manuscripts.

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2. E. Çako, S. Dudziak, P. Głuchowski, G. Trykowski, M. Pisarek, A. F. Borzyszkowska, K. Sikora, A. Zielińska-Jurek, *Heterojunction of (P, S) co-doped g-C₃N₄ and 2D TiO₂ for improved carbamazepine and acetaminophen photocatalytic degradation*, Separation and Purification Technology, 311 (2023) 123320.
3. E. Çako, C. Gomez-Polo, G. Trykowski, M. Pisarek, K. Sikora, A. Zielińska-Jurek, *Dual approach for effective photodegradation and mineralization of carbamazepine using a ternary ZnFe₂O₄/(P, S)-g-C₃N₄/two-dimensional TiO₂ composite*, ACS Omega, 11 (2026) 7486-7500.
4. E. Çako, C. Gomez-Polo, M. Kowalkińska, M. Pisarek, A. Zielińska-Jurek, *Comparison of ibuprofen photodegradation by persulfate-assisted and magnetic field-assisted photocatalysis processes*, Chemical Engineering and Processing - Process Intensification, 222 (2026) 110740.

In the above studies, I contributed with conceptualisation, supervision, methodology, resources, writing, review and editing, and funding acquisition.


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Research activity related to dissertation

Publications:

1. E. Çako, S. Dudziak, P. Głuchowski, G. Trykowski, M. Pisarek, A. F. Borzyszkowska, K. Sikora, A. Zielińska-Jurek. Heterojunction of (P, S) co-doped g-C₃N₄ and 2D TiO₂ for improved carbamazepine and acetaminophen photocatalytic degradation. *Separation and Purification Technology*, 311, (2023) 123320. <https://doi.org/10.1016/j.seppur.2023.123320>. (Published). [IF = 9, CS = 15.1, MNiSW = 140]
2. E. Çako, K. D. Gunasekaran, S. Rajendran, A. Zielińska-Jurek. Recent advances on magnetic carbon-related materials in advanced oxidation processes of emerging pollutants degradation. *Water Resources and Industry*, (2024) 100241. <https://doi.org/10.1016/j.wri.2024.100241>. (Published). [IF = 7.5, CS = 10.6, MNiSW = 200]
3. E. Çako, C. Gomez-Polo, G. Trykowski, M. Pisarek, K. Sikora, A. Zielińska-Jurek, Dual approach for effective photodegradation and mineralization of carbamazepine using a ternary ZnFe₂O₄/(P, S)-g-C₃N₄/Two-Dimensional TiO₂ composite. *ACS Omega*, 11 (5) (2026) 7486-7500. <https://doi.org/10.1021/acsomega.5c08594>. [IF = 4.3, CS = 7.1, MNiSW = 70]. (Published).
4. E. Çako, C. Gomez-Polo, M. Pisarek, K. Sikora, A. Zielińska-Jurek, Comparison of ibuprofen photodegradation by persulfate-assisted and magnetic field assisted photocatalysis process. <https://doi.org/10.1016/j.cep.2026.110740>. [IF = 3.9, CS = 7.9, MNiSW = 140]. (Published).

Conferences:

1. Conference activity (Oral presentation)/ E. Çako, A. Zielińska-Jurek, 'Removal of pharmaceuticals by chemical functionalised graphitic carbon nitride'. 8th Green and Sustainable Chemistry Conference/ Dresden, Germany, 13-15 May 2024.

2. Conference activity (Poster)/ E. Çako, A. Zielińska-Jurek, 'Degradation of carbamazepine (CBZ) by magnetically modified ternary heterocomposite combined with SR-AOPs'. 24th Polish Conference of Chemical and Process Engineering, 13-16 June 2023.
3. Conference activity (Oral presentation)/ E. Çako, A. Zielińska-Jurek, 'The 6-th international conference on the new photocatalytic materials for energy, environment and sustainability (NPM-6)' and 'The 7-th international conference on photocatalytic and advanced oxidation technologies for treatment of water, air, soil and surfaces (PAOT-7)' Ljubljana, Slovenia, April 4-6, 2022.
4. Conference activity (Poster)/ E. Çako, A. Zielińska-Jurek, 'The 5-th international conference on applied surface science'. Palma, Mallorca, Spain, April, 25-28, 2022.

Internships:

1. Public University of Navarra, Pamplona, Spain (2022). 'Magnetic characterisation of spinel ferrite modified photocatalysts, and their application in photocatalysis and photocatalysis combined magnetic field'. The internship was conducted under the supervision of Prof. Dr. Cristina Gomez-Polo.
2. Technical University of Munich, Munich, Germany (2024). Photocatalytic reduction of CO₂ using carbon nitride based photocatalysts. Electrodeposition of Cu₂O and Fe₂O₃ on FTO for photoelectrochemical applications. The internship was conducted under the supervision of Prof. Dr. Jennifer Strunk.