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Photocatalytic Degradation of Methylparaben using semiconductor/carbon catalysts

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List of symbols and abbreviations

B	Full width at half maximum at Scherrer equation
B	Affinity coefficient
BET	Brunauer-Emmett-Teller
BWO	Bismuth tungstate, Bi_2WO_6
CB	Conduction Band
CBET	BET constant
cm	Centimeter
CN	Graphite carbon nitride, g- C_3N_4
CNT	Carbon nanotubes
$^{\circ}\text{C}$	Degree Celsius
d	Interatomic distance
DMF	Dimethyl formamide
DRS	Diffuse Reflectance Spectroscopy
e^-	Electron
E_g	Band gap
eV	Electron volt
$F(R_{\infty})$	Kubelka-Munk function
FTIR	Fourier transform infrared Spectroscopy
FWHM	Full Width at Half Maximum
h	Hour
h^+	Hole
H	Hydrothermal synthesis
h ν	Photon energy
I	Current intensity
I^{ss}	Photocurrent intensity (normal electrolyte)
I^{ss}_{wo}	Photocurrent intensity (normal electrolyte without scavenger)
I^{ss}_{scav}	Photocurrent intensity (normal electrolyte with scavenger)
$\eta_{transfer}$	$I^{ss}_{wo} / I^{ss}_{scav}$
ITO	Indium Tin Oxide
IUPAC	International Union of Pure and Applied Chemistry
K	Crystal shape factor at Scherrer equation
K	Absorption constant at Kubelka-Munk equation

List of symbols and abbreviations

λ	Wavelength
L	Crystallite size
LDH	Layered double hydroxide
M	Molarity
MeP	Methyl paraben
mg	Milli-gram
mL	Milli-liter
mM	Milli-molarity
min	minutes
mV	Millivolt
m/z	Mass/ion charge ratio
μg	Microgram
μL	Microliter
n	Electronic transition at modified Kubelka-Munk equation
NHE	Normal Hydrogen Electrode
nm	Nanometer
OCP	Open Circuit Potential
%	Percentage
p	Pressure
p/p ₀	Relative pressure
p ₀	Gas saturated equilibrium vapour pressure
PL	Photoluminescence
ppm	Milli-gram per liter
θ	Diffacted angle at Bragg and Scherrer equations
R _∞	Absolute diffuse reflectance
rpm	Round per minutes
s	Second
S	Scattering coefficients at Kubelka-Munk equation
SC	Semiconductor
SBET	Specific surface area (BET method)
SEM	Scanning Electron Microscopy
STP	Standard Temperature and Pressure
UV	Ultraviolet

VB	Valence Band
Vis	Visible
V_{meso}	Mesopores volume
V_{Total}	Total pore volume
W_0	Micropore volume (DR equation)
WHO	World Health Organization
wt	Weight
XRD	X-Ray Diffraction
XPS	X-ray Photoelectron Spectroscopy

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Layout

This thesis meets all the requirements for the degree of Doctor of Philosophy in Chemistry, in accordance with the regulations of the doctoral school Énergie, Matériaux, Sciences de la Terre et de l'Univers (EMSTU) at the Université d'Orléans, France. The entire thesis is written in English with the approval of the EMSTU doctoral school, and includes a brief summary (résumé) in French.

The main goals of this PhD thesis are to explore the degradation of endocrine disruptors present in wastewater using photocatalytic Advanced Oxidation Processes based on hybrid semiconductor/carbon materials. The efficiency and cycleability of the catalysts will be discussed in terms of the pollutant conversion and the nature of the intermediate compounds formed. New insights on the mechanism that govern the degradation performance using different process will be evaluated by photocatalytic, photoelectrochemical efforts and quenching tests to rationalize and identify the nature of the catalytic sites and the degradation mechanisms. The possible photocatalytic degradation pathways are analyzed through the identification of degradation intermediates and the use of radical scavengers.

The first chapter provides an introduction on the fundamentals of heterogeneous photocatalysis, and a description of the general goal of the thesis, along with the specific objectives programmed for its achievement.

The second chapter gives a detailed description of the materials used, as well as the fundamentals of the characterization techniques along with the experimental procedures followed during the research work.

The third, fourth and fifth chapter focuses on the g-C₃N₄/carbon, Bi₂WO₆/carbon and LDH/carbon mixtures, analysing the effect of each additive on the physicochemical characteristics, photoelectrochemical response and photocatalytic activity of the mixture. In the three chapters, the photocatalytic degradation of methyl paraben (MeP) was evaluated by g-C₃N₄/carbon, Bi₂WO₆/carbon and LDH/carbon catalysts in comparison to the bare semiconductor. The effect of optical, textural and surface nature of the catalyst on the photocatalytic performance is analyzed.

Finally, sixth chapter provides a conclusion of the whole work, and a vision of the perspectives on the topic.

Résumé

Maintenir la qualité de l'eau dans l'environnement naturel constitue l'un des défis majeurs de notre époque. Les principaux enjeux liés au traitement et à la réutilisation de l'eau concernent la matière organique, les pathogènes et la résistance antimicrobienne, ainsi que les polluants émergents (médicaments, perturbateurs endocriniens, etc.). Les stations d'épuration (STEP) devraient servir de barrières sûres contre ces menaces, mais la plupart de ces contaminants ne sont pas entièrement éliminés par les traitements conventionnels, finissant par atteindre les eaux réceptrices, principales voies d'introduction des micropolluants dans l'environnement.

L'application des procédés d'oxydation avancée (POA) pour la dépollution des eaux usées a suscité un intérêt croissant ces dernières années, en raison de l'apparition de polluants émergents récalcitrants non éliminés efficacement par les traitements classiques. Les POA regroupent diverses techniques, notamment l'ozonation, la réaction de Fenton, les méthodes électrochimiques, les ultrasons et la photocatalyse. Parmi celles-ci, la photocatalyse solaire et durable s'est imposée comme une solution prometteuse pour la dégradation des polluants organiques persistants, tels que les polluants organiques. Des études expérimentales ont confirmé que les systèmes photocatalytiques hétérogènes présentent une efficacité supérieure dans l'élimination des parabènes, atteignant une minéralisation accrue du polluants organiques via des voies d'oxydation médiées par les radicaux hydroxyle.

Les parabènes font partie des perturbateurs endocriniens et leur consommation est liée à leur utilisation dans les cosmétiques, les crèmes pour la peau, les aliments et les produits pharmaceutiques. Les rejets d'eaux usées domestiques et industrielles et les traitements inefficaces dans les stations d'épuration sont les principales voies d'entrée des parabènes dans l'environnement. Toutefois, en raison de l'utilisation extensive, de la consommation élevée et de l'élimination inappropriée des produits contenant des parabènes, ces derniers ont été largement détectés dans les eaux de surface, les eaux souterraines, l'eau potable, les eaux usées, l'air et la poussière au cours des dernières années. Leur présence dans les cours d'eau est devenue un problème environnemental critique en raison de leur toxicité pour les écosystèmes aquatiques et des risques potentiels pour la santé humaine, car ils peuvent être bioaccumulés et altérer le système endocrinien.

Au niveau local, la région Centre-Val de Loire a identifié plusieurs produits

pharmaceutiques et cosmétiques, dont les parabènes, comme des polluants prioritaires détectés dans les eaux usées et les sources d'eau. Parmi tous les parabènes, le parabène méthylique (MeP) est le produit chimique le plus détecté dans les eaux usées, en raison de la longueur de la chaîne alkyle, de la solubilité et de l'activité antimicrobienne, reflétant leur utilisation répandue dans les produits de consommation courante, avec des concentrations allant de ng/L à µg/L. S'appuyant sur les preuves empiriques de la persistance et de la pseudo-persistance du parabène méthylique dans l'environnement ($t_{1/2} > 28$ d dans les systèmes aquatiques) et de son pouvoir de perturbation endocrinienne, ce composé a été stratégiquement choisi comme polluant modèle dans la présente étude, représentant 68 % des dérivés du parabène détectés dans les effluents d'eaux usées municipales.

Si la photocatalyse à base de semiconducteurs (TiO_2 , Bi_2WO_6 , g- C_3N_4 , etc.) a été largement étudiée pour le traitement de l'eau, son déploiement dans les STEP se heurte à des limites telles que l'agrégation des particules et leur séparation. Des travaux récents montrent que les composites hybrides (associant semiconducteurs, carbone nanoporeux, oxydes métalliques, etc.) surpassent les performances des semiconducteurs seuls, grâce à des propriétés photocatalytiques synergétiques. Toutefois, le principal défi scientifique réside dans les propriétés intrinsèques des photocatalyseurs nanostructurés, notamment leur cinétique redox de surface et leur configuration de bande interdite. Une large bande interdite limite l'absorption optique au spectre UV étroit (4-5 % du rayonnement solaire), tandis que la recombinaison rapide des paires électron-trou photo-générées réduit drastiquement l'efficacité quantique, avec un faible rendement de séparation des porteurs de charge sous illumination.

Collectivement, l'intégration stratégique de deux matériaux dans des systèmes photocatalytiques orchestre un mécanisme d'amélioration tétragonale : (1) permettre la migration directionnelle des porteurs de charge pour supprimer la recombinaison électron-trou, (2) élargir l'absorption de la lumière visible par l'ingénierie de la structure de bande sur mesure, (3) établir un alignement de bande optimisé par le biais d'un rétrécissement contrôlé de la bande interdite, et (4) générer d'abondants sites actifs exposés. Ce trio synergique reconfigure fondamentalement le paysage photophysique, amplifiant l'efficacité quantique tout en repoussant les limites de l'utilisation spectrale.

Cette thèse vise à dégrader le méthylparabène - un polluant organique émergent dans l'eau - en utilisant la photocatalyse hétérogène et des photocatalyseurs hybrides semi-conducteurs/carbone, afin d'explorer l'impact des matériaux carbonés en tant

qu'additifs aux semi-conducteurs dans le processus global de photodégradation. L'efficacité et la réutilisabilité des catalyseurs seront évaluées en fonction de la conversion des polluants et de la nature des composés intermédiaires formés. Une analyse approfondie des mécanismes de dégradation (tests de piégeage de radicaux, études photoelectrochimiques) permettra d'identifier les sites catalytiques actifs et les voies réactionnelles. Les intermédiaires de dégradation et l'utilisation d'inhibiteurs spécifiques éclaireront les mécanismes photocatalytiques possibles.

Pour atteindre cet objectif, trois types de photocatalyseurs hybrides semi-conducteurs/carbone ont été synthétisés : (1) La préparation des photocatalyseurs binaires carbone-carbone a été réalisée par une méthode hydrothermique, en utilisant C₃N₄ et des concentrations croissantes de carbone nanoporeux (CQ) allant de 2 à 10 % en poids (échantillons étiquetés CN/CQ-x % en poids, où x représente la quantité de carbone nanoporeux); (2) La préparation des photocatalyseurs binaires BWO-carbone a été réalisée par une méthode hydrothermale, en utilisant différentes quantités de CQ et de CN comprises entre 2 et 10 % en poids. Les échantillons ont été étiquetés BWO/A-x wt.%, où A est l'acronyme du matériau carboné utilisé comme additif (c'est-à-dire CQ ou CN) et x représente la quantité d'additif carboné incorporé ; et (3) la préparation d'un photocatalyseur hybride par l'immobilisation de g-C₃N₄ dans l'espace intercouche d'un NiZnAl-LDH trimétallique via la méthode de co-précipitation, en utilisant une quantité accrue de g-C₃N₄ (de 5 % en poids à 50 % en poids), étiqueté LDH/CN-Y%, où Y représente la quantité de poudres de nitrure de carbone dispersées dans les suspensions. Une caractérisation approfondie des propriétés optiques, structurelles et texturales des matériaux préparés a été réalisée, afin de corrélérer ces propriétés avec l'activité photocatalytique pour la dégradation du méthylparabène sous lumière UV-VIS.

La caractérisation des catalyseurs de la série CN/CQ a montré que l'incorporation de l'additif de carbone ne modifie pas de manière significative les propriétés structurelles du g-C₃N₄ vierge, mais que les composites absorbent plus de lumière visible que le g-C₃N₄ nu. La porosité des composites CN/CQ obtenus ne suit pas la règle générale des mélanges, ce qui indique que les nanopores de l'additif CQ ne sont pas accessibles à l'adsorption de gaz, très probablement en raison du blocage partiel par les particules du semi-conducteur. De même, l'incorporation de CN et de CQ en tant qu'additifs au BWO n'a pas modifié les propriétés structurelles du semi-conducteur BWO nu. Pour les composites BWO/CQ, une meilleure absorption de la lumière visible a été observée ainsi qu'un léger décalage vers le bleu du bord d'absorption du BWO.

Pour les composites BWO/CN, un net décalage vers le rouge a été observé à mesure que la quantité de CN augmentait. Dans l'ensemble, la caractérisation suggère que les additifs CN et CQ sont incorporés dans la matrice BWO plutôt que déposés en surface. D'autre part, l'incorporation réussie de CN dans l'espace entre les couches d'un composé LDH NiAlZn a été confirmée par XRD et Raman.

En ce qui concerne l'activité photocatalytique, la cinétique de dégradation du méthylparabène a été accélérée pour les composites dans tous les cas (séries CN/CQ, BWO/CQ, BWO/CN et LDH/CN), par rapport aux semi-conducteurs nus (ou au composé de type hydrotalcite NiZnAl seul), la cinétique de dégradation étant légèrement améliorée avec la quantité d'additifs. L'activité photocatalytique a également été examinée en termes de conversion et de nature des composés intermédiaires du méthylparabène. Il convient de mentionner que la dégradation du méthylparabène à l'aide des catalyseurs BWO/CQ a généré des intermédiaires polyhydroxylés, tandis que pour les séries CN/CQ et LDH/CN, deux intermédiaires ont été clairement détectés : des intermédiaires polyhydroxylés et du phtalate de diéthyle.

Pour toutes les quantités testées d'additif CQ, l'incorporation de l'additif CQ au CN a augmenté l'élimination du MeP, en particulier après le deuxième essai photocatalytique. La dégradation des intermédiaires n'a pas été améliorée dans le premier essai, alors que des fractions plus élevées de phtalate de diéthyle intermédiaire ont été trouvées dans le deuxième essai photocatalytique par rapport au premier. Dans le cas des catalyseurs de la série BWO/CQ, BWO/CQ-2wt.% a montré la meilleure performance photocatalytique, tandis que pour les catalyseurs de la série BWO/CN, BWO/CN-10wt.% a montré la meilleure performance photocatalytique. Les séries de photocatalyseurs BWO/CQ et BWO/CN présentent toutes deux une cinétique de dégradation similaire pour le MeP. Pour certains composites (par exemple, la série BWO/CQ), la conversion des intermédiaires a également été améliorée. En ce qui concerne la série LDH/CN, l'échantillon contenant 15 % en poids de CN a révélé la meilleure conversion du MeP. Ces composites ont montré une bonne performance cyclique sur plusieurs cycles consécutifs, avec une faible accumulation d'intermédiaires de phtalate de diéthyle après 20 heures d'illumination. Nous attribuons ce résultat à plusieurs facteurs tels que la séparation efficace des électrons-trous photogénérés par l'introduction du CN et le nanoconfinement du CN dans la structure en couches du LDH pour la série LDH/CN.

En résumé, en ce qui concerne la dégradation du MeP, les échantillons de la série

CN/CQ ont affiché une meilleure performance photocatalytique que BWO/CQ, BWO/CN et LDH/CN. En ce qui concerne la dégradation des intermédiaires polyhydroxylés, les échantillons de la série BWO/CQ ont montré une quantité plus faible que les autres. En ce qui concerne le phtalate de diéthyle intermédiaire, les échantillons BWO/CQ et BWO/CN ont généré la plus faible quantité (inférieure à la limite de détection de notre méthode HPLC).

Comme le montre la caractérisation photoélectrochimique, le nitrure de carbone préparé dans cette thèse présente des propriétés de semi-conducteur de type p, contrairement au BWO qui est un semi-conducteur de type n. Comparativement, l'incorporation de l'additif carbone nanoporeux (CQ) à un semi-conducteur de type p a favorisé la dégradation du MeP (cinétique accélérée dans la série CN/CQ), alors que son impact était plus évident dans la conversion des intermédiaires lorsqu'il était ajouté au BWO (semi-conducteur de type n, série BWO/CQ). L'amélioration des performances photocatalytiques est observée lors de l'introduction de CN dans le BWO ou le LDH.

De nouvelles perspectives sur le mécanisme qui régit la performance de dégradation en utilisant différents piègeurs ont été évaluées en couplant l'expérience photocatalytique et l'approche photoélectrochimique pour rationaliser et identifier la nature des sites catalytiques et les mécanismes de dégradation.

La combinaison du piégeage chimique et des essais photoélectrochimiques a fourni des informations supplémentaires intéressantes sur le mécanisme de dégradation. Pour les photocatalyseurs CN/CQ, l'oxydation par $\bullet\text{O}_2^-$ a un impact plus important, que ce soit en présence d'un piègeur de $\bullet\text{O}_2^-$ ou en l'absence d' O_2 . L'oxydation du polluant par $\bullet\text{OH}$ ou directement par les trous a un impact sur les catalyseurs, mais ne semble pas être le mécanisme de dégradation dominant (chute d'environ 50 %). Dans le cas des photocatalyseurs BWO/carbone, des mécanismes de dégradation distincts ont été mis en évidence : BWO/CQ s'appuie principalement sur les radicaux hydroxyles ($\bullet\text{OH}$), et BWO/CN utilise principalement les radicaux superoxydes ($\bullet\text{O}_2^-$). Pour le composite LDH/CN, la réaction médiée par l'hydroxylation est la principale voie d'oxydation dans la dégradation du méthylparabène ; cela se produit principalement lors de la réaction avec les trous photogénérés - également dans des environnements anoxiques -, et dans une moindre mesure lors de la réaction des électrons photogénérés avec l'oxygène dissous dans la solution.

Pour tous les photocatalyseurs, le piégeage des électrons photogénérés a accéléré

Résumé

la vitesse de dégradation du méthylparabène et des intermédiaires, soulignant le rôle important de l'oxydation des trous dans le mécanisme global de dégradation (le piégeage des électrons a réduit la recombinaison des paires trous/électrons, favorisant ainsi la réactivité des trous, soit par oxydation directe des trous, soit par la formation d'espèces radicalaires $\bullet\text{O}_2^-$).

Abstract

Parabens are a part of endocrine disruptors, and their consumption is related to use in cosmetics, skin creams, foods, and pharmaceuticals. The discharge of domestic and industrial wastewater and the inefficient treatments in wastewater treatment plants are the main routes of entry of parabens in the environment. On the other hand, advanced oxidation processes have gained attention in wastewater remediation. In photocatalytic processes, carbon materials and semiconductor have revealed to be efficient for the generation of radical species capable of promoting degradation of organic pollutants in solution.

The objective of this thesis is to explore the degradation of methyl paraben present in water using based on photocatalytic approaches and hybrid materials under UV and Vis irradiation. g-C₃N₄/nanoporous carbon photocatalysts, Bi₂WO₆-based hybrid photocatalyst using g-C₃N₄ or nanoporous carbon as additive and carbon nitride immobilized in a porous NiZnAl hydrotalcite-like compound, have been prepared and characterized to explore their photocatalytic activity for the degradation of parabens from solution.

Data showed the presence of additive affected the visible light absorption, adsorption edge and textural features, but the structural impact is minimal. The photocatalytic conversion of the studied pollutants as well as their intermediates was accelerated for the composites in all the cases (series CN/CQ, BWO/CQ, BWO/CN and LDH/CN), compared to the bare semiconductors (or the NiZnAl hydrotalcite-like compound alone). However, each of them has its own focus, with CN/CQ, BWO/CN and LDH/CN being better for the degradation of methylparaben, and BWO/CQ being better for the degradation of both the main pollutant and its intermediates. All studied photocatalysts showed good photocatalytic performance over long-term illumination (ca. 10-20 consecutive hours). The mechanism that governs the degradation performance was evaluated by coupling chemical scavenger experiments and photoelectrochemical studies. The use of scavengers showed that hydroxylation-mediated reactions involving •OH and the photoholes are the main degradation pathways for BWO/CQ, BWO/CN and LDH/CN. In contrast, the oxidation by •O₂⁻ radicals is the dominant degradation pathway for the series of photocatalysts CN/CQ. The photocurrent responses further validated that the current intensity of composites was enhanced compared to the corresponding bare material, indicating the occurrence of an effective electron transfer

Abstract

at the interfaces. The mechanisms were also validated by the photoelectrochemical responses in the presence of scavengers in the electrolyte.

Chapter 1. Introduction and objectives

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1.1 Water pollution

Maintaining water quality in the natural environment is one of the major challenges of our time. Unfortunately, human activity has a major impact on the balance of our ecosystem: from industry to the simple use of water by households, very large quantities of pollutant-loaded effluents have to be treated by wastewater treatment plants. And yet, even if existing treatment systems are considered to be efficient, many molecules with proven toxicity are found in all water bodies. Despite physico-chemical and biological treatment in wastewater treatment plants, thousands of molecules are not completely eliminated. This insidious pollution disrupts the functioning of all organisms, from humans to animals. The most problematic of these, known as micropollutants, act as endocrine disruptors (antibiotics, pesticides, detergents, dyes, etc.). Against this backdrop, public authorities are imposing increasingly stringent discharge standards, which are constantly evolving, forcing manufacturers and water suppliers to innovate in the treatment of these effluents. New techniques are being developed to meet these new requirements.

Contaminants are recalcitrant to conventional water treatments (also known as micropollutants) can be classified according into three broad categories [Michael-Kordatou et al. 2015]:

- Water from human activities: domestic, artisanal, road traffic or industrial;
- Water after reuse in contact with urban spaces (maintenance of green spaces, facades...)
- Residual water from rainfall or pavement cleaning in contact with urban surfaces

Certain molecules are under particular scrutiny because of the impact they can have on our ecosystem. Their presence in water poses multiple problems, such as degradation of human and animal health, crop damage and the impossibility of reusing collected water [Krzeminski et al. 2019]. As an example, endocrine disruptors, have been scientifically validated to interfere with hormonal systems in both wildlife populations and human populations [Zamri et al. 2021]. Furthermore, these compounds have been implicated in the pathogenesis of multiple health conditions, including but not limited to neurological disorders, cardiovascular diseases, various malignancies, and reproductive health complications in humans [Vieira et al. 2021; Kasonga et al. 2021; Vieira et al. 2020].

The hazardous nature of these molecules at very low concentrations has been widely demonstrated [Luo et al. 2014; Margot et al. 2015]. And yet, they are systematically detected in effluent from wastewater treatment plants (WWTPs). It is clear that monitoring and controlling their occurrence in effluent leaving WWTPs is necessary to preserve the equilibrium of the natural environment. The goal remains the complete elimination of these molecules and their metabolites and transformation products, as their long-term effects are not yet fully understood.

In the European Union, the monitoring and regulation of micropollutants have gained significant legislative traction, driven by growing environmental and public health concerns. The revised Urban Wastewater Treatment Directive (UWWTD) and related policies outline a comprehensive framework to address these contaminants. The updated directive mandates quaternary treatment for micropollutant removal in wastewater treatment plants (WWTPs) serving $\geq 150,000$ population equivalents (p.e.), with staggered implementation until 2045. Facilities must achieve $\geq 80\%$ removal of 6 out of 13 priority micropollutants, including pharmaceuticals (e.g., diclofenac, carbamazepine) and industrial chemicals (e.g., benzotriazole) [EU urban wastewater treatment directive 2023; Novo 2024]. The EU's 2015/495 Watch List includes endocrine disruptors (e.g., 17- α -ethinylestradiol), antibiotics (e.g., clarithromycin), and pesticides (e.g., imidacloprid), necessitating advanced analytical methods for detection [Barbosa et al. 2016]. Despite legislative mandates, member states like Croatia, Romania, and Ireland lag in WWTP upgrades, with $< 50\%$ compliance in some regions. Enforcement relies on slow infringement procedures [Directorate-General for Environment 2024]. The EU's approach to micropollutants combines strict legislative mandates, industry accountability, and advanced technological integration. However, significant challenges remain in balancing energy cost reduction with improved removal efficiency in practical applications.

In addition, legislation requires the monitoring of a list of molecules known as Environmental Quality Standards, made up largely of micropollutants (benzene, chloroalkanes, cyclodiene pesticides, diuron, glyphosate, etc.). For these molecules, the thresholds are much lower, even at the limit of detection in some cases (generally 1,000 times lower). Not all micropollutants are directly covered by the legislation - drugs, for example, are exempt - but this list of 65 molecules is constantly evolving, with new ones appearing regularly. It is therefore necessary to propose new water

treatment techniques to achieve better purification performance.

1.1.1 Endocrine Disruptors aqueous pollutants

Endocrine disruptors are chemicals or chemical mixtures that interfere with the normal functioning of the hormonal system, defined by the U.S. Environmental Protection Agency (EPA) [Kabir et al. 2015]. Endocrine disruption is predominantly reported in molluscs, crustaceans, fish, reptiles, birds and mammals as early as the 1930s [Belgiorno et al. 2007]. Their effect for human health was first reported in 1962 [WHO 2002]. As the research progressed, marking the emergence of a dedicated field focused on studying endocrine disruptors since 1991 [Colborn et al. 1992; Kabir et al. 2015; Wang et al. 2020]. According to a landmark 2013 joint report by the World Health Organization (WHO) and the United Nations Environment Programme (UNEP), endocrine-disrupting chemicals (EDCs).

These endocrine-disrupting compounds are pervasively present in modern consumer products and industrial applications, notably including polymer-based materials (plastics), agrochemical formulations (pesticides and fungicides), pharmacotherapeutic agents, industrial/household chemical products, electronic components, and synthetic colorants. The extensive industrial and domestic utilization of EDCs has led to ubiquitous environmental contamination through wastewater discharge systems, establishing this pathway as a significant environmental vector for EDC dissemination [Belgiorno et al. 2007; Zamri et al. 2021; Huang et al. 2021; Vieira et al. 2021]. It is worth mentioning that the removal efficacy of EDCs in wastewater treatment systems is predominantly governed by the physicochemical characteristics of target contaminants and the specific parameters of their respective aquatic matrices [Azizi et al. 2022].

Parabens, considered as weak endocrine-disrupting chemicals, are ubiquitously quantified in municipal wastewater effluents [Sousa et al. 2023]. The presence of these substances in water was first confirmed and reported in 1996 [Haman et al. 2015]. However, their potential health effects remain a topic of ongoing debate [Haman et al. 2015]. Parabens are a class of synthetic alkyl esters derived from p-hydroxybenzoic acid, found in many fruits and vegetables, and are widely employed in the formulation of highly consumed products, due to their chemical stability (for a wide temperature interval and pH ranging from 4.5 to 7.5), low production cost and systemic toxicity, and broad regulatory acceptance. Parabens are one of the most

prevalent preservative groups since their first introduction for pharmaceutical products in the 1920s [Fransway 1991; Fransway et al. 2019]. These compounds demonstrate particular effectiveness in personal care formulations (including cosmetics and toiletries), pharmaceutical preparations, and processed food systems, where they function by inhibiting microbial growth through membrane disruption and enzyme activity interference [Pereira et al. 2023; Srnovršnik et al. 2023].

The US Food and Drug Administration (FDA) and the European Union (EU) regulations have approved that parabens are classified as “generally regarded as safe” (GRAS) compounds and could be used as preservative for different application [Błędzka et al. 2014; EU Scientific committee on consumer safety 2024], such as in foods, cosmetics and so on. But, the content of single paraben should be less than 0.4 % (w/w), and 0.8 % (w/w) for combination in cosmetics and rarely exceed 1 % (w/w) in pharmaceutical products [Haman et al. 2015].

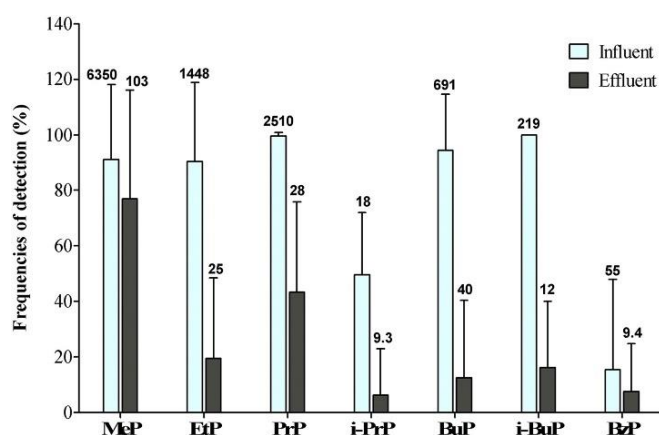


Figure 1.1 Average detection frequencies and relative standard deviations of parabens (methyl-, ethyl-, propyl-, isopropyl-, butyl-, isobutyl- and benzyl-parabens) in WWTP influents and effluents of parabens. Values above each bar are the average concentrations in ng/L [Haman et al. 2015].

However, due to the extensive utilization, high consumption and an improper disposal of products containing parabens, parabens have been widely detected in surface water, groundwater, drinking water, sewage, air and dust in the last years. Their presence in water courses has become a critical environmental issue due to their toxicity to aquatic ecosystems and potential risks to human health, as they can be bio-accumulated and may alter the endocrine system [Bolujoko et al. 2021; Nguyen et al. 2021]. As reported, the average total daily exposure to parabens per person is approximately 76 mg, mainly from the cosmetics and personal care products (ca. 67%)

[Fransway et al. 2019]. Like many other pollutants of emerging concerns, parabens can cause estrogenic activity and have been associated with various types of cancer (breast tumors in women and sperm DNA damage in men), reproductive and immunological complications, as well as allergy and skin irritations [Mehdi Amin et al. 2019; Álvarez et al. 2020].

At the local level, the Région Centre-Val de Loire has identified several pharmaceuticals and cosmetics compounds, including parabens, as priority pollutants detected in wastewater and water sources [Agence de l'Eau 2021; Region Centre Val de Loire 2020]. Of all the parabens, methyl paraben (MeP) is the most detected chemical in wastewater, due to the alkyl chain length, solubility, and antimicrobial activity, as showed in Figure 1.1, reflecting their widespread use in common consumer products, with concentrations from ng/L to µg/L [Miao et al. 2022; Haman et al. 2015]. Building upon the empirical evidence of methyl paraben's environmental persistence, pseudo-persistence ($t_{1/2} > 28\text{d}$ in aquatic systems), and endocrine-disrupting potency, this compound was strategically selected as the model pollutant in the present investigation, representing 68% of paraben derivatives detected in municipal wastewater effluents [EU Scientific committee on consumer safety 2024].

Wastewater treatment plants

A wastewater treatment plant (WWTP) typically has 4-5 core operational stages, depending on the level of treatment required and regulatory standards. The key stages are: pre-treatment, primary treatment, secondary (biological) treatment, tertiary treatment and quaternary treatment [Qasim 2017]. The purpose of pre-treatment is removing coarse solids, grit, grease, and debris to protect downstream equipment. Micropollutant could not be removed during pre-treatment process. Primary treatment involves physically separate suspended organic solids via sedimentation. The solids are allowed to settle as sludge (primary sludge), removing ~50–60% of total suspended solids (TSS) and ~25–35 % of organic matter. Yet, removal of particle-bound micropollutants (e.g., microplastics, some hydrophobic chemicals) are limited. Secondary (biological) treatment utilizes microbial activity to degrade dissolved organic matter and nutrients (N, P), mainly with the help of activated sludge or biofilm. Thus, some biodegradable micropollutants (e.g., caffeine, ibuprofen) are broken down by microbes. However, it is not effective in removing persistent compounds (e.g. carbamazepine, PFOS). Tertiary treatment is an advanced polishing

process to meet stringent discharge standards, increasingly critical for micropollutant removal under EU regulations. It includes: (1) chemical oxidation to degrade recalcitrant micropollutants via reactive oxygen species (e.g., •OH radicals); (2) adsorption of hydrophobic compounds (e.g., pesticides, pharmaceuticals) by granular/powdered activated carbon; (3) removal of microplastics, PFAS, and dissolved ions by membrane filtration and (4) UV Disinfection of neutralizes pathogens. The emerging quaternary treatment, as defined by the UWWTD in 2024 [Directorate-General for Environment 2024], targets priority micropollutants combined by advanced oxidation process (AOPs) and other techniques. The role in micropollutant management was showed in table 1.1.

Table 1.1 Role in micropollutant management

Stage	Micropollutant Removal	EU Legislative Alignment
Pre/Primary	Limited (particle-bound pollutants)	Baseline compliance
Secondary	Partial (biodegradable organics)	Focus on organic load reduction (BOD/TSS)
Tertiary	High (AOPs, GAC, membranes)	Mandated for large WWTPs under UWWTD
Quaternary	Targeted (priority micropollutants)	Enforced for $\geq 150,000$ p.e. by 2045 [Directorate-General for Environment 2024]

Cost-effective and efficient technological solutions to upgrade existing WWTP are needed to face contaminants of emerging concern. Many conventional water treatment may stopped at secondary treatment (3 stages), which can only convert non-biodegradable constituents into sludge, which generates secondary wastes that need to be disposed of or recycled in an expensive manner [Okab et al. 2023; Wang et al. 2016]. Therefore, the transfer of simpler plants to advanced plants, including tertiary/quaternary (4-5), is urgent, especially in areas with strict regulations (e.g. the EU's Municipal Wastewater Treatment Directive). As a result, research into more effective processes has gained interest in water remediation. In this sense, the use of advanced oxidation processes (AOP) coupled with adsorption technologies seems a

good alternative.

1.2 Advanced Oxidation processes for the treatment of wastewater

The application of AOP for the remediation of wastewater has gained attention in recent years owing to the appearance of recalcitrant emerging pollutants that are not easily removed by conventional treatments [Dhaka et al. 2017; Deng et al. 2015]. AOPs are cutting-edge water treatment technologies designed to degrade and mineralize persistent organic pollutants, micropollutants (e.g., pharmaceuticals, pesticides), and emerging contaminants (e.g., PFAS, microplastics) that resist conventional treatment methods. The advanced oxidation process was first proposed in the 1980s and proved to be an effective means of removing organic pollutants from wastewater due to the generation of sufficient quantities of strong hydroxyl radicals ($\bullet\text{OH}$) and other reactive oxygen species (ROS) to break down complex molecules into harmless byproducts like CO_2 and H_2O . AOPs are pivotal in tackling the "invisible" pollution crisis, aligning with global sustainability goals and stricter regulations like the EU's Green Deal.

AOPs encompass a range of techniques, including ozone-based treatments, the Fenton reaction, electrochemical methods, ultrasound, and photocatalysis. Among different options, solar-driven and sustainable photocatalysis have attracted significant attention for the degradation of recalcitrant organic pollutants in wastewater, as parabens [Khan et al. 2024; El Gaini 2024; Frontistis et al. 2017; Kotzamanidi 2018].

Experimental investigations have validated that heterogeneous photocatalytic systems demonstrate superior efficacy in parabens remediation, achieving higher total organic carbon (TOC) mineralization through hydroxyl radical-mediated oxidation pathways [Bolujoko et al. 2021]. Semiconductor photocatalysis has been much investigated for water treatment (such as TiO_2 , Bi_2WO_6 and g- C_3N_4 photocatalyst), but a major bottleneck for use in WWTP is also related with separation & aggregation. Recent studies have demonstrated that hybrid composites can overcome these issues attaining superior performance over semiconductors, due to the photocatalytic properties of additive (such as nanoporous carbon, metal oxides, semiconductor and so on). Yet the predominant scientific challenge in photocatalysis originates from the intrinsic properties of nanostructured semiconductor photocatalysts, particularly their surface redox kinetics and band structure configuration [Li et al. 2021; Okab et al.

2023; Wang et al. 2020]. Wide bandgap energies restrict the optical absorption to the narrow UV spectrum, comprising merely 4-5% of the solar irradiance. Furthermore, rapid recombination kinetics of photogenerated electron-hole pairs in many photocatalysts severely diminishes their quantum efficiency, with a low charge carrier separation yields under illumination [Ajiboye et al. 2021].

The works of semiconductor-based photocatalysis research were established in 1972 through seminal work [Fujishima et al. 1972] that first demonstrated photoelectrochemical water splitting using Titanium dioxide (TiO_2) electrodes. Subsequently, the photocatalytic degradation of organic pollutants was first demonstrated in 1976 using TiO_2 [Carey et al. 1976]. Following these seminal discovery, photocatalytic material development has expanded exponentially, with diverse semiconductor architectures being engineered for enhanced organic pollutant degradation, such as TiO_2 , ZnO , MoS_2 , CdS , Nb_2O_5 , Bi_2WO_6 and so on [Meng et al. 2019; Lee et al. 2016; Wu et al. 2018; Cheng et al. 2018; Ahmad et al. 2024; Zhang et al. 2011; Belousov et al. 2023], due to their low cost, non-toxicity and high chemical stability. While TiO_2 remains a benchmark photocatalyst in heterogeneous catalysis [Lin et al. 2009; Lin et al. 2011; Velegraki et al. 2015], its practical application under solar irradiation is fundamentally constrained by a wide bandgap of 3.2 eV (UV-driven), limiting light absorption primarily to the UV spectrum.

Owing to the poor activity of TiO_2 powders under solar light, significant efforts are being directed towards exploring alternative photocatalysts with enhanced activity under natural solar light. Recent advances in narrow-bandgap semiconductor design have identified bismuth tungstate (BWO, Eg: 2.9 eV) and graphitic carbon nitride (g- C_3N_4 , Eg: 2.7 eV) as promising alternatives [Wang et al. 2014; Carmona et al. 2015; Kang et al. 2015; Fu et al. 2018; Zhu et al. 2021].

As mentioned above, the primary limitation of pristine semiconductor materials stems from the rapid recombination of photogenerated charge carriers, which significantly compromises their photocatalytic efficiency. Advanced heterojunction engineering can be substantially augmented for the visible-light utilization efficiency of single-component semiconductor. Heterojunction photocatalysts can be systematically categorized into four fundamental types based on interface engineering principles [Wang et al. 2014]:

- **Semiconductor-Semiconductor (S-S) Heterojunctions.** These systems (e.g.,

g-C₃N₄/TiO₂) enable staggered charge transfer through built-in electric fields, achieving higher carrier separation efficiencies, particularly via artificial Z-scheme, S-scheme, conventional type II, and p–n heterojunction configurations charge transfer architectures [Zhang et al. 2022; Cai et al. 2019; Yang 2021; Wu et al. 2020a].

- **Semiconductor-Carbon (S-C) Heterojunctions.** Incorporating carbonaceous materials (graphene, CNTs, activated carbon) creates 3D conductive networks, improving charge mobility and providing high surface area for reactant adsorption [Yu et al. 2016; Gómez-Avilés et al. 2019; Asencios et al. 2022; Eshete et al. 2023].

- **Semiconductor-Metal (S-M) Schottky Systems.** Noble metal nanoparticles (Au, Pt) deposited on semiconductors (e.g., Au/TiO₂) induce localized surface plasmon resonance (LSPR), enhancing visible-light absorption (400-800 nm) while reducing charge recombination rates through electron sink effects [Jovic et al. 2013].

- **Multi-component Heterostructures.** Advanced systems combining S-S/M/C components (e.g., Bi₂WO₆/g-C₃N₄/rGO) demonstrate synergistic effects, achieving higher quantum yields than binary systems through cascade charge transfer pathways [Jo et al. 2018; Ma et al. 2016].

The rational design paradigm of heterojunction architectures fundamentally relies on orchestrating directional charge transfer pathways through band alignment engineering, which strategically separates photogenerated electrons (e⁻) and holes (h⁺) across spatially distinct phases. These strategic designs mimic natural photosynthetic systems by establishing directional charge transfer pathways that simultaneously enhance light harvesting, suppress carrier recombination, and preserve strong redox potentials effectively resolving the intrinsic compromise between bandgap narrowing and redox capability in monolithic photocatalysts [Di Liberto et al. 2021; Low et al. 2017].

1.2.1 Bi₂WO₆ as photocatalyst

In this thesis we have used Bi₂WO₆ based on the experience of the team. The pioneering synthesis of Bi₂WO₆ (labelled as BWO) photocatalysts was achieved through solid-state methods in 1999 [Kudo et al. 1999], with subsequent methodological innovations (e.g., sol–gel method, hydrothermal synthesis) significantly improving their visible-light-driven photocatalytic degradation efficiency. The crystal structure of BWO features alternating [Bi₂O₂]²⁺ layers and perovskite-like

[WO₄]²⁻ sheets, where oxygen atoms are coordinatively shared between adjacent layers to form a three-dimensional network [Wang et al. 2018]. Constructing heterojunction structures by combining carbon materials with BWO is an effective strategy to enhance the photocatalytic performance of individual materials, such as CQDs, multi-walled carbon nanotubes (MWNTs), carbon fibers, activated carbon (AC) and g-C₃N₄.

Wang et al [Wang et al. 2018] synthesized carbon quantum dot-modified Bi₂WO₆ (CQDs/m-BWO) ultrathin nanosheets through a facile hydrothermal approach, demonstrating significantly enhanced full-spectrum photocatalytic activity. The composite exhibited ~3-fold and ~2-fold higher degradation efficiencies toward BPA and MO, respectively, compared to pristine BWO. This enhancement is attributed to the formation of strong interfacial C-O-W covalent bonds between CQDs and [Bi₂O₂]²⁺ layers, which substantially modified the electronic structure through charge redistribution. Then, CQDs can absorb near-infrared light and subsequently emit shorter wavelengths, promoting the generation of electron-hole pairs. Additionally, CQDs can function as electron reservoirs, capturing electrons released from m-BWO particles under visible light irradiation and thereby suppressing electron-hole recombination [Qian et al. 2016; Nie et al. 2021]. What's more, MWNTs serve as an efficient cocatalyst in Bi₂WO₆-based systems, significantly enhancing photocatalytic performance through dual functional mechanisms [Yue et al. 2015]. The high surface area and π -conjugated structure of MWNTs establish strong π - π stacking interactions with aromatic pollutants, improving surface adsorption capacity compared to bare BWO. More critically, MWNTs create continuous electron transport pathways at the BWO interface, reducing charge transfer resistance and extending electron-hole pair lifetime, effectively suppressing charge-carrier recombination. Spiral carbon fibers exhibited comparable cocatalytic enhancement effects to MWNTs in boosting BWO photocatalytic performance [Lei et al. 2020]. Electrochemical impedance spectroscopy observed the reduction of charge transfer resistance at the carbon fibers/BWO interface, confirming effective separation of photogenerated charge pair. This structural advantage originates from the carbon fibers unique spiral architecture, which provides both enhanced π -electron delocalization and interlayer charge transport channels similar to MWNTs.

The incorporation of AC into BWO matrices can induce an enhancement in visible-light absorption (450-800 nm) as evidenced by UV-Vis diffuse reflectance

spectroscopy; this may be attributed to the presence of photosensitive functional groups on the carbon matrix [Carmona et al. 2015].

The integration of oxygen-rich graphitic carbon nitride (OCN) with bismuth oxide containing oxygen vacancies (BWO-OV) significantly improves photocatalytic efficiency by enhancing light absorption and increasing the availability of active reaction sites [Huo et al. 2021]. The oxygen vacancies promote the exposure of these sites, while the oxygen-rich structure of OCN boosts light-harvesting capability. This synergistic effect results in outstanding photocatalytic activity, especially in the degradation of pollutants such as tetracycline.

1.3 Carbon materials in photocatalysis

In water purification, beyond traditional adsorption applications, carbon materials have been extensively explored as a versatile functional material serving as a support for heterogeneous catalysts to enhance dispersion and reactivity [Ania et al. 2020; Serp and Figueiredo 2008]. Carbon materials could combine with other materials (e.g., TiO_2) to form photocatalytic composites, where the carbon material improves charge separation and light utilization efficiency, and engineered into carbon-based hybrid materials (e.g., activated carbon (AC)/graphene frameworks) to synergize adsorption and catalytic degradation mechanisms [Leary et al. 2011; Reddy et al. 2015; Thambiliyagodage 2022; Tohamy et al. 2023]. Photocatalytic based on the use of carbon materials as both catalysts and adsorbents are emerging as an efficient and economical new process on the quest of water supply assessment in most vulnerable areas.

The synergy between porous activated carbons and TiO_2 as semiconductor was first systematically explored by Herrmann and co-workers, demonstrating the improved degradation efficiency of various organic pollutants in TiO_2 /carbon mixtures due to the improved mass transfer provided by the porosity of the activated carbon [Matos et al. 1998; Herrmann 1999; Matos et al. 1999; Matos et al. 2001; Matos et al. 2007]. The studies reported that the AC acts as both an adsorbent and a support, concentrating pollutants near TiO_2 's active sites while reducing electron-hole recombination, thereby enhancing photocatalytic activity. Since then, the potential role of carbon materials as supports in semiconductor/carbon composites has been investigated in a number of photocatalytic degradation reactions both in liquid and gas phase [Leary et al. 2011; Serp et al. 2008]. The enhanced photoconversion yield of

carbon/semiconductor composites has been attributed to either single or collective factors based on the combination of the photo-activity of the immobilized semiconductor and the structural, textural and electronic features of the carbon support. Several mechanisms on the role of carbon have been postulated, mainly associated to i) modification of the absorption properties, ii) increased reaction rates due to the confinement of the pollutant in the porosity of the carbon support via adsorption, iii) interfacial electronic effects between the carbon and the semiconductor leading to efficient charge carrier transfer and separation, iv) carbon acting as photosensitizer by injecting electrons into the conduction band of the semiconductor, v) increased stability of the catalyst inhibiting photocorrosion.

Most recently, the self-photochemical activity of certain carbon materials (carbon nitride, nanoporous carbons) has been demonstrated, owing to their ability to form oxygen radical species [Velasco et al. 2010; Velasco et al. 2012; Bandosz et al. 2018]. The combination of adsorption and photocatalysis allowed the simultaneous degradation of pollutants and on-site regeneration of the spent nanoporous carbon, as demonstrated in other studies [Gangu et al. 2019; Chenab et al. 2020; Abbo et al. 2021; Gomis-Berenguer et al. 2017; Velasco et al. 2014].

g-C₃N₄, as a semiconductor and carbon material, has gained emerged and prominent photocatalyst due to its unique physicochemical properties [Fu et al. 2018; Zhu and Zhou 2021; Chen et al. 2020; Ismael 2020]. The catalytic potential of g-C₃N₄ was first demonstrated in 2006 when it successfully facilitated the Friedel-Crafts reaction, marking its debut in heterogeneous catalysis [Goettmann et al. 2006]. This two-dimensional material subsequently revealed its photocatalytic abilities in 2009 through a groundbreaking application in water decomposition to generate hydrogen gas [Wang et al. 2022]. g-C₃N₄ offers several distinct advantages:

1. **Visible-Light Responsiveness.** With a moderate bandgap (~2.7 eV), g-C₃N₄ efficiently absorbs visible light (wavelength < 460 nm) [Jitae et al. 2025], enabling solar energy utilization without requiring UV irradiation.

2. **Chemical and Thermal Stability.** The robust covalent C-N framework ensures exceptional stability under harsh conditions (high temperatures, acidic/alkaline environments, and prolonged irradiation), minimizing material degradation during reactions.

3. **Eco-Friendly and Low-Cost Synthesis.** Synthesized from abundant precursors (e.g., melamine, urea) via thermal polycondensation, it is cost-effective and scalable

for industrial applications.

4. Tunable Electronic Structure. Its electronic properties (e.g., bandgap, charge-carrier dynamics) can be tailored through doping, nano-structuring, or forming heterojunctions with other semiconductors, enhancing photocatalytic efficiency.

5. Non-Toxicity and Biocompatibility. As a metal-free polymer, g-C₃N₄ avoids heavy-metal leaching risks, making it environmentally benign and suitable for biomedical or ecological applications.

6. Effective Charge Separation. The layered structure and π -conjugated system facilitate electron-hole pair separation, critical for driving redox reactions.

7. Surface Functionalization Potential. Rich surface amino groups (-NH₂) and defects allow easy modification with co-catalysts (e.g., carbon materials, Bi₂WO₆, MoO₃, TiO₂...) or integration into hybrid systems to boost activity.

These attributes position g-C₃N₄ as a sustainable and versatile platform for advancing solar-driven photocatalytic technologies, such as efficient water splitting for hydrogen production, degradation of a variety of pollutants and reducing CO₂ to solar fuels (e.g., CH₄, CH₃OH) through generated reactive oxygen species (ROS), due to their favorable band gap structure, good chemical stability, low toxicity and abundance of precursors [Stefa et al. 2023; Ismael 2020; Jiang et al. 2018; Imgharn et al. 2024; Li et al. 2022]. However, the practical implementation of g-C₃N₄ faces significant challenges stemming from two intrinsic limitations: (1) inherently low specific surface area (~16 m²/g) and (2) rapid recombination of photogenerated electron-hole pairs and limited redox potential for specific reactions.[Qiu et al. 2015]. These structural constraints severely restrict accessible active sites and quantum efficiency, forming critical bottlenecks for photocatalytic applications. While g-C₃N₄'s drawbacks are undeniable, they have spurred innovative modifications to tailor its properties [Tofil et al. 2025].

To address these issues, researchers have developed various modification strategies, incorporated with carbon materials to build heterojunctions configurations [Cao et al. 2015; Zhao et al. 2020; Tang et al. 2019], which synergistically enhance charge separation dynamics while optimizing surface reactivity. Substantial advancement in g-C₃N₄'s photocatalytic performance requires concerted improvements in three critical stages: (1) broadband photon harvesting efficiency governed by bandgap engineering, (2) charge carrier dynamics (generation, separation, and transport) mediated by heterojunction architectures, and (3) surface redox kinetics

accelerated through active site engineering [Cao et al. 2015].

Coupling carbon materials with g-C₃N₄ has been proved to be a significant scientific method due to the ability of these materials to enhance photocatalytic activity by utilizing their unique advantages. Carbon materials can function as electron acceptors, facilitate charge transfer, provide reactive sites, and enhance visible light absorption. Indeed, a variety of carbon materials have been used in wastewater remediation, either alone or in combination with other carbon materials (CDs, biochar, CNTs, rGO and so on) [Yang et al. 2023; Liu et al. 2020; Xiao et al. 2018; Asadzadeh-Khaneghah et al. 2020; Li et al. 2022; Li et al. 2013; Feng et al. 2023], with excellent results with heterojunctions based on different carbon allotropes with g-C₃N₄ material.

Fang et al. [Fang et al. 2016] engineered a carbon dot-modified g-C₃N₄ composite that exhibited a threefold enhancement in photocatalytic activity compared to unmodified g-C₃N₄. C-dots acted as electron-sinks, which played an effective role in suppression of electron-hole pair recombination [Liu et al. 2019; Zhao et al. 2020]. In addition, carbon dots can be strategically intercalated into the interlayer galleries of g-C₃N₄, inducing controlled interlayer expansion while simultaneously enhancing the accessible surface area [Xu et al. 2022]. This structural modulation simultaneously amplifies the density of catalytically active sites and establishes electron transport networks across the stratified architecture, synergistically elevating the overall photocatalytic efficiency through dual spatial and electronic optimization mechanisms. Biochar also has emerged as a strategically significant co-catalyst for optimizing the photocatalytic performance of g-C₃N₄ [Pi et al. 2015; Lin et al. 2022; Meng et al. 2020]. The hierarchical porous architecture of biochar substantially enhances substrate adsorption capacity, concentrating organic pollutants at reactive interfaces. Furthermore, its conductive carbon matrix (π -conjugated electron systems) establishes electron transfer highways with g-C₃N₄. Crucially, the biochar/g-C₃N₄ heterojunction achieves a self-regulating equilibrium between contaminant sequestration and photo-induced regeneration, where adsorbed pollutants are continuously mineralized while maintaining active catalytic surfaces through controlled charge transfer dynamics. The introduction of Carbon nanotubes could enhance the visible light absorption of the g-C₃N₄. Carbon nanotubes (CNTs) synergistically enhance the charge separation efficiency in g-C₃N₄ photocatalytic systems by serving as conductive bridges for rapid electron transport [Liu et al. 2020; Xu et al. 2020; Shi et al. 2022]. The nanostructure

of CNTs provides directional pathways for photogenerated electrons to migrate from g-C₃N₄, thereby suppressing electron-hole recombination through spatial separation of charge carriers. This electron-shuttling mechanism not only prolongs the lifetime of reactive holes but also establishes interfacial charge transfer channels that optimize redox reaction kinetics. The incorporation of reduced graphene oxide (rGO) with g-C₃N₄ demonstrated analogous photocatalytic enhancement, rooted in a dual-mechanistic synergy: (1) the 2D conductive framework of rGO establishes rapid electron highways, accelerating charge carrier mobility to suppress recombination, and (2) its high surface-to-volume ratio generates abundant exposed catalytic domains. This structural-electronic interplay amplifies interfacial charge transfer kinetics while maintaining a favorable band structure for visible-light-driven redox processes [Fu et al. 2020; Tang et al. 2019].

The carbon matrix effectively traps photogenerated electrons from the semiconductor's conduction band, thereby suppressing charge recombination. This electron transfer process prolongs the lifetime of photogenerated charge carriers compared to pristine semiconductors. Carbon incorporation could induce a reduction in the semiconductor's bandgap through interfacial electron coupling effects. This band structure modification extends light absorption into the visible spectrum while maintaining adequate redox potentials for photocatalytic reactions.

1.4 Layer-double hydroxide compound in photocatalysis

Heterojunctions of semiconductors with two-dimensional materials also have recently attracted the attention as a means to improve the lifetime of the photogenerated charge carriers due to the reduced distances within the 2D structures [Wang et al. 2022; Ong et al. 2016; Du et al. 2023]. Among these two-dimensional materials, hydroxide-like compounds -also known as layered double hydroxides (LDHs)- are promising candidates to improve the performance of semiconductors in photocatalytic applications [Meza-Fuentes et al. 2020]. LDHs are highly advantageous for constructing 2D/2D heterojunctions with g-C₃N₄ due to their tunable band alignment and compositional flexibility. The inherent adjustability of LDHs' metal cation ratios (e.g., Ni/Fe, Co/Al) enables precise modulation of their conduction and valence band positions, which synergistically align with those of g-C₃N₄ to facilitate interfacial charge separation. Additionally, their layered morphology promotes intimate 2D face-to-face contact with g-C₃N₄ nanosheets, minimizing

charge transfer resistance and enhancing photocatalytic activity for applications such as water oxidation or pollutant degradation [Du et al. 2023; Ding et al. 2023]. LDHs are characterized by lamellar arrangements composed of positively charged layers formed by divalent and trivalent metal cations coordinated with hydroxyl groups and anions to compensate the surface charge [Valdivieso-Vera and Guerrero-Pérez 2024; Cuevas et al. 2003]. The layered structure of LDHs is expected to facilitate the separation and migration of the charge carriers, while the ability to host diverse cations and anions within the interlayer space can enhance the light absorption in the visible range [Du et al. 2023; Nguyen et al. 2024; Wu et al. 2023; Lu et al. 2023]. The synergistic effect of photocatalytic heterostructures based on LDH and g-C₃N₄ has been reported for the degradation of pollutants and the generation of hydrogen from water splitting [Du et al. 2023; Wu et al. 2023; Lu et al. 2023; Xiong et al. 2020; Megala et al. 2020; Tripathi et al. 2020; Gandamalla et al. 2021; Tripathi and Hussain 2021], such as g-C₃N₄/MgFe-LDH [Wu et al. 2020a; Wu et al. 2020b], g-C₃N₄/NiAl-LDH [Wu et al. 2023; Megala et al. 2020], g-C₃N₄/CoAl-LDH [Lu et al. 2023; Xiong et al. 2020], g-C₃N₄/MgAl-LDH [Megala et al. 2020; Hao et al. 2024], C₃N₄/ZnAl-LDH [Li et al. 2020; Tripathi et al. 2020; Gandamalla et al. 2021; Tripathi et al. 2021] and so on. g-C₃N₄ is assembled with M(II)M(III)-LDH via adjusting the mass ratio of MII to MIII and the M(II)M(III)-LDH to g-C₃N₄. Then, the microstructure, optical and photoelectrochemical properties of composite could be affected, which will improve the removal efficiency toward pollutant [Hao et al. 2024].

As an example, g-C₃N₄ supported on ZnAl-LDH has been reported display better photocatalytic activity under visible light due to a red shift in the optical absorption edge of immobilized carbon nitride [Wu et al. 2023; Tripathi et al. 2020; Tripathi et al. 2021]. The enhanced photocatalytic performance of g-C₃N₄/NiAl-LDH can also be attributed to the compact interfacial contact and the synergistic interaction between pristine g-C₃N₄ and NiAl-LDH [Yuan et al. 2017]. This combination facilitates efficient mass transfer and promotes the effective separation of photogenerated charge carriers. Furthermore, g-C₃N₄/NiAl-LDH demonstrate excellent stability, retaining their photocatalytic efficiency over four consecutive cycles with no significant performance loss [Salehi et al. 2018]. In a pioneering study by Wang et al. [Wang et al. 2019], a vertically aligned MgAl-LDH/g-C₃N₄ heterostructure was engineered, featuring MgAl-LDH nanosheets grown perpendicularly on g-C₃N₄ nanosheets. This architecture provides a high density of

exposed edges, resulting in a pronounced synergistic effect between adsorption and charge separation. Additionally, the positively charged LDH layers promote the accumulation of anionic contaminants around the g-C₃N₄ surface. These electrostatic interactions effectively reduce diffusion distances and accelerate contaminant degradation.

What's more, it was found that the addition of third divalent cation could contribute to the improvement of reductivity of composite without changing the laminated structure. For example, the introduction of zinc can increase the reductivity aluminum with nickel cations, which further favors the decomposition of pollutants in the photocatalytic reaction [Fuentes et al. 2011]. Sherry et al. reported the synthesis of a trimetallic g-C₃N₄/NiCoAl-LDH heterojunction with excellent structural stability and improved activity for hydrogen production due to optimized charge transfer pathways [Sherry et al. 2024]. Feng et al. [Feng et al. 2022] have also described the synthesis of a g-C₃N₄/NiZnAl-LDH heterojunction with good performance for the photocatalytic degradation of methyl orange and tetracycline. Despite the favorable results reported so far for a variety of LDH/carbon nitride heterojunctions prepared by different synthetic routes [Du et al. 2023], the challenge remains in the control of the incorporation of the semiconductor in the interlayer spacing of the 2D structure of the LDH and the understanding of the charge transfer mechanisms occurring at the interface between both phases.

Collectively, the strategic integration of two materials into photocatalytic systems orchestrates a tetragonal enhancement mechanism: (1) enabling directional charge carrier migration to suppress electron-hole recombination, (2) broadening visible-light absorption through tailored band structure engineering, (3) establishing optimized band alignment via controlled bandgap narrowing, and (4) generating abundant exposed active sites. This synergistic trifecta fundamentally reconfigures the photophysical landscape, amplifying quantum efficiency while expanding spectral utilization boundaries. What's more, all these studies highlighted a critical threshold: excessive loading of additive paradoxically formed electron-hole recombination centers, ultimately diminishing the photocatalytic performance of the hybrid material.

1.5 Objectives of this PhD thesis

The main goals of this PhD thesis are to explore the degradation of methylparaben (an endocrine disruptor present in wastewater) using photocatalytic based on hybrid semiconductor/carbon materials. The efficiency and cyclability of the catalysts will be discussed in terms of the pollutant conversion and the nature of the intermediate compounds formed. New insights on the mechanism that govern the degradation performance using different process will be evaluated by photocatalytic, photoelectrochemical efforts and quenching tests to rationalize and identify the nature of the catalytic sites and the degradation mechanisms. The possible photocatalytic degradation pathways are analyzed through the identification of degradation intermediates and the use of radical scavengers.

The specific objectives set in order to achieve the main purpose of this thesis were:

- To explore the photocatalytic activity of various semiconductor/porous support hybrid photocatalysts prepared by blending various semiconductors (BWO and carbon nitride) and porous matrices (nanoporous carbon, 2D layered double metal hydroxides). The adequate balance between the π -electron density, structural defects and electronic conductivity of the hybrid photocatalysts is expected to improve charge separation efficiency of photogenerated electron-hole pairs and thus alter the photocatalytic properties.
- To examine the effect of the characteristics of the components of the hybrid photocatalysts (e.g., crystallinity, porosity, composition, optical features...) in their photocatalytic activity and stability for the degradation of methylparaben over consecutive photocatalytic cycles.
- To explore the photocatalytic degradation mechanism of methylparaben in each system, and to correlate this with the characteristics of both components in the hybrid photocatalysts. For this, the photocatalytic reaction will be studied under the effect of various quenchers of the photoinduced reactive species (i.e. photogenerated h^+ , e^- , $\bullet OH$ and $\bullet O_2^-$), and by photoelectrochemical responses under different illumination conditions. This will allow determining the effectiveness of the charge carriers separation, their surface recombination and the modulation of interfacial charge dynamics in the hybrid photocatalysts upon their physicochemical properties.

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2.1 Target pollutant

In my thesis, methylparaben (labelled as MP; Sigma-Aldrich, CAS No.99-76-3) was selected as a target pollutant in all the photocatalytic experiment. MP (a synthetic compound) is currently regulated as a preservative (Annex V, entry 12) in a concentration up to 0.4 % (as acid) when used on its own or up to 0.8% for mixtures of esters (Annex V, entry 12, column g), an opinion on MP, published by European Scientific Committee on Consumer Safety in 2024. It has been found that MP was widely employed in the cosmetic, food, and pharmaceutical industries over 50 years to exert the intended antimicrobial affect, due to its relatively non-irritating, non-sensitizing, and of low toxicity. Methyl paraben is especially effective in inhibiting the growth of molds and yeasts [Soleimani et al. 2024; Soni et al. 2002]. The MP has a high stability over a wide pH range. It is stable in air and resistant to hydrolysis in hot and cold water, as well as in acidic solutions. But It hydrolyses could occur in alkaline solutions. All my experiments are carried out at pH ~6.99 (the pH of pure water), and the MP is stable at the aqueous solution (the pH of MP solution is ~6.98). The chemical structure of MP is depicted in Figure 2.1.

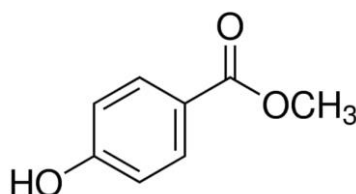


Figure 2.1 The chemical structure of Methyl paraben.

2.2 Materials

2.2.1 Bismuth tungstate

Bi_2WO_6 (BWO) was prepared by following a hydrothermal procedure, as reported in our previous work [Carmona et al. 2015]. First, 4.85 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 10 mL of glacial acetic acid. Meanwhile, 1.65 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 90 mL of distilled water. Second, the two solutions were combined to form a white suspension (~pH 2), which was stirred for 30 minutes before being transferred into a Teflon lined stainless steel autoclave. The autoclave was moved to the oven at 140°C for 20 hours for hydrothermal treatment. Then, the obtained yellowish precipitate was filtered, thoroughly washed with distilled water, and dried overnight at 120°C. Finally, the dried powder was further calcined at 300°C for 4 hours.

2.2.2 Carbon Nitride

Bulk graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) was prepared by thermal decomposition of melamine as reported elsewhere [Jin et al. 2017; Zhong et al. 2014]. Briefly, melamine was heated at 520 °C for 4 hours in a muffle furnace (heating rate of 10 °C/min) under air atmosphere. The sample labeled as CN.

2.2.3 Nanoporous Carbon

A commercial nanoporous carbon (brand name Aquasorb 2000, Jacobi Carbons) obtained by steam activation of bituminous coal was selected; it was labelled as CQ.

2.2.4 Layer-double hydroxide compound

The Ni–Al–Zn hydroxide-like compound (LDH) was synthesized via the co-precipitation method [Benedicetto et al. 2018; Reyero et al. 2013]. Briefly, an aqueous solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was prepared as the source of Ni, Zn and Al. The chemical composition obtained corresponded to a Ni: Al: Zn molar ratio of 2:1:1. Firstly, 12.36 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 9.75 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 3.54 g of ZnCl_2 were dissolved in distilled water. A second solution was prepared by dissolving 4.68 g of Na_2CO_3 and 3.18 g of NaOH in 50 mL of deionized water (to adjust the pH of the synthesis). Secondly, 50 mL of Ni–Al–Zn solution and 50 mL of the selected alkaline solution were slowly and simultaneously added dropwise under vigorous stirring in a beaker for 45 minutes. The temperature was maintained around 25 °C, and the pH was controlled during the addition. The resulting mixture was kept stirring for 15 minutes. Then, the suspension was stored in a plastic container and was put in oil bath at 80 °C for 24 hours. After cooling, the solids were recovered by filtration, washed with 500 mL distilled water and dried overnight in ambient environment. Finally, the solid was dried in a vacuum oven at 65 °C until constant weight. The obtained sample was grinded by mortar before adding to the photocatalytic reactor.

2.2.5 Synthesis of the Composites

2.2.5.1 CN/CQ composite

A series of binary carbon/carbon heterojunctions has been prepared by blending carbons with activated carbons. The hybrid carbon nitride/carbon photocatalysts were prepared by a hydrothermal method, using variable amounts of the CQ additive, ranging from 2 to 10 wt. %. Firstly, the carbon materials (2g of the total) were mixed in water (75mL) and sonicated for 15 min to assure a good dispersion. Then, the suspension was transferred into a Teflon-lined stainless-steel autoclave and maintained at 140 °C for 20 h. Finally, the precipitate was filtered, washed with

distilled water and dried at 120 °C overnight. The composites were labelled as CN/CQ-Y%, where Y refers to the amount of CQ powders dispersed in the suspensions. What's more, the compared CN was obtained under the same hydrothermal method without the addition of carbon Q. It was used as a control group and called CN(H).

2.2.5.2 BWO/carbon composite

BWO/CQ and BWO/CN materials were prepared by following a similar synthesis procedure with BWO. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (Sigma–Aldrich, ACS reagent) were used as precursors. Thus, 4.85 g of the Bi precursor was dissolved in 10 mL of glacial acetic acid and 1.65 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 90 mL of distilled water. These two solutions were finally mixed to form a white suspension (~pH 2) which was kept under stirring for 15 min. Then, the necessary amount of pre-treated carbon material was added to the suspension in order to have different carbon to BWO weight ratios (2, 5 and 10 wt %), and the mixture was sonicated for 15 min and kept under stirring for other 15 min. At this part, the carbon additives used were CQ and CN. Teflon-lined stainless-steel autoclave is exploited to proceed the hydrothermal treatment, performed at 140°C for 20 h in oven. Next, the yellowish precipitate was then filtered, repeatedly washed by distilled water and dried overnight at 120°C. Finally, the obtained powder was calcined at 300°C for 4 h. The composites were labelled as BWO/CQ-Y% and BWO/CN-Y%, where Y refers to the amount of additive powders dispersed in the suspensions.

2.2.5.3 LDH/CN composite

First of all, 12.36 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 3.54g of ZnCl_2 and 9.75 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 50 mL of deionized water. A second solution was prepared by dissolved 4.68 g of Na_2CO_3 and 3.18 g of NaOH in 50 mL of deionized water (to adjust the pH of the synthesis). Both solutions were mixed dropwise into an Erlenmeyer flask under vigorous stirring at 25 °C. secondly,carbon nitride powders was added to the solution mixture containing the LDH precursors, followed by 3 hours of sonication to ensure its uniform dispersion. Then, the mixture was allowed to age in an oven at 80 °C for 24 hours. After cooling, the solid was recovered by filtration, washed with distilled water, and dried overnight at 100 °C. The composites were labelled as LDH/CN-Y%, where Y refers to the amount of carbon nitride powders dispersed in the suspensions.



Figure 2.2 Images of all the synthesized photocatalysts.

2.3 Characterization

2.3.1 X-ray diffraction (XRD) spectroscopy

X-ray diffraction (XRD) spectroscopy is a powerful and efficient analytical technique for characterizing the crystalline phases of materials. The principle of X-ray diffraction: based on three rules: (1) any phase has a special diffraction spectrum. (2) diffraction spectrums are different for two phases. (3) Diffraction peaks of multiphase samples are mechanical superposition of each phase. This method provides detailed structural information, including unit cell dimensions, by exposing the sample to high-energy electromagnetic radiation in the X-ray wavelength range of 0.01 to 10 nm. XRD represents a rapid, non-destructive analytical technique for determining atomic-scale structural characteristics of crystalline materials. This method enables precise characterization of atomic/ionic/molecular arrangements within crystal lattices and

provides comprehensive structural parameters. The fundamental principle of X-ray diffraction is governed by Bragg's law (Equation 3.1) [Bragg et al. 1913], which mathematically describes the conditions for constructive interference of coherently scattered X-rays by crystalline planes:

$$n \lambda = 2d \sin \theta \quad \text{Equation 2.1}$$

where λ represents the wavelength of the incident X-ray radiation (nm), d corresponds to the interplanar spacing (nm) between atomic lattice planes, and θ denotes the Bragg angle (radians) at which constructive interference occurs.

In this study, the crystallinity of obtained materials was characterized using X-ray diffraction analysis performed on a Bruker D8 Advance diffractometer equipped with a Cu K α radiation source ($\lambda = 0.15406$ nm), operating at 30 kV and 40 mA. The diffraction patterns were collected in the 2θ range of 10° to 80° with an optimized step size that was adjusted according to the specific material characteristics. The crystallite sizes of both pristine semiconductors and their corresponding carbon composites were determined through application of the Scherrer equation (Equation 2.2) to the dominant XRD peaks.

$$L = \frac{K\lambda}{B \cos \theta} \quad \text{Equation 2.2}$$

In the Scherrer equation, L represents the crystallite size (nm), B denotes the full width at half maximum (FWHM) of the diffraction peak in radians, and K is the dimensionless shape factor, which depends on the crystallographic orientation and typically ranges between 0.62 and 2.08, with a commonly adopted value of 0.89 for spherical crystallites.

2.3.2 UV-Vis diffuse reflectance spectroscopy

UV-Vis diffuse reflectance spectroscopy (DRS) is a highly sensitive analytical technique widely employed for characterizing the optical properties of materials, particularly for determining their band gap energy. The band gap represents the minimum energy required to promote an electron from the valence band to the conduction band, resulting in the formation of bound electron-hole pairs (excitons). When the incident photon energy exceeds both the exciton binding energy and the fundamental band gap energy, these excitons dissociate into free charge carriers (electrons and holes), which are essential for initiating photocatalytic reactions. This technique is particularly valuable for semiconductor characterization as it provides crucial information about the electronic structure and optical absorption properties of

materials.

UV-Vis diffuse reflectance spectra were acquired using a Shimadzu UV-2700 spectrophotometer equipped with an ISR-2600 Plus integrating sphere assembly, employing barium sulfate (BaSO_4) as a reflectance standard. Measurements were performed in the 200–800 nm spectral range (limited by the detector configuration of the integrating sphere assembly) under diffuse reflectance mode. Particulate materials were mechanically homogenized using an agate mortar and pestle for 120 seconds to achieve particle size uniformity. The processed powders were then uniaxially compressed into cylindrical sample holders with standardized dimensions (30 mm diameter $\times$ 5 mm depth). For materials exhibiting insufficient reflectance properties, thin-layer deposition was performed on optically polished quartz substrates (3 mm thickness) to minimize scattering artifacts.

To determine the optical band gap from diffuse reflectance spectra, the raw reflectance data were mathematically converted into equivalent absorbance units using the Kubelka-Munk transformation [Kubelka et al. 1931]. In this transformation, (R) represents the relative reflectance, aiding in the precise evaluation of the band gap. The Kubelka-Munk theory describes the interaction of light within a dispersing medium as a function of its scattering (S) and absorption coefficients (k), as expressed in Equation 2.3:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{k}{S} = \alpha \quad \text{Equation 2.3}$$

where, α represents the absorption coefficient derived from the Kubelka-Munk function, where R_∞ denotes the absolute diffuse reflectance of an optically thick sample (typically >5 mm thickness) measured relative to a non-absorbing reference standard (typically BaSO_4) across the spectral range.

The approximation $F(R_\infty) \approx \alpha$ has been extensively validated for optical band gap determination in semiconductor materials [Gesesse et al. 2020; López et al. 2012]. This approximation is particularly reliable for crystalline semiconductors where discrete electronic transitions dominate the absorption characteristics. However, for amorphous or structurally disordered semiconductors, the presence of localized tail states near the band edges (Urbach tails) significantly modifies the absorption profile. These tail states arise from structural defects, compositional fluctuations, and thermal disorder, resulting in exponential absorption edges rather than sharp band transitions. For such materials, the Tauc method (Equation 2.4) provides a more appropriate

framework for band gap evaluation, accounting for the energy-dependent density of states in disordered systems:

$$\alpha h\nu = B (h\nu - E_g)^n \quad \text{Equation 2.4}$$

where $h\nu$ represents the photon energy (h is Planck's constant - 4.136 1015 eV/s), B is the Tauc constant, E_g denotes the optical band gap, and n is the transition characteristic exponent ($n=2$ for direct allowed transitions, $n=1/2$ for indirect allowed transitions and $n = 3/2$ for direct forbidden transitions).

2.3.3 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful analytical technique for characterizing molecular vibrations and identifying functional groups in materials. When a sample is exposed to infrared radiation in the mid-IR range (typically 4000-400 cm^{-1}), specific frequencies are absorbed corresponding to the vibrational modes of molecular bonds, while non-absorbed frequencies are transmitted. The interferogram generated by the Michelson interferometer is Fourier-transformed to produce a characteristic absorption spectrum, where each absorption band corresponds to specific molecular vibrations. These vibrational modes, appearing at characteristic wavenumbers, can be precisely assigned to particular functional groups. The resulting FTIR spectrum serves as a molecular fingerprint, enabling qualitative and quantitative analysis of chemical composition through comparison with reference spectral databases.

In this study, IR spectra were recorded under vacuum in a Nicolet spectrometer equipped with a DTGS detector. Dried powders of the materials were mixed (agate mortar) and pressed with KBr (dilution 1:250) using uniaxial compression (10-ton load, 5 min dwell time) in a hydraulic press (Specac Atlas Series) to form 13-mm-diameter transparent pellets. Before the measurements, the pellets were dried at 60°C for 12 h. Each spectrum resulted from the accumulation of 64 scans, recorded with a spectral resolution of 4 cm^{-1} in the mid-IR range (4000-400 cm^{-1}) spectral domain. A blank KBr pellet was used as reference.

2.3.4 Photoluminescence

Photoluminescence (PL) is an optical phenomenon wherein a material absorbs photons (typically in the UV-Vis-NIR spectrum) and undergoes electronic transitions from ground states to excited states, followed by radiative recombination processes that emit photons with characteristic wavelengths. This photophysical process,

governed by quantum mechanical selection rules, serves as a critical probe for investigating electronic structures and energy transfer dynamics in diverse systems.

In my study, dispersions of the photocatalyst (ca. 0.1 g/L) in water were studied through steady state fluorescence emission spectra on a Horiba Fluoromax 4P spectrofluorometer, using 300 and 375 nm as excitation wavelength. The emission of obtained samples was collected to study the radiative recombination. Radiative recombination refers to the direct band-to-band transition of an electron from the conduction band to the valence band, accompanied by the emission of a photon. This process is essentially the reverse of photon absorption.

2.3.5 X-ray photoelectronic spectroscopy

X-ray photoelectronic spectroscopy (XPS) is a highly sensitive, quantitative spectroscopic technique based on the photoelectric effect. It enables the identification of elements present within a material (elemental composition) or on its surface (within 1–10 nm of a material's surface), along with their chemical states, overall electronic structure, and density of electronic states. XPS is particularly powerful because it not only reveals the elemental composition but also provides insights into the chemical bonding between elements.

In this study, XPS experiments were collected in a K-Alpha ThermoScientific spectrometer (ThermoScientific, Waltham, MA, USA) using monochromatic AlK α (1486.6 eV) radiation at 3 mA $\times$ 12 kV. The spectra of dried samples were recorded using a 400 μ m diameter analysis area. Processing of the XPS spectra was performed in Advantage software (v5), with energy values referenced to the C1s peak of adventitious carbon located at 284.8 eV, and a Shirley-type background.

2.3.6 Texture characterization

The International Union of Pure and Applied Chemistry (IUPAC) defines the texture of a materials as a detailed geometry of void space in the particles [Robert et al. 1976; Thommes et al. 2015]. Porosity is a concept related to texture, referring to the pore (void) space in a material; it is usually defined as the ratio of the volume of pores (open and closed) and to the volume occupied by a solid. However, it should be considered that porosity is not a characteristic of a material, since it depends on the method used to determine it [Rouquerol et al. 2014]. In this context, the textural characterization of a material typically includes the determination of:

- Specific surface area, the surface area per unit mass of solid.

- Pore volume, the volume of pores per unit mass of solid determined by stated method.
- Pore size or width, is the distance between the two opposite walls of cylindrical pore or a slit.
- Pore size distribution, is associated to the presence of pores in the adsorbent between a certain pore size.

According to their size, IUPAC classification of pores is as follows [Thommes et al. 2015]: Macropores, are pores with widths exceeding about 50 nm.; Mesopores, are pores of widths between 2 nm and 50 nm; Micropores, are pores with widths not exceeding than 2 nm. Recently, IUPAC has accepted the term *nanopores* to include pores with an upper limit close to 100 nm width [Thommes et al. 2015]. In order to characterise the texture of solid materials and to determine the main textural parameters mentioned above (e.g. surface area, pore volume, pore width, pore size distribution), IUPAC recommends the use of gas adsorption (various gases and temperatures).

Adsorption is a spontaneous process that occurs when a surface is exposed to a fluid (i.e. gas or liquid); it can be defined as an increase in the concentration of a fluid (e.g. an enrichment of molecules, atoms or ions) at the interface of a condensed phase due to the operation of surface forces [Calvert 1990]. Depending on the interaction between the solid and fluid, a distinction can be made between physical adsorption (physisorption) in which weak interactions are involved (e.g. Van der Waals), or chemical adsorption (chemisorption) in which the adsorbed molecules are chemically bonded to the surface. The solid is called the adsorbent, whereas the fluid is adsorbible (before being adsorbed) or adsorbate (in adsorbed state).

The amount of gas adsorbed by an adsorbent (n) per mass of solid (m), depends on several factors as pressure (p), temperature (T) and the nature of the gas–solid system. For a given gas–solid pair, and at a constant temperature below the critical temperature of the gas, the amount of adsorbed (n) can be expressed by the following general expression (Equation 2.6) of an adsorption isotherm [Rouquerol et al. 2014].

$$n(p) = f\left(\frac{p}{p_0}\right)_{T, \text{gas}, \text{solid}} \quad \text{Equation 2.6}$$

where, p_0 is the gas saturated equilibrium vapour pressure at temperature T , and p/p_0 is the relative pressure.

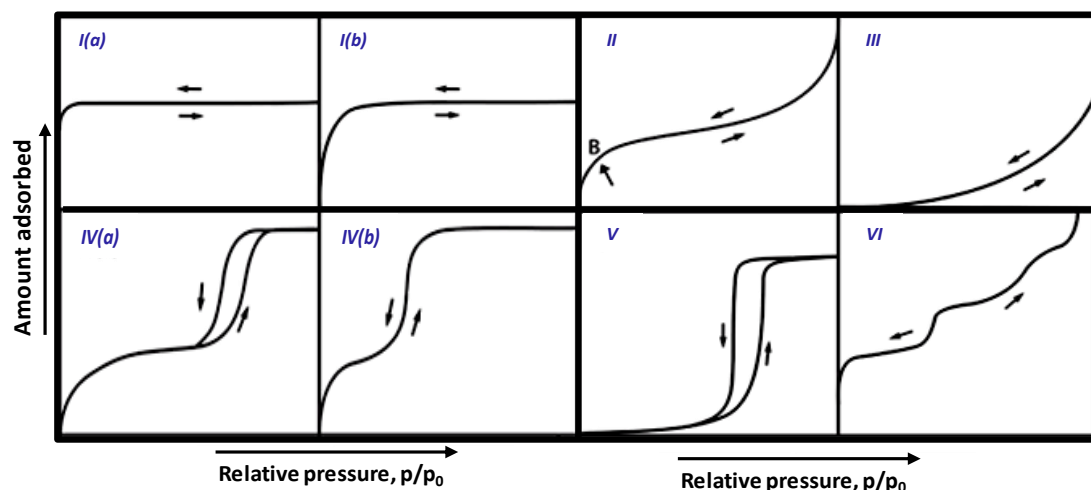


Figure 2.3 IUPAC classifications of adsorption isotherms. Adapted from [Thommes, 2015].

The adsorption isotherms are a graphical representation of amount of gas adsorbed in a solid as a function of relative pressure at constant temperature. The quantity of gas in the adsorption isotherms may be expressed as mass of gas (e.g. grams, mols) or volume of gas (usually expressed in STP, standard temperature and pressure conditions). According to IUPAC, the majority of gas/vapours isotherms may be classified into six groups (Figure 2.3) or their combinations [Rouquerol et al. 2014; Thommes et al. 2015]. Each type of isotherm is associated to a particular mechanism (physical adsorption, chemical adsorption, capillary condensation), thus, the analysis of the experimental adsorption isotherms can provide useful information about the pore structure of the adsorbent and the nature of the gas solid interactions, allowing to draw some conclusions on the porous texture of the analysed material. When an isotherm presents a shape as a combination of several of the proposed shapes, such an isotherm is described as displaying a hybrid or a composite shape.

Type I(a) and I(b) isotherms are characterized by a limiting value of the amount adsorbed, which is reversible and concave to the relative pressure axis. These isotherms are rise steeply at a low relative pressure to reach a plateau, and a high adsorbate-adsorbent interaction is expected. They are commonly obtained for microporous solids presenting high internal surface areas, as is the case for activated carbons and zeolites. Type I(a) isotherms are characteristic of microporous materials having mainly narrow micropores and very small external surface area, whereas Type I(b) isotherms indicate the presence of wider micropores and a certain contribution of mesopores.

Type II isotherms are concave to the relative pressure up to a certain point (Point B), where multimolecular adsorption occurs. If the knee is sharp, the uptake at point B represents the completion of monolayer coverage. This shape of isotherm is common for nonporous or macroporous adsorbents such as clays, pigments, cements. Rouquerol has proposed a subdivision of Type II isotherms depending on the reversibility of the desorption branch [Rouquerol, 2014]: reversible desorption-adsorption Type II(a) isotherm, indicating the normal monolayer-multilayer adsorption on an open and stable surface; and Type II(b) isotherm exhibiting a hysteresis loop (H3) characteristics of inter-particle capillary condensation commonly due to aggregation.

Type III isotherms are convex in the complete range of the p/p_0 axis (there is no point B), which indicates the weak adsorbate-adsorbent interactions, typically on nonporous or macroporous adsorbents. Type IV isotherms are characteristic of mesoporous materials, such as many oxide gels and some molecular sieves. The shape of the initial region of the isotherm is related to Type II, reaching a saturation plateau at high relative pressures. Type IV(a) isotherms exhibit a hysteresis loop associated with the emptying of the mesopores by capillary condensation that occurs when pore exceeds a certain critical width, depending on the adsorption system and temperature. In contrast, Type IV(b) isotherms are completely reversible and are associated to adsorbents having mesopores of small widths. Type V isotherms are convex to the p/p_0 axis and, to a certain pressure value, similar to the isotherms of Type III, indicating relatively weak adsorbent-adsorbate interactions. Although the adsorbate-adsorbent interaction is weak, this type of isotherm occurs on a microporous or mesoporous adsorbent (e.g. water adsorption on microporous carbons). Type VI isotherms, sometimes called stepwise isotherms are associated to layer-by-layer adsorption on highly uniform surfaces. Type VI isotherms are typically obtained for the adsorption of argon or krypton at low temperatures on graphitized carbon blacks.

In this thesis, the textural features of the samples were characterized by measuring physisorption of N_2 at $-196\text{ }^\circ\text{C}$ in a volumetric analyser (Micromeritics). Before the measurements, the samples were outgassed under vacuum at $120\text{ }^\circ\text{C}$ ($2\text{ }^\circ\text{C}/\text{min}$) for 17 h. The adsorption isotherms were used to determine the specific surface area, the total pore volume, the micropore volume and mesopore volume. The mathematical description of each model that used to determine the textural parameters is explained below.

Since it was first developed in the 1930s, the Brunauer-Emmett-Teller (BET) equation has found widespread use to calculate surface areas of all type of materials, and has become one of the most used models for this purpose, and is now the IUPAC gold standard for the characterization of nanoporous materials [Thommes et al. 2015]. Despite of this, it is generally recognized that the theory is based on an oversimplified model of multilayer adsorption and that the reliability of the BET method is questionable unless certain conditions are prescribed.

The BET equation was formulated based on several assumptions, among them: (i) adsorption takes place on an array of fixed sites; (ii) all sites are energetically identical; (iii) no allowance is made for lateral interactions between adsorbed molecules; (iv) the adsorption rate is equal to the desorption rate; (v) the heat of adsorption from the second layer is constant and equal to the vapour condensation heat; (vi) when p is equal to p_0 , the vapour condenses as a liquid and the ordinary number of adsorbed layers is infinite.

The equation is written as follows (Equation 2.7):

$$n(p) = \frac{n_m C_{BET} p}{(p_0 - p) [1 + (C_{BET} - 1) (p/p_0)]} \quad \text{Equation 2.7}$$

where, $n(p)$ is the amount of gas adsorbed at pressure p , n_m is the amount of gas adsorbed required to fill a monolayer surface on the surface of the adsorbent, p_0 is the vapour equilibrium saturation pressure, and C_{BET} is a constant associated to the adsorbate-adsorbent interactions.

The application of the equation requires the determination of the amount adsorbed at the monolayer (n_m). BET equation can be linearized in different forms; in this thesis, the one proposed by Parra [Parra et al. 1995] has been used (Equation 2.8).

$$\frac{1}{n(1-x)} = \frac{1}{n_m} + \frac{1}{n_m C_{BET}} \left(\frac{1-x}{x} \right) \quad \text{Equation 2.8}$$

where, x represents p/p_0

Once the amount adsorbed at the monolayer is determined, the specific surface area (S_{BET}) of the adsorbent is estimated by knowing the area occupied by each molecule; in the case of nitrogen the area is 0.162 nm^2 , assuming that it is adsorbed in a closed-packed system.

BET equation needs to be applied with extreme caution as it may be very difficult to detect the formation of the monolayer from the multilayer adsorption and micropore filling, as well as to locate the linear range of the BET plot. IUPAC has

addressed this concern in a recent review [Thommes et al. 2015], recommending a procedure to overcome this difficulty and to avoid any subjectivity in evaluating the BET monolayer capacity. The procedure is based on various criteria; among them: i) the C_{BET} constant should be a positive value; ii) the application of the BET equation should be restricted to the range where the term $n(1 - p/p_0)$ continuously increases with p/p_0 ; iii) the p/p_0 value corresponding to the monolayer (n_m) should be comprised within the selected BET range.

The total pore volume was calculated as the volume of gas adsorbed at a relative pressure of 0.99, expressed in terms of cm^3/g , using the density of liquid gas to convert the amount of gas adsorbed in STP conditions. In the case of N_2 at -196°C , the equation is as follows (Equation 2.9):

$$V_{\text{Total}}(\text{cm}^3/\text{g}) = V_{\text{gas adsorbed}}(\text{cm}^3/\text{g, STP}) \times 0.00154643 \quad \text{Equation 2.9}$$

2.3.7 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) employing in-lens schottky plus field emission gun (FEG) technology was utilized for high-resolution microstructural characterization of catalyst materials in this investigation. The MERLIN Compact analytical SEM system (JSM-IT810) operated at optimized parameters: 5 kV accelerating voltage and 3.0 mm working distance. Secondary electron imaging was performed using an upper hybrid detector (UHD) combined super hybrid lens (SHL), which could reduce the charging effects. The UHD system, integrating secondary electron (SE) and backscattered electron (BSE) detection capabilities, is specifically engineered for high-resolution imaging of beam-sensitive nanomaterials under low-dose operating conditions. This approach enabled nanoscale visualization of surface morphology while preserving native surface chemistry through non-destructive analysis.

2.4 Photocatalytic degradation of MeP

2.4.1 The source of light

A simulated UV-Vis irradiation (125 W Helios ItalQuartz 900 W/m^2) was used as illumination source. The spectral photon flux distribution, critical for assessing light-matter interaction dynamics, was quantitatively characterized using a calibrated spectroradiometer and is systematically presented in Figure 2.4.

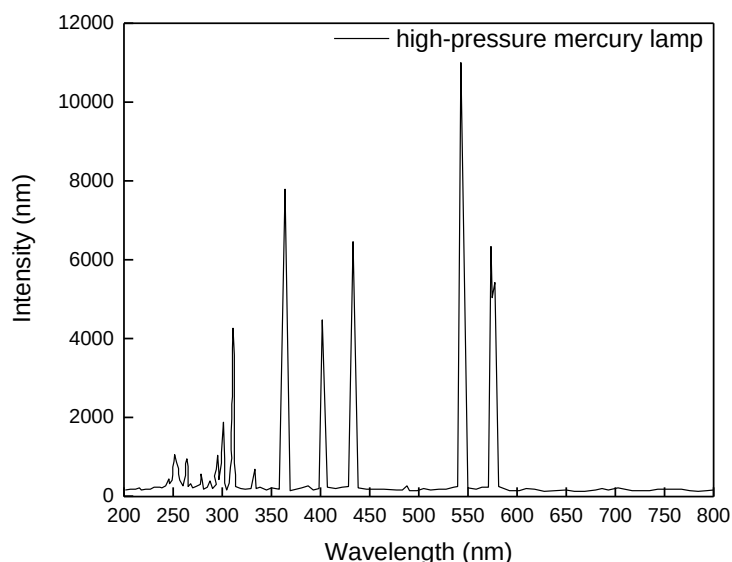


Figure 2.4 Emission spectrum of high-pressure mercury lamp [Gomis Berenguer 2016].

The broadband light source (Hg-Xe arc lamp) generates polychromatic radiation spanning 200–600 nm, exhibiting characteristic emission lines at 253.7 nm (Hg I), 365 nm (Hg I), 435.8 nm (Hg II), and a continuous spectrum >400 nm (Xe plasma). This spectral configuration enables simultaneous investigation of carbon-based materials' photoactivity under both UV-C (200–280 nm), UV-A (315–400 nm), and visible light (400–600 nm) irradiation.

2.4.2 Adsorption under dark conditions

Dark-phase adsorption analysis was systematically conducted to quantify the surface retention capacity of photocatalysts toward methylparaben prior to photoactivation. This critical pretreatment step enables discrimination between pollutant removal mechanisms: physisorption/chemisorption (non-destructive) versus photocatalytic degradation (destructive). Experimental Protocol:

- Catalysts (100 mg/L) were equilibrated with methylparaben solution (50 ppm) in amber vials under constant agitation (500 rpm, room temperature)
- Temporal concentration profiles monitored via UV-Vis spectrometer ($\lambda=255$ nm) for 6 hours

Adsorption saturation thresholds inform optimal catalyst loading to minimize masking effects during photocatalytic evaluations. This methodology provides essential baseline correction for accurate quantum yield calculations in subsequent photodegradation experiments, particularly crucial for carbon-modified catalysts exhibiting high specific surface areas.

2.4.2 Experimental protocol for the photocatalytic assays

The photocatalytic degradation of the methylparaben was carried out at room temperature in 500 ml batch reactor at concentration of 10 ppm after dark adsorption. The mercury lamp, with a double-walled cylindrical quartz jacket, was cooled by flowing water to protect the treated solution from high temperature during the photocatalytic assays, and vertically immersed in the aqueous solution. The catalyst equilibrated in solution in dark conditions for 30 min before starting irradiation to account for the adsorption on the porous catalysts. Then suspension was irradiated for 300 min. By supplying a continuous air flow, an excess of oxygen was supplied during all the photocatalytic processes. Aliquots of the solution were periodically taken out and filtered (0.45 mm nylon filter), then analyzed by reverse-phase HPLC to determine the residual concentration of the pollutant.

The details of HPLC are as follows: C18 column 125 mm $\times$ 4 mm; 45:55 methanol: 28mM phosphate buffer at pH 2.5 as mobile phase; 40 °C of oven temperature; flow rate of 0.7 mL/min; injection volume 10 μ L; photodiode array detector. The degradation of MP without photocatalysts and with the bare graphite carbon nitride were carried out as well. The photodegradation experiments were performed with a fixed loading of the photocatalysts (ca. 0.25g/L). In terms of detection of the intermediates during the photocatalytic reaction, mass spectrometry analyses were performed using an Orbitrap Q Exactive mass spectrometer (mass accuracy <1 ppm RMS, resolution 140,000 at m/z 200), collaborated with ICARE-CNRS. Flow injection analysis (FIA) was employed, utilizing a motorized syringe to continuously introduce samples into the ionization source at a flow rate of 1–3 μ L/min for 1 min. For total organic carbon (TOC) analysis, samples were filtered with 0.45 μ m filters (Whatman, Maidston, UK) and measured in a Shimadzu VCSN TOC analyzer.

In this part study, ultrapure water and distilled water were produced by Millipore Direct-Q system with resistivity 18.2 M Ω .cm and conductivity 0.056 μ S/cm at 25°C. HPLC gradient grade methanol ($\geq 99.9\%$) was purchased from Fisherbrand™. Methyl-paraben (Reagent Plus®, $\geq 99.0\%$, crystalline), sodium phosphate dibasic (Na₂HPO₄), sodium phosphate monobasis (NaH₂PO₄ • 2H₂O) were purchased from Sigma-Aldrich. All of the chemicals what were used in my work are analytical grade without further purification.

Radicals' trapping experiments were conducted to elucidate the mechanistic pathways of photocatalytic activity. Prior to dark adsorption, designated scavengers were introduced into the reactor to mitigate potential catalyst-scavenger interactions. Four specific scavengers were employed in this investigation: isopropyl alcohol (IPA) for hydroxyl radicals ($\bullet\text{OH}$), benzoquinone (BQ) for superoxide radicals ($\bullet\text{O}_2^-$), methanol (MeOH) for holes (h^+), and acetone for electrons (e^-). Scavenger concentrations were systematically optimized through a two-phase protocol: initial low-dose conditions (IPA: 0.17 mM and BQ: 0.09 mM, controlled based on MP concentration (10ppm)), followed by high-dose administration (IPA: 257.32 mM, BQ: 9.25 mM, MeOH: 484.06 mM and acetone: 26.81 mM). To further inhibit $\bullet\text{O}_2^-$ generation, the reactor was purged with helium atmosphere (detailed mechanistic analysis will be presented in Chapter 3). Subsequent experimental procedures strictly adhered to standard photocatalytic testing protocols without scavengers.

2.5 Photoelectrochemical responses

2.5.1 The preparation of electrodes

ITO-coated glass slides ($2.5\text{ cm} \times 1\text{ cm} \times 2\text{ mm}$; geometrical area: 1 cm^2) were employed as conductive substrates for electrode fabrication. Prior to modification, the substrates underwent sequential ultrasonic cleaning in acetone, ethanol, and deionized water (15 min per solvent) followed by thorough drying under ambient conditions.

Electrode fabrication for C₃N₄, BWO, and composite materials involved suspending 200 mg of powdered sample in 2.5 mL of N,N-dimethylformamide (DMF) under 20 min magnetic stirring. Approximately 100 μL of the homogeneous dispersion was deposited via syringe onto pre-cleaned ITO substrates (sheet resistivity: 15–25 Ω/sq) and spin-coated at 2500 rpm for 30 s, following established protocols [Haro et al. 2012]. Sequential layer deposition (three cycles) ensured full ITO coverage, with each layer air-dried for 10 min at ambient temperature. Final thermal processing comprised drying at 100 $^\circ\text{C}$ for 10 h followed by air annealing at 200 $^\circ\text{C}$ for 30 min (ramp rate: 5 $^\circ\text{C}/\text{min}$). The annealing temperature was specifically selected to preserve the carbonaceous components' structural integrity during oxidative treatment. A schematic of the electrode preparation workflow is provided in Figure 2.5.

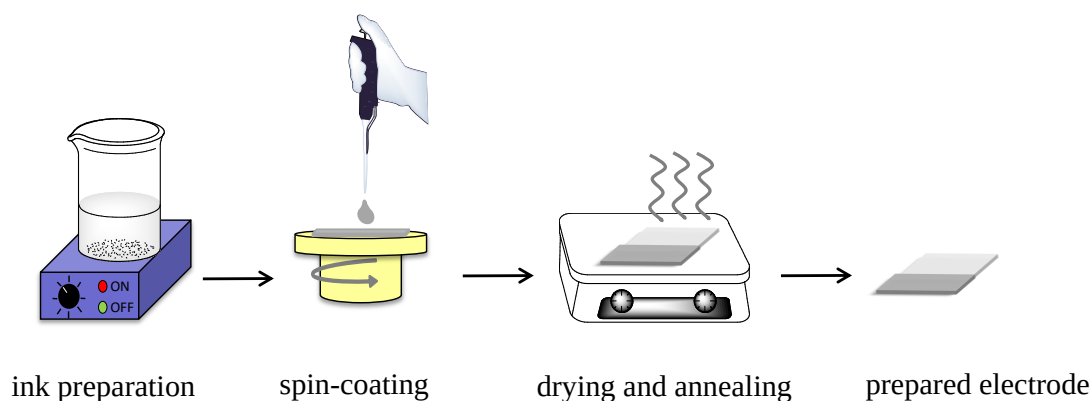


Figure 2.5 Representation of the preparation of electrodes using spin-coating technique on ITO support [Gomis Berenguer 2016].

2.5.2 Photoelectrochemical measurements

Electrochemical characterization was performed using a Biologic VMP3 potentiostat in a standard three-electrode configuration (Figure 2.6). The working electrode comprised the synthesized materials (size: 1cm*1cm) cast onto ITO substrates (size: 1cm*2.5cm), while a graphite rod served as the counter electrode and a solid-state Ag/AgCl electrode functioned as the reference.

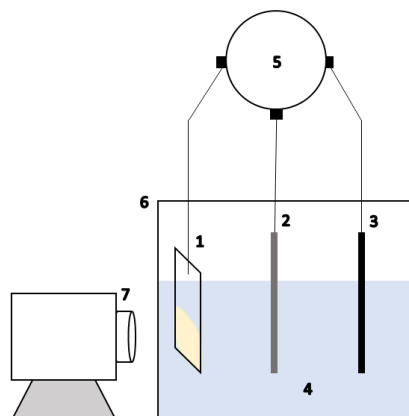


Figure 2.6 Potentiostatic three-electrode experimental set-ups: (1) working electrode, (2) reference electrode, (3) counter electrode, (4) electrolyte solution, (5) potentiostat, (6) quartz cell, (7) light source.

Photoelectrochemical characterization was conducted in 0.5 M Na_2SO_4 electrolyte (50 mL, pH~2) using a three-electrode configuration. Prior to testing, the working electrode was immersed in the electrolyte for 12 h to ensure full wettability, then positioned in a quartz cell at 0.5 cm distance from the light source. A PTFE-insulated platinum connector was employed to isolate the electrode from extraneous illumination effects. Control experiments confirmed negligible background photocurrent (<2% of total signal) from bare ITO substrates under irradiation. All

measurements were performed at ambient temperature ($25\pm 1^\circ\text{C}$) with triplicate testing across multiple electrodes to validate reproducibility (inter-electrode RSD <5%) and repeatability (intra-electrode RSD <3%).

Three complementary electrochemical techniques were employed to evaluate photoresponse characteristics:

(a) Open-circuit potential (OCP) monitoring under dark cycles.

(b) Cyclic voltammetry (CV) measurements versus the Ag/AgCl reference electrode revealed distinct redox potential ranges for the synthesized materials:

- g-C₃N₄: Cathodic/anodic peaks at -0.40 V and +0.55 V
- BWO: Characteristic redox pairs at -0.30 V and +0.70 V
- C₃N₄/CQ 10 wt%: Enhanced charge separation with shifted potentials (-0.40 V, +0.45 V)
- BWO/C₃N₄-10 wt%: Intermediate behavior showing -0.25 V to +0.70 V
- BWO/CQ 10 wt%: Narrowest potential window (-0.175 V to +0.70 V)

(c) Chronoamperometry at fixed bias under modulated illumination.

Cyclic voltammetry

The open-circuit potential (OCP) was monitored before measuring the cyclic voltammetry and chronoamperometry. OCP, known as rest potential or corrosion potential, represents the equilibrium electrode potential established when there is zero net current flow between the working electrode and electrolyte, typically measured under open-circuit conditions without external polarization. In this experimental investigation, the OCP values of the studied electrode materials were systematically recorded after achieving stable electrochemical equilibrium under dark conditions to eliminate potential photoelectrochemical interference, as showed in Figure 2.7.

Cyclic voltammetry (CV), a cornerstone electrochemical characterization technique, employs a triangular waveform potential excitation to probe interfacial redox mechanisms and coupled electron transfer processes. This potential-controlled methodology applies a linearly scanned potential (forward sweep) across the working electrode within a three-electrode configuration while monitoring the resultant faradaic current response. Upon reaching the vertex potential, the scan direction reverses (backward sweep) to complete a full redox cycle, with multiple consecutive cycles typically performed to assess reaction reversibility and electrochemical stability. In photoelectrochemical systems, CV enables critical differentiation between

photo-induced charge transfer phenomena and dark electrochemical processes, providing essential insights into light-driven charge separation efficiency and energy conversion capabilities - key figures of merit for evaluating photoactive materials. The present study acquired cyclic voltammograms using a rigorously optimized potential window (determined through preliminary scans to prevent electrolyte decomposition and minimize parasitic reactions) with a scan rate of 20 mV/s, ensuring sufficient temporal resolution while maintaining quasi-steady-state conditions through multiple measurement cycles.

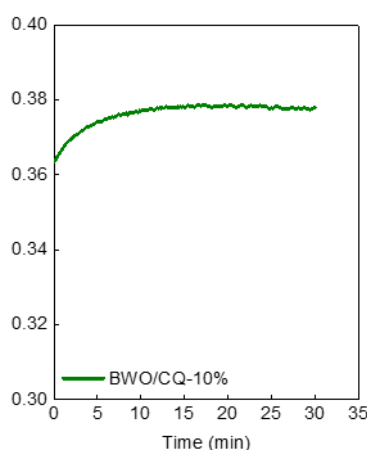


Figure 2.7 the OCP values of the studied electrode material (BWO/CQ-10wt.%) under dark conditions.

Chronoamperometry

Chronoamperometry (CA), a time-resolved potentiostatic technique, involves monitoring the temporal evolution of faradaic and non-faradaic currents under a fixed potential perturbation to elucidate dynamic interfacial phenomena. This methodology enables quantitative assessment of (i) incident photon-to-current conversion efficiency (IPCE), (ii) charge carrier separation-recombination kinetics, and (iii) interfacial charge transfer dynamics of photoexcited species at electrified semiconductor/electrolyte junctions. In this investigation, time-dependent photocurrent profiles were acquired using a standardized three-electrode electrochemical cell under modulated irradiation, with precisely positioned illumination geometry (optically calibrated lamp-to-electrode distance = 0.5 cm). Details of the light sources selected are as follows (see spectrum in Figure 2.8):

(1) LED 340 nm (Thorlabs M340L4): nominal wavelength of 340 nm, minimum output power 53 mW, maximum irradiance 0.22 mW.

(2) LED 470 nm (Thorlabs M470L3): nominal wavelength of 470 nm, minimum output power 650 mW, maximum irradiance 2.19 mW.

(3) LED cold white (Thorlabs MCWHP1): color temperature of 6500 K, minimum output power 2350 mW, maximum irradiance 4.13 mW.

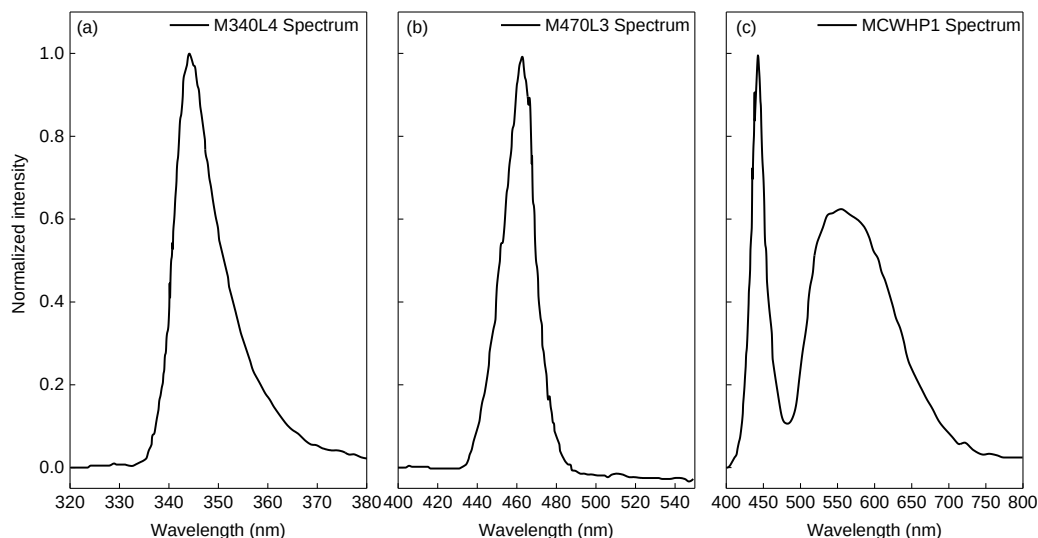


Figure 2.8 Emission spectrum of the light sources selected (a) 340nm; (b) 470nm and (c) cold white.

Experimental protocols followed a sequential dark/light activation procedure: application of predetermined onset potentials → dark current stabilization (1 min) → controlled irradiation cycles (1 min light ON/OFF intervals). The observed current transients exhibited characteristic non-faradaic charging behavior (double-layer capacitance current) during potential step application, decaying exponentially to steady-state faradaic current. Photoinduced current generation manifested as bias-dependent anodic/cathodic responses, with onset potentials correlating to the material's flat-band potential (V_{fb}), a critical parameter determining depletion layer formation and recombination suppression efficacy.

To explore the electron-hole separation mechanism, different scavengers were added to the electrolyte. The volume of electrolyte is 50 ml (one tenth), so the scavengers' concentrations were controlled based on the setup in photocatalytic reaction (showed in 2.4.2 section). We played the photocurrent by changing the scavengers, as showed: benzoquinone (BQ) for superoxide radicals ($\bullet O_2^-$), MeOH and KI [Li et al. 2017; Li et al. 2023] for holes (h^+), and acetone for electrons (e^-). Two kind hole scavengers were used in this section. The KI solution was controlled at 0.06 mM. For each scavenger, the experimental protocols followed a sequential dark/light

activation procedure: application of predetermined onset potentials → dark current stabilization (1 min) → controlled irradiation cycles (1 min light ON/OFF intervals for three cycles) → add the scavenger → dark current stabilization (1 min) → controlled irradiation cycles (1 min light ON/OFF intervals for three cycles).

Chapter 3. Photocatalytic activity of carbon/carbon heterojunctions for the degradation of MeP

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In this chapter, the photocatalytic activity of binary carbon-carbon photocatalysts, by blending nanoporous carbons with carbon semiconductor g-C₃N₄ (CN), have been prepared and explored for the photocatalytic degradation mechanism of methyl paraben (MeP) from aqueous solutions. As described in chapter 2, the preparation of the binary carbon-carbon photocatalysts was made by a hydrothermal method, using CN and increasing concentrations of the nanoporous carbon (CQ) from 2-10 wt.% (samples labelled as CN/CQ-x wt.%, where x stands for the amount of nanoporous carbon). The characterization of the optical, structural and textural properties of the prepared materials will be first introduced and discussed, to finally correlate it with the photocatalytic activity for the degradation of methylparaben under artificial UV-VIS light. In addition, the photocatalytic degradation mechanism of the CN/CQ photocatalysts was further explored by performing photocatalytic assays and an advanced electrochemical characterization in the presence of chemical scavengers.

3.1 Characterization of the CN/CQ samples

The X-ray diffraction patterns of the prepared samples are shown in Figure 3.1 (a-f). The pattern of the carbon nitride showed two clear peaks corresponding to (210) and (002) lattice planes (peaks indexed to reference NO.00-066-0813 in the ICDD (International Centre for Diffraction Data), characteristic of the orthorhombic geometry and lattice parameters of $a=16.4\text{Å}$, $b=12.4\text{Å}$, $c=6.49\text{Å}$ and $\alpha = \beta = \gamma = 90^\circ$. The sharp, well-defined diffraction peak at 27.46° corresponds to the (002) plane and it has been associated to the interlayer stacking of aromatic structures with a graphitic-like structure in carbon nitrides [Li et al. 2023a; Yang et al. 2018]. A second peak (less intense) at 12.93° is ascribed to the (210) plane and associated to parallel chains of tri-s-triazine units [Fina et al. 2015]. The d-spacing for the (002) and (210) planes are 0.33 and 0.68 nm, respectively. To evaluate the impact of the hydrothermal treatment in the structure of bulk carbon nitride, a control sample -sample CN(H)- was prepared by exposed the latter to the hydrothermal treatment conditions used in the preparation of the composites, but in the absence of the carbon additive CQ. The XRD profile show in Figure 3.1b shows small differences between CN(H) and CN concerning the width of the main 210 peak (position remained unchanged) that become narrower (smaller FWHM value) after the hydrothermal treatment, indicating a larger crystallite size. Similar observations reported in the literature have been

attributed to the appearance of network defects and grain boundaries during the hydrothermal treatment [Pazouki et al. 2021]. A small diffraction peak at 10.9° appeared after the hydrothermal treatment in all the samples (CN(H) and the CN/CQ composites). We did not find the peak assigned to any relevant compound (melamine or different structures of C_3N_4), and that it could be attribute to to an impurity.

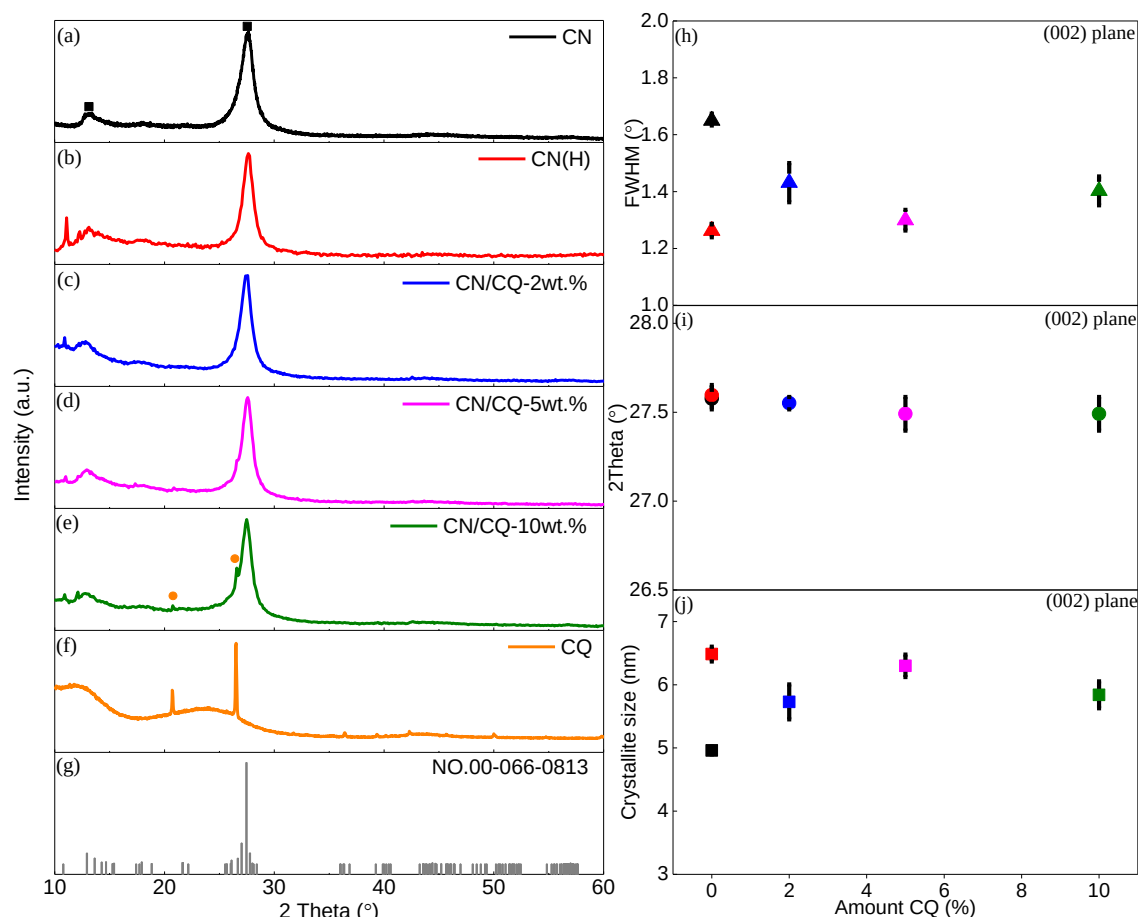


Figure 3.1 (a-f) XRD patterns of the prepared samples compared to the pattern of the structure NO.00-066-0813 identified in the database as showed in (g); (h-j) correlation between crystallographic parameters - FWHM, 2θ and crystallite sizes of (002) plane- and the amount of nanoporous carbon incorporated in the composites.

The incorporation of the CQ additive brought about minor modifications in the XRD profiles. As seen, the intensity of peak (210) gradually decreased with increasing the amount of nanoporous carbon CQ increasing, which suggests that the particles of sample CQ prevent the stacking of CN to some extent [Aboubakr et al. 2020] and the in-plane network is gradually destroyed [Shi et al. 2022]. Additional diffraction peaks characteristic of amorphous carbons at 20.70° and 26.52° (that can also be observed in pristine CQ) were noticeable only in sample CN/CQ-10wt.%. The narrow peaks in the profile of carbon CQ at assigned to the inorganic content (mainly

silicon oxide and aluminum oxide) of the nanoporous carbon [Velasco et al. 2013]. The low content of carbon CQ in the other two composites may be the reason why these are not observed in the latter. Similar observations regarding the lack of the characteristic peaks of the carbon additive in composites with a low amount of the latter have been reported for g-C₃N₄ modified by carbon quantum dots (CQDs) [Wang et al. 2021].

The Figure 3.1 (h-i) shows the correlation between the amount of CQ and the main structural parameters calculated from the XRD patterns (such as 2θ position and full width at half maximum (FWHM) of the mean diffraction peak and crystallite size). Overall, it can be concluded that the incorporation of the CQ does not modify the lattice structure of carbon nitride. The minor structural modifications in the lattice of carbon nitride would seem to be mainly due to the hydrothermal treatment itself and not to the amounts of sample CQ, since they are also observed in the control sample CN(H). The position of the main peak remained constant with the incorporation of sample CQ, and the crystallite size slightly increased with the amount of CQ, compared to sample CN(H).

The optical properties of carbon nitride and the CN/CQ composites were collected by UV-visible diffuse-reflectance spectra within the range of 200-800 nm (Figure 3.2(a)). The reflectance spectrum of carbon nitride aligns with previously reported data for this material in the literature [Kumar et al. 2018; Zhu et al. 2021; Dong et al. 2014]. As displayed in Figure 3.2(a), the profile of carbon nitride shows the strong adsorption edge for each material between 400-500 nm, indicating the high absorption of this material in the visible light region. The profile of sample CN(H) was similar to that of CN, with a small blueshift in the absorption edge indicating somewhat modified absorption features in the visible light. The corresponding bandgaps of both samples, estimated from the Tauc graphical representation (Figure 3.2(b)) were 2.83 and 2.95 eV for CN and CN(H), respectively. This change after the hydrothermal treatment of carbon nitride could be assigned to the small changes in the crystalline structure of the material (i.e., the crystallite size of CN(H) -ca. 6.49 nm- was larger than that of pristine CN -ca. 4.96 nm-), as also reported for other semiconductors [Peng et al. 2018; Klubnuan et al. 2016].

For the CN/CQ composites, the reflectance profiles showed the edge of carbon nitride, and a sharp decrease in the signal between 500-800 nm as the amount of CQ was increased. This behavior is attributed to the absorption of visible light of the

nanoporous carbon additive [Gesesse et al. 2020]. The estimation of the bandgap values in the composites showed values similar to those of the pristine semiconductor, demonstrating that the incorporation of the nanoporous carbon additive does not modify the bandgap of carbon nitride.

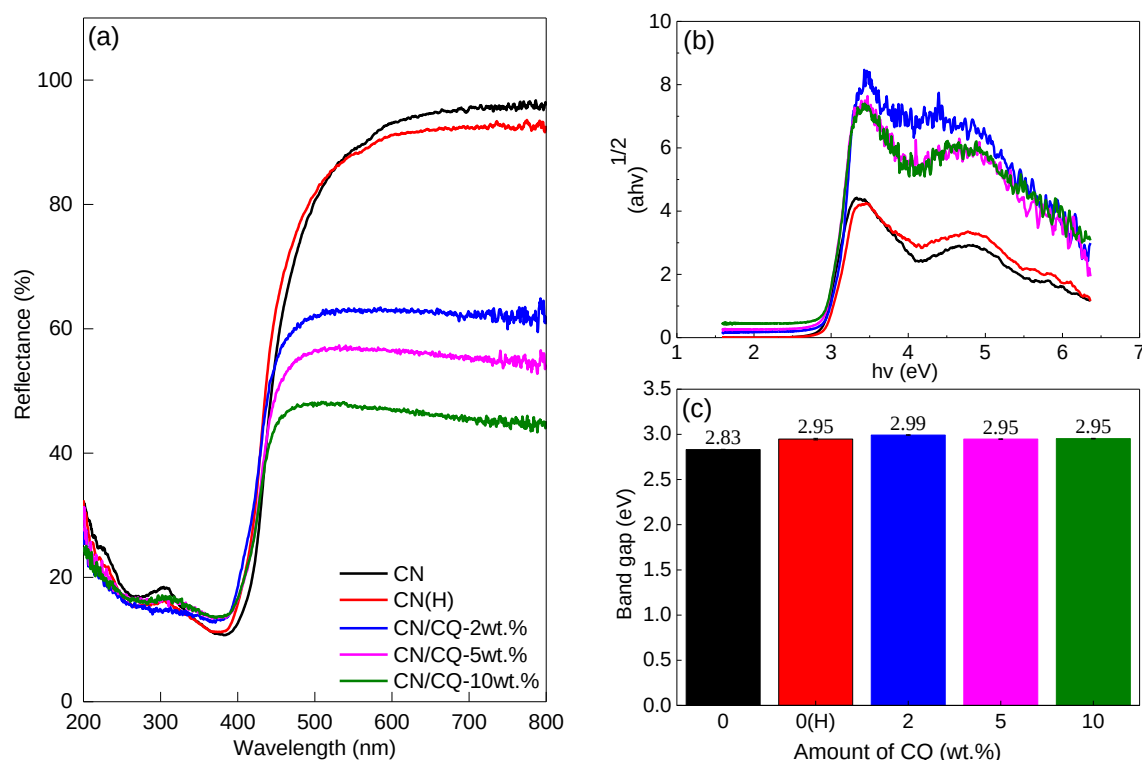


Figure 3.2 (a) Diffuse reflectance spectra and (b) Tauc graphical representations for the composites; (c) evolution of the calculated bandgap with the amount of CQ in the composites.

The porosity of the photocatalysts was analyzed by N_2 adsorption-desorption isotherms (Figure 3.3(a)). The carbon material used as additive of carbon nitride has a well-developed porous network in the micropore range, as seen the characteristic type I nitrogen adsorption isotherm according to the IUPAC classification [Thommes et al. 2015]. For carbon nitride, the nitrogen adsorption isotherm displayed a type II shape indicative of materials with a low porosity. The amount of gas adsorbed is very low up to relative pressures of 0.8, increasing exponentially at larger relative pressures. This indicates the presence of mesopores.

The hydrothermal treatment of carbon nitride slightly modified the porosity, with higher amounts of gas adsorbed in the whole range of relative pressures, and spanning the hysteresis loop into a wider range of relative pressures (from 0.7 to 0.5). This is indicative of the presence of a wider mesopore network after the hydrothermal treatment (most likely due to an expansion of the lattice at nanometric scale), in

agreement with the increased surface area and pore volumes. Similar features were observed for the composites, with a gradually higher amount of gas in the low relative pressure range inherited by the microporosity of the nanoporous carbon additive. This is in line with the increased volume of micropores with the amount of CQ (Figure 3.2d).

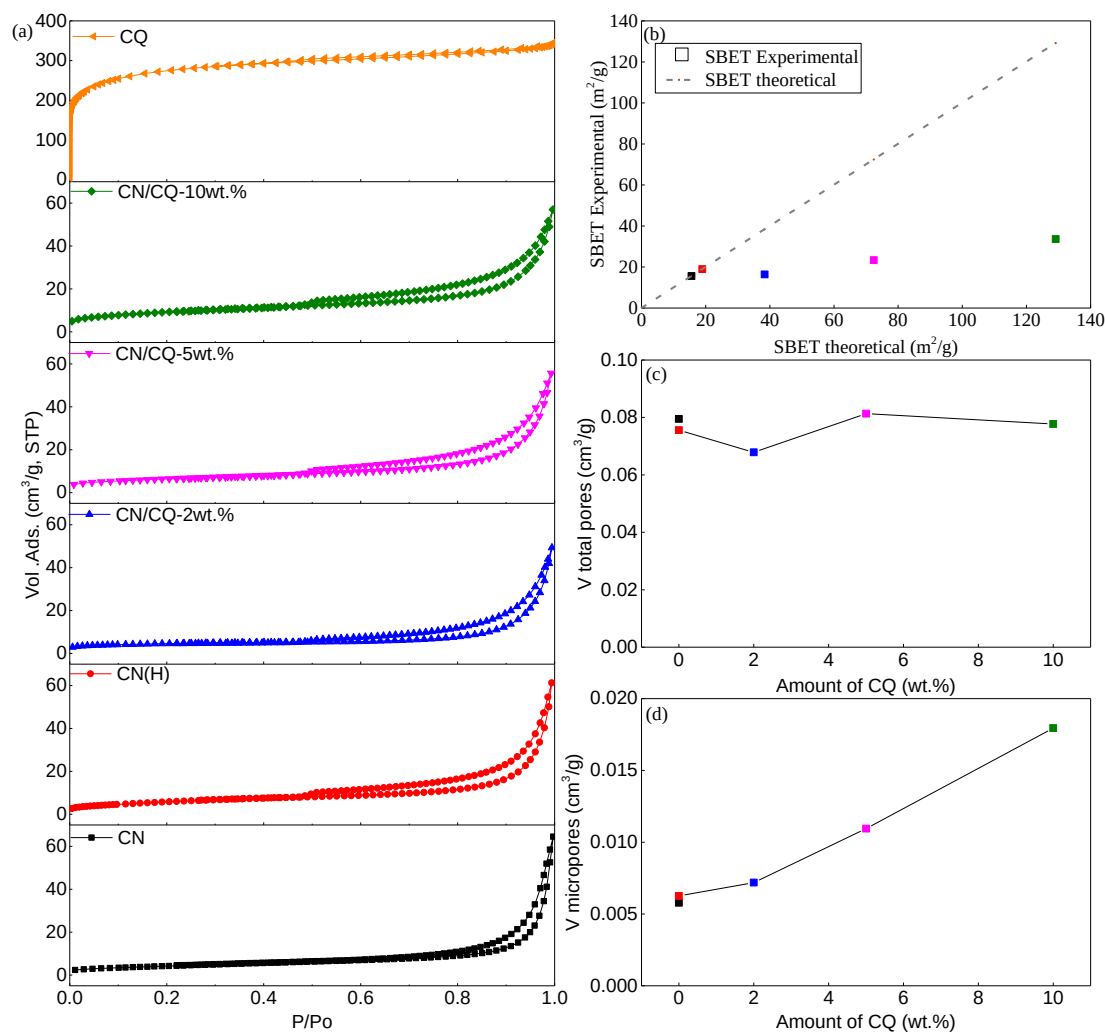


Figure 3.3 (a) N_2 adsorption isotherms at $-196\text{ }^{\circ}\text{C}$ of the prepared photocatalysts; Correlation of (b) the experimental and theoretical specific surface area; (c) Evolution of the total pores volume (d) and the volume of micropores vs the amount of CQ in the composites.

To evaluate the impact of the synthetic method on the porosity of the resulting composites, the specific surface area obtained from the nitrogen adsorption isotherms was further analyzed considering the rule of the mixtures. The theoretical specific surface area was calculated considering the composition of the CN/CQ composites and compared to the experimental values (Figure 3.3b). As seen, the predicted surface

areas calculated by a general mixing rule are smaller than the experimental values for all the samples (all the points are below the bisector line), indicating that the porosity inherited by the nanoporous carbon additive is not fully accessible in the composites (by nitrogen probe at -196 °C). In other words, that the fraction of pores present in the composites due to the amount of CQ additive are somehow blocked by the matrix of the carbon nitride. This indicates that the distribution of CQ in the composites does not take place in the external surface (where all the pores would be accessible, as in composites prepared by physical mixture), but rather located within the layers of carbon nitride. This is in agreement with the observations of the XRD profiles. The CN/CQ composites displayed increasing volume of micropores (yet below the theoretical values based on the composition) and the total pore volume followed a constant trend with the amount of CQ incorporated in the composites. This confirms that the latter parameter is defined by the matrix of carbon nitride (the major component in the composites).

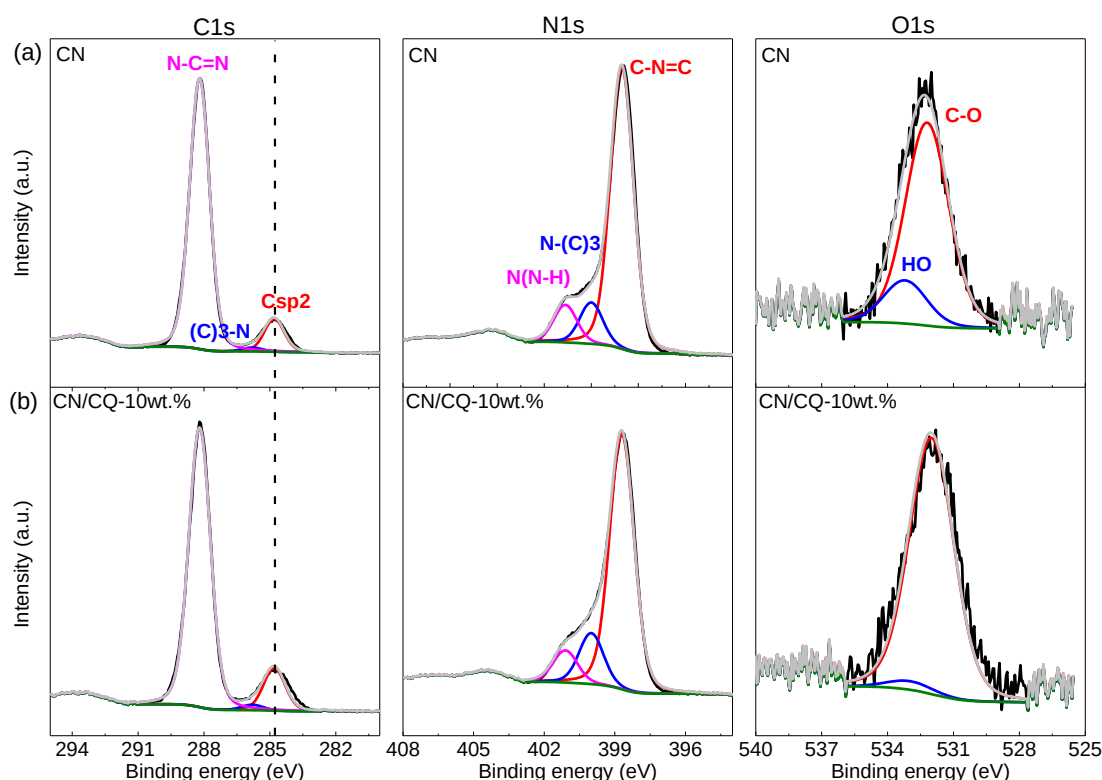


Figure 3.4 XPS analysis of C1s, O1s and N1s high resolution spectra for (a) CN and (b) CN/CQ-10wt.% composite.

The surface chemical composition of bare CN and the composite with the highest amount of carbon additive (sample CN/CQ-10 wt.%) were further investigated by XPS. The XPS survey spectra (Figure S1 in Annex I) confirmed the

presence of C, N, and O elements. In the case of C element, the C1s peak exhibits relatively high intensity and corresponds to the lowest binding energy, which is also observed for N1s and O1s. The high-resolution spectra of C1s, N1s and O1s core levels of bare CN and both selected samples are shown in Figure 3.4. The signal of the C1s core level was deconvoluted into various components at 284.8 eV (Csp²), 285.8 eV ((C)₃-N) 288.2 eV (N-C=N). In the case of N1s core level, three chemical states assigned to C-N=C (398.7 eV), N-(C)₃ (400.0 eV) and N(N-H) (401.1 eV) were found in both samples. For the O1s spectra, peaks centered at 532.2 and 533.2 eV, are assigned to the C-O and O-H, respectively. All these assignments are consistent with previously reported results for carbon nitride [Caudillo-Flores et al. 2021; Li et al. 2023b; Meng et al. 2021].

Table 3.1 Atomic concentrations, relative abundance and binding energy of the main components obtained from the deconvolution of the C1s and N1s core levels of sample CN and CN/CQ-10wt.%.

		CN			CN/CQ-10wt.%	
Component		B.E. (eV)	Atomic Concentration (at.%)	Relative abundanc ce (%)	Atomic Concentration (at.%)	Relative abundanc e (%)
C1s	Csp2	284.8		4.54		5.71
	(C) ₃ -N	285.8	42.51	0.54	43.96	0.73
	N-C=N	288.2		37.42		37.51
	C-N=C	398.7		43.43		39.76
N1s	N-(C) ₃	400.0	55.59	6.38	52.72	7.95
	N(N-H)	401.1		5.79		5.01
	C-O	532.2		1.57		3.21
O1s	O-H	533.2	1.90	0.33	3.32	0.11
Atomic C to N ratio			0.76	--	0.83	--

Table 3.1 displays the atomic concentration (at.%), relative abundance (%), and carbon to nitrogen atomic ratio of the main components obtained from the analysis of the C1s and N1s core levels in the XPS spectra of samples CN and CN/CQ-10wt.%. As expected, the carbon to nitrogen atomic ratio of sample CN/CQ-10 wt.% (ca. 0.83) is higher than that of sample CN (ca. 0.76, being the theoretical value for carbon

nitride of 0.75) owing to the incorporation of the carbon additive. A similar behavior is observed in the increase in the Csp² component, since the nanoporous carbon additive is mainly composed of aromatic carbon atoms. In contrast, the calculated mass percentage concentration of carbon was rather similar for both samples (ca. 38 and 40 wt.% for CN and CN/CQ-10wt.%, respectively). While this could attribute to the low amount of CQ in the composite, it also indicates that the carbon additive is not accumulated in the external surface of the hybrid photocatalysts, but would be rather dispersed in the bulk.

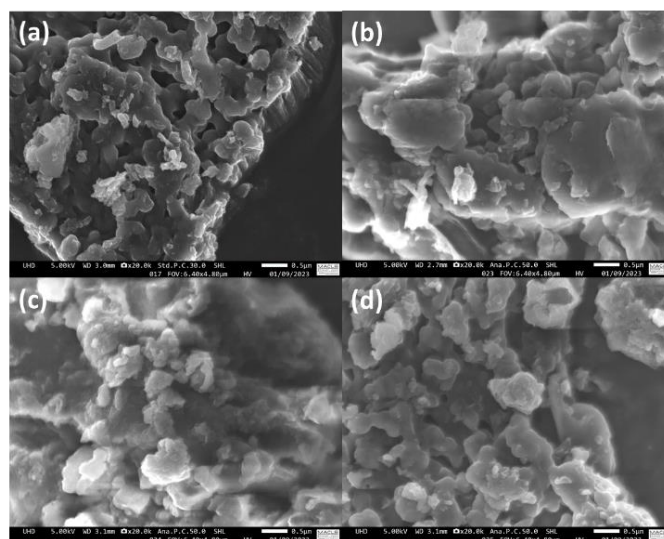


Figure 3.5 SEM images of samples (a) CN; (b) CN(H); (c) CN/CQ 2wt.%; (d) CN/CQ 5wt.% (magnification 0.5 μ m).

Selected SEM images of the prepared composites are shown in Figure 3.5. All the images show similar globular particles corresponding to the carbon nitride [Huang et al. 2019; Pan et al. 2022], with no evidences of a second matrix (i.e., particles of the carbon additive CQ). The images also show that the hydrothermal of the bulk carbon nitride did not affect its morphology.

3.2 Photocatalytic activity of CN/CQ series samples

3.2.1 Role of the carbon additive in the photocatalytic system

Due to the above-mentioned differences in the porosity among the CN/CQ composites, the dark adsorption of the target pollutant was initially evaluated for all the samples (before the photocatalytic assays). The aim was to determine the amount of methylparaben removed by adsorption in the porosity of the photocatalysts (in the absence of light, thus to discriminate the adsorption from the photodegradation

reaction).

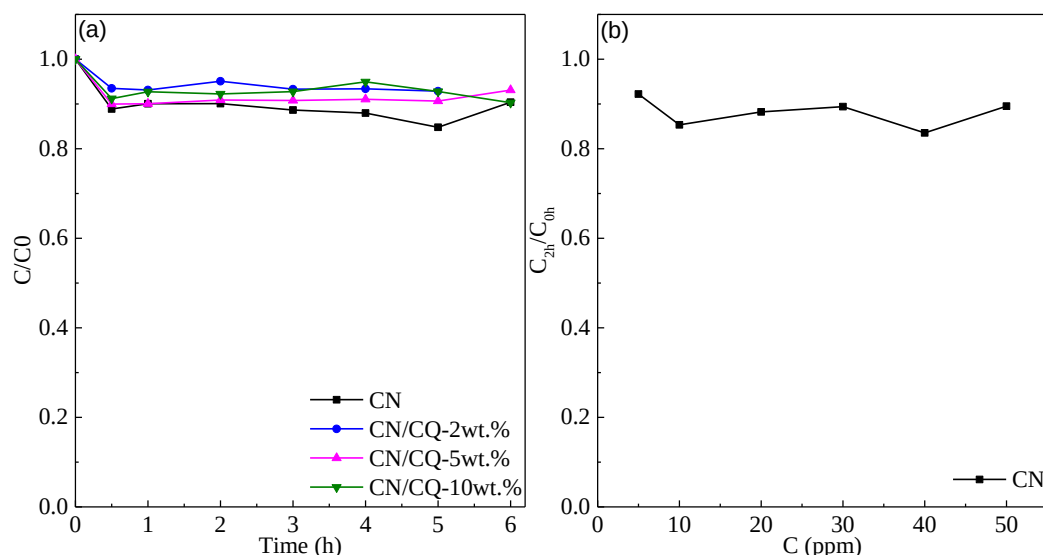


Figure 3.6 (a) Kinetics of adsorption of MP on catalysts of the series CN/CQ materials; (b) Kinetics of adsorption of MP on CN catalyst of the series concentration of MP.

Figure 3.6 (a) shows the kinetic profiles for the adsorption of a solution of methylparaben of 50 ppm of initial concentration, in contact with 20 mg of the photocatalysts (in the dark). As seen, the kinetics of the adsorption under the assayed conditions is fast, reaching the equilibrium after 30 minutes. All the samples displayed a similar drop in the concentration of methylparaben (ca., 10 %) regardless the amount of CQ in the composites. This contrast with the trend of the volume of micropores (i.e., the active sites for the adsorption of methylparaben in porous carbons), but is in line with the observations of a partial blockage of the porosity of CQ in the composites. The adsorption kinetics in the dark of various concentrations of methylparaben in contact with 20 mg of CN is displayed in Figure 3.6 (b). As we could see, a similar drop in the concentration of methylparaben (ca., 10 %) is observed for all the concentrations.

As indicated in the experimental section (Chapter 2, section 2.4.3), and based on the data about the uptake in the dark, the initial concentration of methylparaben in the photocatalytic assays was recalculated in order to have a similar amount (10 ppm as controlled) in all the systems after a 30 minutes equilibration in the dark. This allows a straightforward comparison of the experimental data in all the samples (neglecting differences in the rate of adsorption and/or rate of photolysis with the initial concentration of the pollutant).

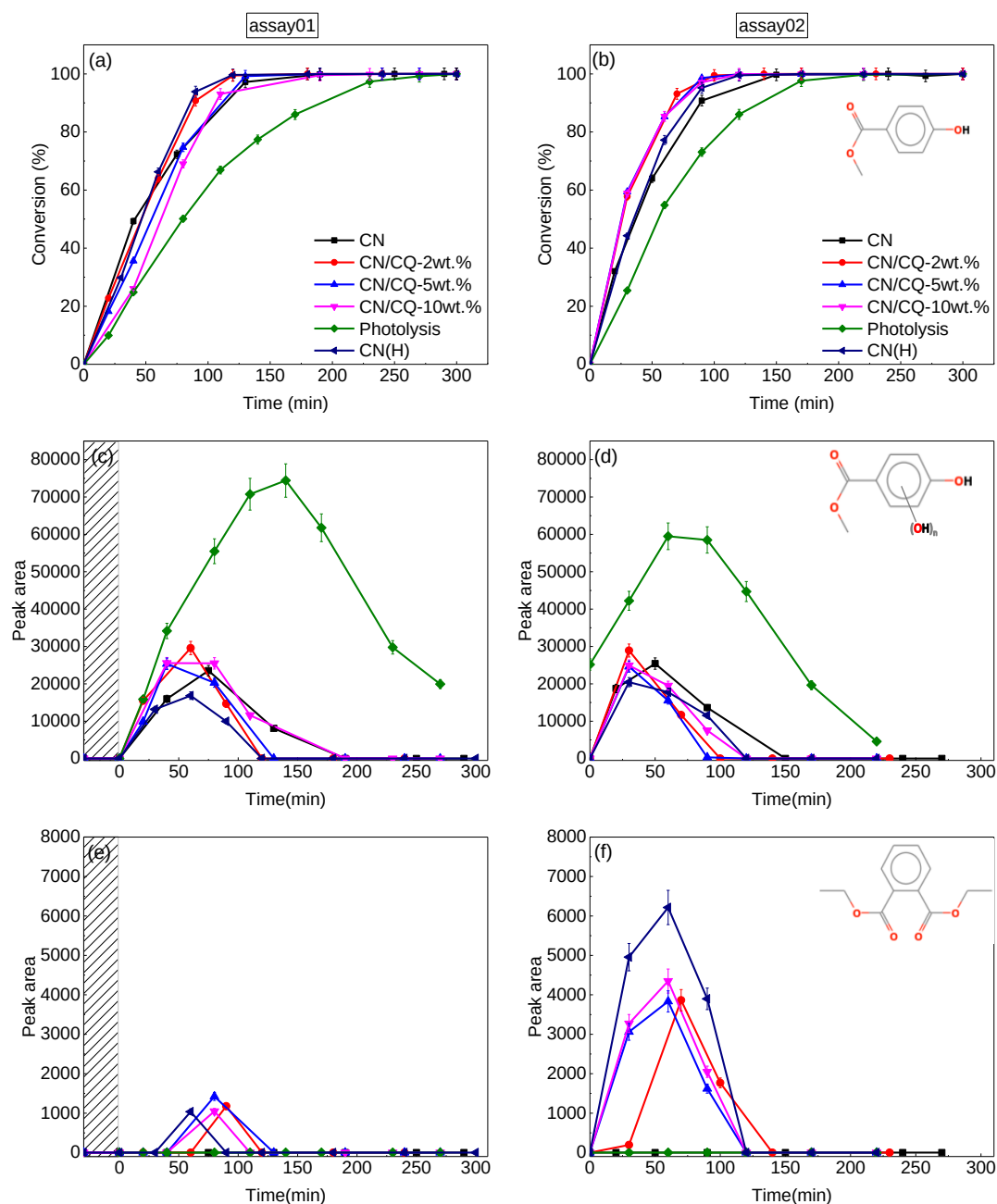


Figure 3.7 (a, b) Conversion of methylparaben during two consecutive photocatalytic assays; (c-f) evolution of the photodegradation intermediates detected by HPLC.

Figure 3.7a shows the conversion of methylparaben with the irradiation time on the series of prepared photocatalysts, compared with the photolytic reaction (i.e., absence of catalyst). Data corresponding to the chromatographic peaks detected by HPLC and corresponding to degradation intermediates are shown in Figure 3.7 (b,c). The conversion of methylparaben in the photolytic reaction is relatively high for the lamp used in our study, as seen by the conversions of ca. 50 and 100 % reached after 90 and 300 minutes of illumination.

The full conversion of methylparaben during the photolysis is not accompanied by the degradation of the intermediates, as seen in the evolution of the areas of the peaks corresponding to those intermediates detected by HPLC (Figure 3.7c). This indicates that the photolytic reaction is not efficient for the full degradation of methylparaben and intermediates. The conversion of methylparaben is largely accelerated upon the use of carbon nitride (both samples CN and CN(H)), reaching a full conversion after ca. 180 min of irradiation. The amount of intermediates is also much lower than for the photolytic reaction, indicating the more efficient performance of these materials. The hybrid CN/CQ photocatalysts also outperformed the photolytic reaction, reaching the full conversion of methylparaben after 120 min for sample CN/CQ-2wt.% and 150 min for the rest of the series of the composites. Interestingly, the profiles of the photodegradation intermediates are lower for the composites with 5 and 10wt.% of the carbon additive; for all the samples no intermediates were detected after 150 min of irradiation.

HPLC coupled to mass spectrometry revealed that the intermediates corresponded to polyhydroxylated derivatives of methylparaben: di-hydroxymethyl paraben and tri-hydroxymethyl paraben (m/z 167, 183, 199) and diethyl phthalate (m/z 222). The photocatalysts were used in a consecutive photocatalytic assay (assay 02 in Figure 3.7), and data showed that the performance decreased (compared to the first assay) for the carbon nitride, but all the CN/CQ composites showed a better performance than CN and compared to the first cycle, both in terms of conversion of methylparaben and intermediates. However, it should be mentioned that higher fractions of diethyl phthalate (m/z 222) intermediate were found in the second photocatalytic assay, despite it was no longer detected after 120min.

In order to compare the photocatalytic performance for these materials, the rate constant (k_{app}) was calculated by fitting the experimental data to the first-order kinetics mechanism. In my work, the degradation rate of methylparaben was independent of the initial concentration of the pollutant (between 5-10 ppm; see Figure S2 Annex I). But, we found the rate constant showed a similar kinetic trend (see Figure S3 Annex I). Figure 3.8 shows the values of the rate constants obtained for the studied photocatalysts. As expected, the degradation rate constants of methylparaben were higher when photocatalysts were used (compared to the photolytic reaction), and also higher for the CN/CQ composites (compared to bare carbon nitride). The effect was more pronounced for the second photocatalytic assay.

No clear correlation was observed between the rate constant of methylparaben and the amount of CQ in the composites (Figure 3.8b). Interestingly, the constant rates corresponding to the appearance of the intermediates (Figure 3.8 c,d) followed different trends with the amount of carbon additive.

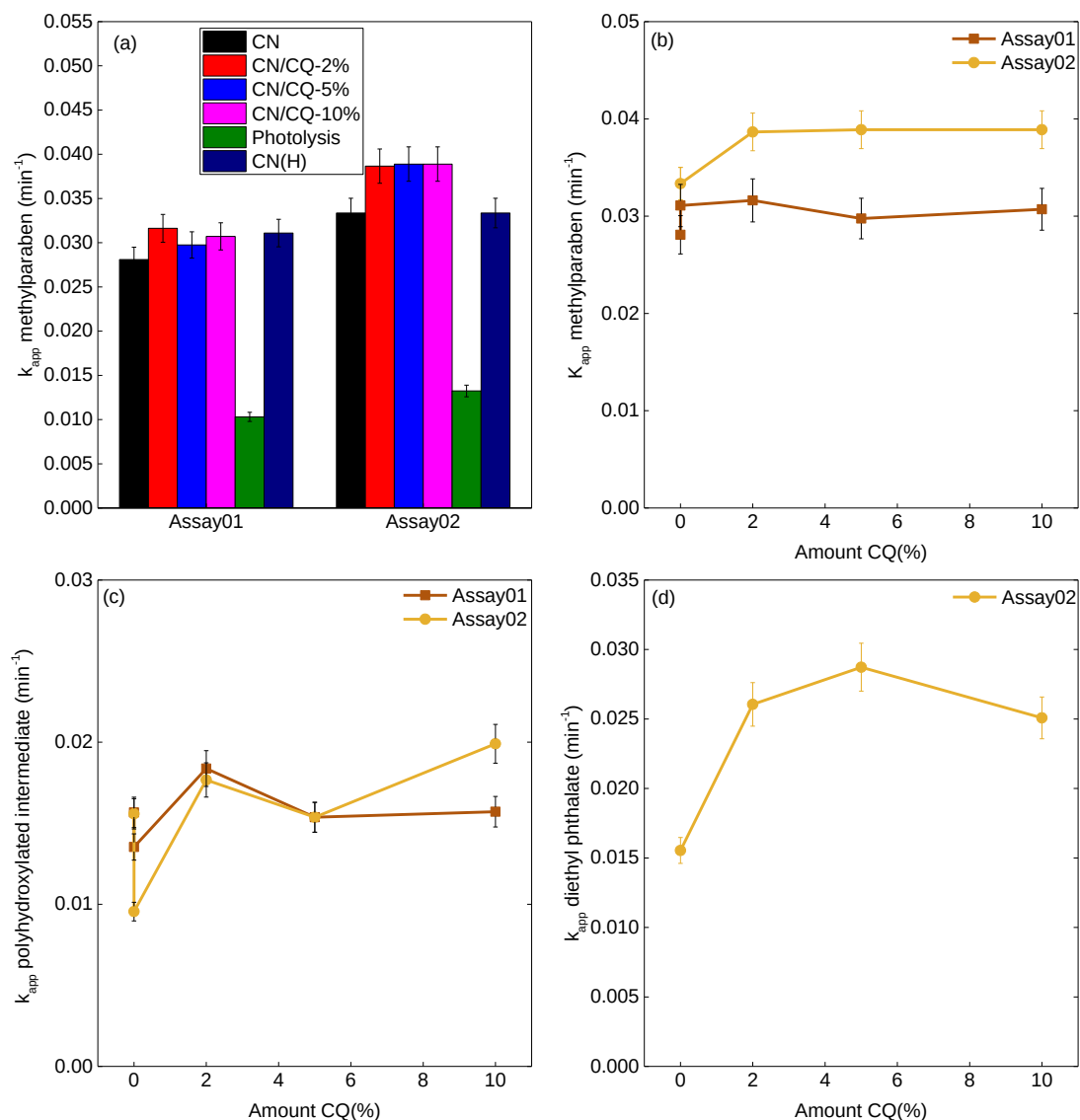


Figure 3.8 (a,b) Degradation rate constant of methylparaben in the two consecutive photocatalytic assays; (c,d) Degradation rate constants of the (c) polyhydroxylated intermediates and (d) diethyl phthalate.

The rate constant for the formation of the polyhydroxylated intermediates, decreased with the amount of carbon additive present in the composite for the first assay, and showed a similar value for the second assay. On the other hand, the degradation rate constant of the diethyl phthalate (observed higher amount in the second cycle) showed an increasing trend with the amount of CQ, indicating that the

incorporation of the nanoporous carbon accelerates the degradation of this intermediate. This improved performance in the second consecutive assay possibly could be attributed to increased surface hydroxylation of the catalyst during recycling, which enhances the adsorption capacity or light absorption properties. In our previous work about C_3N_4/MoO_3 composite [Imgharn et al. 2024], we found that the O-H component fraction increased significantly after three cycles. Alternatively, the photocatalyst has a reduced particle size and improved dispersion over multiple uses, thereby increasing the effective surface area.

3.2.2 Role of the carbon additive in the photocatalytic mechanism

3.2.2.1 Optimization of the dose of chemical scavengers of $\bullet OH$ and $\bullet O_2^-$

It is widely known that the formation of oxygen radical species (such as $\bullet OH$ and $\bullet O_2^-$) plays an important role in most photocatalytic processes for the degradation of a variety of pollutants [Ghattavi et al. 2020; Samsudin et al. 2020; Bresolin et al. 2020; Yang et al. 2016; Foroughipour et al. 2023; Chen et al. 2017; Muñoz-Flores et al. 2022; Yang et al. 2023; Zhao et al. 2014]. Thus the determination of the density of radicals species formed during the irradiation of different photocatalysts has become an interesting tool to elucidate changes in reaction mechanisms. However, recent studies have raised concerns about the usefulness of the use of chemical scavenger for this purpose, due to the occurrence of interference reactions, lack of specificity and the use of (often) optimized operating parameters inspired/inherited from other works based on different semiconductor systems [Puga et al. 2024; Schneider et al. 2020]. Taking this into account, in this PhD thesis we have first proceeded to optimize the protocol concerning the use of chemical scavengers of radical species frequently reported in the literature. Based on this literature search, we have selected isopropanol (IPA) as scavenger of hydroxyl radicals, and benzoquinone (BQ) as scavenger of superoxide radicals literature [Muñoz-Flores et al. 2022; Puga et al. 2024; Schneider et al. 2020].

According to the literature, hydroxyl radicals react with IPA through hydrogen abstraction reactions involving alkoxy radicals and carbon-centered radicals [Ding et al. 2023; Frias Batista et al. 2019]. On the other hand, BQ reacts with superoxide radicals at neutral pH [Fónagy et al. 2021; Schneider et al. 2020; Puga et al. 2024], but it can act as direct electron scavenger through the formation of hydroquinone at sufficiently high concentrations (ca. above 2 mM) [Fónagy et al. 2021], and be

photodegraded by hydroxyl radicals produced in the photocatalytic reaction. Thus, BQ is suitable as scavenger of oxygen radical species and electrons, but not exclusively for the quantification of superoxide radicals [Zamadar et al. 2013; Rao et al. 1973; Schuchmann et al. 1998; Sonntag et al. 2004].

Based on the above, we have explored two doses of scavengers, which correspond to values commonly reported in the literature: namely 0.17 and 257 mM for IPA (ca. 3 and >4000 times higher than the amount of methylparaben to be degraded: i.e., 0.066 mM) and 0.09 and 9.25 mM for BQ (ca. 1.5 and > 140 times higher than the amount of methylparaben to be degraded). It should be noted that the amount of photocatalyst was 0.25 g/L, that corresponds to ca. 4.4 mM for C_3N_4 and 0.6 mM for Bi_2WO_6 . Thus, higher than the lowest dose of scavenger (assuring an excess of photogenerated species) and lower than the highest dose of scavenger (assuring an excess of scavenger).

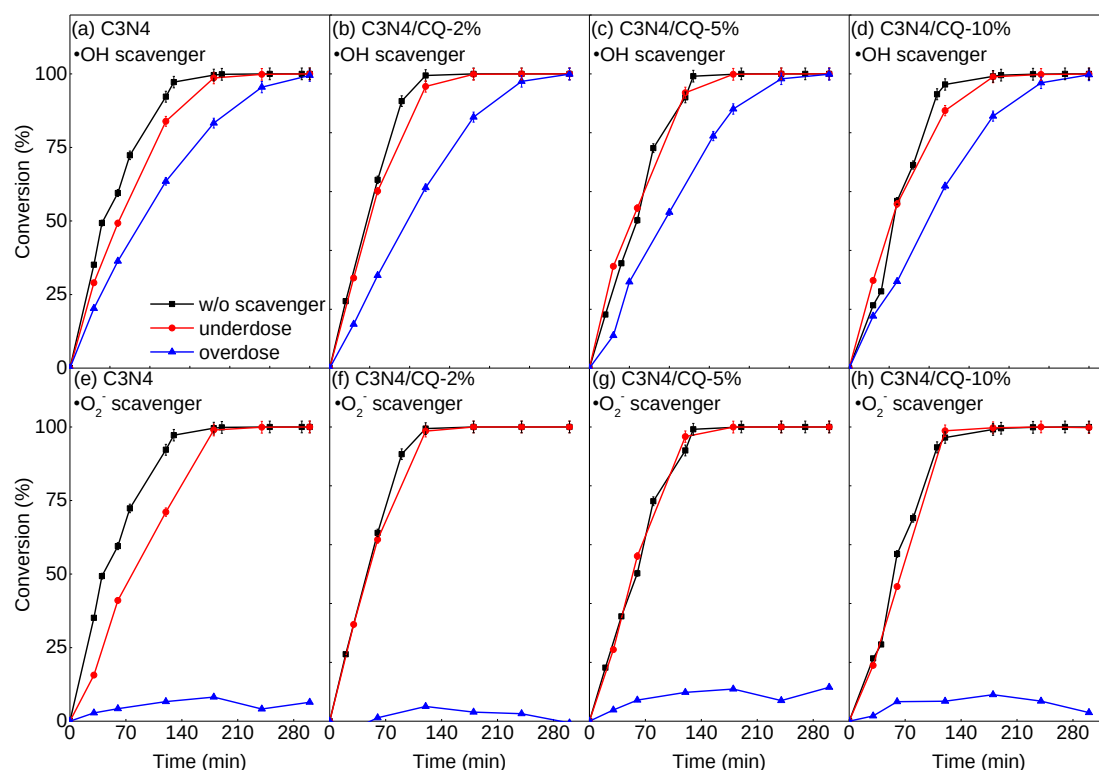


Figure 3.9 Conversion of methylparaben in the presence of $\bullet OH$ scavenger (IPA) and $\bullet O_2^-$ scavenger (benzoquinone) for samples CN, CN/CQ-2%, CN/CQ-5% and CN/CQ-10%.

Figure 3.9 shows the conversion of methylparaben in the presence and absence of IPA (considered as $\bullet OH$ scavenger) and benzoquinone (considered as scavenger of $\bullet O_2^-$, $\bullet OH$ and/or electrons) for the series of CN/CQ photocatalysts investigated. As

expected, the presence of the chemical scavengers had a strong impact in the conversion of methylparaben, with reduced conversion for all the photocatalysts. The impact was more pronounced for bare carbon nitride, even when low doses of both chemicals were used. In the case of the CN/CQ composites, low doses of IPA and BQ did not modify the conversion of methylparaben, being the effect only observed when high doses of the scavengers were applied. This demonstrates the importance of the adequate choice of the dose of the scavenger to achieve a complete scavenging effect in the degradation of the studied compound (avoiding the total consumption of the scavenger).

The analysis of the degradation kinetic rates in the presence of IPA and BQ scavengers also confirmed this trend (Figure S4 in Annex I). A decrease in the kinetic rate for the degradation of methylparaben of 12% and 28% was observed for the photocatalytic assays in the presence of under-dose $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ scavengers, respectively; the reduction accounted for ca. only 5 % for the CN/CQ composites. There are two plausible explanations for this behavior: (1) the CN/CQ composites display a more efficient exploitation of the hydroxyl radicals formed upon irradiation of the photocatalysts (usually referred to in the literature as a reduced recombination of pairs e^- and h^+), or (2) they promote the formation of a larger density of hydroxyl radicals (thereby counteracting the effect of the chemical scavenger). It was necessary to increase the amount of IPA chemical scavenger by 1500 times to observe a decrease in the performance for methylparaben and the intermediates. Similar observations were obtained in the photoelectrochemical assays where the photocurrent generated upon illumination of the catalysts was recorded in the presence of the scavengers. This will be discussed in section 3.2.2.3.

A different trend was observed for the degradation of the intermediates (Figure 3.10). Similarly to methylparaben, low doses of IPA did not modify the amount of the first hydroxylated intermediate, as seen in the similar area profiles compared to the photocatalytic assay in the absence of any scavenger. In contrast, a high dose of IPA increased the amount of intermediate (larger area) for all the catalysts, although the effect was more pronounced for the CN/CQ composites. This accumulation in the amount of the intermediate when hydroxyl radicals are trapped indicates the important role of this species in the degradation of methylparaben intermediates. For the excess of BQ, the conversion of methylparaben was negligible, and the polyhydroxylated intermediates were not detected. In this case, we attribute this to a strong interference

of BQ at those high concentrations due to light shielding effect (the solution became too colored/opaque, which may hinder the exposure of the catalysts to light) [Mergbi et al. 2023; Low et al. 2017], and to the photodegradation of benzoquinone itself as dominant reaction at such high concentrations (Figure S5 in Annex I shows the degradation of BQ reached ca. 80 % after 5h irradiation). Thus, despite the multiple scavenging effect of BQ, it is important to control its concentration in scavenging assays to avoid interferences that may be misinterpreted in terms of the degradation mechanism.

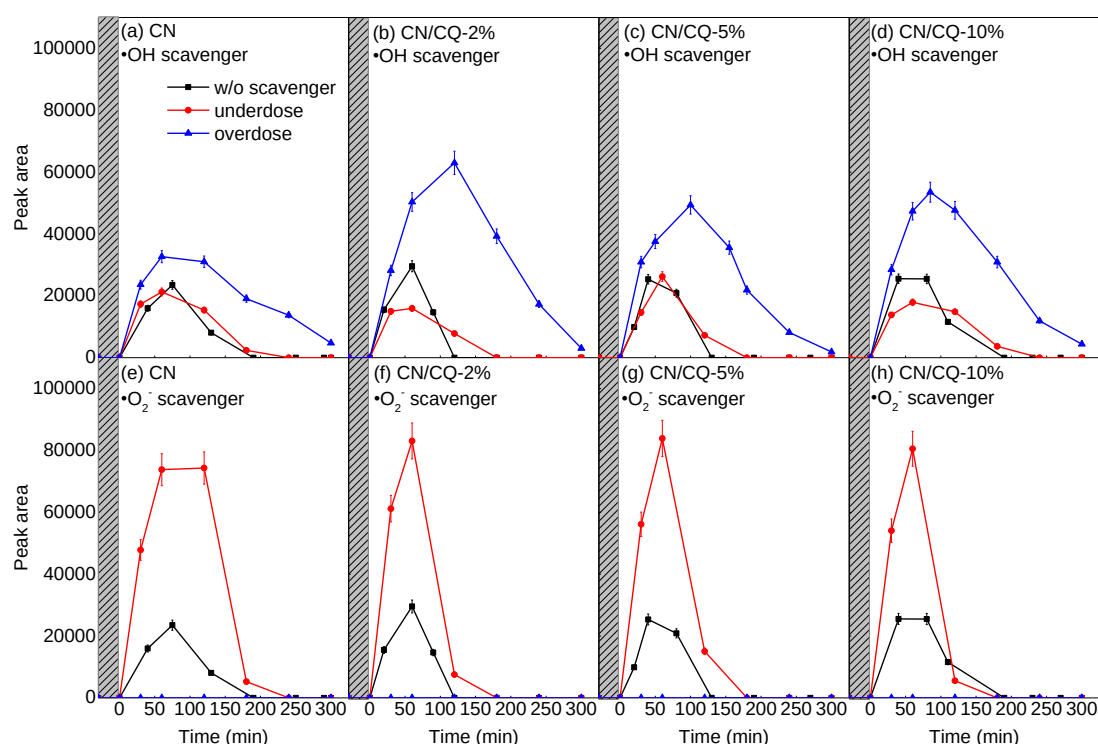


Figure 3.10 Evolution of the amount of degradation polyhydroxylated intermediates (in-1) in the presence of $\bullet\text{OH}$ scavenger (IPA) and $\bullet\text{O}_2^-$ scavenger (benzoquinone) for samples CN, CN/CQ-2%, CN/CQ-5% and CN/CQ-10%.

Based on all this, we decided to avoid the use of benzoquinone as scavenger of superoxide radicals, and we explored a different approach based on the application of O_2 -free conditions to avoid the formation of superoxide radicals [Yang et al. 2016; Schneider et al. 2020; Puga et al. 2024]. In this PhD thesis, the solution was deoxygenated by sonicated and using a continuous helium flow.

Figure 3.11 shows the comparison of the conversion of methylparaben in the presence of an excess of benzoquinone as $\bullet\text{O}_2^-$ radical scavenger and in O_2 -free conditions provided by bubbling helium for 60 minutes through a previously sonicated solution of the pollutant to eliminate the dissolved oxygen, maintaining a

helium atmosphere in the top of the reactor during the photocatalytic assays (to avoid redissolution of oxygen). For bare carbon nitride, the complete removal of oxygen from the reaction medium resulted in a decrease in the conversion, reaching ca. 90% in 300 min at O_2 -free condition. This indicates the important role of $\bullet O_2^-$ in the conversion of this pollutant. The effect was more pronounced for the CN/CQ composites, where the reduction in conversion in the de-aerated solutions accounted for 20-25 % after 5 hours irradiation, for samples CN/CQ-2%, samples CN/CQ-5% and samples CN/CQ-10%, respectively. The reduction is lower than that for the excess of benzoquinone, confirming the interference of the former due to the competitive degradation and light shielding. The reduced conversion in the de-aerated solutions suggests that suppressing the reaction of the photogenerated electrons with dissolved oxygen to generate $\bullet O_2^-$ radicals seems to increase the recombination of the electron/holes pairs, particularly in the CN/CQ composites [Syoufian et al. 2008; Chen et al. 2017].

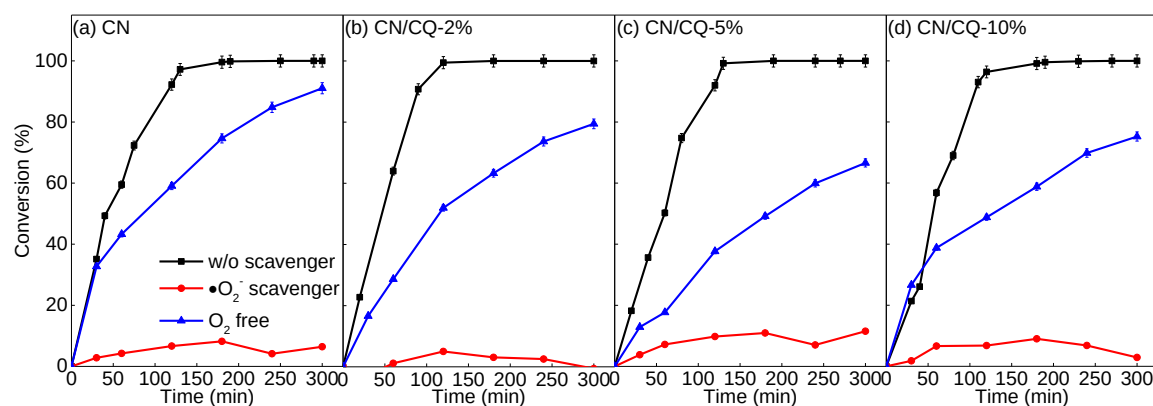


Figure 3.11 Conversion of the methylparaben in the presence of an excess of benzoquinone as $\bullet O_2^-$ radical scavenger, compared to the photocatalytic assay in oxygen-free conditions.

3.2.2.2 Scavengers of photogenerated e^- and h^+

Besides the scavenging of hydroxyl and superoxide radicals as indirect evidences of the reactivity of the photogenerated electrons and holes to create O -radical species, we have explored directly the reactivity of the photogenerated electrons and holes. According to literature, methanol is among the most popular and efficient hole scavenging agent frequently used in photocatalytic applications [Chen et al. 2018; Jung et al. 2021; Fakhrul Ridhwan Samsudin et al. 2018; Bresolin et al. 2020; HART and FIELDEN 1965; Augustin et al. 2024; Wei et al. 2019], outperforming

other alcohols (e.g., ethanol and ethylene glycol) in the interfacial hole scavenging efficiency owing to the fast kinetics of the oxidation of methanol by the holes [Chen et al. 2018; Jung et al. 2021]. On the other hand, acetone acts as electron scavenger due to the fast redox reactivity of the polar carbonyl moiety to form secondary alcohol and/or an acetone radical intermediate [HART et al. 1965; Kurpil et al. 2019].

Figure 3.12 shows the comparison of the kinetic profiles of the conversion of methylparaben in the presence of IPA (hydroxyl radical scavenger), methanol (hole scavenger), acetone (electron scavenger) and in oxygen-free conditions (to avoid superoxide formation) for the series of CN/CQ photocatalysts.

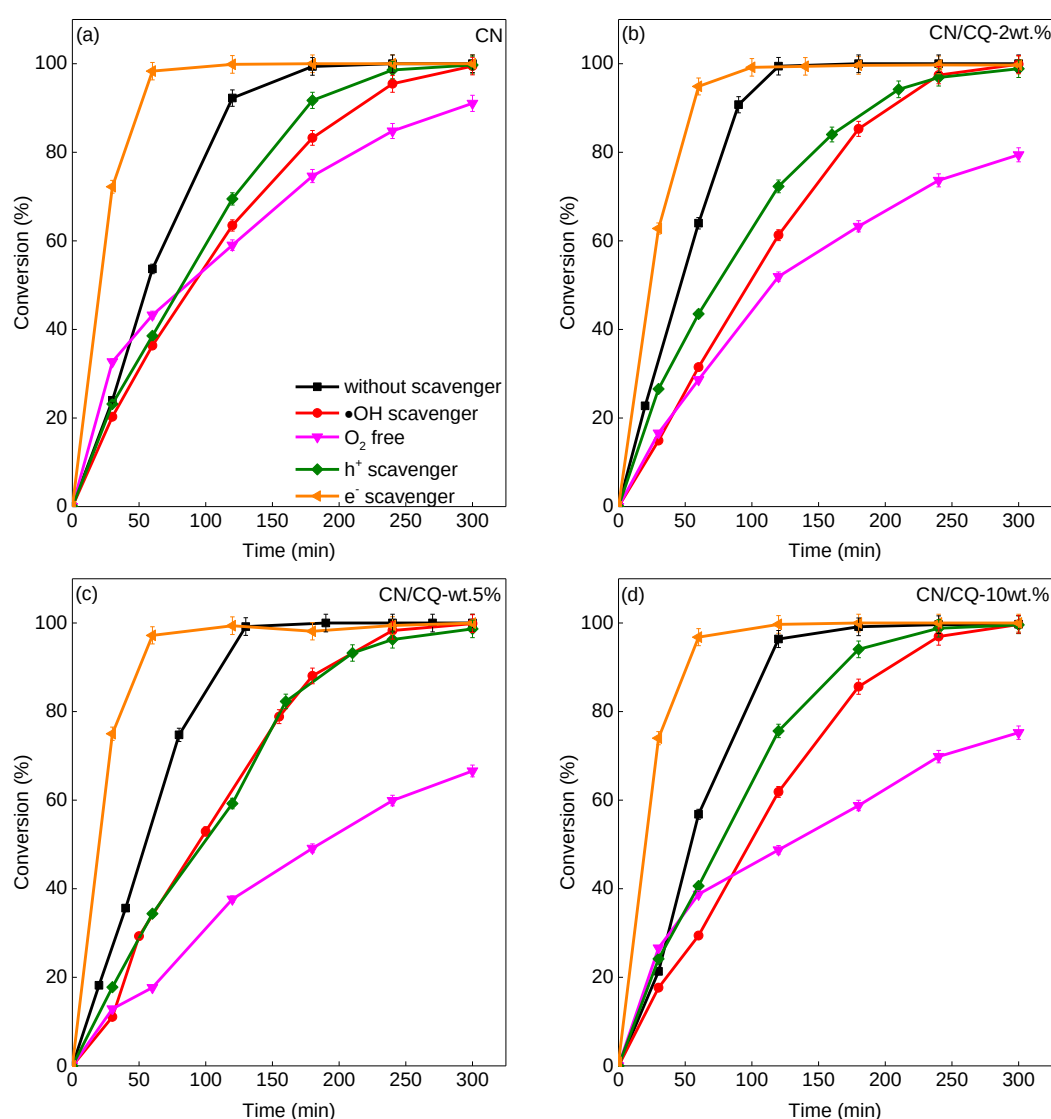


Figure 3.12 Conversion of the methylparaben in the presence of •OH radical, photogenerated h⁺ and e⁻ scavenger and in O₂-free conditions for samples (a) CN, (b) CN/CQ-2%, (c) CN/CQ-5% and (d) CN/CQ-10%.

With the exception of the assay carried out in the presence of acetone as electron

scavenger, the conversion of methylparaben was significantly reduced in the presence of IPA, methanol and in oxygen-free conditions. The effect was more pronounced for the photocatalytic assays carried out in the oxygen-free environments, emphasizing the important role of superoxide radicals in the mechanism and/or of the direct oxidation of the holes (since the reaction of the photoelectrons with dissolved oxygen to generate the superoxide radicals would reduce the recombination of the holes).

Regarding the composition of the photocatalysts, the impact of the oxygen-free environment was more pronounced in the CN/CQ composites, suggesting the important role of the reaction of the electrons with dissolved oxygen to avoid a decrease in the conversion likely due to the recombination of electron hole pairs. The chemical scavenging of the hydroxyl radicals and of the photogenerated holes also decreased the conversion of methylparaben, although the effect was less pronounced than for the oxygen free conditions. This indicates that the hydroxylation-mediated oxidation reaction is the predominant pathway in the degradation of methylparaben and its intermediates, and that the photogenerated holes play an essential role in these reactions.

In contrast, when the electrons were scavenged upon the incorporation of acetone, the conversion of methylparaben degradation became very fast for all the photocatalysts, reaching 100% of conversion after 60 minutes (compared to ca- 200-300 min needed in the absence of the scavenger) with no degradation intermediates observed for any of the materials (Figure 3.13). This was further evidenced by the kinetic rates shown in Figure 3.14), showing that the CN/CQ composites tend to degrade polyhydroxylated intermediate faster than bare CN in the presence of $\bullet\text{OH}$ radical and photogenerated h^+ scavenger. Indeed, a clear correlation can be found between the rate constants and the amount of CQ in the composites (Figure 3.14). As discussed above, the degradation rate constants of methylparaben in the absence of scavenger increased smoothly with the amount of carbon additive in the composites. In the presence of IPA and methanol (hydroxyl radical and hole scavengers, respectively), the degradation rate constants of methylparaben were rather similar regardless the amount of CQ in the composites, but the degradation kinetic rate decreased with the amount of carbon additive when the photocatalytic assays were carried out in oxygen-free environment. The lowest rate constant of O_2 -free condition indicates that oxidation by $\bullet\text{O}_2^-$ has a larger impact (drop of ca. 10-33%), particularly in the semiconductor/carbon composite. The highest rate constants were obtained in

the presence of the scavenger of electrons (ca.2-3 times higher than in the absence of scavenger), with similar values regardless the amount of carbon additive.

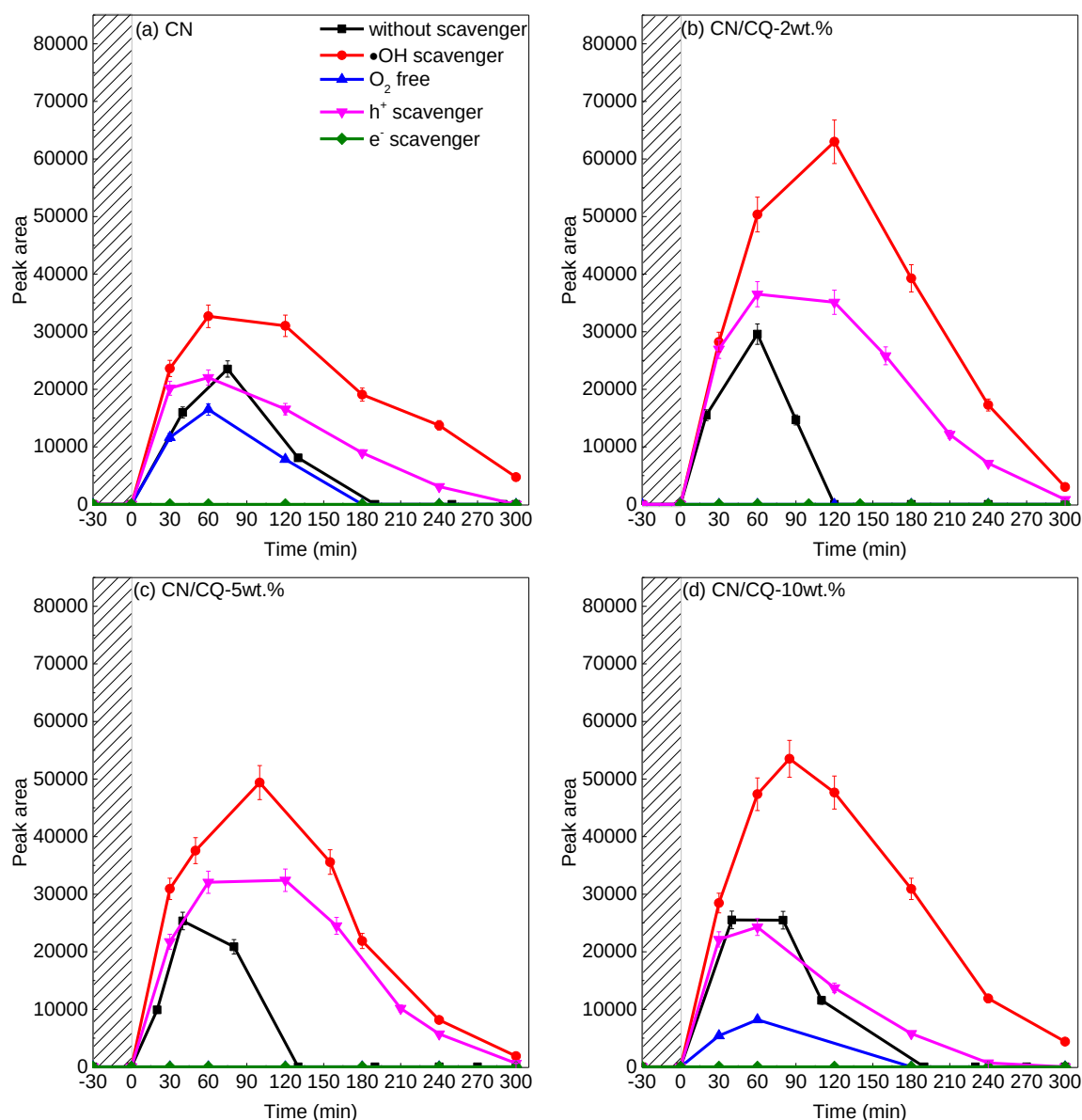


Figure 3.13 The evolution of the amount of degradation polyhydroxylated intermediates in the presence of different scavengers and in O₂-free conditions for obtained samples.

In summary, the degradation rate followed the order: e⁻ scavenger > without scavenger > h⁺ scavenger ≥ •OH scavenger > O₂-free, for all the catalysts. Therefore, the contribution of radicals in the photocatalytic system follows the order: •O₂⁻ > •OH > h⁺ > e⁻, which agrees with the performance of CN reported in the literature [Yang et al. 2016; Bai et al. 2014; Chen et al. 2014]. This also points out that the oxidation via •O₂⁻ radicals may be the dominant pathway in photocatalytic degradation of

methylparaben, as also reported in the literature for other systems [Velegiraki et al. 2015]. This is consistent with the energy levels of the conduction band and the valence band of carbon nitride estimated using the Butler and Ginley method [Butler and Ginley 1978; Wierzyńska et al. 2023; Peng et al. 2018]. The position of the conduction band (-1.18 eV) is more negative than the standard redox potential of the pair $O_2/\bullet O_2^-$ (-0.33 eV vs NHE), thus confirming the capacity of the photogenerated electrons in the semiconductor to react with dissolved oxygen to generate $\bullet O_2^-$ radicals [Imgharn et al. 2024; Huang et al. 2021].

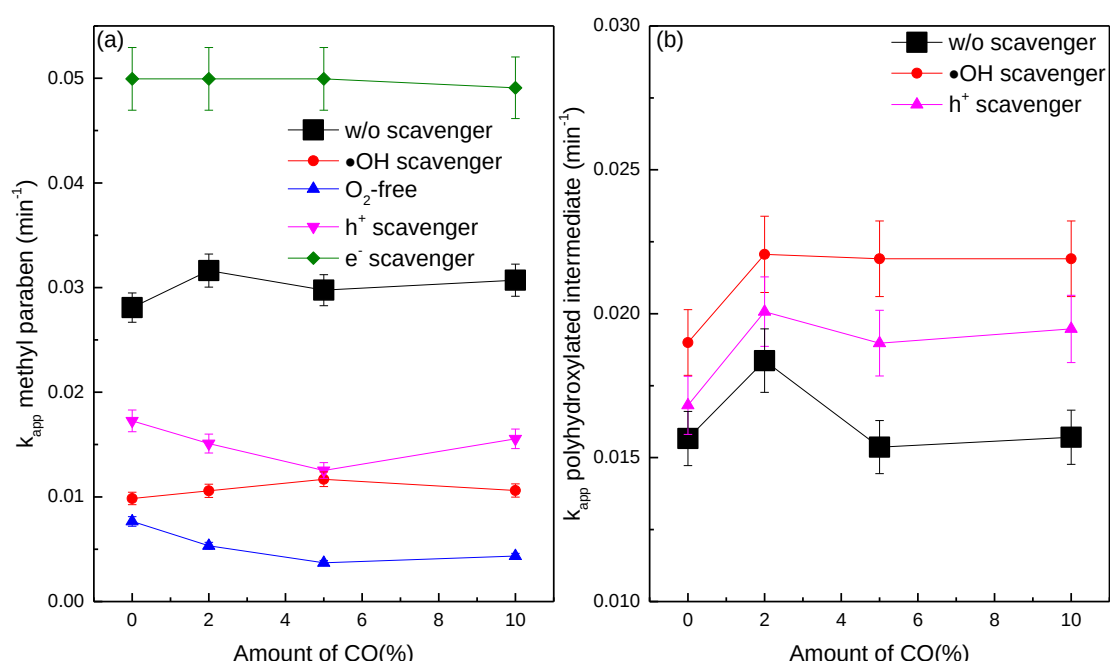


Figure 3.14 Rate constants for the degradation of MP (a) and the degradation of the polyhydroxylated intermediates (b) in the composites at different scavengers.

3.2.2.3 Photoelectrochemical characterization of the photocatalysts

Most organic pollutant in photocatalysis are removed through oxidation reactions, thus promoting the reactivity of the photogenerated holes would be preferred over electrons. In this context, holes are known to prevail over electrons as photogenerated carriers in *p*-type semiconductors (with a higher density of holes than electrons), thus *p*-type semiconductors should be (in principle) more suitable for the photocatalytic degradation of pollutants than *n*-type counterparts. However, most *p*-type semiconductors present low shallow valence bands potentials that limit the oxidation performance of the photogenerated holes [Luo et al. 2017; Zhang et al. 2010]. In this context, C_3N_4 displays amphoteric semiconductor properties (it can be synthesized as both *n*-type and *p*-type semiconductor) [Jing et al. 2021], and many

efforts are directed to control and switch the semiconducting behavior of this material. On the other hand, it has been reported that the photogenerated holes from the valence bands of C_3N_4 have a high oxidation potential and therefore should be able to oxidize most organic pollutants. However, the recombination rate is very high.

To evaluate the recombination rate of the photogenerated charge carriers, and the impact of the carbon additive on it, we have performed photoelectrochemical measurements of the prepared photocatalysts under varied illumination conditions. The charge transfer of the photogenerated exciton can be assessed from transient photocurrent measurements upon on/off illumination of the photocatalysts at a bias potential. The applied potential in the transient photocurrent measurements was chosen in the depletion region of the semiconductor (between -0.4 V and +0.6 V vs Ag/AgCl), that corresponds to area where the voltammogram exhibits a flat current and there are not interferences with charge transport through the electrode from secondary reactions [Imgharn et al. 2024; Bard et al. 2002].

Figure 3.15 shows the photocurrent transients of C_3N_4 and CN/CQ-10% upon illumination at various conditions and after adding the chemical scavengers. It should be noted that acidic electrolyte conditions (0.5 M Na_2SO_4 , pH-2) were selected to amplify the signal and avoid limitations of low sensibility (owing to the typically low photocurrents). The transient photocurrent curves upon on/off illumination of bare carbon nitride showed a sharp (negative) photocurrent spike that follows a smooth decay over time (sometimes accompanied with a sharp current overshoot). This indicates that our prepared C_3N_4 presents p-type semiconductor properties, and thus that photogenerated holes are the majority charge carriers. The photocurrent transient measurements were reproducible for various electrodes and upon repeated on/off illumination cycles. For the CN/CQ 10wt.%, the transient photocurrents show a similar shape that those of CN, indicating the p-type character of the composite. This is expected considering the amount of carbon additive in the composite. On average, the magnitude of the photocurrent was larger for the composites than for bare carbon nitride, which indicates the lower recombination of the charge carriers in the composites (thus in line with the improved photocatalytic performance for the degradation of methylparaben).

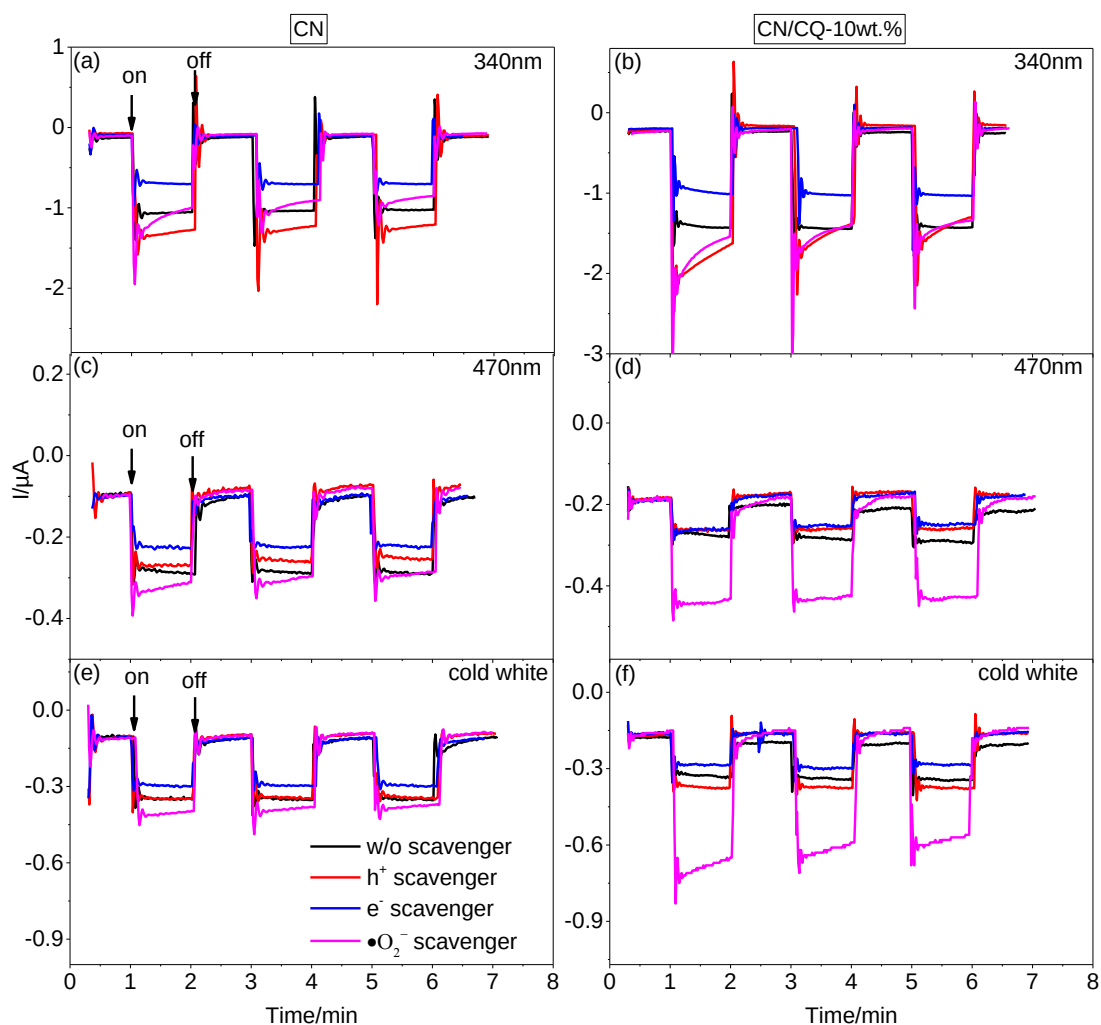


Figure 3.15 Photocurrent transients of CN and CN/CQ-10wt.% after adding different scavengers upon illumination at various conditions: 340 nm, 470 nm and simulated solar light (cold white), recorded at -0.3 V (CN) and -0.2 V (CN/CQ-10wt.%) vs Ag/AgCl in 0.5 M Na₂SO₄ (pH 2). To facilitate the comparison, the transients have been shifted to the same initial value of dark photocurrent (corresponding to the measurement during the first minute).

When a p-type semiconductor is immersed in an electrolyte, a space charge region is generated at the semiconductor/electrolyte interface, (causing the band bending of the semiconductor in this interfacial region) due to the migration of the majority charge carriers (holes for a p-type semiconductor) to the interface with the electrolyte. When the equilibrium is reached, an excess positive charge is generated in the solution side of the interface, and excess negative charges in the semiconductor side [Thorne et al. 2015; Peter et al. 2020]. The ‘instantaneous’ photocurrent observed when the light is switched on corresponds to rapid separation of photogenerated electron/hole pairs in the space charge region, with holes accumulated in the valence band being transferred to the counter electrode through the external circuit (to oxidize

water to generate O_2) and electrons moving to the interface to charge the space charge region and being injected to the electrolyte (used to reduce water into H_2). The rise of the instantaneous photocurrent typically occurs in less than 1 ms, and its decay is attributed to the build-up of photogenerated minority carriers (electrons in this case) at or near the interface which causes some recombination. The steady state is reached when the rates of photogeneration and consumption are balanced. The under/overshoots observed when the light is switched off arises because the hole flux is interrupted abruptly, and only the electron flux of the polarization is recorded (which will decay until all excess holes have been consumed).

The magnitude of the photocurrent increased in the presence of the hole scavenger, and decreased in the presence of superoxide and electron scavengers for both samples, being the effect more pronounced for the electron scavenger. The decreased photocurrent in the presence of the electron scavenger is expected since the measured photocurrent corresponds to the reduction of the electrolyte due to the photogenerated electrons, as indicated above. Similar trends were obtained regardless the illumination conditions, although the intensities of the photocurrents corresponding to the signals in the presence of superoxide scavenger were much higher under visible light (470 nm and simulated solar light) than under UV. In addition, the magnitude of the photocurrent for CN/CQ-10 wt.% was higher than that of pristine C_3N_4 (1.4-fold enhancement) upon illumination at 340 nm, indicating a more efficient electron injection in the conduction band in the composite. We attribute this to the π electron density of the nanoporous carbon that would facilitate the electron mobility and would effectively suppress the competing recombination of excitons. Similar results have been reported for mesoporous carbon/CdS composites [Banerjee et al. 2021]. This suggests that the carbon additive acts as an acceptor of electrons from the VB of g- C_3N_4 . In contrast, higher photocurrents were recorded for carbon nitride alone than for the composite when illuminated at 470 nm and simulated solar light. This indicates that the increased efficiency in the photogeneration of the charge carrier upon the incorporation of the CQ additive affects mainly the UV region. This aligns well with the photocatalytic performance discussed in Section 3.2.1.

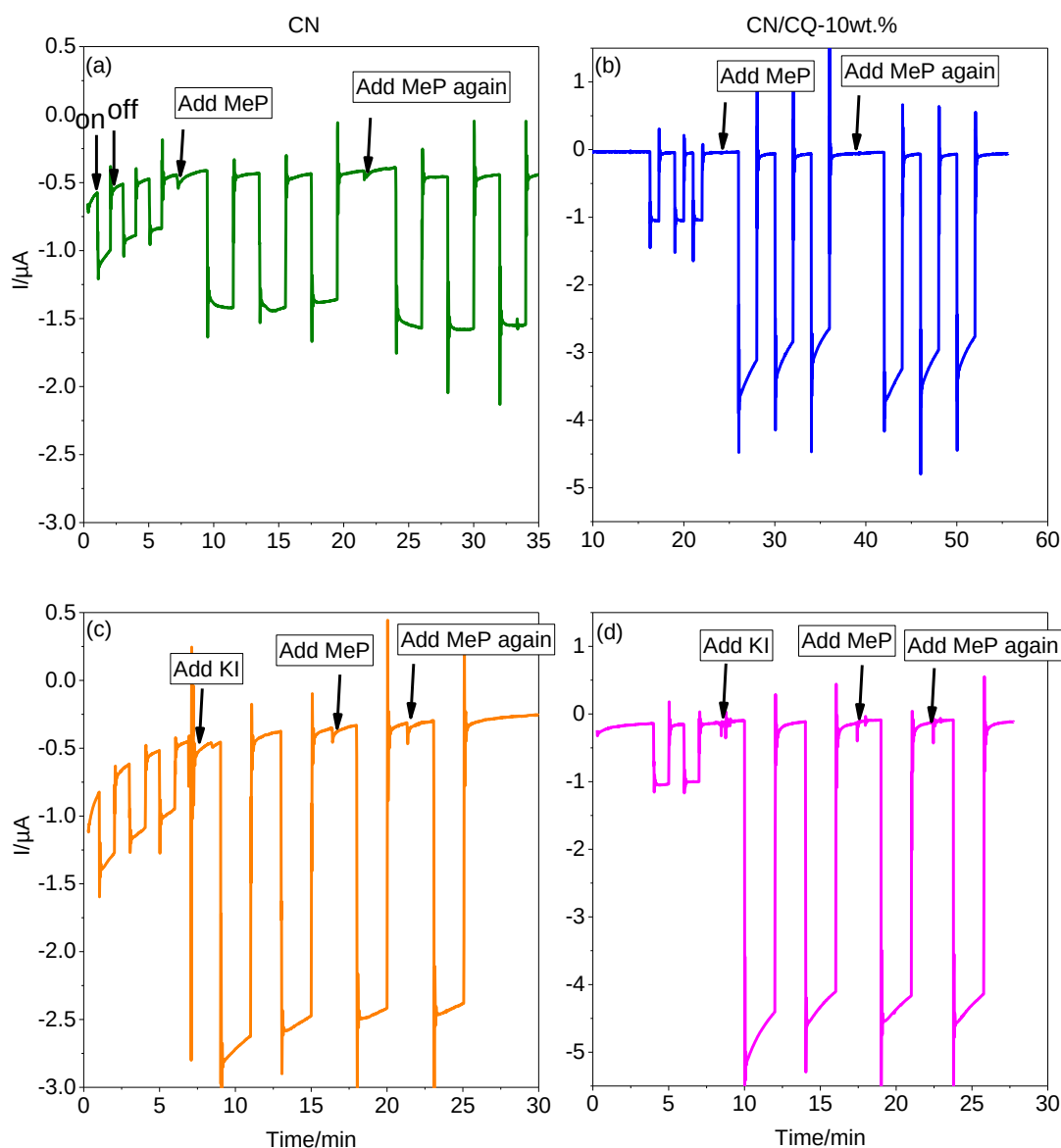


Figure 3.16 Photocurrent transients of CN and CN/CQ-10wt after adding KI (another hole scavenger) and MeP upon illumination at 340 nm, recorded at -0.3 V (CN) and -0.2 V (CN/CQ-10wt.%) vs Ag/AgCl in 0.5 M Na₂SO₄ (pH 2).

We have further explored the photoresponse of CN and CN/CQ-10wt.% upon illumination at 340 nm in the presence of methylparaben and KI as hole scavenger (Figure 3.16). As we can see in Figure 3.16 (a, b), the incorporation of methylparaben increased the magnitude of the photocurrent detected in both catalysts, being the effect more pronounced in the composite. This evidences the charge carriers transfer to the selected pollutant. In the presence of KI as hole scavenger, the photocurrent increased significantly indicating the higher density of electrons in the system (owing to the reduced recombination).

To better compare the data, we have calculated the steady-state photocurrent (I^{ss})

of each system in the normal electrolyte (without scavenger, $I^{\text{ss}}_{\text{wo}}$) and in the electrolyte containing the scavenger ($I^{\text{ss}}_{\text{scav}}$). The ratio of both magnitudes ($\eta_{\text{transfer}} = I^{\text{ss}}_{\text{wo}} / I^{\text{ss}}_{\text{scav}}$) was used as an indicator of the charge carrier transfer efficiency (Table 3.3, Figure 3.7). Note that the steady-state photocurrent (I^{ss}) corresponds to the variation between dark and illumination conditions (i.e., I^{ss} values are calculated subtracting the dark current).

Table 3.2 Values of the steady-state photocurrent in the presence ($I^{\text{ss}}_{\text{scav}}$) and absence ($I^{\text{ss}}_{\text{wo}}$) of scavengers and/or methylparaben, and ratio η_{transfer} ($I^{\text{ss}}_{\text{wo}}/I^{\text{ss}}_{\text{scav}}$) for CN and CN/CQ 10wt.% upon illumination at various conditions.

	340nm		470nm		Cold white	
I^{ss} (μA)	CN	CN/CQ-10wt.%	CN	CN/CQ-10wt.%	CN	CN/CQ-10wt.%
w/o scavenger	-0.74	-1.17	-0.18	-0.08	-0.22	-0.14
h^+ scavenger (MeOH)	-1.11	-1.50	-0.22	-0.09	-0.17	-0.21
e^- scavenger	-0.50	-0.82	-0.17	-0.07	-0.23	-0.12
$\bullet\text{O}_2^-$ scavenger	-0.90	-1.36	-0.12	-0.24	-0.28	-0.45
MeP (alone)	-1.56	-3.60	--	--	--	--
h^+ scavenger (KI)	-3.00	-5.92	--	--	--	--
MeP after KI	-2.89	-5.67	--	--	--	--
η_{transfer}						
h^+ scavenger (MeOH)	1.50	1.28	1.22	1.13	0.77	1.50
e^- scavenger	0.68	0.70	0.94	0.88	1.05	0.86
$\bullet\text{O}_2^-$ scavenger	1.22	1.16	0.67	3.00	1.27	3.21
MeP (alone)	2.11	3.08	--	--	--	--
h^+ scavenger (KI)	4.05	5.06	--	--	--	--
MeP after KI	3.91	4.85	--	--	--	--

When a hole scavenger is added to the electrolyte (methanol), the photocurrents in both the pristine g-C₃N₄ and the composite are higher than the corresponding measurements in the normal electrolyte. This indicates a more efficient transfer of the electrons to the electrolyte. A similar result was observed when BQ was added to the medium, although the photocurrents were smaller than in the presence of methanol, indicating a less efficient charge transfer. When acetone is added to the electrolyte as electron scavenger, the photocurrent decreased indicating the effective scavenging of the photogenerated electrons.

3.2 Photocatalytic activity of CN/CQ series samples

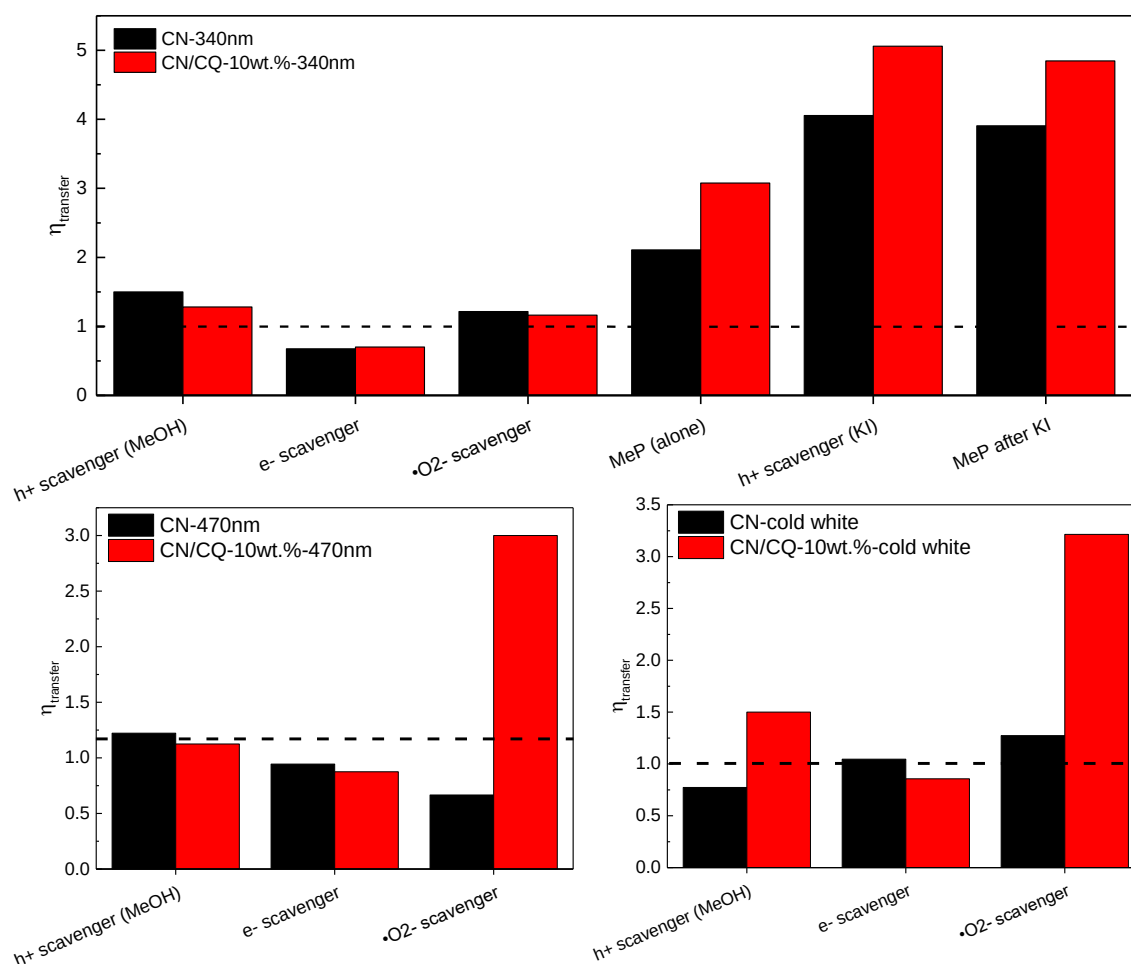


Figure 3.17 Representation of $\eta_{transfer}$ ($I_{ss_{wo}} / I_{ss_{scav}}$) for the different assays carried out in the presence of scavengers and/or methylparaben (MeP) upon illumination at various conditions for CN and CN/CQ 10wt.%.

3.3 Partial Conclusions

The photocatalytic degradation of methylparaben has been investigated in aqueous solution by using carbon nitride/carbon composites, using a nanoporous carbon as additive to carbon nitride. The characterization of the materials prepared upon hydrothermal synthesis indicated that the incorporation of the carbon additive in a concentration range between 2-10 wt.% does not significantly modify the structural properties of the pristine semiconductor, but the composites absorb more visible light than bare CN. The porosity of the resulting CN/CQ composites did not follow the general rule of the mixtures, indicating that the nanopores of CQ additive are not accessible by gas adsorption, most likely due to the partial blockage by the particles of the semiconductor. All the materials displayed an effective degradation of both methylparaben and its intermediate, being the kinetics of the degradation slightly improved with the amount of the carbon additives. The composites also showed a good cyclic performance over two consecutive irradiation cycles, with a low accumulation of intermediates. The combination of chemical scavenging and photoelectrochemical assays threw interesting information about the degradation mechanism. The degradation of methylparaben proceeds through a multiple oxidation step reactions involving the formation of polyhydroxylated intermediates. The presence of dissolved oxygen seems to be important to promote the formation of superoxide radicals (particularly in the CN/CQ composites). The increased performance in the presence of chemical scavengers of the photogenerated electrons indicates the key role of the reactivity of the photogenerated holes, either in direct oxidation reactions or through the formation of oxygen radical species. Indeed, the degradation kinetics increased significantly after the scavenging of the photogenerated electrons for all the studied catalysts.

Chapter 4. Investigation of BWO/carbon photocatalyst for degradation of MeP

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In this chapter, the incorporation of carbon materials (g-C₃N₄ and CQ) as additives to semiconductor (BWO) have been studied, and the photocatalytic activity of the resulting materials has been explored for the degradation of methylparaben from solution. We have investigated the impact of adding small amounts of these carbon materials on the light absorption features of the BWO, the photocatalytic performance and on the fate of the photogenerated excitons to form radical reactive species responsible for the degradation of methylparaben under artificial UV-VIS light. The preparation of the binary BWO-carbon photocatalysts was made by a hydrothermal method as described in the experimental chapter, using various amounts of the CQ and CN ranging between 2-10 wt.%. The samples were labeled as BWO/A-x wt.%, where A is the acronym of the carbon material used as additive (i.e., CQ or CN) and x stands for the amount of carbon additive incorporated.

4.1 Characterization of structure and texture of the materials

X ray diffraction was used to analyze the crystal structure of obtained catalysts. The XRD pattern of pristine BWO and BWO/carbon composite were showed in Figure 4.1. It is clear that the pattern of BWO has five peaks between 10° and 60 °. All of the peaks were well indexed to russellite phase with an orthorhombic geometry structure and the space group Pca2₁ (reference NO. 96-901-1800) and lattice parameters of $a=5.43 \text{ \AA}$, $b= 16.43 \text{ \AA}$, $c=5.45 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$. These peaks could correspond to [131], [060], [202], [191] and [262] lattice planes, locating at 28.30°, 32.68°, 47.15°, 55.67° and 58.55 °, respectively, as reported in literature [De Jesus Silva Chaves et al. 2019; Zhang et al. 2012; Carmona et al. 2015]. As discussed in chapter 3, there are two peaks in the XRD pattern of CN at the 12.9° and 27.6°, and two peaks of CQ at 20.70° and 26.52°. However, no other diffraction peaks, associated to carbon phases (either CN or CQ), were detected for the composite. It could be attributed to the relatively low loading of carbon material and low intensity of the reflections of the carbons. For BWO/CN samples, it may also due to low crystallinity of CN, and the two phases of [131]

(28.3°) and [002] (27.6°) were too close to be separated. Similar observations regarding the lack of the characteristic peaks of the carbon additive in composites with a low amount of the latter have been reported for BWO modified by carbon materials (e.g. carbon fibers, graphene oxide, carbon and g- C_3N_4) [Huo et al. 2021; Lei et al. 2020; Cui et al. 2013; Song et al. 2016; Tian et al. 2013b]. The absence of diffraction peaks corresponding to bismuth and tungsten oxides indicates that the BWO precursors underwent complete self-assembly during the hydrothermal synthesis in the presence of carbon additives. A similar finding has been reported by Gomis-Berenguer et al. 2019.

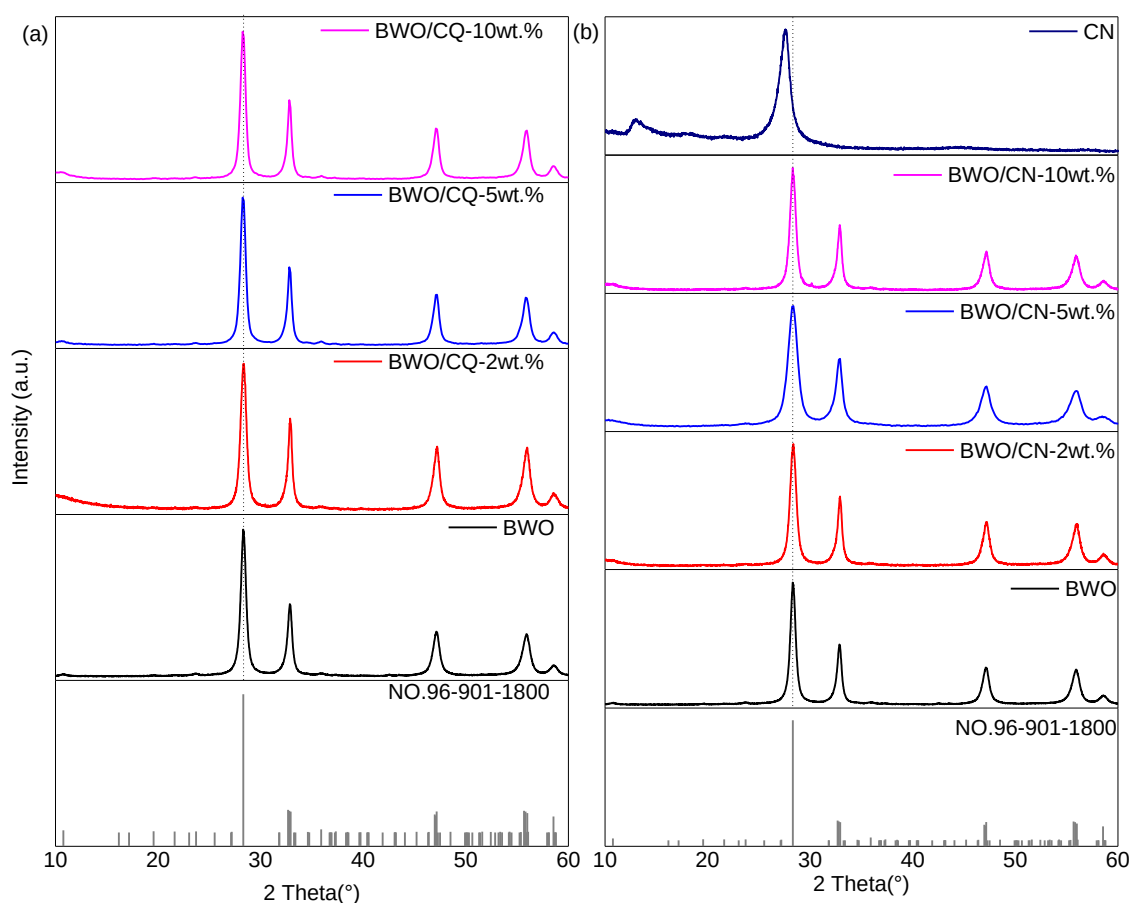


Figure 4.1 The XRD pattern for all the (a) BWO/CQ and (b) BWO/CN composite.

Figure 4-2 displays the correlation between the amount of CQ and the main structural parameters calculated from the XRD patterns (such as 2θ position and FWHM and crystallite size of [131] phase). A slight shift to a lower 2θ position is observed when both the CQ or CN material was introduced to BWO. Interestingly,

there is no shift of 2θ position between composites. According to Bragg's law, this tiny decrease in the 2θ value can be attributed to an increase in lattice parameters, which alters the crystal structure, consequently, changes the interplanar spacing (BWO: 0.160 nm; BWO/carbon composite 0.163 nm) [Huang et al. 2014]. Crystallite sizes, calculated by Scherrer equation, increased as the amount of additive was raised. The change in crystallite sizes indicates a tiny distortion of the lattice of BWO. In addition, the intensity of [131] plane has barely changed for any of the composites, which suggests that the incorporation of the increasing amount additive did not alter the support to a large extent. The reduction in FWHM indicates an increase in the long-range order and a more organized crystal structure, as reported for BWO in the literature [Pinatti et al. 2020].

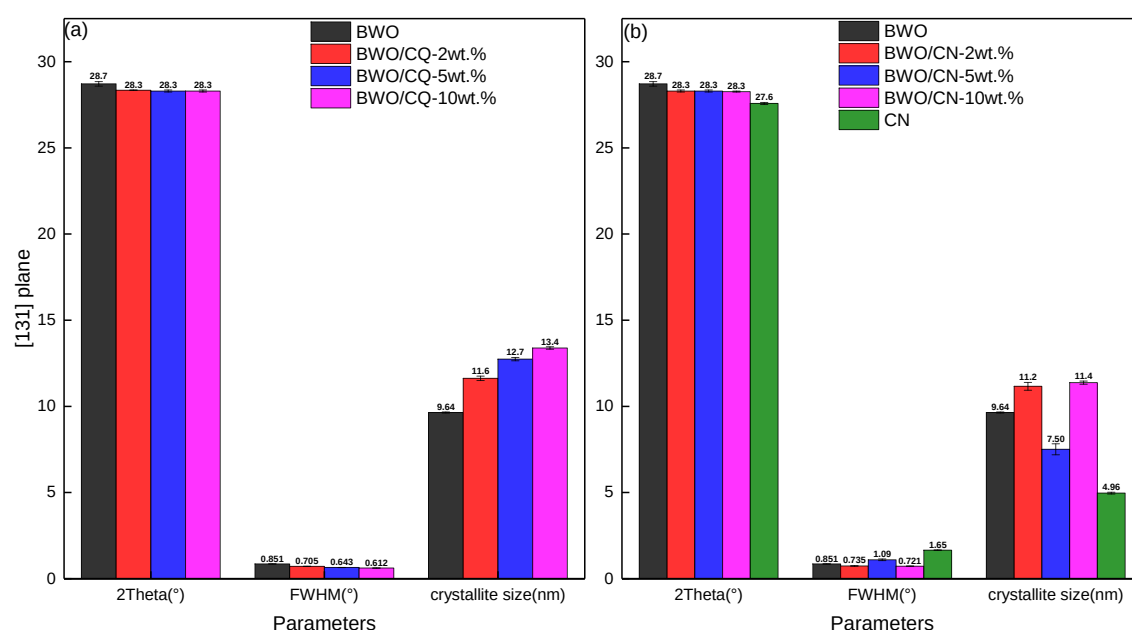


Figure 4.2 The parameters of [131] phase for all the (a) BWO/CQ and (b) BWO/CN composite.

Optical properties are a key property of photocatalysis and relate to the ability of the catalyst to utilize which types of light (e.g. UV, UV-Vis, Vis-NIR, or NIR) can be used [Tian et al. 2013a]. In particular, the positions of the band edges play a critical role in determining the photoactivity of materials, as reported for TiO₂-based materials [Beranek 2011]. Diffuse reflectance of all the obtained samples were showed in Figure 4.3(a)(b).

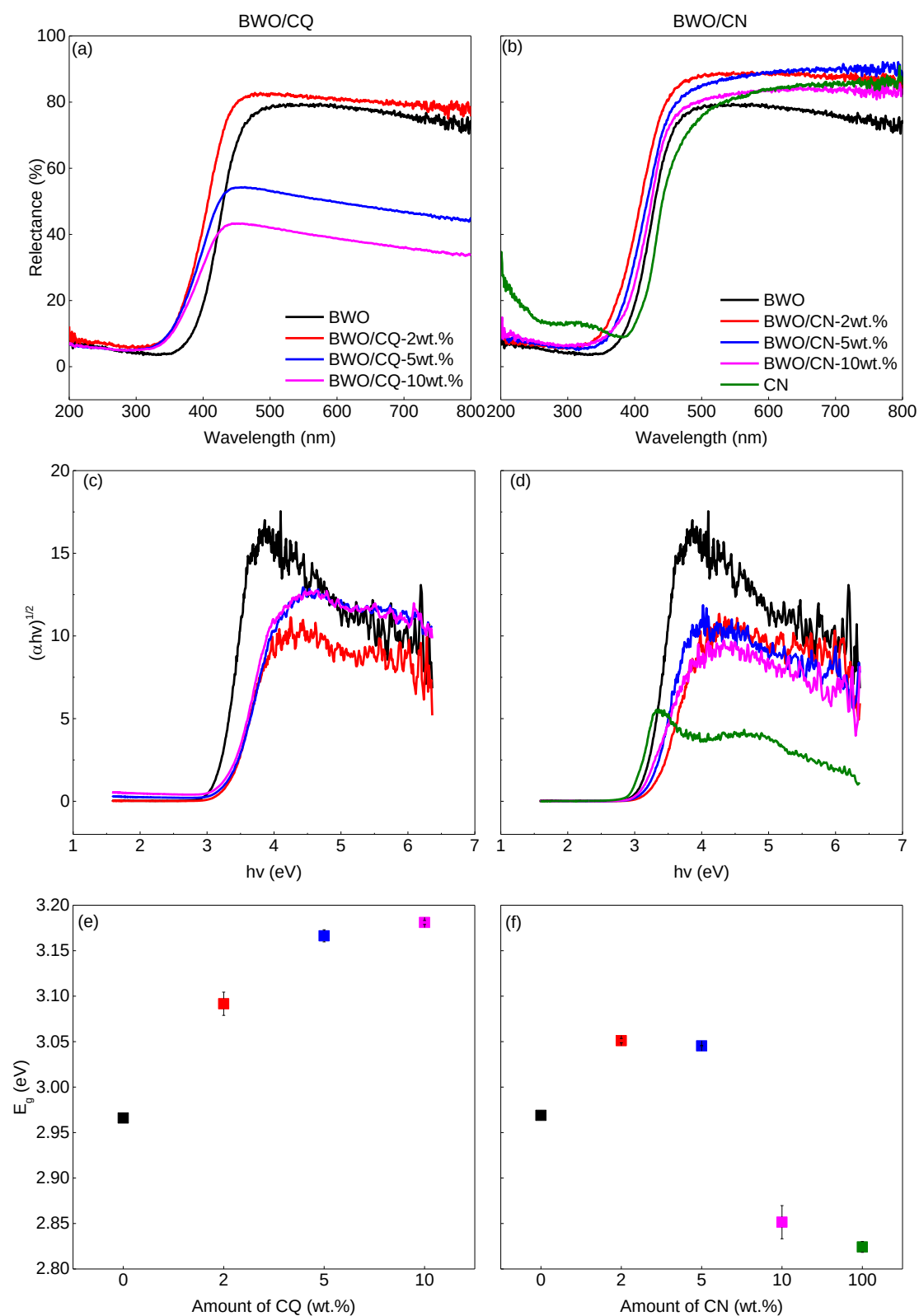


Figure 4.3 The diffuse reflectance (a) (b), Tauc plot and (c) (d) and energy gap (e) (f) of the obtained BWO/CQ and BWO/CN materials.

A strong adsorption edge was observed in the reflectance below 450nm for all

samples. Compared to bare BWO, all composite exhibited a blue shift in their adsorption edge due to the incorporation of carbon additives, regardless of the type and amount of the carbon additives. For the BWO/CQ materials, BWO/CQ-2wt.% exhibits a reflectance similar to that of pristine BWO in the visible light range, which is attributed to the low loading of the CQ additive. However, as the CQ content increases from 2wt.% to 10wt.%, the BWO/CQ composites are able to absorb more visible light in the range of 450–800 nm, attributed to the presence of a greater amount of residual carbon [Murcia-López et al. 2013]. Carbon materials contain the high density of C=C double bonds, it could trigger the harvesting of light in the visible range [Gesesse et al. 2020], as discussed in chapter 3. Additionally, no shift is observed in the absorption edge of the BWO/CQ composites. This can be attributed to the fact that excess carbon may lead to the formation of new defect sites or recombination centers, which promote the recombination of photogenerated electrons and holes, ultimately resulting in a reduction in photocatalytic activity [Cui et al. 2013]. As showed in Figure 4-3 (b), CN exhibited the highest light absorption due to its blackbody nature [Huo et al. 2021]. The absorption edge followed the trend: BWO/CN-2wt.% < BWO/CN-5wt.% < BWO/CN-10wt.% < CN < BWO < 500 nm. It can be observed that BWO/CN composites showed less dependence on the CN content in the visible adsorption (450-800 nm). Moreover, BWO/CN-2wt.% exhibits the most significant blue shift in the absorption edge among the composites and bare samples. When the CN content exceeds 2 wt.%, the absorption edge shifts slightly toward longer wavelengths, indicating that the CN percentage in the complexes significantly influences light energy utilization and electron-hole pair generation. This, in turn, impacts photocatalytic activity, as reported in previous study [Qi et al. 2021].

The obtained reflectance data has been analyzed by the Kubelka-Munk and Tauc plot approaches coupled with double linear fitting in order to calculate the energy gap of the catalysts. We can see that BWO/CQ composite overlapped each other in the linear part. The bandgap, in Figure 4-3(e), revealed increasing bandgap of BWO/CQ composite (>3.05 eV), which are bigger than the pure BWO (2.97 eV).

This suggested that the introduction of CQ can influence the electronic structure of BWO, although the quantity of CQ did not modify the light adsorption edge. The plots in Figure 4-3 (d) and (f) indicate that the doping of CN modifies the bandgap of BWO. Unlike the CQ addition, the impact of CN on the bandgap varies with changes in the amount of CN. The bandgap of composite was enlarged with incorporating 2wt.% of CN. Then, bandgap of the composite decreases as the amount of CN increases, 3.05 eV, 3.04 eV and 2.85 eV, respectively. These conclusions are consistent with the changes observed in the absorption edge.

The N₂ adsorption-desorption isotherms of BWO/CQ and BWO/ CN samples were recorded, showed in Figure 4-4 (a)(b). The IUPAC pseudo-type II gas adsorption isotherms were observed for all these samples [Sing et al. 2004], which means all these materials had low porosity. And it indicated that these obtained materials are mesopores with a hysteresis loop of H3, which suggests that the internal porosity of the obtained materials is predominantly slit-shaped and panel-shaped [Huo et al. 2021]. To a larger extent, the shape of hysteresis loop could endow a valuable interpretation of the pore structure. Thus, analysing hysteresis loops allows for an indirect assessment of the pore structures of various materials [Wang et al. 2012].

For BWO, the volume of gas adsorbed is very low ($\sim 50 \text{ cm}^3/\text{g,STP}$), with a wider range of relative pressures of hysteresis loop (from 1 to 0.5). This indicates the presence of mesopores. In Figure 4-4(a), it is evident that the hysteresis loop of the BWO/CQ composite shifts to a higher relative pressure range (from 0.5 to 0.8), and the area of the hysteresis loop decreases upon doping CQ into BWO. It indicates that the amount of micropore is increasing by incorporating with CQ. However, there is no observed significant hysteresis loop shift between the BWO/CQ composites, indicating that the amount of CQ did not affect the mesopore network, in agreement with the unchanging pore volumes (Figure 4.4 (e)). Concerning BWO/CN composite, when the 2 wt.% of CN was doped into BWO, the hysteresis loop shifted from 0.5 to 0.75 in terms P/P₀, which could be assigned to the high relative pressure hysteresis loop for bare CN (P/P₀:0.8). Then, the hysteresis loop

shifted back to 0.5 (P/P₀) again as the loading of CN are 5 and 10 wt.%. All of these results revealed that pore structure could be modified by incorporating with different amount of CN.

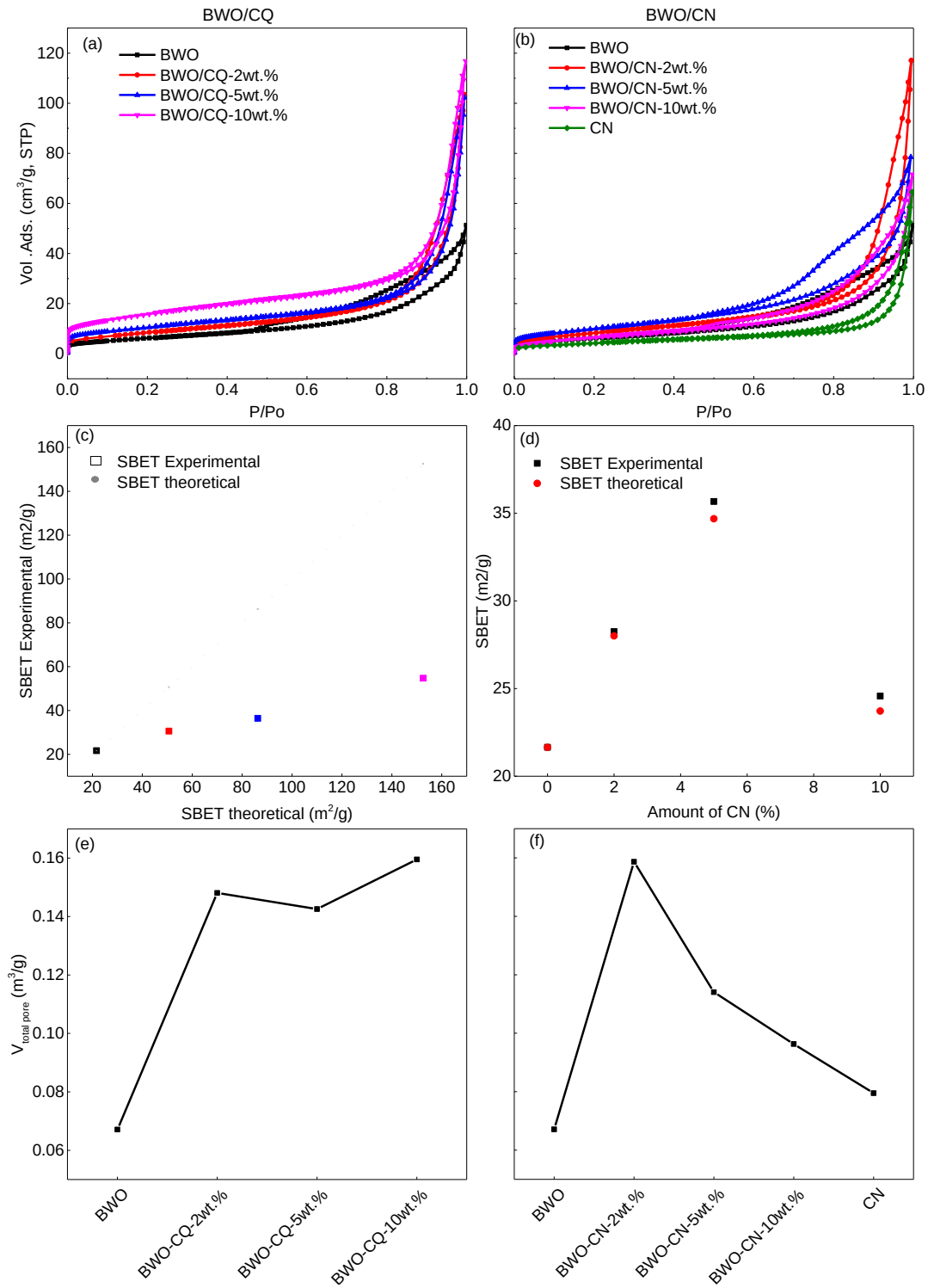


Figure 4.4 (a)(b) The N₂ adsorption-desorption isotherms, (c)(d) specific surface area and (e)(f) volume of total pores (@ P/P₀ of 0.99) of BWO/CQ and BWO/CN samples.

The SBET of these materials showed a slight increase when either CQ or CN was used as an additive, as illustrated in Figure 4-4(c)(d). The experimental data for the BWO/CQ samples exhibited a gradually increased trend of SBET with the rising of CQ content, attributed to the large specific surface area of CQ ($\sim 1033 \text{ m}^2/\text{g}$). The experimental values are lower than the theoretical values calculated based to the rules of the mixtures. This may be due to the fact that the pores in the CQ additive within the composite are not accessible to N_2 , in agreement with CN/CQ samples' results in chapter 3. In addition, the BWO/CN composite exhibits a larger specific surface area than both bare CN and BWO, suggesting that the combination of BWO and CN may create new pores, thereby enhancing the overall surface area. BWO/CN-5 wt.% exhibited the largest specific surface area within BWO/CN composites.

These observation indicates that the CQ additive interacts closely with the semiconductor particles, likely integrating within the layered structure of the WO_6 octahedra and $(\text{Bi}_2\text{O}_2)^{2+}$ units, rather than existing as isolated particles [Gomis-Berenguer et al. 2019]. Otherwise, the material would exhibit the computational features of the physical mixing rules of the catalyst components, as in the case of the BWO/CN complexes.

SEM was utilized to explore the morphology of the obtained samples. Studies proved that the morphology is a critical factor to affect photocatalytic performance [Yi et al. 2019]. As reported in our previous studies, the hydrothermal synthesis of BWO under our experimental conditions renders flower-like shaped microspheres (as showed in Annex I Figure S11) with average particle size between $3\text{-}8 \text{ }\mu\text{m}$ [Carmona et al. 2015]. The morphologies of BWO/CN-2wt.% and BWO/CN-5wt.% were showed in the Figure 4.5. As we can see, the addition of CN additives during hydrothermal synthesis had little effect on the morphology of BWO nanoparticles. All the composites were composed of flower-like shaped microspheres, which is consistent with other studies reported in literature [Chen et al. 2021; Carmona et al. 2015]. Isolated carbon particles were not observed in BWO/CN-2 wt.%, indicating good dispersion of the carbon material CN within the BWO particles. However,

some catalysts containing 5 wt.% carbon additives (e.g., BWO/CN-5 wt.%) exhibited the opposite behavior, which could be assigned to the increasing amount of CN additive [Gomis-Berenguer et al. 2019].

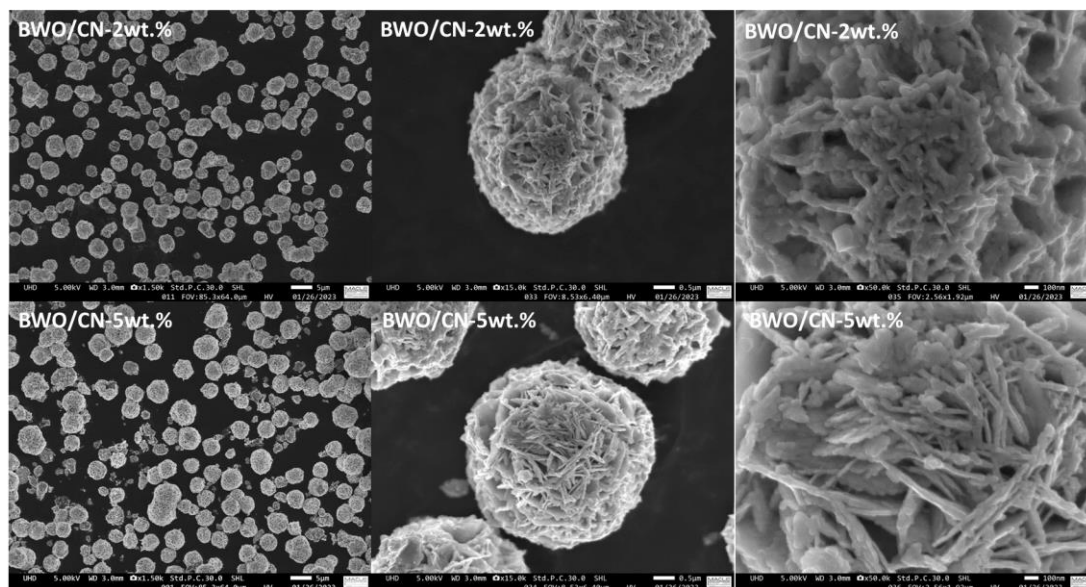


Figure 4.5 SEM images of selected samples: BWO/CN-2wt.% and BWO/CN-5wt.% synthesized by hydrothermal method.

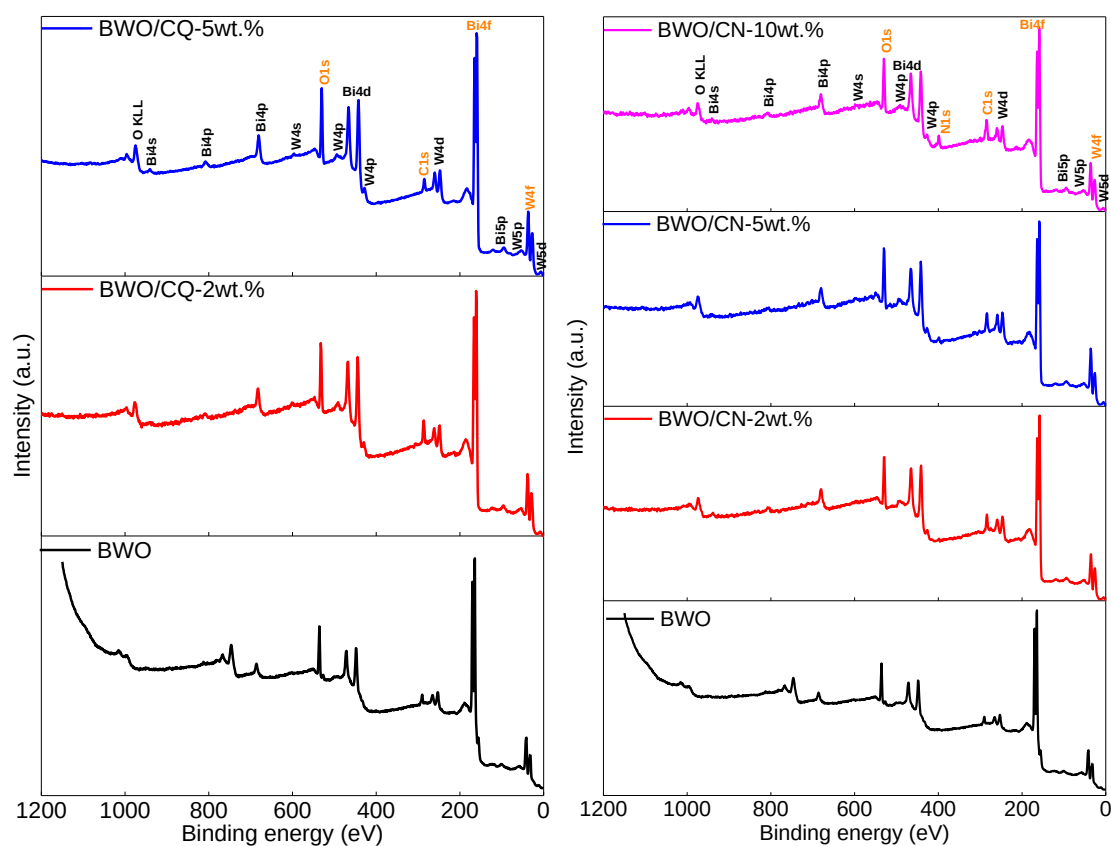


Figure 4.6 XPS survey spectra of as-prepared BWO/CQ (left) and BWO/CN (right) photocatalysts.

XPS analysis was performed to investigate the surface chemical composition and states of BWO, BWO/CQ, and BWO/CN composites. As shown in Figure 4.6, the XPS survey spectra confirm the presence of Bi, W, O, and C elements, with N elements specifically identified in the BWO/CN composites. In the case of W element, the W4f peak exhibits relatively high intensity and corresponds to the lowest binding energy, which is also observed for Bi4f, O1s, C1s, and N1s. The W4f peak in an XPS spectrum could represent the energy distribution of the emitted photoelectrons from the W4f orbital of the W atom. The peak's position and shape can provide insights into the chemical environment of W, such as the presence of different oxidation states or the interaction with other elements in the compound.

The high-resolution spectra of Bi4f was showed in Figure 4.7 (a)(c). For pristine BWO and BWO/Carbon 2wt.% (either CN or CQ additive), two sets of signals for Bi4f 5/2 and Bi4f 7/2 could be well fitted to two peaks. The binding energy were in 164.56 and 159.24 eV (5.32eV of the doublet separation energy), attributed to the oxidation state Bi^{3+} [Zhang et al. 2019]. The other binding energy at the 163.28 and 157.96 eV were ascribed to the lower oxidation state $\text{Bi}^{(3-x)+}$ [Huo et al. 2021]. The existence of oxidation state $\text{Bi}^{(3-x)+}$ suggest the oxygen vacancy (OV) defects of pristine BWO [Kong et al. 2019]. In terms of BWO/Carbon 5wt.% and 10wt.%, another set of signals were observed after deconvolution. It located in 164.8 and 159.48 eV, corresponding to the higher valence state of $\text{Bi}^{(3+x)+}$. Figure 4.7 (b)(d) indicated that the binding energy of W4f has two regions, W4f 5/2 and W4f 7/2. Two oxidation state were found for BWO and BWO/carbon 2wt.%, W^{6+} and W^{5+} . The binding energy of W^{6+} located in 37.59 and 35.46 eV with 2.13eV of the doublet separation energy. Another deconvolution at the 36.43 and 34.3 eV are ascribed to the W^{5+} oxidation state. With respect to the BWO/carbon 5wt.% and 10wt.%, the higher oxidation state of $\text{W}^{(6+x)+}$ was observed at 37.94 and 35.81 eV.

The high-resolution spectra of C1s and O1s for the two series materials were showed in Figure 4.8. The peaks of C1s could be deconvoluted to Csp², C-O and COO component, located at 284.8, 286.38 and 288.8 eV for both BWO/carbon materials. Due to the introduction of CN, high resolution spectra of BWO/CN

composite displayed another two signals, (C)3-N and N-C=N, located to 285.8 and 288.2 eV. For the O1s spectra of BWO/CQ and BWO/CN, peaks centred at 530.01, 530.52 and 532.2 eV are assigned to the crystal lattice oxygen atoms in Bi-O, W-O and C-O, respectively.

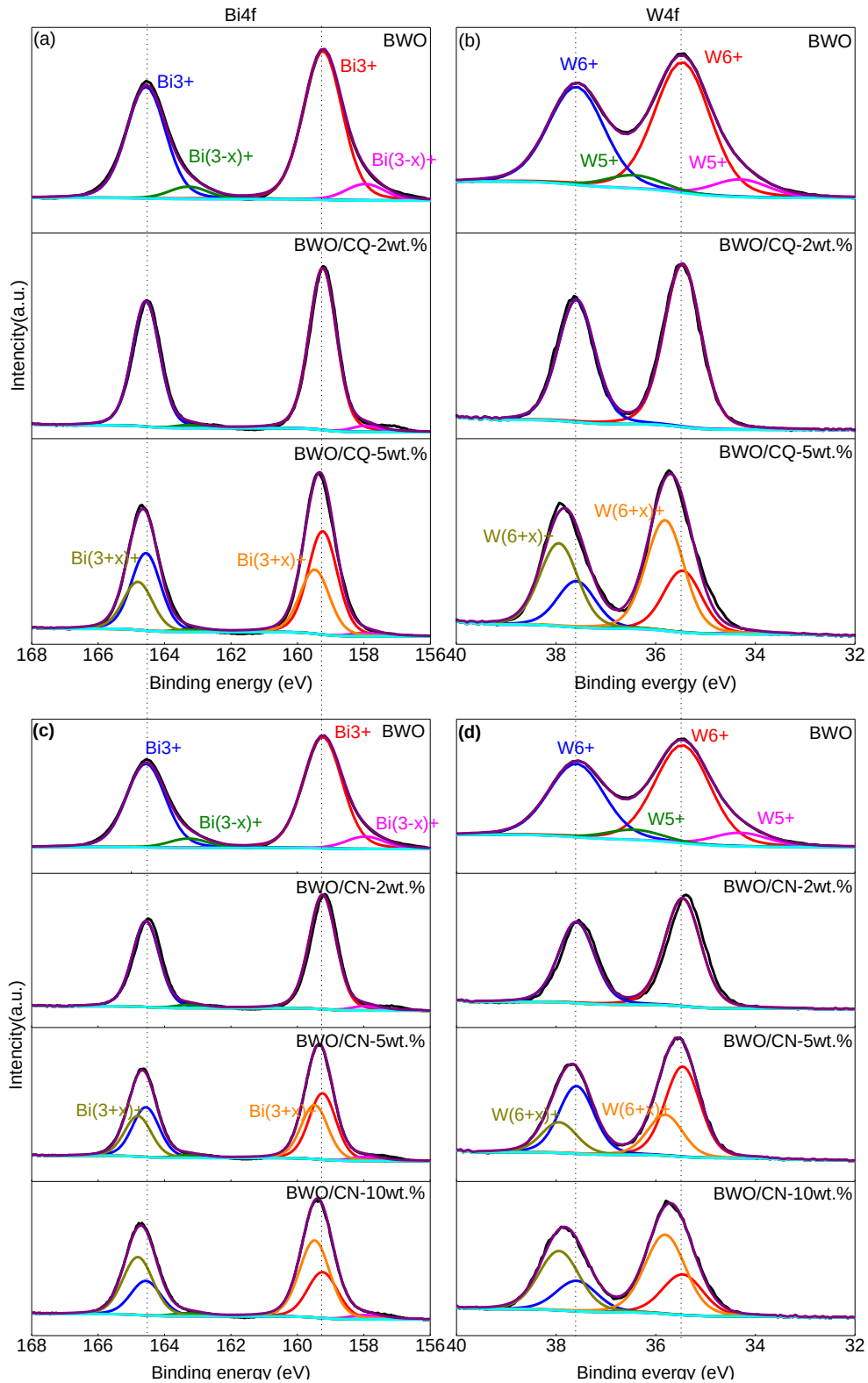


Figure 4.7 XPS analysis of BWO, BWO/CQ and BWO/CN composite: (a) (c) Bi4f and (b) (d) W4f high resolution spectra.

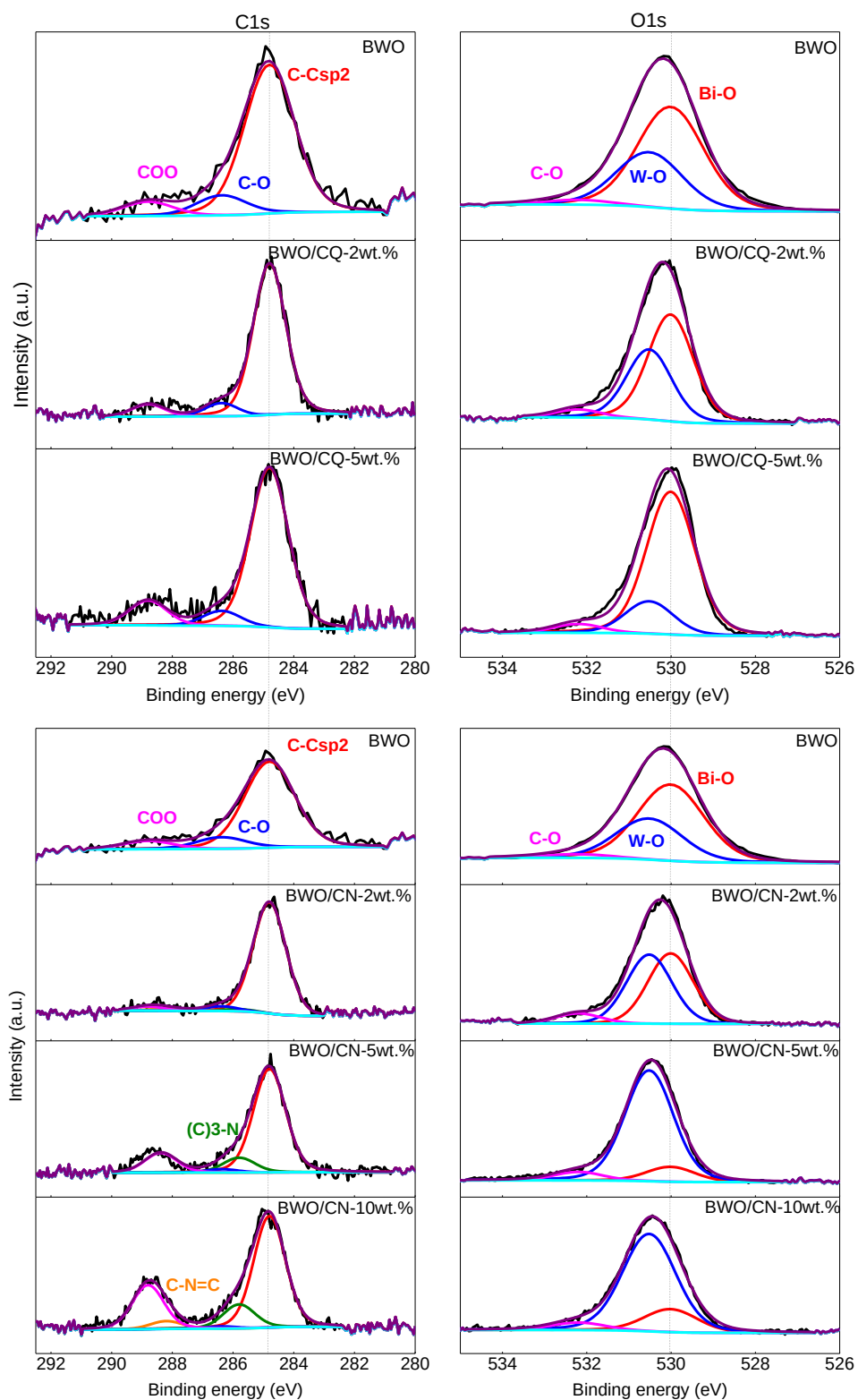


Figure 4.8 XPS analysis of BWO, BWO/CQ and BWO/CN composite: (a) (c) C1s and (b) (d) O1s high resolution spectra.

To understand the influence of carbon additives on the semiconductor (BWO), the correlation between the additive amount and the atomic concentrations are illustrated in Table 4.1, the correlation between the additive amount and relative abundance are showed in Figure 4.9 (Bi 4f and W 4f) and Figure 4.10 (C 1s and O 1s). As we can see, the N 1s atomic concentration increases with the rising CN content in the BWO/CN composite, as shown in Table 4.1. This not only confirmed the presence of CN in the composite but also demonstrated perfect control over CN proportion during the preparation process.

Table 4.1 Atomic concentrations (at.%) and Calculated mass percentage concentration (C-wt.%) of each element of samples : BWO, BWO/CQ composite and BWO/CN composite.

At.%	BWO	BWO/CQ composite		BWO/CN composite		
		2 wt.%	5 wt.%	2 wt.%	5 wt.%	10 wt.%
Bi 4f	28.43	21.94	21.87	18.63	15.53	15.05
W4f	9.74	7.08	7.01	5.78	6.56	4.92
C1s	23.30	33.92	23.19	36.20	36.03	39.76
O1s	38.53	37.05	47.92	36.68	37.27	31.76
N1s	--	--	--	2.71	4.61	8.51
Bi :W :O	2.9 :1 :3.9	3.1 :1 :4.8	3.1 :1 :6.8	3.2 :1 :6.3	2.4 :1 :5.7	3.1 :1 :6.5
C-wt.%						
Bi 4f	68.86	66.57	66.18	64.73	58.54	61.03
W4f	20.75	18.92	18.68	17.66	21.75	17.55
C1s	3.24	5.91	4.03	7.22	7.80	9.26
O1s	7.15	8.61	11.10	9.76	10.76	9.86
N1s	--	--	--	0.63	1.16	2.31

The relative abundance of Bi^{3+} and $\text{Bi}^{(3-x)+}$ decreased with the increasing amount of additive (either CQ or CN). The $\text{Bi}^{(3-x)+}$ oxidation state tended to disappear when the carbon additives were introduced, which revealed the removal

of OV defects. Refer to Figure 4.9 (c) (d), we could find that OV defects primarily arise from the removal of surface oxygen atoms in the W-O layers from BWO/CQ-materials, Bi-O layers from BWO/CN materials [Kong et al. 2019]. For the BWO/CQ composite, the pronounced increase in Bi-O component could be assigned to the $[\text{Bi}_2\text{O}_2]^{2+}$ slabs in BWO.

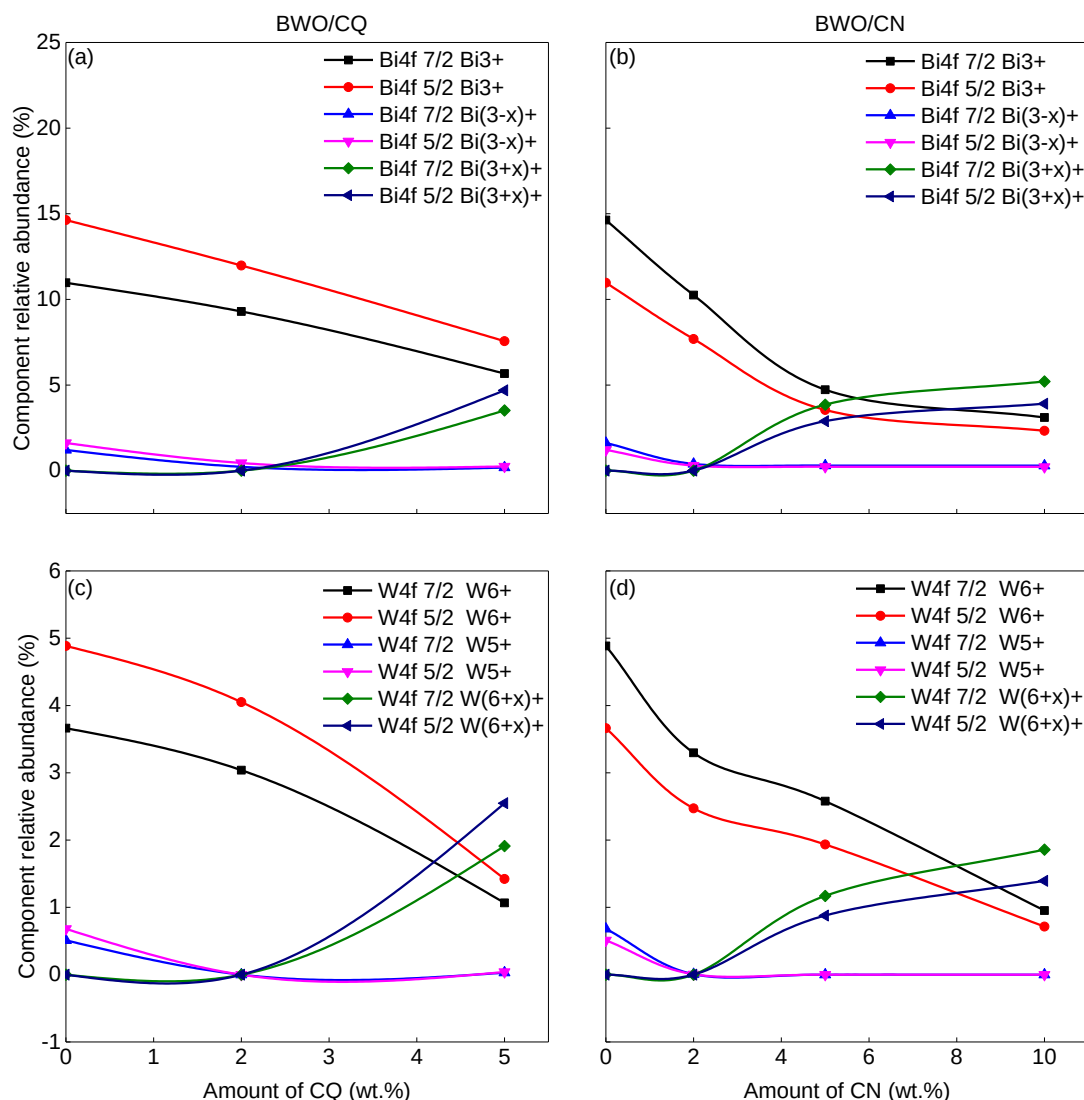


Figure 4.9 The correlation between the amount of additive and the relative abundance is shown in (a) (b) for Bi 4f, and in (c) (d) for W 4f, for the BWO/CQ and BWO/CN samples.

Likewise, the increase of W-O component for BWO/CN materials could be ascribed to the $(\text{WO}_4)^{2-}$ layers in the BWO. A positive correlation is observed between the $\text{Bi}^{(3+x)+}$ concentration and the amount of additives, and same trend was observed for the W4f spectra for both composites. The W^{6+} and W^{5+} concentrations

are negative correlation with the loading of carbon materials. On the contrary, the $W^{(6+x)+}$ concentration gradually increases, with higher additive amounts resulting in higher $W^{(6+x)+}$ concentrations.

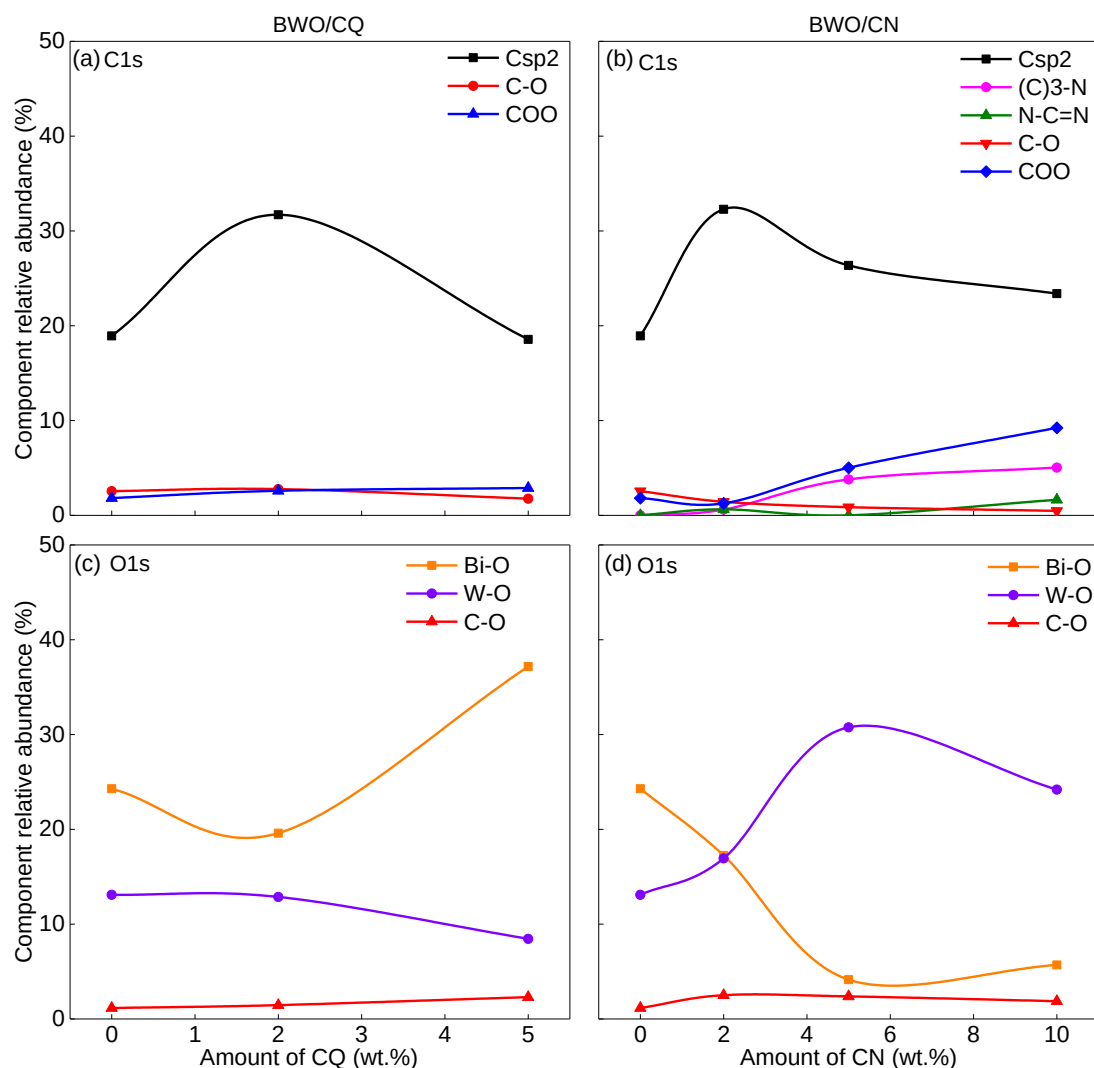


Figure 4.10 The correlation between the amount of additive and the relative abundance is shown in (a) (b) for C 1s, and in (c) (d) for O 1s, for the BWO/CQ and BWO/CN samples.

The positive binding energy shift means that the W and Bi elements lose more electrons upon the introduction of carbon materials, suggesting that electrons are transferred from BWO to the additive. The electron migration pathway implied that the BWO acted as an electron donor in the composite, both for BWO/CQ and BWO/CN. And the carbon materials served as an electron acceptor. This further

confirms that the introduction of carbon materials establishes a new mechanism to inhibit the electron-hole recombination in BWO.

4.2 Photocatalytic activity

4.2.1 Dark adsorption

As discussed above regarding porosity, contaminants in aqueous solutions can be adsorbed onto the surface of the catalyst pores, thereby influencing the pollutant concentration. Consequently, the adsorption capacity of the pores for MeP is measured prior to light exposure, ensuring control over the initial concentration at the start of the photocatalytic process, as done in chapter 3. The adsorption equilibrium of MeP on the different BWO/carbon samples are presented in Figure 4.11.

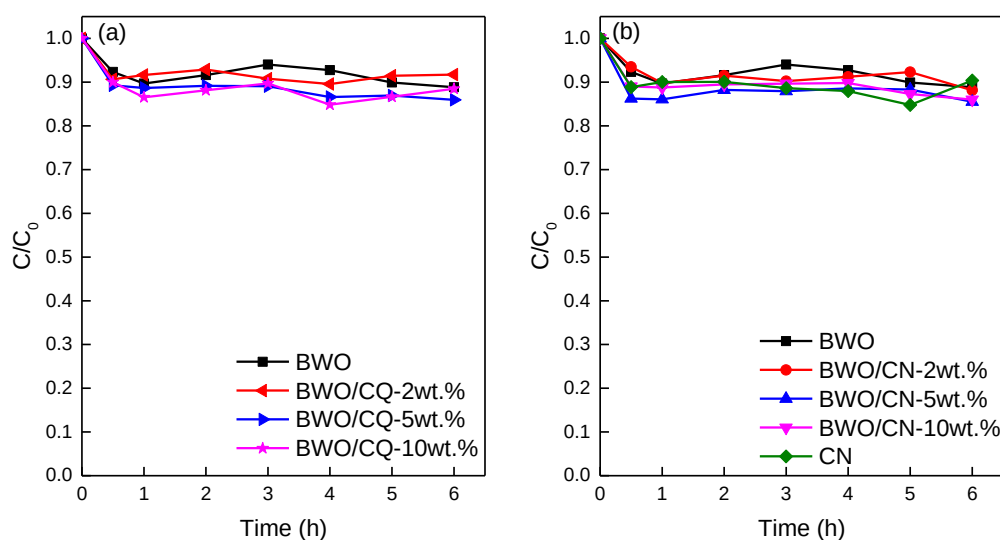


Figure 4.11 Adsorption equilibrium of MP in dark adsorption (a) BWO/CQ Ywt.% and (b) BWO/CN Ywt.%, Y referring to the amount of additive.

It can be observed that all the composites and bare BWO exhibit similar adsorption behavior, despite differences in the porosity of the materials. This is attributed to the low carbon loading in the composites, with a maximum of 10 wt.% in my study. In contrast, all the catalysts reached a similar uptake (~10%) of MeP within 30 minutes, which remained stable over 6 hours of contact with the aqueous solution. Concerning the adsorption capacity, an equilibrium time of 30 minutes was selected for all the catalysts before adding the irradiation.

4.2.2 The photocatalytic reaction under irradiation

The photocatalytic assays were carried out following the dark adsorption. To evaluate the impact of CQ and CN additives on BWO in degrading MeP, a series of photocatalytic experiments were conducted. The MeP conversion after 5 hours of light exposure was shown in Figure 4.12. Two cycles (assay01 and assay02) were conducted to evaluate the photocatalytic performance and stability of these two series of materials, BWO/CQ in (a)(b) and BWO/CN in (c)(d). As observed, all the materials achieved 100% conversion of MeP after 5 hours of irradiation. Among the BWO/CQ mixed materials, BWO/CQ-2wt.% exhibited the best performance, outperforming both the other composites and bare BWO. Regarding the BWO/CN samples, the photocatalytic performance of BWO/CN-2wt.% and BWO/CN-10wt.% showed a notable improvement over bare BWO. Nevertheless, the degradation of MeP by the BWO/CN complex remained slightly slower than that achieved by CN samples alone.

The first-order reaction rate mechanism was used again to determine the apparent rate constants (k_{app}). The fitted data corresponded to 99% methylparaben conversion, and the rate constants for MeP degradation were calculated (Figure 4.13). The data exhibited that the rate constants for methylparaben degradation by the BWO/CQ-2wt.% was higher than other two composites and BWO alone, indicating faster pollutant degradation. BWO/CN-10wt.% showed a bigger k_{app} than others. This trend persisted across two consecutive photocatalytic cycles for both kind samples. The highest rate constants for the degradation of methylparaben, achieved with sample BWO/CQ-2wt.% and BWO/CN-10wt.%, are approximately ~2 times (in two assays) that of bare BWO.

It is worth noting that, while two distinct intermediate products were identified in the previous chapter (referring to CN/CQ photocatalysts), only one prominent intermediate product peak, corresponding to polyhydroxylated intermediates, was observed when the BWO/carbon series catalysts were used to degrade MeP under irradiation, showed in Figure 4.14.

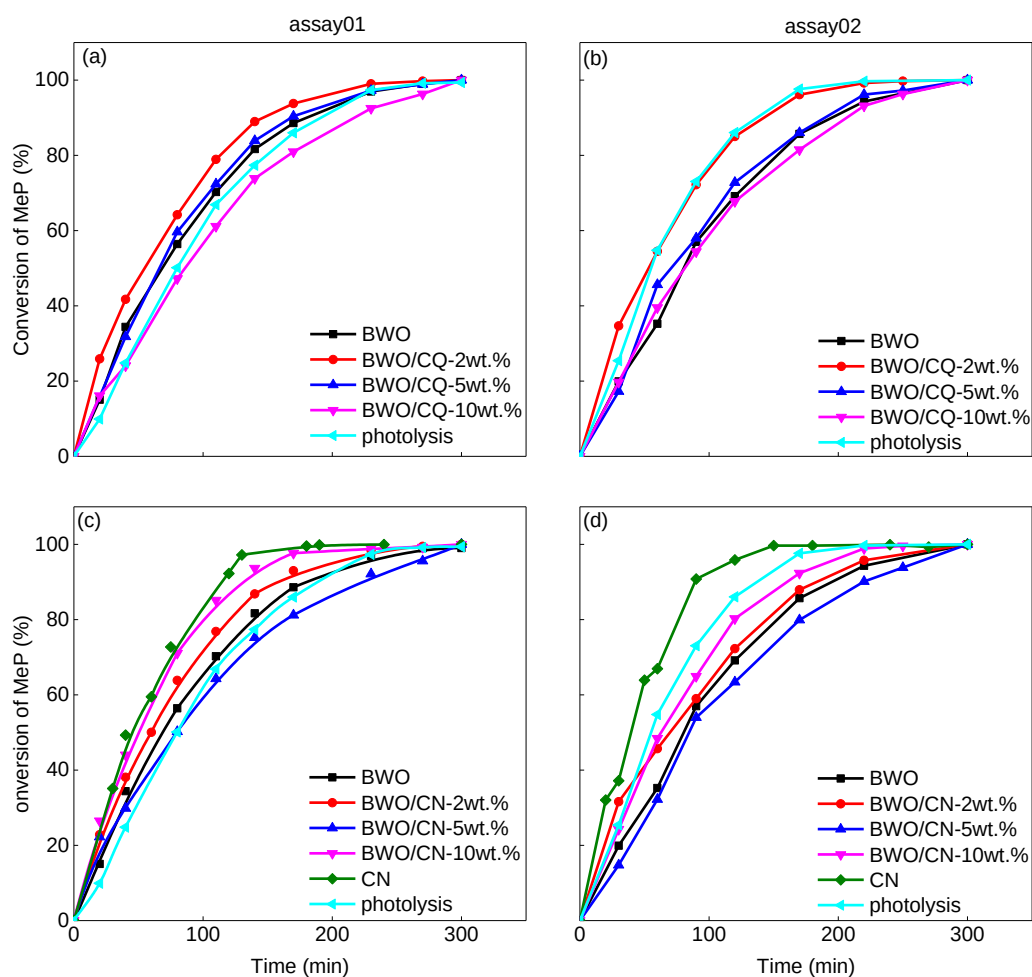


Figure 4.12 Conversion of methylparaben during two consecutive photocatalytic assays (a,b) BWO/CQ Ywt.% and (c,d) BWO/CN Ywt.%, Y referring to the amount of additive.

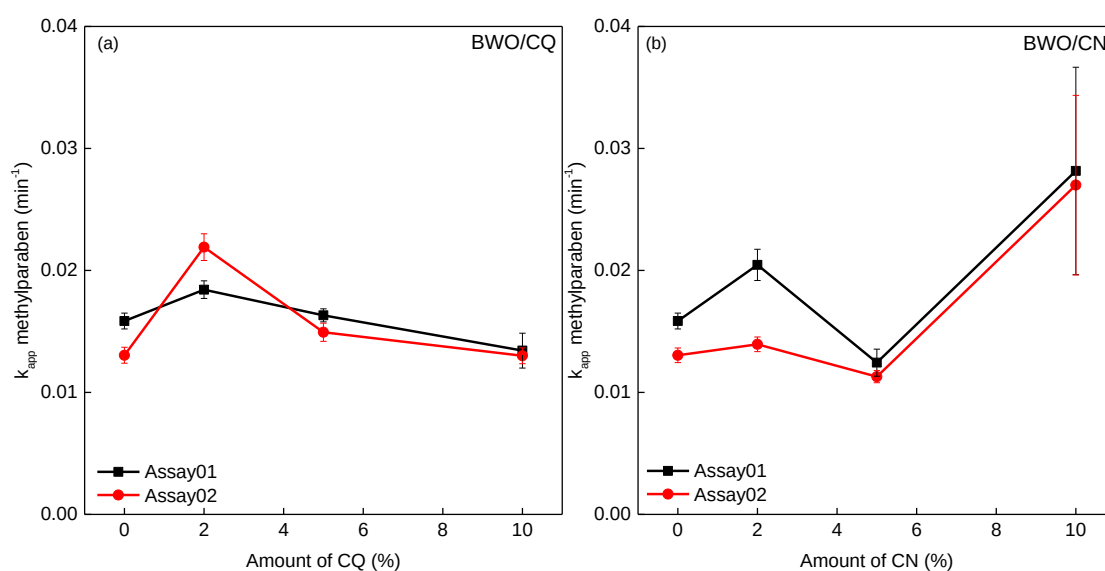


Figure 4.13 Rate constants for the degradation of methylparaben degradation: (a) BWO/CQ and (b) BWO/CN samples.

Interestingly, the amount of polyhydroxylated intermediates reduced when the BWO/CQ composites are used as photocatalysts. The greater the amount of CQ, the more significant impact on hindering the formation of polyhydroxylated intermediate. Therefore, the amount of polyhydroxylated intermediate for BWO/CQ-10wt.% is minimal compared to the others. Unlike the addition of CQ, the CN additives did not affect the total amount of polyhydroxylated intermediates. However, it significantly accelerated the rapid generation and degradation of polyhydroxylated intermediates within 3 hours (BWO/CN-10wt.% showed the best performance). The rate constants for the degradation of the polyhydroxylated intermediate compounds were also calculated, showed in Table 4.2).

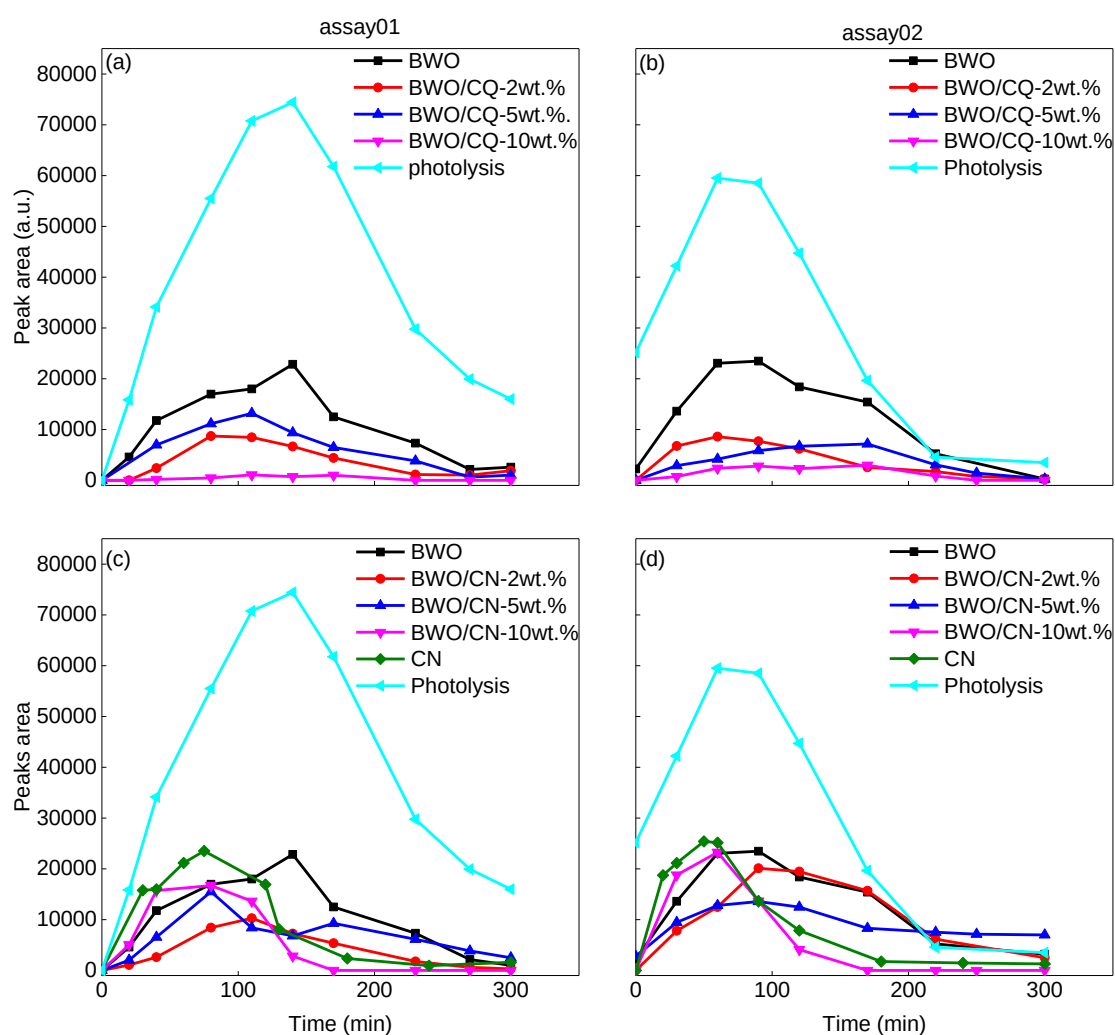


Figure 4.14 Evolution of the degradation polyhydroxylated intermediate detected in solution for the (a)(b) BWO/CQ and (c)(d) BWO/CN composites in consecutive photocatalytic assays.

Table 4.2 Rate constants (k_{app}) for the polyhydroxylated intermediate at two consecutive photocatalytic assays.

k_{app} (min ⁻¹)	assay01	assay02
	Polyhydroxylated intermediates	
BWO	0.014	0.013
BWO/CQ-2wt.%	0.017	0.018
BWO/CQ-5wt.%	0.016	0.014
BWO/CQ-10wt.%	0.025	0.025
BWO/CN-2wt.%	0.015	0.014
BWO/CN-5wt.%	0.007	0.009
BWO/CN-10wt.%	0.021	0.022
CN	0.017	0.016

4.2.3 Mechanism investigation

As found above, when the two materials, CQ and CN, were incorporated with BWO, the resulting complexes exhibited markedly different photocatalytic properties, either for MeP or intermediate. To investigate the reasons behind this difference, we analyzed the photocatalytic behavior of composites (BWO/CQ-10wt.% and BWO/CN-10wt.%) and bare catalysts (BWO and CN) in the presence of different scavengers, depicted in Figure 4.15.

The conversion of MeP is significantly reduced (drop ca.10%-15%) for the bare BWO and the two composites (BWO/CQ-10wt.% and BWO/CN-10wt.%) in the presence of $\bullet\text{OH}$ and h^+ scavengers. Notably, the three materials exhibit the completely identical effect on MeP degradation when h^+ and $\bullet\text{OH}$ radicals are trapped, respectively. Obviously, the $\bullet\text{OH}$ was generated in the valence band of BWO, because the E_{VB} of BWO is more positive than the standard redox potential of $\bullet\text{OH}/\text{OH}^-$ (+2.3 eV vs NHE) [Torad et al. 2021]. These results indicated that hydroxylation-mediated oxidation is the primary pathway for the MeP degradation, while the reaction of photogenerated h^+ with H_2O serves as the sole pathway for hydroxyl radical formation. Although the using of CN catalyst exhibited a subtle difference in MP conversion in the case of $\bullet\text{OH}$ radicals and h^+ being trapped, it did not impact the performance of BWO/CN-10 wt.%. This may be due to the low loading of CN in composite.

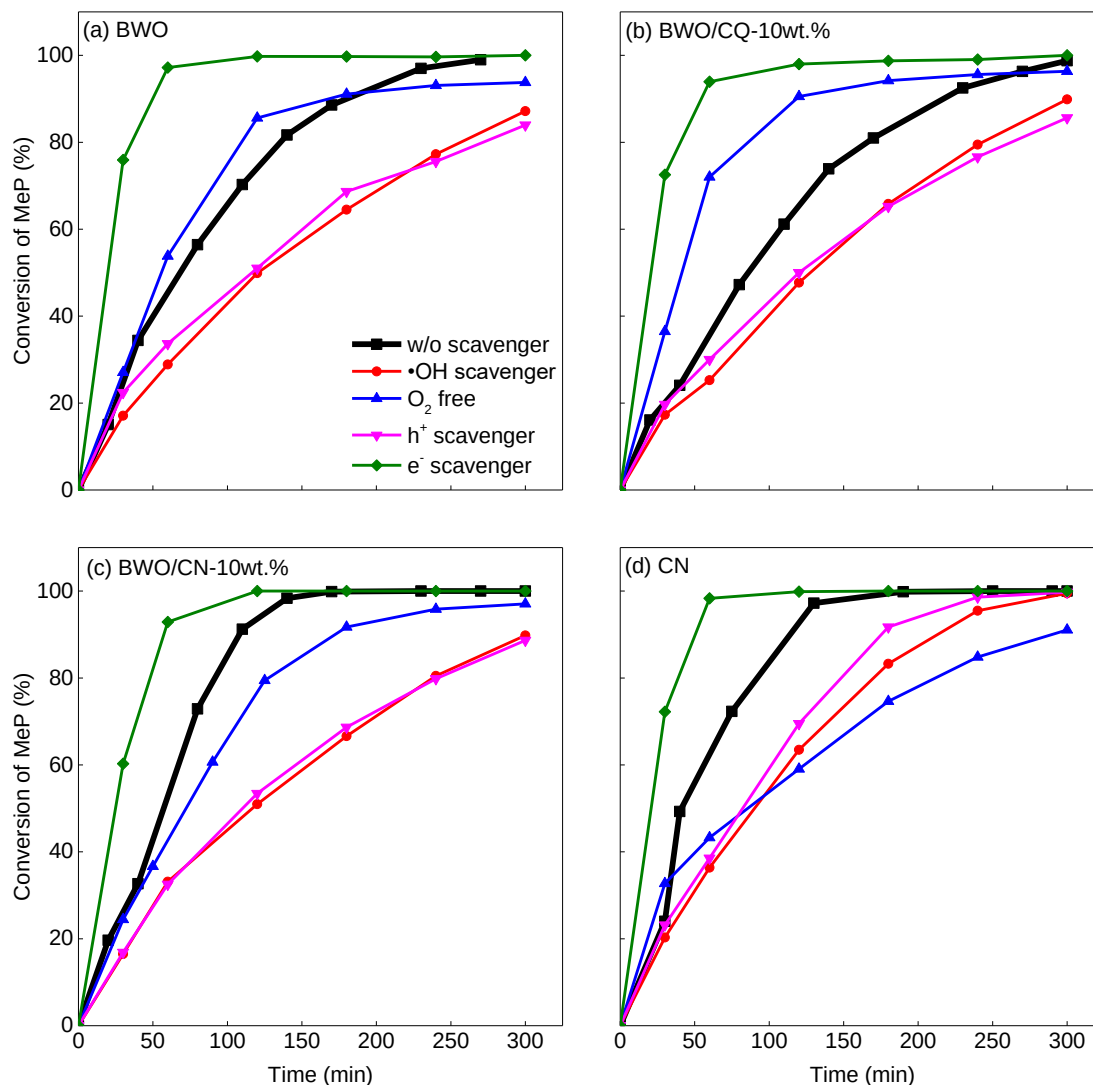


Figure 4.15 Conversion of MeP in the presence of •OH, h⁺, e⁻ scavenger and in oxygen-free conditions for (a) BWO; (b) BWO/CQ-10wt.%; (c) BWO/CN-10wt.% and (d) CN.

As reported [Oluwole et al. 2023], the standard redox potential of O₂/•O₂⁻ is -0.33 eV vs NHE (lower than +0.21 eV), which suggested that the generation of •O₂⁻ radicals in conduction band of BWO were insufficient. For pristine BWO, the MeP conversion under the O₂-free condition revealed a different trend to that of without scavenge. The conversion of MeP reached ca.97% for samples BWO/carbon materials in the absence of •O₂⁻ radicals, which was more pronounced than the bare BWO (ca.93%) and CN (ca.90%), showed in Figure 4.16.

In the case of BWO, the removal of O₂ slightly accelerated the degradation of MeP. Meanwhile, the MeP degradation were largely increased with the introduction

CQ to BWO. It could be assigned to the low recombination of h^+ and e^- when the C acted as an electron acceptor [Bai et al. 2014]. However, BWO/CN-10wt.% exhibits exact opposite result, observed a largely reduction of MeP conversion under O_2 -free condition, which indicated that the activation of O_2 through its reaction with photogenerated e^- plays a crucial role for MeP decomposition as well. These results implied a possible charge transfer upon a Z-scheme inside BWO/CN-10wt.% [Senthil et al. 2017; Liu et al. 2021]. For all catalysts tested, the absence of photogenerated e^- significantly enhanced MeP removal (approximately ca. 99% within 60 min). This is attributed to the effective suppression of electron-hole recombination, which, in turn, promoted MeP degradation by $\bullet OH$, $\bullet O_2^-$ radicals and photogenerated h^+ . The rates constant with and without scavengers, in Figure 4.16, favored to the above conclusion.

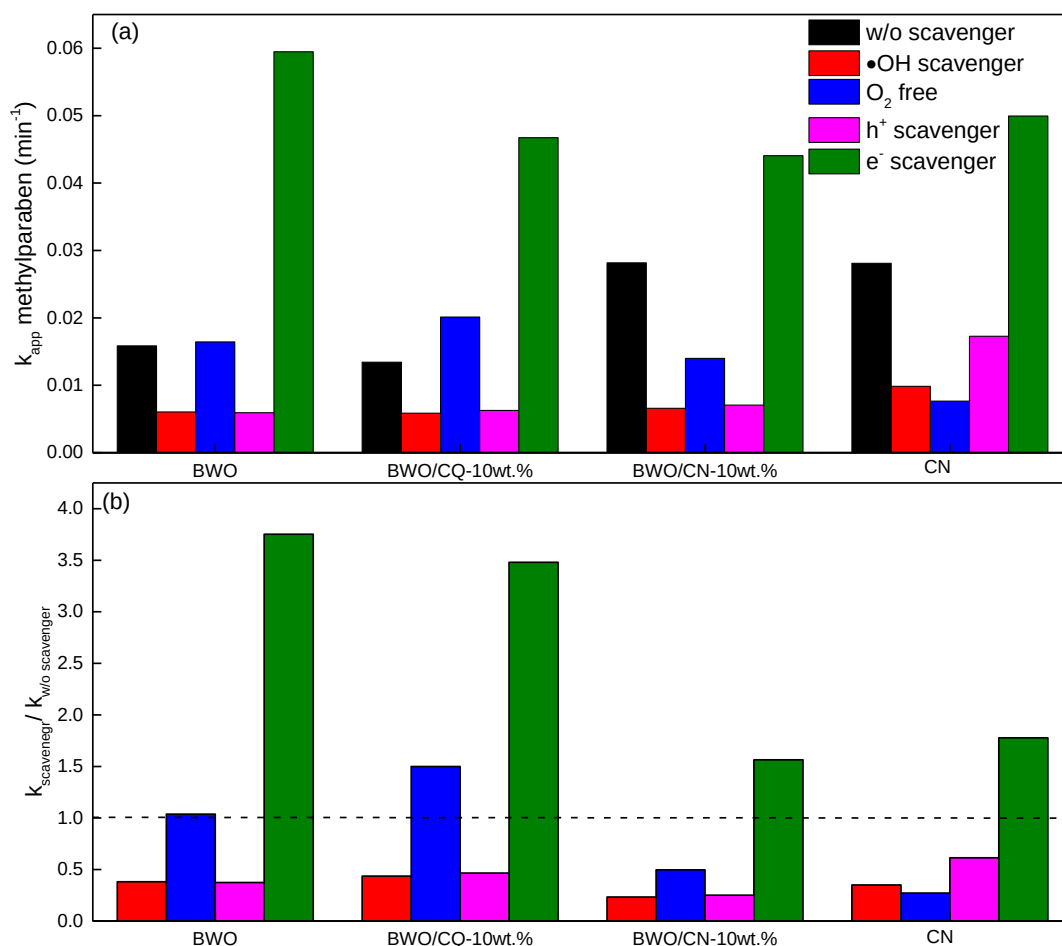


Figure 4.16 Rate constant (K_{app}) and the ratio $K_{scavenger}$ to $K_{w/o\ scavenger}$ of methylparaben degradation in the presence of $\bullet OH$, h^+ , e^- scavenger and in oxygen-free conditions for BWO; BWO/CQ-10wt.%; BWO/CN-10wt.% and CN.

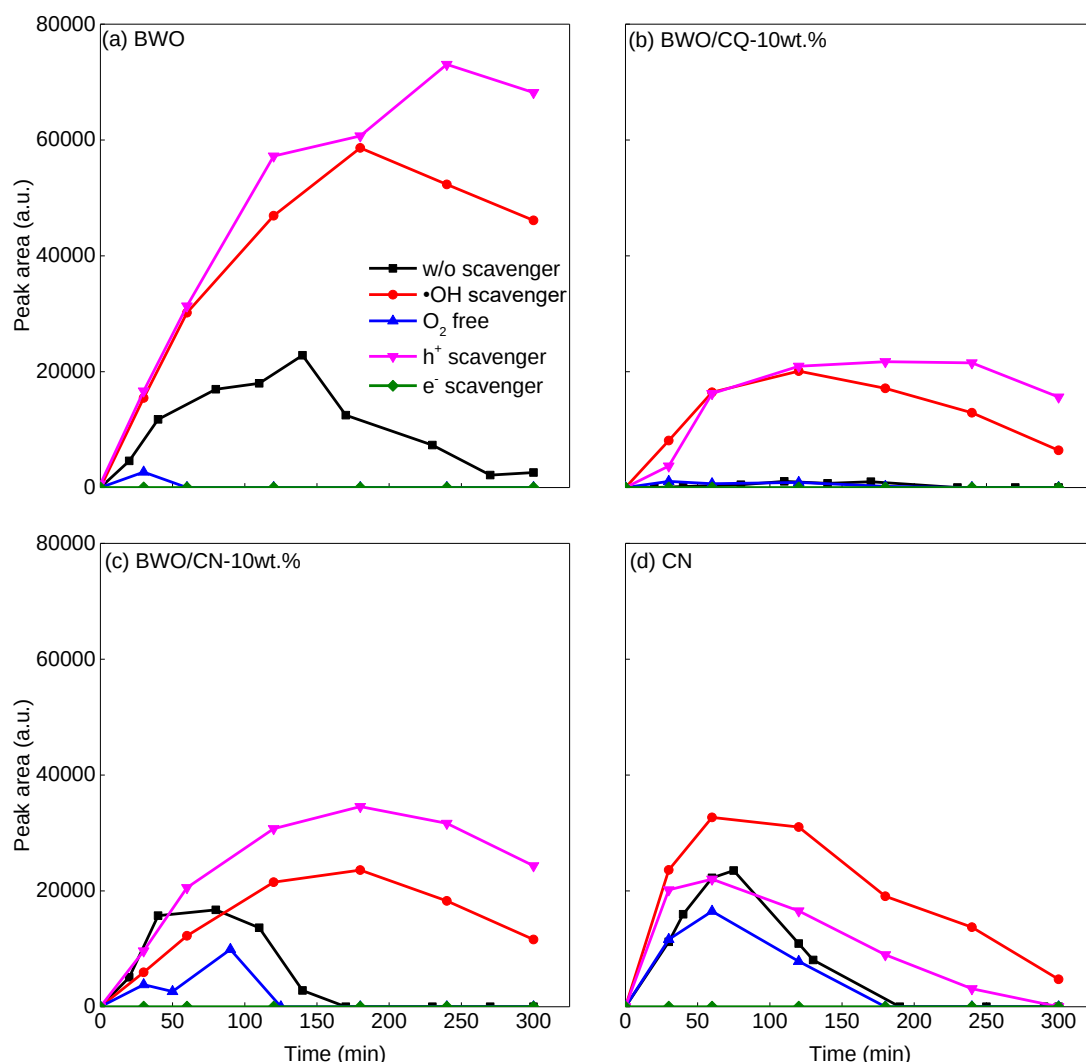


Figure 4.17 Evolution of its degradation polyhydroxylated intermediates in the presence of $\bullet\text{OH}$, h^+ , e^- scavenger and in O_2 free conditions for (a) BWO; (b) BWO/CQ-10wt.%; (c) BWO/CN-10wt.% and (d) CN.

The evolution of degradation polyhydroxylated intermediates were displayed in Figure 4.17 in the presence of scavengers. In terms of the all the materials, the polyhydroxylated intermediates concentration begins to increase and persists for a longer duration in the absence of $\bullet\text{OH}$ radicals and photogenerated h^+ . And concerning BWO sample, the yield of intermediate is the largest compared to other catalysts (BWO/carbon composite and bare CN). However, when BWO was integrated with both CQ and CN, the yield of intermediates was drastically reduced. This indicates that the hydroxylation-mediated oxidation is the also the dominant pathway to remove polyhydroxylated intermediate. The introduction of carbon

materials contributed to improve the oxidation of intermediate. What's more, the absence of $\bullet\text{O}_2^-$ radicals could accelerate the formation and degradation of polyhydroxylated intermediate, similar to the results observed in the absence of photogenerated e^- .

In order to further investigate the photocatalytic mechanism, the photocurrent transients of BWO, BWO/CQ-10% and BWO/CN-10% upon illumination are measured at various conditions and after adding the chemical scavengers, displayed in Figure 4.18. The transient photocurrent curves upon on/off illumination of bare BWO showed a sharp (positive) photocurrent spike that follows a smooth decay over time (sometimes accompanied with a sharp current overshoot). This indicates that our prepared BWO presents n-type semiconductor properties, and thus that photogenerated electrons are the majority charge carriers.

For the BWO/CQ 10wt.%, the transient photocurrents show a similar shape that those of BWO, indicating the n-type character of the composite. On the contrary, BWO/CN 10wt.% showed a negative photocurrent, indicating a p-type semiconductor properties, which could be attributed to the p-type semiconductor properties of bare CN. On average, the magnitude of the photocurrent was larger for the composites (either BWO/CQ 10wt.% or BWO/CN 10wt.%) than for bare BWO, which indicates the lower recombination of the charge carriers in the composites (thus in line with the improved photocatalytic performance for the degradation of methylparaben).

The magnitude of the photocurrent increased in the presence of the hole scavenger, and decreased in the presence of superoxide and electron scavengers for BWO. In the case of BWO/CQ-10wt.%, the magnitude of the photocurrent increased in the presence of the hole and superoxide scavenger, and decreased in the presence of electron scavengers. For BWO/CN-10wt.%, the photocurrent increased in the presence of the superoxide scavenger, and decreased in the presence of hole and electron scavengers. All these results revealed that the effect of the electrons' scavenger is more pronounced.

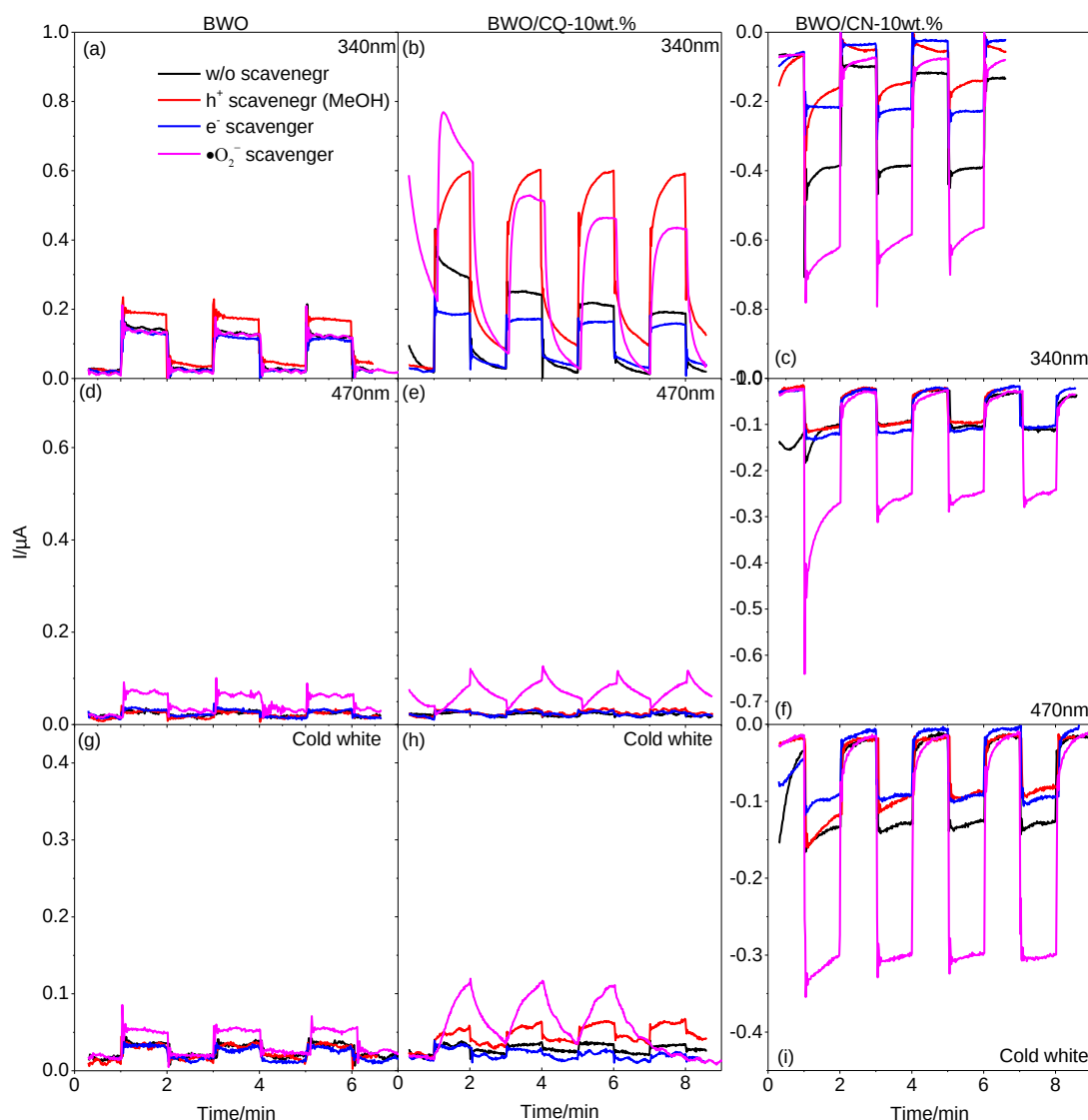


Figure 4.18 Photocurrent transients of BWO, BWO/CQ-10wt.% and BWO/CN-10wt.% after adding different scavengers upon illumination at various conditions: 340 nm, 470 nm and simulated solar light (cold white), recorded at 0.7 V (BWO and BWO/CQ) and -0.15 V (BWO/CN-10wt.%) vs Ag/AgCl in 0.5 M Na_2SO_4 (pH 2).

The decreased photocurrent in the presence of the electron scavenger is expected since the measured photocurrent corresponds to the reduction of the electrolyte due to the photogenerated electrons. Similar trends were obtained regardless the illumination conditions, although the intensities of the photocurrents corresponding to the signals in the presence of superoxide scavenger were much higher under visible light (470 nm and simulated solar light) than under UV. In addition, the magnitude of the photocurrent for BWO/CQ-10 wt.% and

BWO/CN-10.wt.% were higher (2 and 2.7 times enhancement) than that of pristine BWO upon illumination at 340 nm, indicating a more efficient electron injection in the conduction band in the composite. We attribute this to the π electron density of the nanoporous carbon that would facilitate the electron mobility for BWO/CQ sample and successful construction of Z-scheme heterojunction for BWO/CN sample, which would effectively suppress the competing recombination of excitons. In contrast, higher photocurrents were recorded for BWO/CN-10.wt.% than for the BWO alone and BWO/CQ-10.wt.% when illuminated at 470 nm and simulated solar light. This indicates that the increased efficiency in the photogeneration of the charge carrier upon the construction of Z-scheme heterojunction. This aligns well with the photocatalytic performance discussed in Figure 4.13.

The steady-state photocurrent of each system in the normal electrolyte (without scavenger, $I^{\text{ss}}_{\text{wo}}$) and in the electrolyte containing the scavenger ($I^{\text{ss}}_{\text{scav}}$) were calculated (see discussion in chapter 3), as well as the ratio of both magnitudes (η_{transfer}) (Table 4.2).

Table 4.2 Steady-state photocurrent (I^{ss}) in the presence and absence of scavengers and methylparaben upon illumination at various conditions.

	I^{ss} (μA)	w/o scavenger	h^+ scavenger (MeOH)	e^- scavenger	$\bullet\text{O}_2^-$ scavenger
340nm	BWO	0.11	0.14	0.10	0.11
	BWO/CQ-10wt.%	0.22	0.39	0.13	0.20
	BWO/CN-10wt.%	-0.29	-0.13	-0.19	-0.53
	CN	-0.74	-1.11	-0.50	-0.90
470nm	BWO	0.03	0.01	0.01	0.01
	BWO/CQ-10wt.%	0.00	0.01	0.01	-0.01
	BWO/CN-10wt.%	-0.07	-0.07	-0.09	-0.23
	CN	-0.18	-0.22	-0.17	-0.12
Cold white	BWO	0.02	0.02	0.02	0.03
	BWO/CQ-10wt.%	0.01	0.02	0.01	0.02
	BWO/CN-10wt.%	-0.11	-0.09	-0.08	-0.27
	CN	-0.22	-0.17	-0.23	-0.28

When methanol is added to the electrolyte (hole scavenger), the photocurrents in both BWO and BWO/CQ-10wt.% increased, compared to the measurements in

the normal electrolyte, indicating a more efficient transfer of the electrons to the electrolyte. A similar trend was observed for BWO/CQ-10 wt.% and BWO/CN-10wt.% in the presence of BQ scavenger. In contrast, in the presence of acetone the photocurrents decreased indicating the effective scavenging of the photogenerated electrons.

4.3 Partial conclusions

In this chapter, we have investigated how the incorporation of carbon materials of different nature (i.e. a nanoporous carbon and carbon nitride) as additives to BWO semiconductor can modify the mechanism of the photocatalytic activity for the degradation of methylparaben. The characterization results of the two composite materials revealed that the incorporation of carbon additives (CN or CQ) did not significantly alter the structural properties of the pristine semiconductor. CQ introduction enhanced visible-light absorption but triggered a blue shift in the absorption edge of BWO, accompanied by an enlarged band gap. CN integration preserved visible-light absorption capacity despite an initial blue shift; however, a distinct red shift emerged with increasing CN content. Porosity variations exhibited complete dependence on the additive type, with CQ and CN demonstrating divergent impacts on the composite's mesoporous structure. And, we found that both CN and CQ additives were embedded within the BWO matrix rather than surface-deposited, suggesting bulk-phase interactions. In addition, BWO/CQ and BWO/CN composites outperformed pristine BWO in degrading methylparaben (MeP) and its intermediates. In particular, BWO/CQ demonstrated accelerated degradation kinetics for intermediates, whereas BWO/CN exhibited superior efficiency in primary MeP removal. The photocatalytic assays carried out in the presence of chemical scavengers have demonstrated the enhanced charge transfer of the photogenerated electron-hole pairs towards the methylparaben in the presence of the carbon additives. However, distinct degradation mechanisms were revealed: BWO/CQ predominantly relied on hydroxyl radicals ($\bullet\text{OH}$), and BWO/CN primarily utilized superoxide radicals ($\bullet\text{O}_2^-$).

Chapter 5. Photocatalytic activity of LDH/CN composites for the degradation of MeP

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In this chapter, we report the preparation of a hybrid photocatalyst by immobilizing g-C₃N₄ in the interlayer space of a trimetallic NiZnAl-LDH via the co-precipitation method, using an increased amount of g-C₃N₄ (from 5 wt.% to 50wt.%), labelled as LDH/CN-x wt.%, where x refers to the amount of carbon nitride powders dispersed in the suspensions. Different characterisation techniques are utilized to investigate the optical, structural, and textural properties of the synthesized materials, which could facilitates linking to their photocatalytic performance in methylparaben degradation under simulated UV-VIS irradiation. Meanwhile, the degradation mechanism mediated by LDH/CN photocatalysts was elucidated through a combined approach involving photocatalytic activity tests using chemical scavengers and advanced electrochemical analyses (e.g., transient photocurrent measurements).

5.1 Characterization of the photocatalysts

Figure 5.1 (a-e) depicts the XRD patterns of the prepared LDH/CN composites, compared to those of the pristine components LDH-NiZnAl and carbon nitride. The diffraction pattern of the synthesized NiZnAl double layered hydroxide displayed the characteristic peaks corresponding to the LDH structure, indexed to JCPDS-ICDD files of nickel oxide hydroxide (01-089-7111), nickel aluminum hydroxide (04-025-1941), zinc hydroxide (04-013-9365) and zinc hydroxide dehydrate (01-091-1676). The well-defined peaks at $\sim 11^\circ$ (003) $\sim 23^\circ$ (006) and $\sim 34^\circ$ (009) planes indicate a crystalline layered structure with rhombohedral symmetry. The basal spacing distance of the (003) peak was 0.786 nm, which is consistent with values reported for similar LDH materials in the literature [López et al. 2003; Sherryrna et al. 2024; Feng et al. 2022; Benedictto et al. 2018; Reyero et al. 2013].

For the CN (00-066-0813), the characteristic diffraction peak at 27.46° (002) associated to the interlayer stacking of aromatic structures with a graphitic-like structure [Li et al. 2023] was clearly observed, along with an ill-defined peak at 12.93° (210) associated to parallel chains of tri-s-triazine units [Fina et al. 2015].

The XRD patterns of the LDH/CN composites displayed the typical characteristic diffraction peaks of both components NiZnAl-LDH and g-C₃N₄, without evidences of additional peaks corresponding to different phases. Similar observations have been reported for LDH/CN composites prepared by different methods [Gandamalla et al. 2021; Tripathi and Hussain 2021; Sherryrna et al. 2024; Feng et al. 2022; Wang et al. 2014].

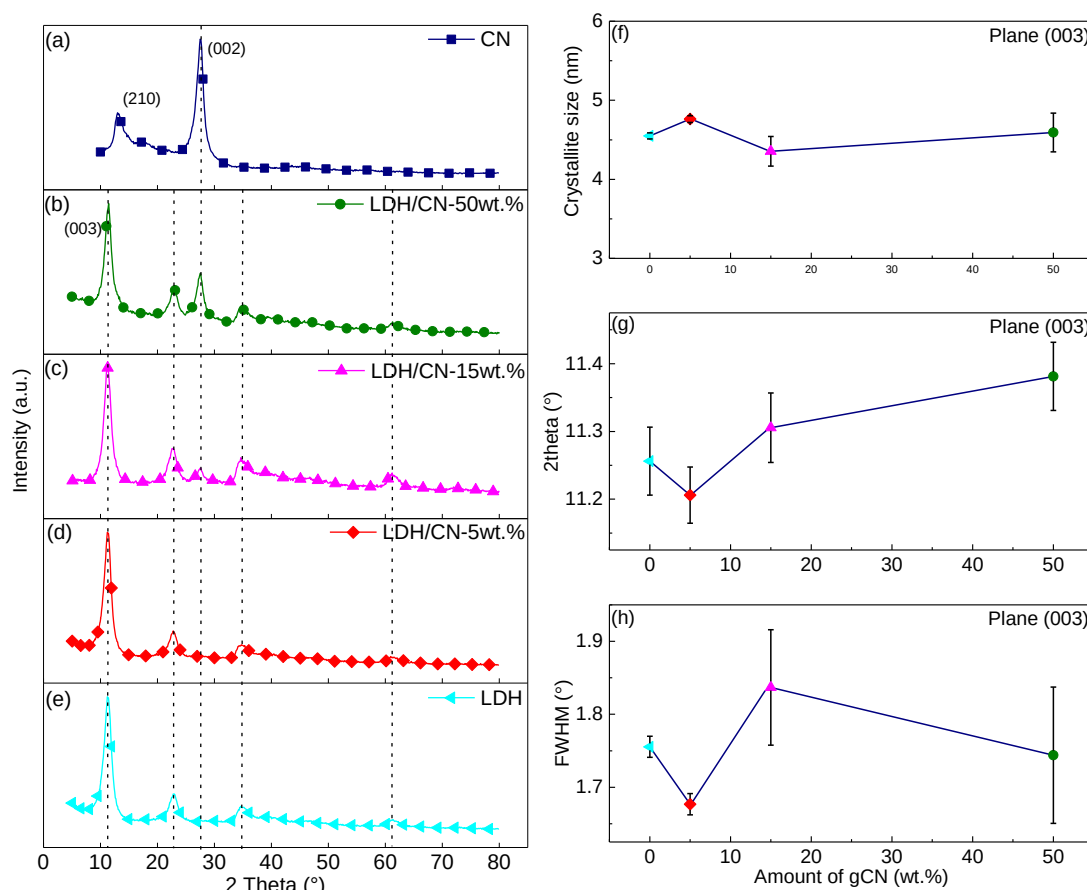


Figure 5.1 (a-f) X-ray diffraction patterns, (g) crystallite size, (h) position and (k) FWHM of the (003) reflection plane of the prepared samples.

A detailed analysis of the crystallinity parameters (position, FWHM, crystallites size) corresponding to the main reflection peak of the LDH shows a correlation with the amount of carbon nitride (Fig. 1f-h). As a general trend, the peak at ~11° (003, LDH) became slightly broader and shifted towards higher 2θ values with the increase in the amount of CN in the composites (Figure 5.1f-h). This indicates a subtle distortion of the structure of the LDH, confirming the incorporation of the CN particles in the interlayer spacing (although differences are

minor). The increase in the amount of CN brought about an increase in the intensity of the diffraction peak at 27.46° corresponding to the (002) reflection of CN. The basal spacing distance of the (003) peak decreased gradually with the amount of CN (from 0.78 nm for LDH/CN-5% up to 0.77 nm for LDH/CN-50%), which confirms the incorporation of the carbon nitride in the interlayer space of the LDH.

The composition of the photocatalysts was further investigated by IR and Raman (Figure 5.2). Both bare components (LDH and CN) showed the characteristic bands widely reported in the literature for both materials [Gandamalla et al. 2021; Feng et al. 2022; Wang et al. 2014; Chen et al. 2021; Boumeriame et al. 2023]. The spectrum of carbon nitride showed the characteristic bands at ca. 3200, 1640-1200 and 810 cm^{-1} , ascribed to the vibrations of terminal uncondensed amino groups, C-N and C=N heterocycles, and triazine rings, respectively [Chen et al. 2021; Boumeriame et al. 2023]. For LDH, a broad band centered at 3400 cm^{-1} (vibrations of surface -OH groups), the intense peak at 1384 cm^{-1} (vibrations of O-C-O groups), and the peaks at 617 and 432 cm^{-1} (vibrations of metal-oxygen and metal-oxygen-metal bonds) were observed.

The LDH/CN composites showed the coexistence of the characteristic bands of LDH and CN, with a decrease in the intensities of the bands assigned to LDH (particularly 1384 and between $3000\text{--}2800\text{ cm}^{-1}$) with the amount of CN. Similar observations have been reported for LDH/CN composites prepared by mixing both components [Boumeriame et al. 2023; Chen et al. 2021], and interpreted as the evidence of specific interactions between both phases. Raman spectra of the photocatalysts are shown in Figure 5.2B. For pristine LDH, the characteristic bands at 480 cm^{-1} (Al-OH stretching), 600 cm^{-1} (Co-O bonds) and 1050 cm^{-1} (C-O stretching of carbonate ions) were observed, in agreement with IR observations. Due to fluorescence interference (Fig. S1), the resolution of the Raman spectra of carbon nitride and all the LDH/CN composites was rather poor (for both 532 and 350 nm lasers), although several weak peaks were observed at 1642, 1558, 1465, 1258, 980, 753, 707, and 486 cm^{-1} corresponding to vibration modes of CN heterocycles [Xu et al. 2013; Jiang et al. 2014]. The peak at 1050 cm^{-1} assigned to carbonate ions in the

LDH was particularly pronounced in sample LDH/CN-15%. The similarities in the Raman spectra in the LDH/CN composites than in bare CN suggests that the confinement in the interlayer space of the LDH does not cause any significant modification in the structural skeleton of the carbon nitride. However, a distinct spectral feature was observed: a small blue shift in the peaks at 980, 753 and 707 cm^{-1} in the composites, which could be attributed to phonon confinement effects in the interlayer of the LDH. Similar observations have been reported for exfoliated CN nanosheets [Xu et al. 2013; Jiang et al. 2014].

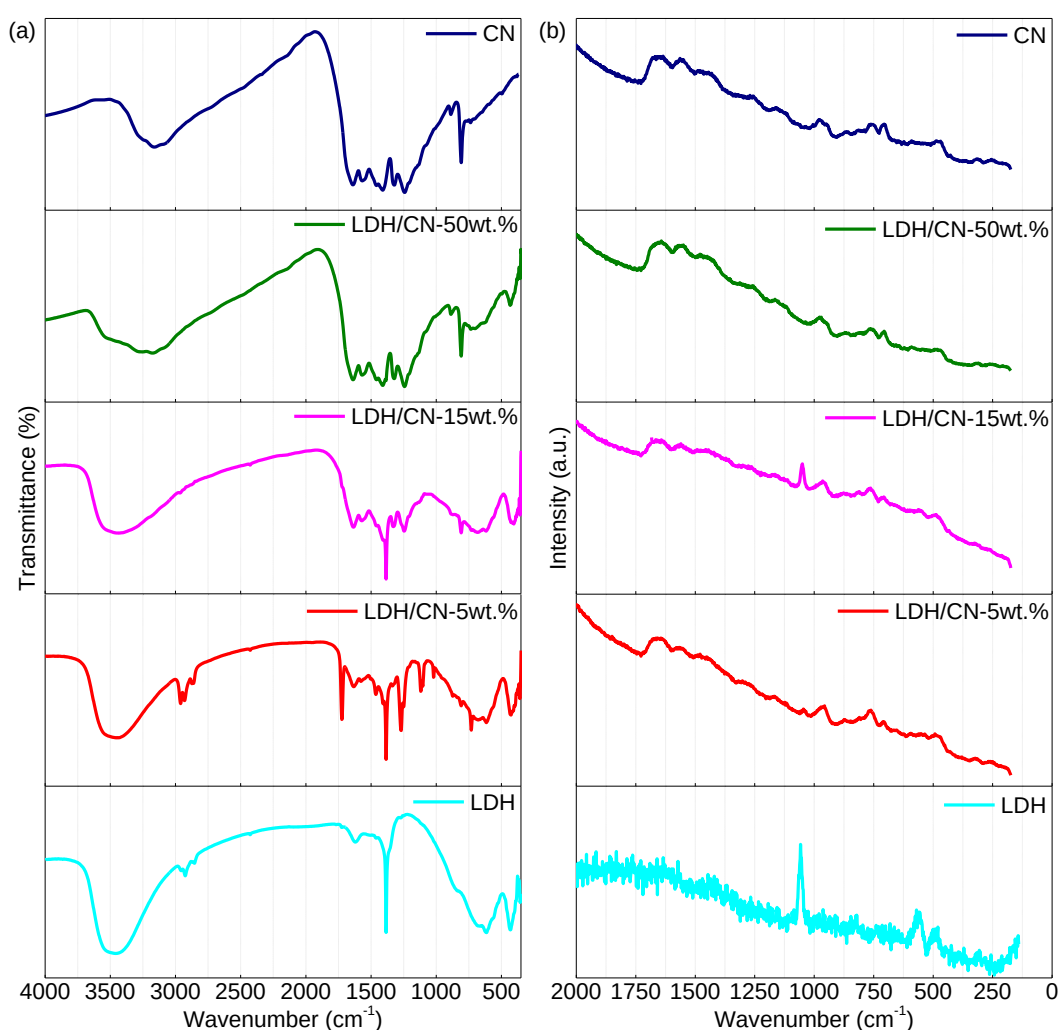


Figure 5.2 (a) IR and (b) Raman spectra of the prepared LDH/CN composites and the pristine components.

The porosity of the LDH/CN composites was determined by gas adsorption and analyzed in terms of the composition and the expected trend considering the rule of the mixtures (Fig. 5.3). The main textural parameters evaluated from the gas

adsorption isotherms are compiled in Table 5.1. The pristine LDH displayed a type II nitrogen adsorption isotherm characteristic of materials with low surface area (ca. $3 \text{ m}^2/\text{g}$). It is well known that several factors (e.g., molar ratio of precursors, synthesis temperature and aging time) influence the porosity of LDH materials obtained from coprecipitation methods [Gandamalla et al. 2021; Feng et al. 2022; Seftel et al. 2008; Nazir et al. 2022]. The low porosity of the pristine LDH compared to some of the studies in the literature [Tripathi and Narayanan 2020; Sherryrna et al. 2024; Wang et al. 2014; Nazir et al. 2022] is attributed to the shorter time and lower temperature of the aging step during the synthesis. On the other hand, the pristine carbon nitride also displayed a type II isotherm but showed a larger amount of gas adsorbed in the whole range of relative pressures. This effect was more pronounced above 0.8, indicating a marked mesoporous/macroporous character in this material.

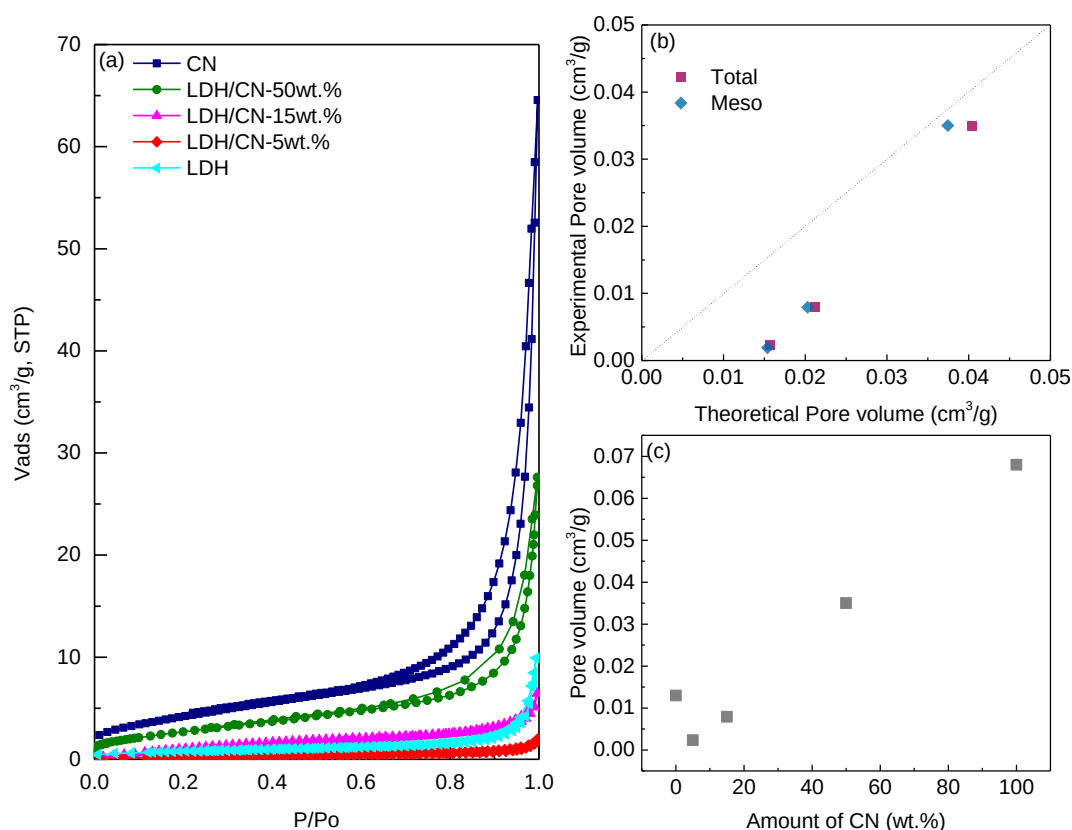


Figure 5.3 (a) N_2 adsorption/desorption isotherms at -196°C of the studied samples; (b) correlation between the theoretical and experimental pore volumes; (c) correlation between the total pore volume and the amount of carbon nitride in the composites.

The LDH/CN composites also displayed low surface areas and pore volumes, as expected based on the porosity of the pristine components. Clear correlations were observed between the textural parameters of the composites and the amount of carbon nitride (Fig. 5.3b, 5.3c). The experimental pore volumes (total pore volume and mesopore volume) of the LDH/CN composites were found to be lower than the expected theoretical values calculated considering the composition of the LDH/CN samples and the rule of the mixtures (Fig. 5.3b). This indicates that the pores of the carbon nitride phase in the composites are not accessible to the nitrogen probe, and suggests that the carbon nitride is confined in the lamellar structure of the LDH (in agreement with the XRD data). Indeed, the porosity of composites prepared by a simple physical mixture of LDH and CN with similar composition followed the trend based on the rule of the mixtures.

Table 5.1 Summary of main textural parameters (specific surface area - S_{BET} -, total pore volume and mesopore volume) of the samples evaluated from the nitrogen adsorption isotherms at -196 °C.

	S_{BET} (m^2/g)	Total Pore Volume (cm^3/g)	Mesopore Volume (cm^3/g)
LDH-NiZnAl	3	0.013	0.013
LDH/CN-5%	1	0.002	0.002
LDH/CN-15%	6	0.008	0.008
LDH/CN-50%	9	0.035	0.034
CN	16	0.068	0.062

The optical bandgap and the light harvesting properties of the obtained catalysts were evaluated from diffuse reflectance spectroscopy. Figure 5.4 shows the absorption edge spectra and the Tauc graphical representation of the diffuse reflectance data of the prepared materials. The pristine LDH-NiZnAl showed three low-intensity broad absorption bands that can be ascribed to several transitions of the metals. The band in the 200-300 nm range is assigned to transitions between oxygen atoms and Ni(II) ions; the two bands in the visible range between 350-500 nm and 600-800 nm correspond to spin-allowed (380, 740 nm) and spin-forbidden

(420, 640 nm) transitions of Ni(II) ions [Megala et al. 2021; Zhou et al. 2022]. No electronic transitions involving Zn(II) ions are expected due to their d10 configuration. For pristine CN, the characteristic sharp absorption edge between 400-500 nm commonly reported for this material was observed [Ismael 2020; Jiang et al. 2018; Imgharn et al. 2024; Wang and Wang 2022], corresponding to a bandgap energy of 2.83 eV.

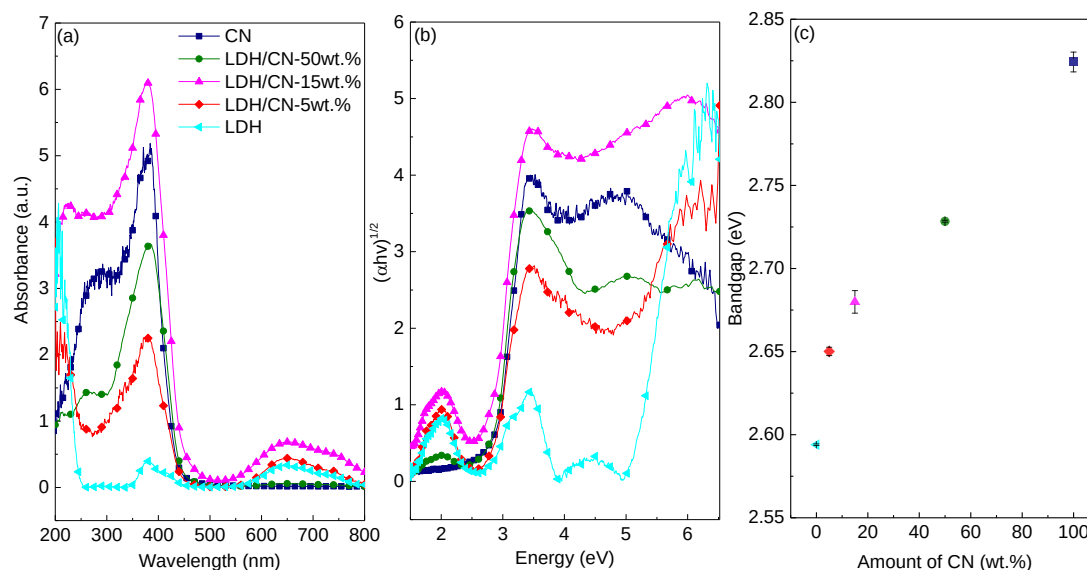


Figure 5.4 (a) Absorption spectra and (b) Tauc graphical representation of the synthesized LDH/CN composites; (c) correlation between the optical band gap and the amount of carbon nitride in the composites. Average values of duplicate measurements (a,b) and error bars (c) are presented (accuracy below 5%).

For the LDH/CN composites, the absorption profiles showed the distinct bands of both components, regardless of the composition: the absorption edge of CN around 430 nm and the band at 600-800 nm of the transitions of the LDH. The position of the absorption edge of CN in the LDF/CN composites showed a slight redshift, indicating an increased light absorption in the visible region owing to the confinement in the layered structure of the LDH. As a result, a slight decrease was observed in the optical band gap values of the composites with the amount of carbon nitride (Fig. 4c). Similar optical redshifts have been reported for LDH-CN heterostructures [Megala et al. 2021; Zhou et al. 2022]. On the other hand, the absorption in the 600-800 nm region was enhanced in the composites with 5 and

15 wt.% of CN, and negligible in the composite with 50 wt.% of CN. This can be attributed to oxygen vacancies in the LDH phase, pointing out differences in the interfacial interactions between both phases upon the amount of carbon nitride.

Photoluminescence emission spectra of the photocatalysts in water were recorded to further probing the optical properties of the prepared photocatalysts (Figure 5.5). Colloidal aqueous suspensions of the materials were used to record the photoluminescence emission spectra, with the same loading than the photocatalytic assays to assure similar environmental conditions -as this may affect surface reactions leading/quenching the radiative recombination of the photogenerated species-. As seen in Fig. 5.5, all the samples displayed a broad emission spectrum upon excitation at 300 nm spanning from 400 to 570 nm.

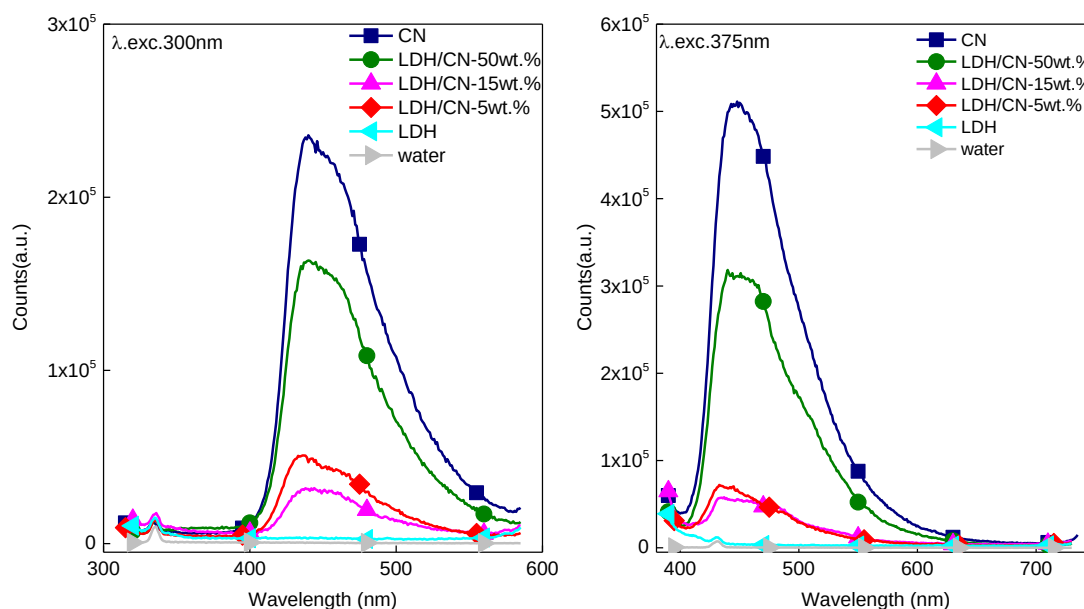


Figure 5.5 Photoluminescence emission spectra of aqueous suspensions of the synthesized photocatalysts (loading is similar to that used in the photocatalytic assays) upon excitation at 300 nm and 375 nm.

The emission band showed a maximum at ca. 440 nm (2.96 eV) and a shoulder at 455 nm (2.87 eV), with a similar shape for all the samples. Upon excitation at 375 nm, the profiles are rather similar, but the emission band is centered between 400 and 650 nm, with a maximum at 450 nm. According to the literature, the emission at 440 nm is associated with different transitions between lone pair state in the valence band and the π^* antibonding state in the conduction

band (e.g., $\pi^*-\pi$, π^* -lone pair, σ^* -lone pair state transitions) [Das et al. 2016; Zhang et al. 2021]. The photoluminescence emission of carbon nitride was substantially quenched in the LDH/carbon nitride composites, as inferred from the lower intensity of the signal, showing that the immobilization of the semiconductor in the layered structure of the hydrotalcite-like compound suppressed the radiative recombination of the electron-hole pairs.

This strongly suggests an effective separation of the photogenerated charge carriers in the composites, likely due to an adequate matching of the energy levels of both materials (e.g., midgap energy levels in LDH matching the defect states in carbon nitride responsible for the radiative emission). The decrease in the intensity of the photoluminescence emission was more noticeable for sample LDH/CN-15%, which agrees with the better photocatalytic performance of this material and the strong impact of water oxidation by the photoholes as a critical step for the degradation of methylparaben.

5.2 Photocatalytic assays

5.2.1 Dark adsorption

As described in the experimental section, the photocatalytic assays were initiated after the equilibration of the materials with the solution of methylparaben in the dark for 30 minutes. All the catalysts showed similar uptakes and adsorption kinetics of methylparaben from solution (Fig. 5.6), thus the initial concentration of methylparaben in solution when the illumination of the catalyst started was similar for all the studied materials. This is important given the rather high conversion of methylparaben in the photolytic reaction (see discussion below), to avoid misinterpretations of the degradation rates that would be related to differences in the initial concentration of the pollutant in solution rather than to the different photocatalytic activity of the materials [Ollis 2018].

5.2.2 The photocatalytic activities under UV-Vis irradiation

Figure 5.7 shows the conversion of methylparaben during the photocatalytic

degradation using the composites prepared with 5, 15 and 50 wt.%. Data corresponding to the photolytic degradation in solution (absence of a catalyst), and the corresponding control assays for carbon nitride and the LDH are also shown for comparison purposes.

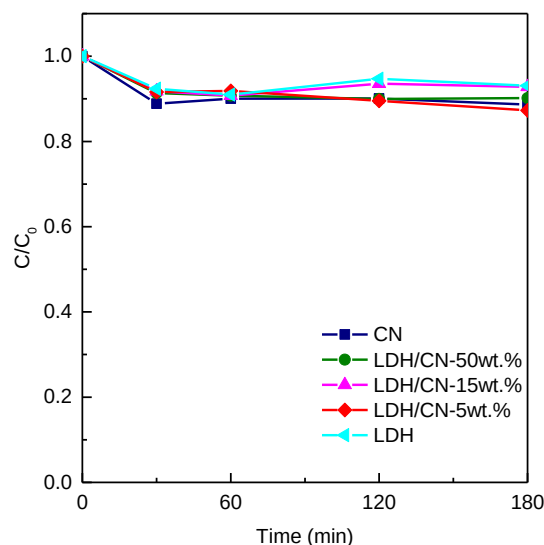


Figure 5.6 Dark adsorption of methylparaben in the prepared photocatalysts.

As seen, the conversion of methylparaben is high in all the cases, reaching 100 % after 180 minutes of illumination for the composites and after 240 min for the photolytic reaction. This was expected due to the low initial concentration of the pollutant. Despite the high conversion, the mineralization of methylparaben is not complete, as inferred from the total organic carbon values of the solution (Fig. 5.7b) and the evolution of the concentration of intermediates. Indeed, the reduction in the total organic carbon of the solution after 2 hours of photolysis represented only 0.4 %, due to a low conversion of the intermediates. Similar values were obtained for the control of the LDH, indicating the poor photocatalytic activity of the bare material. On the contrary, the fall in the total organic carbon for the photocatalytic degradation using carbon nitride was 30 % after 2 hours of irradiation, and ca. 47 % for the composite LDH/CN-15% (the one showing the best performance). Two intermediate peaks were detected by HPLC, polyhydroxylated intermediates for all the studied catalysts and diethyl phthalate intermediate observed for the LDH/carbon nitride composites, as discussed in chapter 3. The polyhydroxylated

intermediates accumulated at short illumination times, and started to decrease after ca. 100 min of irradiation for the studied photocatalysts, confirming the complete degradation of the intermediates. This diethyl phthalate intermediate disappeared after 200 min of illumination in all the assays. Similar degradation intermediates for methylparaben using advanced oxidation processes have been reported in the literature with different catalysts [Lin et al. 2009; Dhaka et al. 2017; Cifre-Herrando et al. 2022].

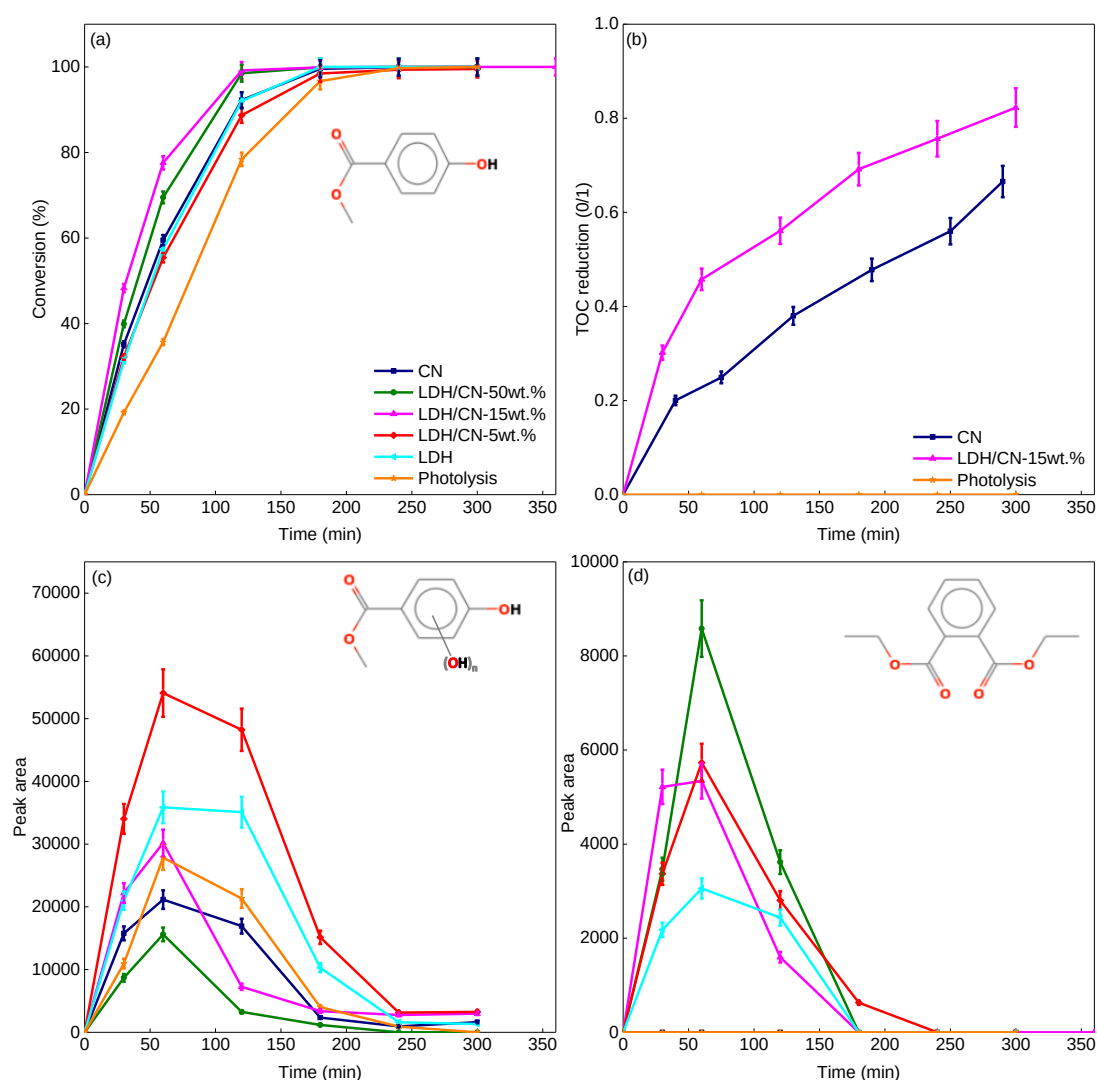


Figure 5.7 (a) Conversion of methylparaben; (b) Total Organic carbon (TOC) reduction; (c,d) evolution of the degradation intermediates detected in solution for the studied photocatalysts. Average values and actual error bars of each measurement are presented (accuracy below 5%).

To compare the performance of the materials, the photocatalytic activity was analyzed assuming a first-order reaction-rate mechanism to calculate the apparent

rate constants (k_{app}). Fitted data corresponded to 99% of methylparaben conversion; the rate constants for the degradation of the intermediate compounds were also calculated (Table 5.2).

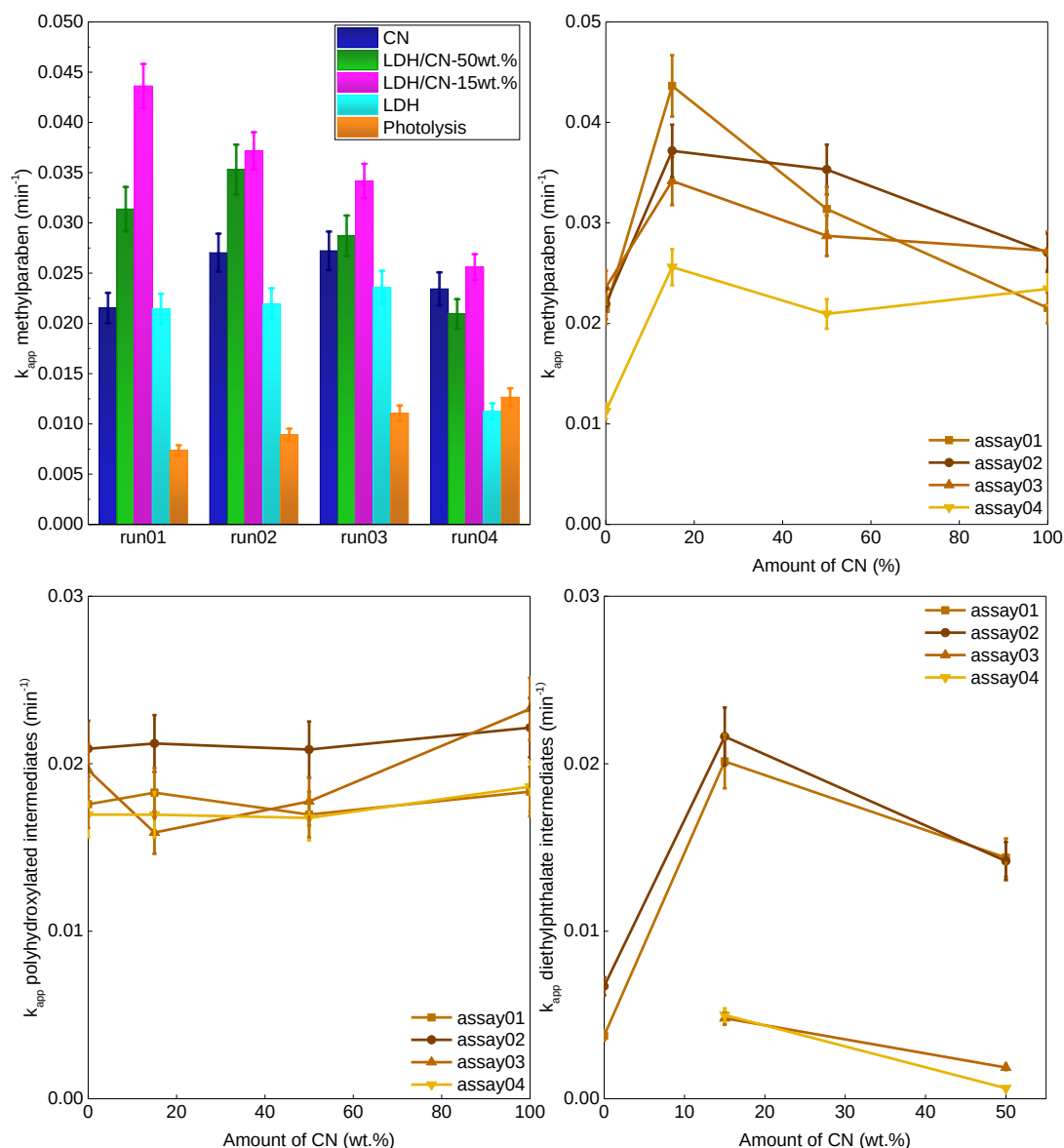


Figure 5.8 (a) Apparent rate constants for the degradation of methylparaben for the investigated photocatalysts during the consecutive photocatalytic assays; (b,c,d) correlation between the apparent rate constants of degradation of methylparaben (b) and its detected intermediates (c,d) with the amount of carbon nitride in the composites.

Data shows that the rate constants of methylparaben degradation of the LDH/CN composites were higher than those of the photolytic reaction and the controls with LDH and carbon nitride alone, demonstrating the faster degradation of

the pollutant. The trend was maintained over several consecutive photocatalytic cycles. The highest rate constants of the degradation of both methylparaben and its intermediates were obtained for sample LDH/CN-15% (ca. twice the value of bare carbon nitride and 1.5 times that of LDH/CN-50%), and decreased with the amount of carbon nitride in the composites (Fig. 5.8).

Table 5.2 Rate constants (k_{app}) for the degradation of methylparaben degradation and the degradation intermediates at consecutive photocatalytic assays.

	assay 01	assay 02	assay 03	assay 04
Methylparaben				
LDH-NiZnAl	0.021	0.022	0.024	0.011
photolysis	0.007	0.009	0.011	0.013
LDH/CN-5%	0.023	--	--	--
LDH/CN-15%	0.044	0.037	0.034	0.026
LDH/CN-50%	0.031	0.035	0.029	0.021
CN	0.022	0.027	0.027	0.023
Polyhydroxylated intermediates				
LDH-NiZnAl	0.018	0.021	0.020	0.017
photolysis	0.020	0.008	0.015	0.012
LDH/CN-5%	0.016	--	--	--
LDH/CN-15%	0.018	0.021	0.016	0.017
LDH/CN-50%	0.017	0.021	0.018	0.017
CN	0.018	0.022	0.023	0.019
Diethyl phthalate intermediate				
LDH-NiZnAl	0.004	0.007	--	--
photolysis	nd	nd	nd	nd
LDH/CN-5%	0.018	--	--	--
LDH/CN-15%	0.020	0.022	0.005	0.005
LDH/CN-50%	0.014	0.014	0.002	0.001
CN	nd	nd	nd	nd
n.d. not detected intermediate				

Figure 5.9 shows the photocatalytic performance of the materials under consecutive illumination assays. The cyclic performance was evaluated by adding a small volume of methylparaben to the dispersions of the photocatalysts after each cycle, so as to increase the concentration of the pollutant up to 10 ppm (ca. the initial concentration used in the first cycle). It is important to note that by doing this,

any un-degraded intermediate from the previous cycles remains in the dispersion. This allows finding out if there is an accumulation of intermediates during the consecutive photocatalytic assays.

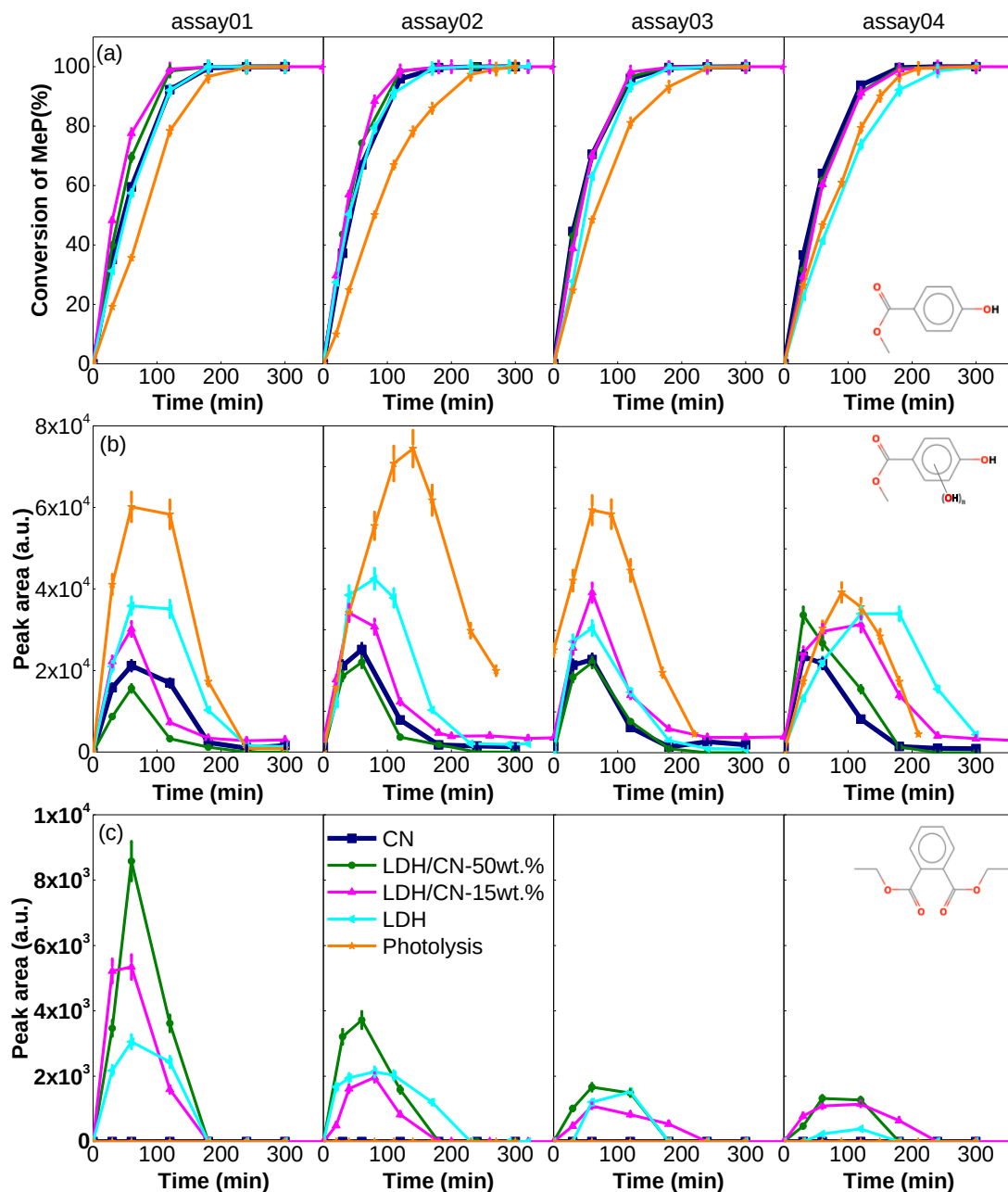


Figure 5.9 (a) Conversion of methylparaben and (b,c) evolution of the degradation intermediates for the studied photocatalysts during several consecutive catalytic assays.

The high conversion of methylparaben was well maintained during the consecutive cycles, with full conversion after 180 min in all the cycles. Differences

are visible when analyzing the intermediates from the solution and the degradation rate constants. The rate constant of methylparaben degradation with the LDH/CN composites decreased slightly with the number of photocatalytic cycles (Fig. 5.8), although the values were still higher than those of the individual components and the photolytic reaction after the fourth cycle. The amount of degradation intermediates was rather similar for the consecutive cycles (Fig. 5.9), with the exception for the photolytic reaction and the control with the LDH where an accumulation of the intermediates is observed. This indicates that both methylparaben and its intermediates are degraded in the consecutive photocatalytic cycles, thus confirming that the activity of the materials is maintained. Interestingly, the apparent rate constant for the degradation of the polyhydroxylated intermediates remained rather constant over the cycles for all the samples (Fig. 5.9b), while the values for the degradation of the second intermediate (Fig. 5.9c) showed a decrease with the number of cycles and the amount of the carbon nitride in the composites.

5.2.3 The trapping experiment in presence of scavengers

To explore the degradation mechanism of methylparaben, the photocatalytic assays for the best performing composite (LDH/CN-15%) and the bare components (LDH and CN) were carried out in the presence of scavengers of hydroxyl and superoxide radicals (Fig. 5.10). The conversion of methylparaben was largely slowed down for sample LDH/CN-15% in the presence of hydroxyl radical scavenger, indicating that the hydroxylation-mediated oxidation reaction is the predominant pathway in the degradation of this compound, and that the photogenerated holes are indispensable for the hydroxylation of methylparaben (see also the trends of the degradation apparent rate constants in the presence of the scavengers in Annex I Fig. S12). The use of a superoxide radical scavenger also decreased the conversion of methylparaben although to a smaller extent, indicating that the hydroxylation can also occur from the reaction of the photogenerated electrons with dissolved oxygen in solution, as frequently reported for TiO_2 [Li et al.

2012].

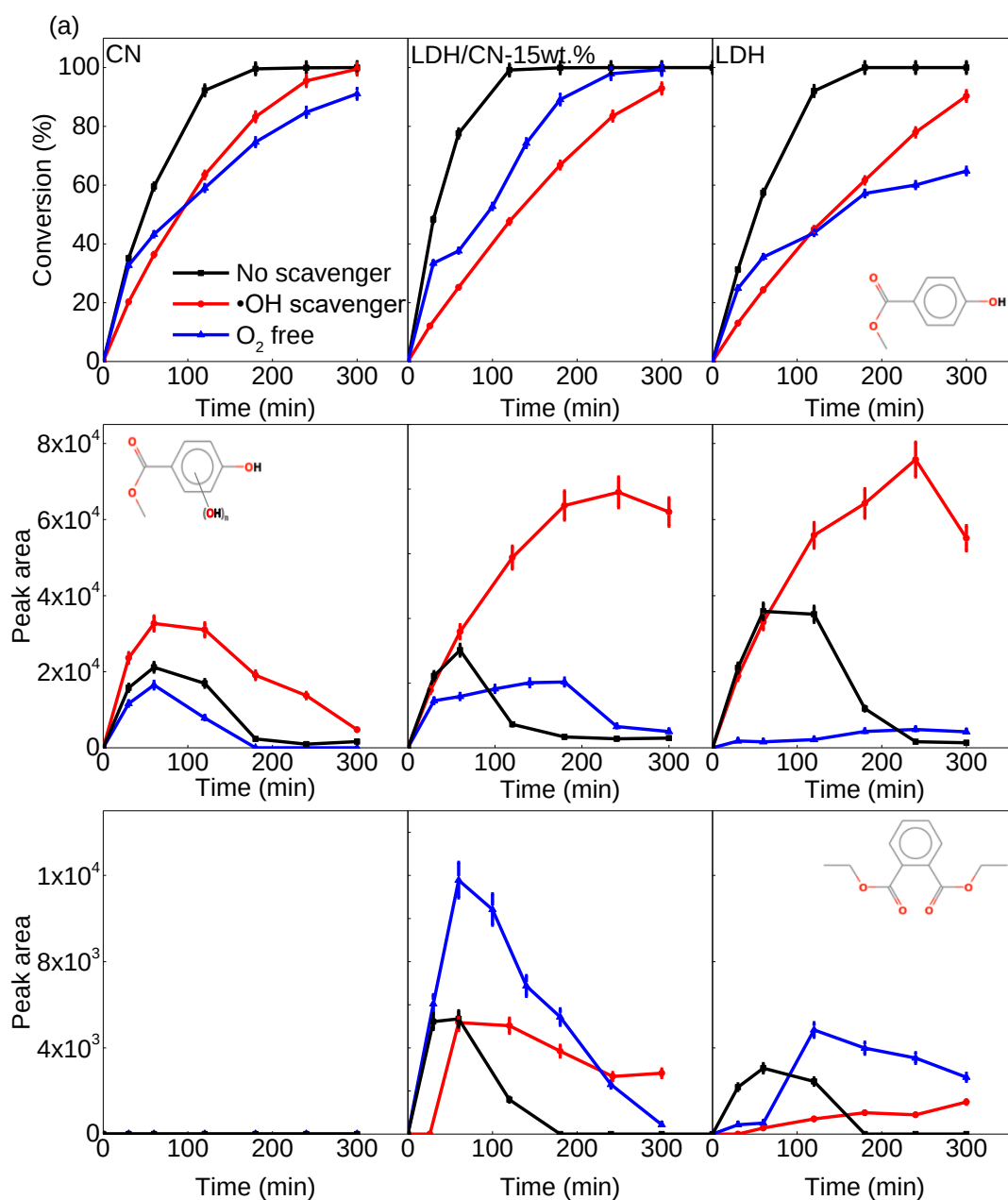


Figure 5.10 Conversion of (a) methylparaben and (b,c) evolution of its degradation intermediates in the presence of hydroxyl radical scavenger and in oxygen-free conditions for samples LDH, CN and LDH/CN-15%.

The intermediates tended to accumulate for longer times when the photocatalytic assays are carried out in the presence of the scavengers, being the effect more pronounced for scavenging the hydroxyl radicals and for the polyhydroxylated intermediate. When carbon nitride or LDH were used alone as photocatalysts, the conversion of methylparaben also decreased and data showed a

rather similar performance for the scavenging of hydroxyl and superoxide radicals. This corroborates that water oxidation by the photoholes is a critical step for the degradation of methylparaben with sample LDH/CN-15%, and that in the bare materials (carbon nitride and LDH) the activation of oxygen upon reaction with the photogenerated electron is also important.

5.3 Partial Conclusions

A series of hybrid photocatalysts have been synthesized by the co-precipitation of a NiZnAl hydrotalcite-like compound in the presence of increasing amounts of carbon nitride powders, and used for the degradation of methylparaben in aqueous solution. The incorporation of CN particles inside the interlayer spacing of the LDH was confirmed by XRD by the gradual decrease in the basal spacing distance with the CN content. A blue shift in the signals of CN in the Raman spectra of the LDH/CN composites also revealed the confinement effect of CN. Data has shown that the photocatalytic activity of the pristine carbon nitride was efficiently increased in the hybrid LHD/carbon nitride materials, owing to the immobilization of the carbon nitride in the layered structure of the LDH. Those hybrid photocatalysts showed faster degradation rates for both the main pollutant (methylparaben) and its degradation intermediates, and displayed better photocatalytic performance upon consecutive assays (after 20 hours of consecutive illumination), than the bare carbon nitride -and the NiZnAl hydrotalcite-like compound alone-. Our synthetic route allowed a good interfacial contact between the carbon nitride confined in the lamellar structure of the hydrotalcite-like compound. The reduced recombination via radiative emission in the hybrid photocatalysts points out to an adequate matching of the energy levels of both materials owing to the confinement of the semiconductor. This enables a more efficient exploitation of the photogenerated charge carriers (hence increased photocatalytic performance) in those hybrid photocatalysts. The photocatalytic assays carried out in the presence of selective scavengers of the hydroxyl radicals, and in an oxygen-free environment -to prevent the formation of superoxide radicals-

revealed that the confinement of carbon nitride in the layered structure of the NiZnAl hydrotalcite-like compound also modified the degradation mechanism of methylparaben. The hydroxylation-mediated reaction is the main oxidation pathway in the degradation of methylparaben; this occurs predominantly upon reaction with the photogenerated holes -also in anoxic environments-, and to a minor extent upon reaction of the photogenerated electrons with dissolved oxygen in solution.

Chapter 6. Conclusions and perspectives

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6.1 Conclusions

This thesis aimed for the degradation of methylparaben -an organic emerging pollutant in water- using heterogeneous photocatalysis and hybrid semiconductor/carbon photocatalysts, to explore the impact of carbon materials as additives to semiconductors in the overall photodegradation process. To attain this aim, three kinds of hybrid semiconductor/carbon photocatalysts have been synthesized: (1) carbon nitride/nanoporous carbon (CN/CQ series) via hydrothermal process; (2) Bi_2WO_6 -based hybrid photocatalyst using C_3N_4 (BWO/CN series) and a nanoporous carbon (BWO/CQ series) as additives via a hydrothermal process; and (3) carbon nitride immobilized in a porous NiZnAl hydrotalcite-like following a co-precipitation method. A deep characterization of the optical, structural and textural properties of the prepared materials was carried out, to correlate those properties with the photocatalytic activity towards the degradation of methylparaben under UV-VIS light.

The characterization of the CN/CQ series catalysts indicated that the incorporation of the carbon additive does not significantly modify the structural properties of the pristine g- C_3N_4 , but the composites absorb more visible light than bare g- C_3N_4 . The porosity of the resulting CN/CQ composites did not follow the general rule of the mixtures, indicating that the nanopores of CQ additive are not accessible by gas adsorption, most likely due to the partial blockage by the particles of the semiconductor. Similarly, the incorporation of CN and CQ as additives to BWO did not alter the structural properties of the bare BWO semiconductor. For the BWO/CQ composites, enhanced visible-light absorption was observed along with a slight blue shift in the absorption edge of BWO. For the BWO/CN composites, a distinct red shift was observed as the amount of CN increased. Overall, the characterization suggested that CN and CQ additives are embedded within the BWO matrix rather than surface-deposited. On the other hand, the successful incorporation of CN inside the interlayer spacing of a NiAlZn LDH compound was confirmed by XRD and Raman.

Regarding the photocatalytic activity, the degradation kinetics of methylparaben was accelerated for the composites in all the cases (series CN/CQ, BWO/CQ, BWO/CN and LDH/CN), compared to the bare semiconductors (or the NiZnAl hydrotalcite-like compound alone), being the kinetics of the degradation slightly improved with the amount of the additives. The photocatalytic activity was also

discussed in terms of the conversion and nature of methylparaben intermediate compounds. It is worth mentioning that the degradation of methylparaben using the BWO/CQ catalysts generated polyhydroxylated intermediates, whereas for the CN/CQ and LDH/CN series, two intermediates were clearly detected: polyhydroxylated intermediates and diethyl phthalate.

For all the tested amounts of CQ additive, the incorporation of CQ additive to CN increased the removal of MeP, especially after the second photocatalytic assay. The degradation of intermediates was not improved in the first assay, whereas higher fractions of diethyl phthalate intermediate were found in the second photocatalytic assay compared to the first one. In the case of the BWO/CQ series catalysts, BWO/CQ-2wt.% showed the best photocatalytic performance whereas for the BWO/CN series catalysts, BWO/CN-10wt.% showed the best photocatalytic performance. Both BWO/CQ and BWO/CN series of photocatalysts exhibit similar degradation kinetics for MeP. For certain composites (e.g., BWO/CQ series), the conversion of the intermediates was also improved. In terms of LDH/CN series, the sample with 15wt.% of CN revealed the best conversion of MeP. These composites showed a good cyclic performance over several consecutive cycles, with a low accumulation of diethyl phthalate intermediates after 20 hours of illumination. We attribute this to several factors such as efficient separation of photogenerated hole-electrons by introduction of CN and the nanoconfinement of CN in the layered structure of LDH for the LDH/CN series.

In sum, considering degradation of MeP, the CN/CQ series samples displayed the better photocatalytic performance than BWO/CQ, BWO/CN and LDH/CN. Considering the degradation of polyhydroxylated intermediates, BWO/CQ series samples showed the lower amount than others. In terms of diethyl phthalate intermediate, BWO/CQ and BWO/CN generated the lowest amount (below the detection limit of our HPLC method).

As inferred from the photoelectrochemical characterization, the carbon nitride prepared in this thesis showed p-type semiconductor properties, as opposed to BWO that is an n-type semiconductor. Comparatively, the incorporation of the nanoporous carbon (CQ) additive to a p-type semiconductor favored the degradation of MeP (accelerated kinetics in series CN/CQ), whereas its impact was more evident in the conversion of the intermediates when it was added to BWO (n-type semiconductor, series BWO/CQ). The enhanced photocatalytic performance is observed with

introducing CN to BWO or LDH.

New insights on the mechanism that govern the degradation performance using different scavengers were evaluated by coupling photocatalytic experiment and photoelectrochemical approach to rationalize and identify the nature of the catalytic sites and the degradation mechanisms.

The combination of chemical scavenging and photoelectrochemical assays threw interesting additional information about the degradation mechanism. For CN/CQ photocatalysts, oxidation by $\bullet\text{O}_2^-$ has a larger impact, either in the presence of $\bullet\text{O}_2^-$ scavenger or O_2 -free condition. Oxidation of pollutant by $\bullet\text{OH}$ or direct by holes have an impact in the catalysts, but they do not seem to be the dominant degradation mechanisms (drop ca. 50%). In the case of BWO/carbon photocatalysts, distinct degradation mechanisms were revealed: BWO/CQ predominantly relied on hydroxyl radicals ($\bullet\text{OH}$), and BWO/CN primarily utilized superoxide radicals ($\bullet\text{O}_2^-$). For LDH/CN composite, the hydroxylation-mediated reaction is the main oxidation pathway in the degradation of methylparaben; this occurs predominantly upon reaction with the photogenerated holes -also in anoxic environments-, and to a minor extent upon reaction of the photogenerated electrons with dissolved oxygen in solution.

For all the photocatalysts, scavenging the photogenerated electrons accelerated the degradation rate of both methylparaben and the intermediates, pointing out the important role of the hole oxidation of the overall degradation mechanism (scavenging the electrons reduced the recombination of the holes/electron pairs, thus favoring the hole reactivity either via direct hole oxidation or the formation of $\bullet\text{O}_2^-$ radical species).

6.2 Perspectives

Based on the obtained results, the following lines of research could contribute to further explore the impact of the different carbon additives in the photocatalytic performance of the semiconductor/carbon photocatalysts.

- Conducting experiments under outdoor illumination conditions in -for instance- Concentric Parabolic Compound (CPC) photoreactors would allow evaluating the potential application of the prepared photocatalysts under realistic conditions. These assays would allow to evaluate the effect of a variable illumination over time (that corresponds to the different daylight hours) as opposed to the constant illumination typically carried out when artificial light is applied. Different illumination conditions (in varied outdoor environments corresponding, for instance, to sunny/cloudy days where the photon flux can vary significantly) would also allow determining the threshold illumination conditions for triggering the photocatalytic activity of the materials and/or the impact on their long-term performance.

These assays would need to be complemented by the use of water samples with varied salinity and/or natural organic matter that are known the impact the photocatalytic degradation as they can act as internal scavenger chemicals.

- The toxicity analysis of the final effluents (for instance via de Vibrio Fisheri photoluminescence bioassay) would allow to determine whether if the photocatalytic decomposition of methylparaben generated more toxic by-products. The toxicity assessment is of crucial importance especially if the complete mineralization of the target pollutant is not achieved.

- The analysis of the degradation mechanisms has revealed to be a complex endeavor. To further elucidate the possible pathways, experimental data could be complemented by computational studies. In this regard, DFT calculations could help to understand the mechanism of the photocatalytic reactions involved in the degradation of a given molecule, including the processes of light absorption, electron transfer and surface adsorption, and thus guiding the design of efficient photocatalysts.

Additionally, DFT calculations can predict the energy band structure, electronic structure, surface active sites and other properties of photocatalysts, providing theoretical guidance for the design and optimization of efficient photocatalysts.

- Further exploitation of the photoelectrochemical tests, to determine recombination rates under different illumination conditions would be useful to understand the different degradation kinetics in the presence of the scavengers.
- The mechanistic studies could be complemented by a deep analysis of different chemical scavengers (optimizing concentration and nature) and time resolved techniques (to evaluate lifetimes of transient species).

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Annex I. Supplementary Figures

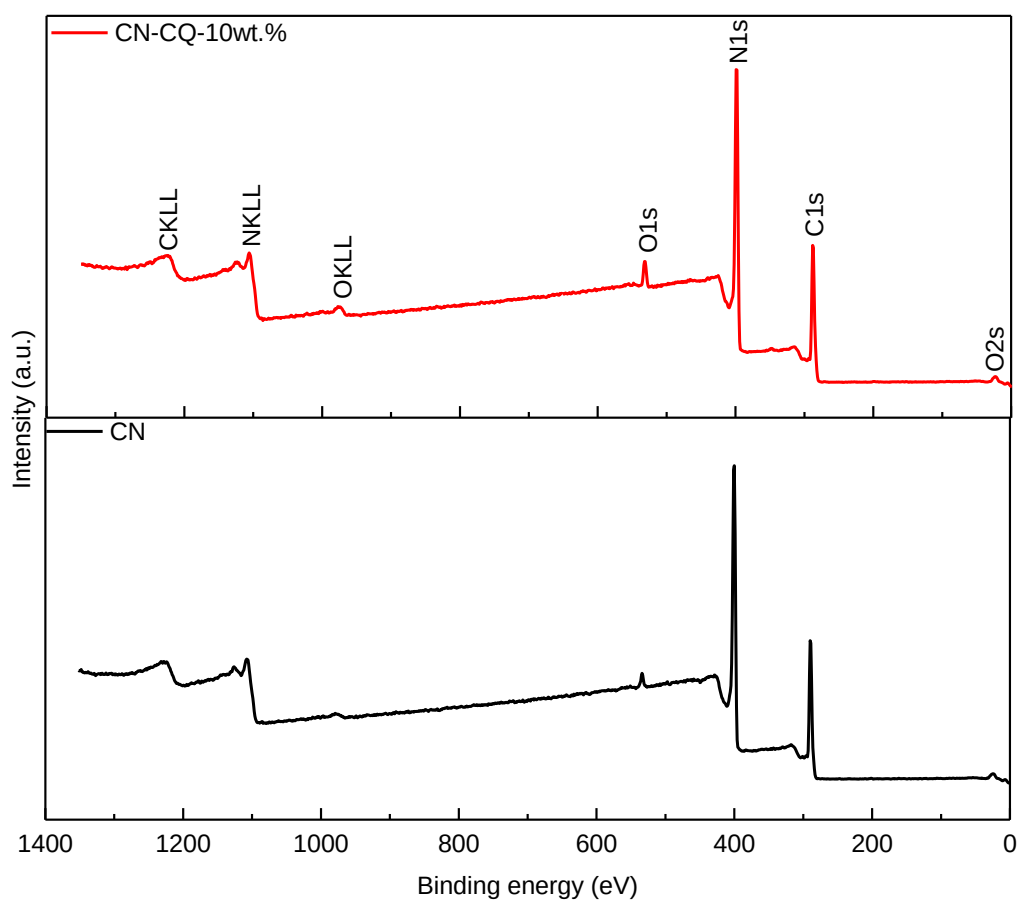


Figure S1 XPS survey spectra of as-prepared CN and CN/CQ-10wt.% photocatalysts.

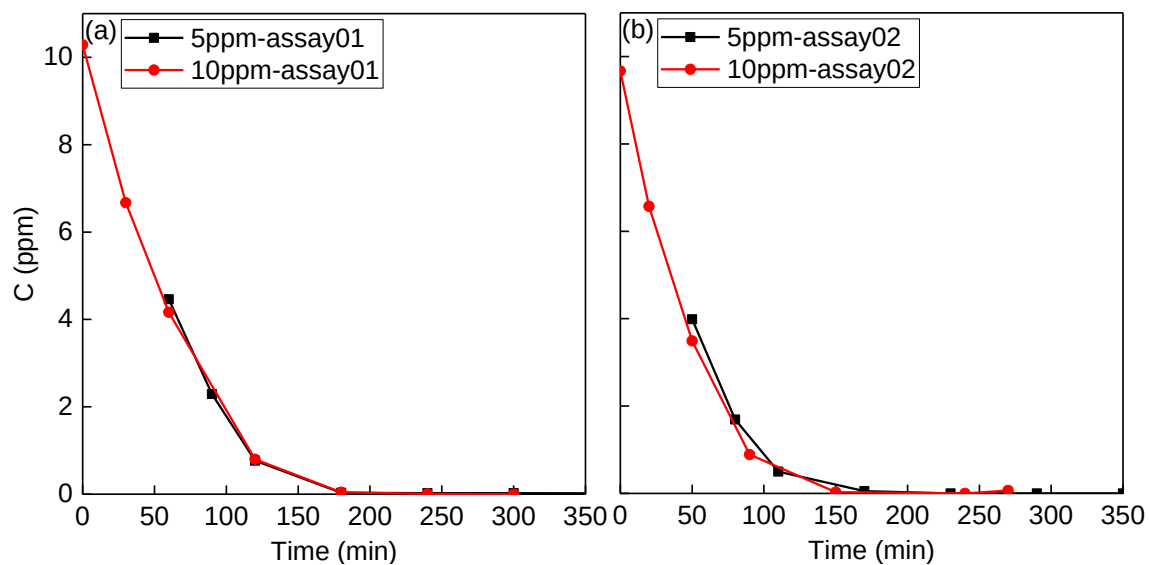


Figure S2 Concentration decay of methylparaben at different initial concentrations.

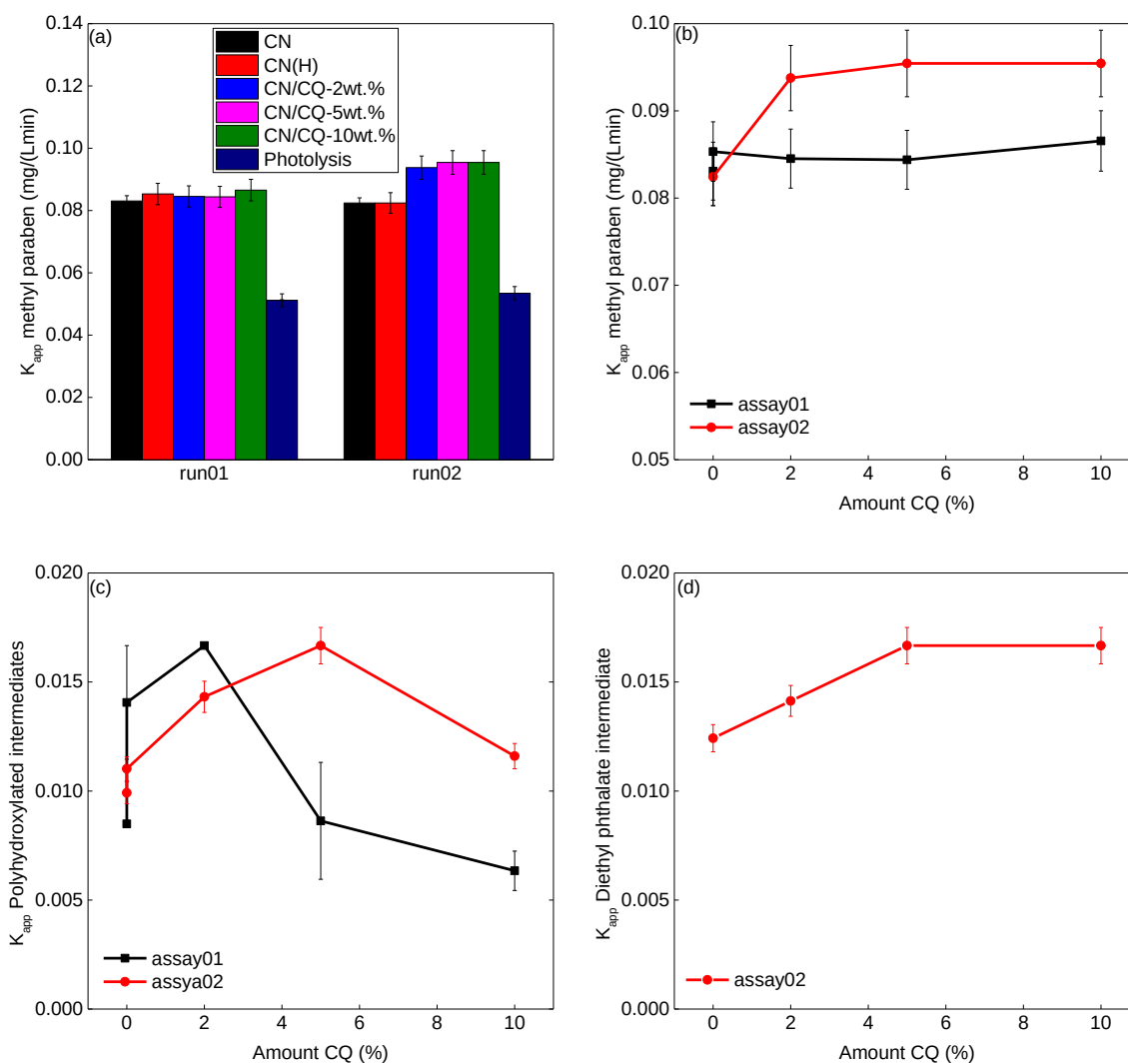


Figure S3 (a,b) Degradation rate constant of methylparaben in the two consecutive photocatalytic assays; (c,d) Degradation rate constants of the (c) polyhydroxylated intermediates and (d) diethyl phthalate based on the zero-order kinetics mechanism.

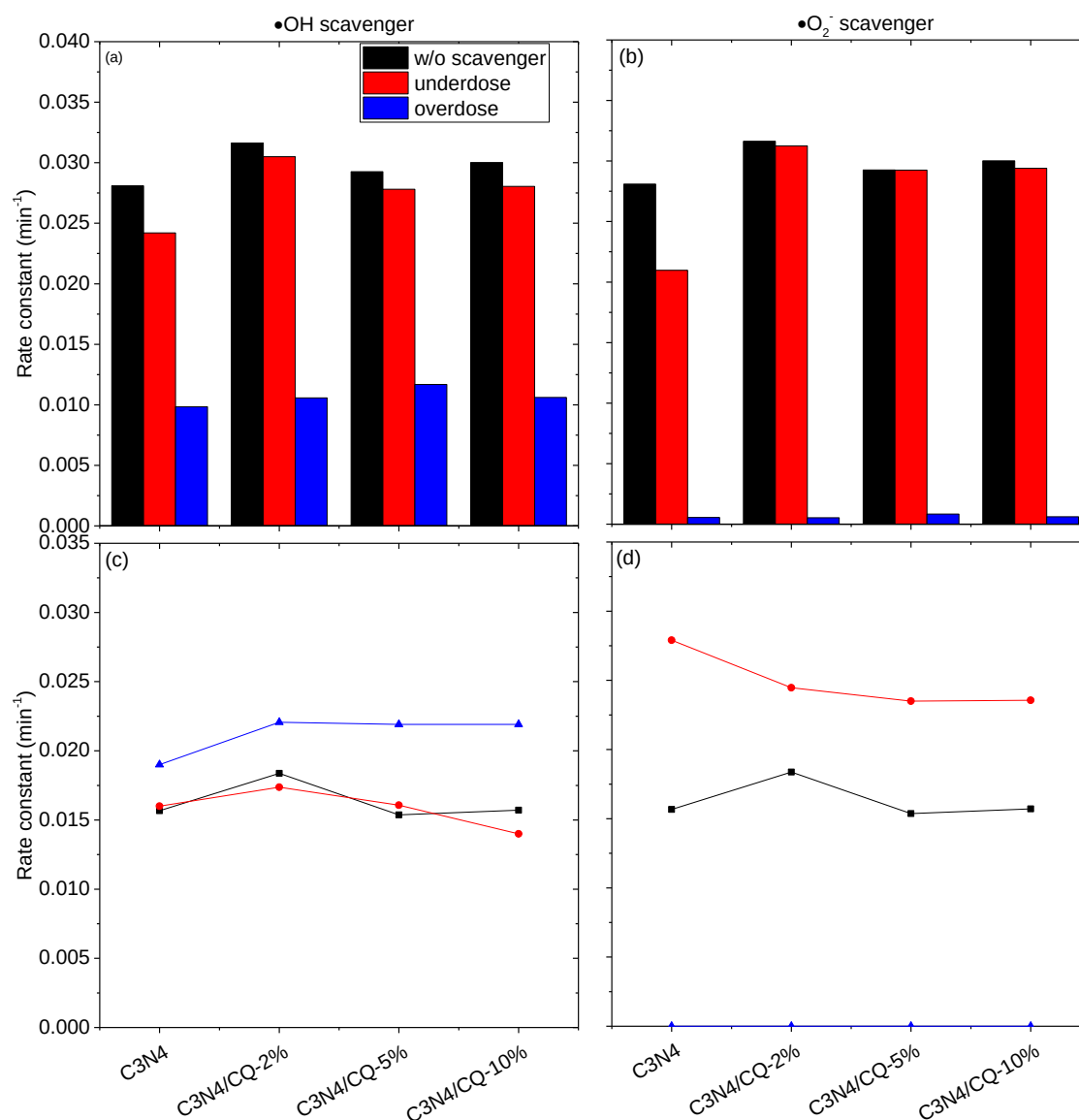


Figure S4 Correlation between the rate constants and the amount of carbon Q for the degradation of (a-b) methylparaben and (c-d) polyhydroxylated intermediates in the composites at different dose scavenger.

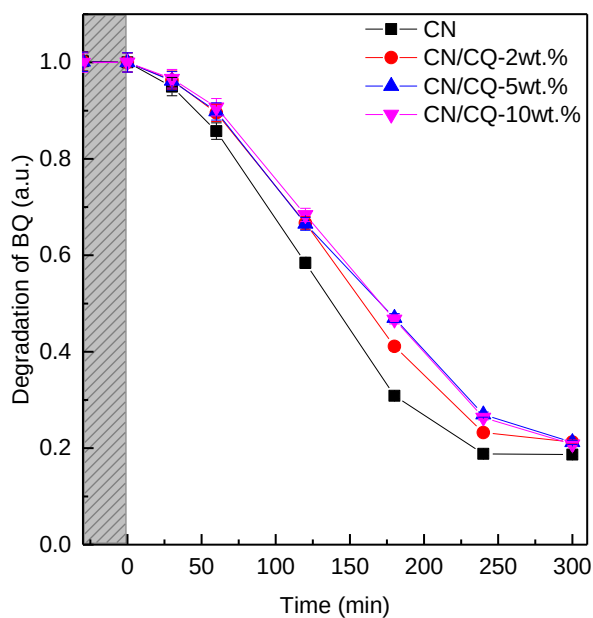


Figure S5 The degradation of benzoquinone for obtained catalysts under UV-Vis irradiation.

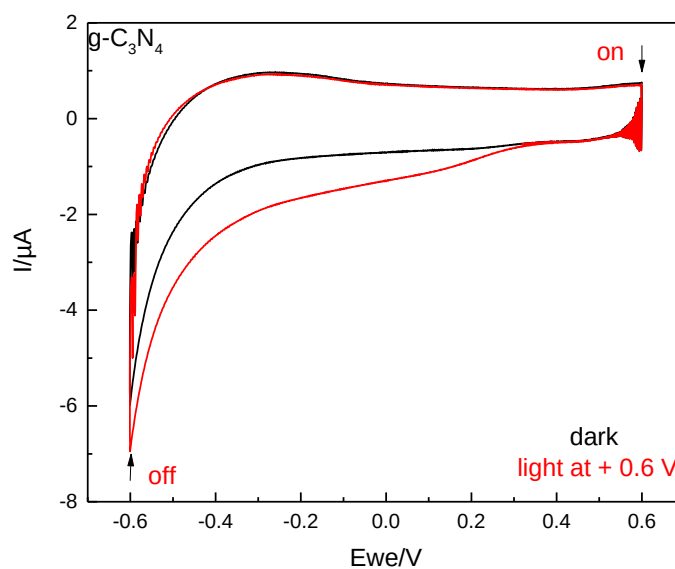


Figure S6 Cyclic voltammograms recorded at 20 mV/s of ITO/g-C₃N₄ electrodes in 0.5 M Na₂SO₄ (pH 2) under dark conditions and illumination using a 340 nm LED.

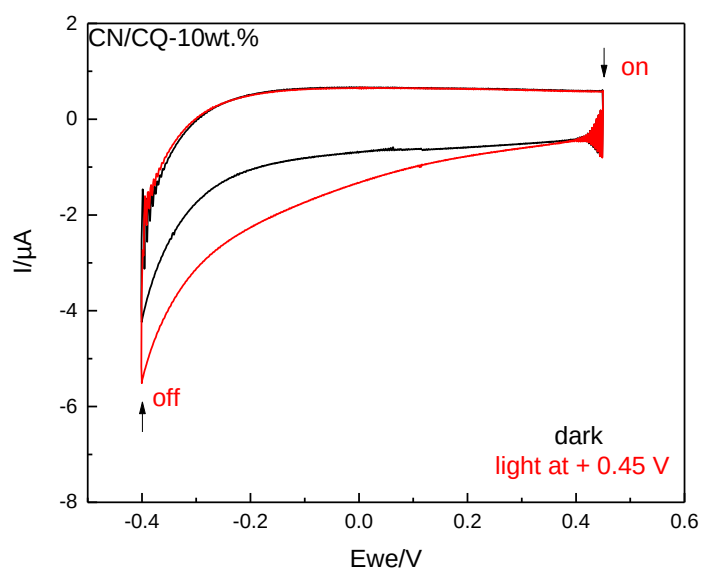


Figure S7 Cyclic voltammograms recorded at 20 mV/s of ITO with CN/CQ-10wt.% electrodes in 0.5 M Na_2SO_4 (pH 2) under dark conditions and illumination using a 340 nm LED.

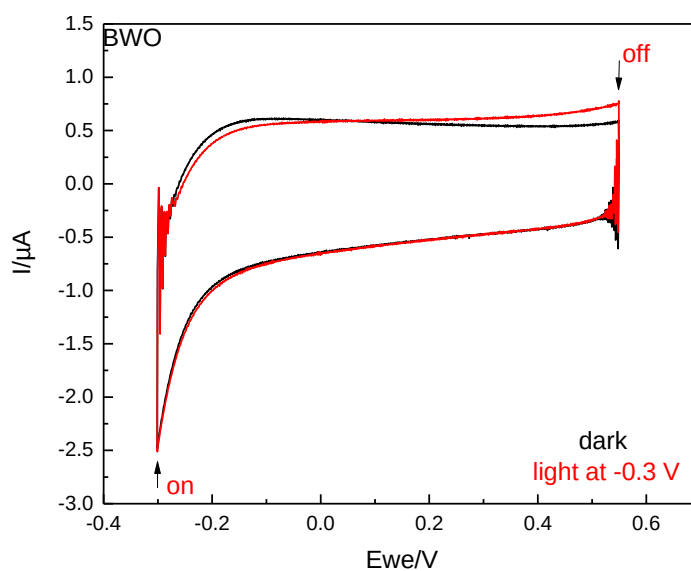


Figure S8 Cyclic voltammograms recorded at 20 mV/s of ITO/BWO electrodes in 0.5 M Na_2SO_4 (pH 2) under dark conditions and illumination using a 340 nm LED.

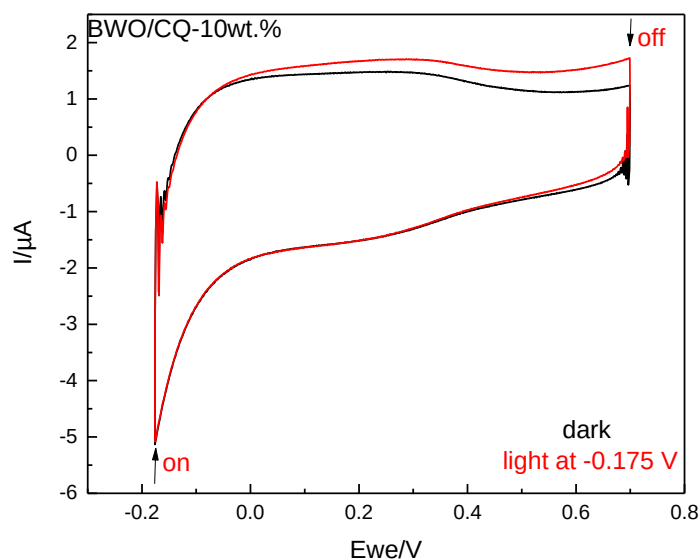


Figure S9 Cyclic voltammograms recorded at 20 mV/s of ITO with BWO/CQ-10wt.% electrodes in 0.5 M Na_2SO_4 (pH 2) under dark conditions and illumination using a 340 nm LED.

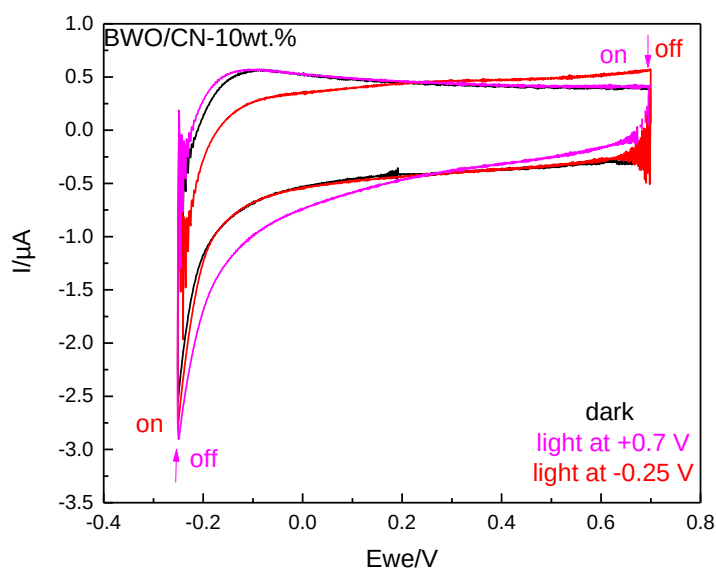


Figure S10 Cyclic voltammograms recorded at 20 mV/s of ITO with BWO/CN-10wt.% electrodes in 0.5 M Na_2SO_4 (pH 2) under dark conditions and illumination using a 340 nm LED.

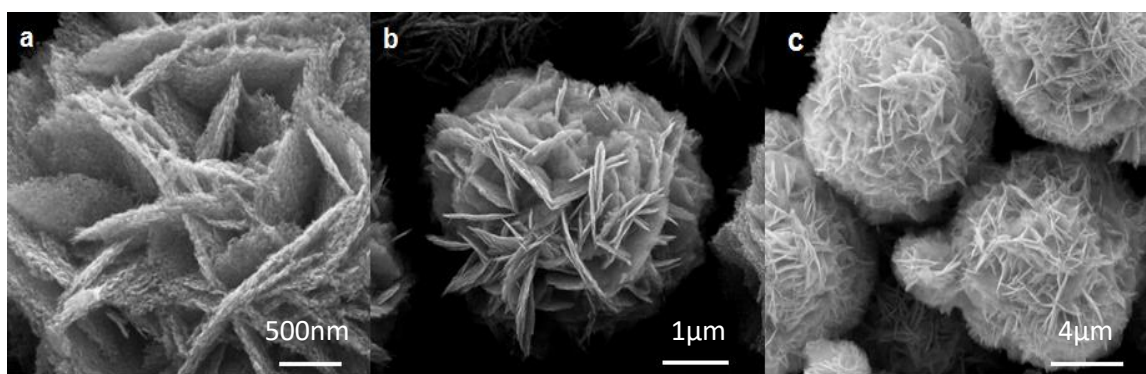


Figure S11 SEM images of sample BWO synthesized by hydrothermal method under different magnifications (a) 500nm; (b) 1 μ m; (c) 4 μ m.

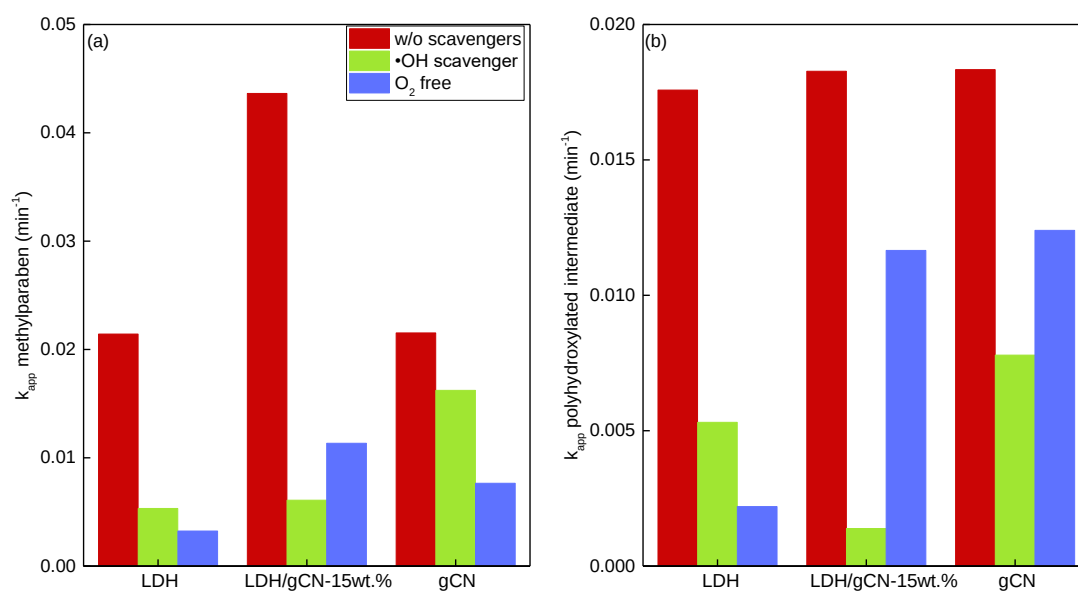


Figure S12 Apparent rate constants for the degradation of methylparaben and its intermediates in the absence of scavengers, in the presence of hydroxyl radicals scavenger and in oxygen-free conditions for samples LDH, CN and LDH/CN-15wt.%.

Annex II. Publications

Article

A Simple Approach to Prepare a C_3N_4/MoO_3 Heterojunction with Improved Photocatalytic Performance for the Degradation of Methylparaben

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Abstract: The adequate optical properties, low cost, and thermal stability of graphitic carbon nitride and molybdenum oxide make them both promising materials for photocatalytic applications. However, they both suffer from strong recombination of their photogenerated charge carriers. Therefore, searching for strategies that enable an efficient charge carrier separation is desirable for improving the photocatalytic performance of both semiconductors. In this work, we have synthesized a $g-C_3N_4/MoO_3$ heterojunction by a facile solid dispersion approach to the pristine semiconductors that allows a uniform dispersion of the two phases in the heterojunction. The resulting hybrid photocatalyst exhibits light absorption features similar to pristine $g-C_3N_4$ and presents an improved separation of the photogenerated charge carriers, likely through a Z-scheme between both semiconductor phases, as inferred by photoelectrochemical measurements. As a result, the $g-C_3N_4/MoO_3$ heterojunction showed better photocatalytic activity than the individual semiconductors and good cycling stability for the degradation of methylparaben and its reaction intermediates. We drew these conclusions based on total organic carbon (TOC) measurements.

Keywords: methylparaben degradation; water emergent contaminants; solid state heterojunction; photocatalysis; carbon nitride; molybdenum oxide

1. Introduction

Recent years have seen an increased awareness of the risks associated with contaminants of emerging concern to the aquatic ecosystems and to human health [1,2]. Among different families of substances, parabens—derivatives of para-hydroxybenzoic acid used as antimicrobial and antibacterial preservatives—are perceived as recalcitrant pollutants to water bodies. Their impacts on human health include their ability to disrupt the endocrine system or to produce pregnancy complications and adverse effects on fetal and childhood growth [3–5]. Parabens occur naturally in many fruits and vegetables, but they are also widely used in the formulation of common consumer products such as cosmetics, pharmaceutical compounds, personal care products, beverages, and in the food industry [5]. Owing to such high utilization, parabens have been detected in human tissues and various types of water (including drinking water, rivers, and seawater). The presence of parabens in water bodies is mostly attributed to discharges from wastewater treatment plants and industrial activities [6]. Since conventional sludge treatment methods have proven to be

inefficient at removing these recalcitrant pollutants, research on more efficient degradation processes has become a topic of interest in water remediation.

Among other alternatives, solar-driven photocatalytic processes seem particularly attractive for the degradation of non-biologically degradable pollutants such as parabens. TiO_2 is considered the benchmark photocatalyst for many applications; however, its poor activity under natural sunlight and the recently raised issues related to its nanoparticulated nature (e.g., the European Union banned the use of TiO_2 nanoparticle suspensions in food products in 2020 [7]) prevent a widespread application to water remediation [8–10]. This has prompted investigations into new materials with enhanced photoactivity under natural sunlight [10–12]. In this context, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) has received much attention in photocatalytic applications. Its interesting electronic band structure, visible-light response, and relatively low cost have made it a potential alternative to transition metal-based semiconductors [13–16]. As for many other semiconductors, the main cornerstone of $\text{g-C}_3\text{N}_4$ for further advances in the field of photocatalysis is the severe recombination of the photogenerated charge carriers.

On the other hand, the use of solid-state heterojunctions (e.g., catalysts composed of distinct phases—typically semiconductors—with different energy levels) has become a promising approach in photocatalysis, with many examples showing improved photocatalytic conversion rates owing to the increased lifetime of the charge carriers. (The close contact between the phases in the heterojunction shortens the path of the charge carriers [13,14,17].) In particular, $\text{g-C}_3\text{N}_4$ -based direct Z-scheme photocatalysis has been extensively applied in water remediation, with remarkable results for several pollutants, namely dyes, tetracyclines, pesticides, and pharmaceuticals [13–17]. Despite the abundant literature on heterojunctions based on $\text{g-C}_3\text{N}_4$, most studies focus on the use of wide bandgap semiconductors (e.g., ZnO , TiO_2) and complex synthetic approaches to obtain controlled optimized interfaces between the semiconductors of the heterojunction, as the interfacial properties define the flow of charge carriers upon illumination [18–24].

In this study we have selected MoO_3 , an n-type gap semiconductor for the preparation of a $\text{g-C}_3\text{N}_4/\text{MoO}_3$ heterojunction as both materials have a staggered energy level structure that should allow the formation of a direct Z-scheme. Furthermore, the favorable optical properties of MoO_3 (e.g., it can be activated under solar light), its low cost, and its stability in aqueous environments make it a viable contender in solar photocatalysis for water remediation [10]. Indeed, the advantages of combining MoO_3 with other photocatalysts have been widely reported in the literature. Some examples include ZnO [25], CuO [26], BiVO_4 [27], or $\text{g-C}_3\text{N}_4$ [19].

In this study, we used a fast and simple solid dispersion method to prepare a $\text{g-C}_3\text{N}_4/\text{MoO}_3$ heterojunction showing enhanced photocatalytic performance for the degradation of a recalcitrant pollutant (methylparaben, MPB). Methylparaben is a pollutant of primary concern in France, owing to its toxicity and frequent detection in aqueous environments after sewage treatment [28,29]. Obtained data has shown that the heterojunction displays better photodegradation efficiency under simulated solar light than the bare semiconductors in terms of conversion of both MPB and its degradation intermediates. Our preliminary results monitoring the by-products formed indicate the presence of short alkyl chain organic acids, with only traces of aromatic derivatives. The enhanced separation of the photogenerated charge carriers (evidenced by the photoelectrochemical measurements) demonstrated the adequate interface contact between both semiconductors in the heterojunction. This resulted in an improved redox ability of the photoelectrons and photoholes retained in the heterojunction, hence accounting for the improved catalytic activity for the photodegradation of methylparaben, with a high mineralization extent (as evidenced by TOC measurements).

2. Results and Discussion

2.1. Characterization of the Catalysts

Figure 1 shows the XRD patterns of the $g\text{-C}_3\text{N}_4/\text{MoO}_3$ heterojunction and the pristine semiconductors $g\text{-C}_3\text{N}_4$ and MoO_3 . The latter shows the diffraction peaks corresponding to the well-reported structures of both materials in the literature [19–26]. The pattern of $g\text{-C}_3\text{N}_4$ exhibits two diffraction peaks, located at 13.11° and 27.52° , which are consistent with the reference diffractogram for this material (JCPDS, 87-1526). The peak at 13.11° corresponds to the in-planar repeated triazine units (100). The peak at 27.52° (002) is associated with the interlayer stacking of aromatic structures and confirms the graphitic-like structure of this material. A crystallite size value of 5.2 nm was calculated using the Scherrer equation (Table S1).

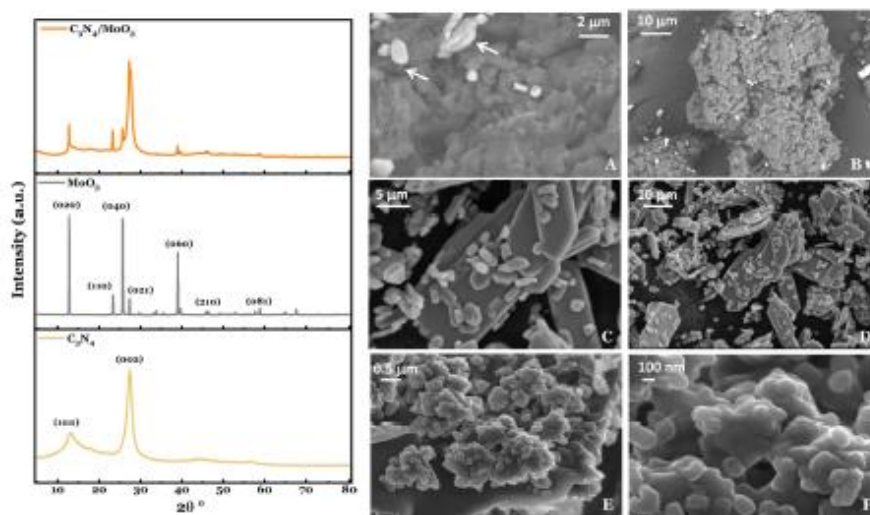


Figure 1. XRD patterns and SEM images of the pristine semiconductors and the heterojunction: (A,B) $g\text{-C}_3\text{N}_4/\text{MoO}_3$; (C,D) MoO_3 ; (E,F) $g\text{-C}_3\text{N}_4$.

For MoO_3 , all the diffraction peaks indexed with the orthorhombic structure (JCPDS, 05-0508) of the semiconductor, with a crystallite size of ca. 61 nm. The XRD patterns of the $g\text{-C}_3\text{N}_4/\text{MoO}_3$ heterojunction revealed the coexistence of the crystalline phases of both semiconductors, with negligible differences in the position and/or widths of the peaks compared to the patterns of the bare semiconductors. The peaks corresponding to the (020), (110), (040), and (060) of MoO_3 are clearly seen in the pattern of the heterojunction, along with the wide (002) peak of $g\text{-C}_3\text{N}_4$. The absence of additional diffraction peaks in the heterojunction confirms the lack of structural modifications to the semiconductors during the synthesis (i.e., solid state dispersion of the individual phases at 100°C). Similarly, the morphology (Figure 1) and porosity (Figure S1) of the heterojunction were similar to that of the pristine semiconductors. More specifically, the heterojunction showed particles of irregular shapes ranging from a few hundred nanometers to several microns that correspond to the morphology of pristine $g\text{-C}_3\text{N}_4$, along with scattered micrometric particles of regular and smooth shape (see arrows in Figure 1) corresponding to the MoO_3 semiconductor. The average particle sizes ranged from a few hundreds of nanometers to several microns. EDS analysis of the heterojunction (Figure S2) revealed the presence of C, N, O, and Mo atoms with atomic ratios C:N and Mo:O of 1.2 (ca. 1.1 wt.%) and 0.01 (ca. 0.6 wt.%), respectively. These atomic ratios are lower than the expected stoichiometric values considering the composition of the heterojunction (0.8 and 0.33 atomic ratio for C:N and Mo:O, respectively). This mismatch could be attributed to either the lack of sensitivity

of EDS analysis preventing a precise estimation of the atomic ratios, or to a homogeneous distribution of MoO_3 particles in the bulk of the heterojunction and not on the surface (EDS being a surface technique). A similar observation was inferred from the XPS analysis, as will be discussed below.

Regarding porosity (Figure S1), all the samples displayed type II N_2 adsorption isotherms characteristic of non-porous solids, and a hysteresis loop relative pressure above 0.8, indicating the presence of large cavities (mesopores and macropores). Furthermore, the main textural parameters of sample $\text{g-C}_3\text{N}_4/\text{MoO}_3$ (pore volumes and surface areas) are similar to the theoretical values predicted by the mixing rules. This was rather expected since the synthetic route used in the preparation of the heterojunction consisted of a solid dispersion of the pristine semiconductors at moderate temperatures.

The optical features of the photocatalysts were evaluated by diffuse reflectance spectroscopy. The corresponding spectra of the heterojunction and the pristine semiconductors, along with Tauc representations for the evaluation of the optical band gap, are shown in Figure 2. As seen, all three materials presented an abrupt decrease in reflectance values associated with the optical absorption edge of the materials. The absorption edge of $\text{g-C}_3\text{N}_4$ and MoO_3 is observed at around 400 nm and 350 nm, respectively, indicating the higher absorption of $\text{g-C}_3\text{N}_4$ in the visible light region. The corresponding bandgaps were calculated assuming direct electronic transitions for MoO_3 and indirect transitions for $\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4/\text{MoO}_3$, as commonly reported in the literature [19,21,25–27]. The obtained values were 2.83 eV for $\text{g-C}_3\text{N}_4$, 3.03 eV for MoO_3 and 2.85 eV for $\text{g-C}_3\text{N}_4/\text{MoO}_3$ (+ 0.01 eV in all cases).

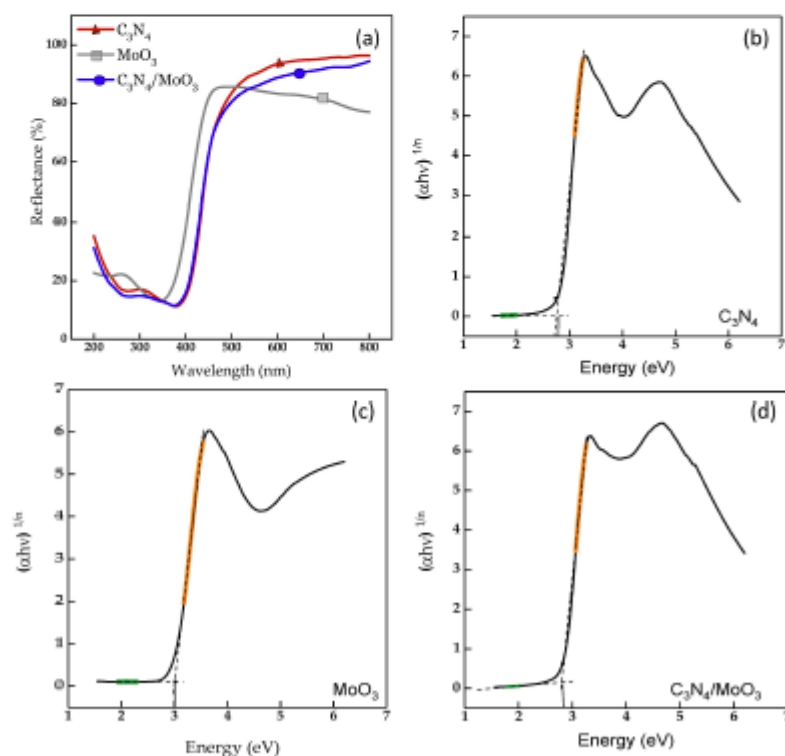


Figure 2. Experimental diffuse reflectance spectra (a) and Tauc graphical representations of the studied catalysts (b–d). In Tauc representations: experimental data (black lines); fitted range (orange line); baseline fitting (green line); dotted lines represent the extrapolation of the double linear fitting ranges.

The calculated optical band gap of the heterojunction is slightly higher than that calculated for g-C₃N₄ (although the differences are subtle). This points out that, despite the differences in the optical band gap of the pristine semiconductors, the incorporation of a small amount of MoO₃ (ca. 10wt.%) in a solid-state dispersion of carbon nitride matrix does not have a strong impact on the optical features of the latter.

The surface composition of the catalysts was analyzed by XPS (Figure 3). For sample g-C₃N₄, the C1s spectrum was deconvoluted into several contributions: a peak at 284.6 eV was assigned to C–C bonds of graphitic carbon; a peak at 285.8 eV attributed to the C–N=C backbone, and the peak 288.2 eV characteristic of sp²-hybridized carbon in an N–C=N configuration. The N1s core level spectrum was deconvoluted into three peaks at 398.7, 400.0, and 401.1 eV, which represent triazine rings of C–N=C, the tertiary nitrogen in N–(C)₃ groups, and the N(H) groups, respectively. The O1s core level spectrum revealed small contributions (ca. 3 at.%) for oxygen species, mainly attributed to adsorbed oxygen/water. All these assignments are consistent with previously reported results for carbon nitride [30,31]. The analysis of pristine MoO₃ showed the characteristic peaks corresponding to Mo 3d3/2 and Mo 3d5/2 at 236.6 and 233.4 eV assigned to Mo⁶⁺, along with two small peaks at 232.10 eV and 235.2 eV that can be assigned to Mo⁵⁺ (oxygen vacancies) [32]. The calculated atomic ratio Mo 3d:O 1s of 1.6 confirms the existence of oxygen vacancies in MoO₃.

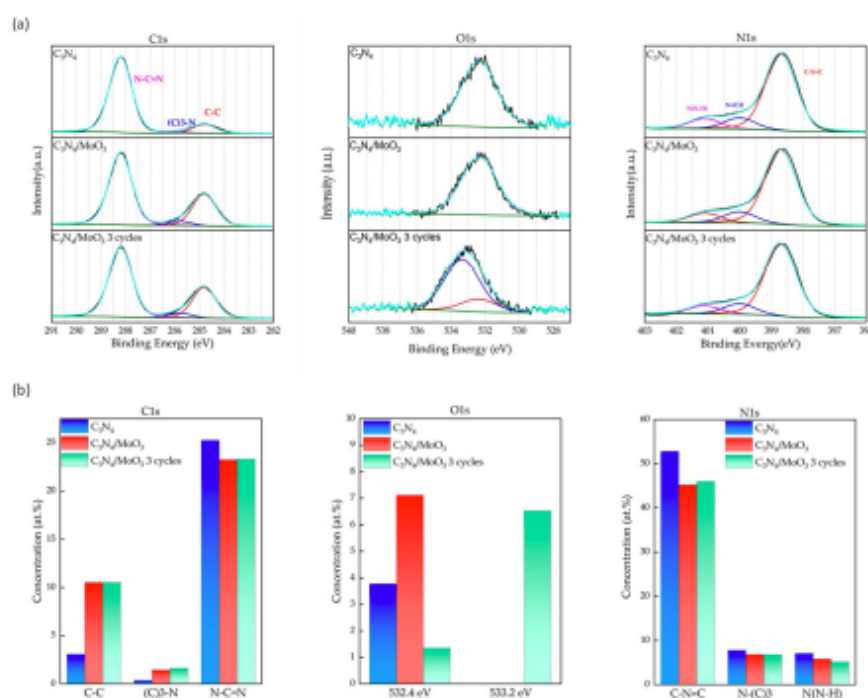


Figure 3. (a) High resolution C1s, O1s, and N1s core spectrum of the studied catalysts before and after three consecutive photocatalytic assays; (b) atomic concentration of the different species.

For the heterojunction, a distribution of species similar to that in g-C₃N₄ was found for all the elements, confirming the minor modification in the surface composition of the heterojunction. On the other hand, the Mo 3d signal was not detected on the heterojunction (the sample was measured three times with similar outcomes). The presence of MoO₃ in the heterojunction was confirmed by ICP-OES (upon acid digestion of the sample) and by the XRD patterns (Figure 1). The lack of a Mo 3d signal indicates that the MoO₃ phase is not

accumulated in the external surface of the heterojunction (note that XPS is a surface analysis technique probing ca. 1–10 nm in the external surface), but rather dispersed in the bulk of the material. (Hence, the surface composition determined by XPS does not represent the bulk material.) A similar conclusion was inferred from the mismatch in the element's atomic ratios detected by EDS analysis (another surface technique), as mentioned above.

2.2. Photocatalytic Performance

Before irradiation, the photocatalysts were put in contact with a solution of methylparaben and stirred in dark conditions for 30 min (see further details in the experimental section below). This takes into account the removal of the pollutant due to adsorption on the catalysts (before irradiation). For clarity purposes, this has been marked as −30 min in Figure 4 (dark contact region). Preliminary kinetic adsorption studies in dark conditions on all of the catalysts confirmed that under our experimental conditions, the uptake of MPB reaches equilibrium conditions (i.e., stable concentration in solution) in 20–30 min. The uptake in dark conditions was relatively low and similar to all three studied catalysts, which is consistent with their low porosity (Figure S2). This assured us that the initial concentration of the pollutant in the solution, when the catalysts are illuminated, is the same for all of them. This is important to the comparison of their photocatalytic performance, disregarding the effects of adsorption rates since it is well-known that photodegradation kinetics is affected by the initial concentration of the pollutant in the solution. Also, this experimental approach allows us to discriminate between pollutant removal due to (non-degradative) adsorption and the photocatalytic degradation reaction, which may occur simultaneously in porous catalysts.

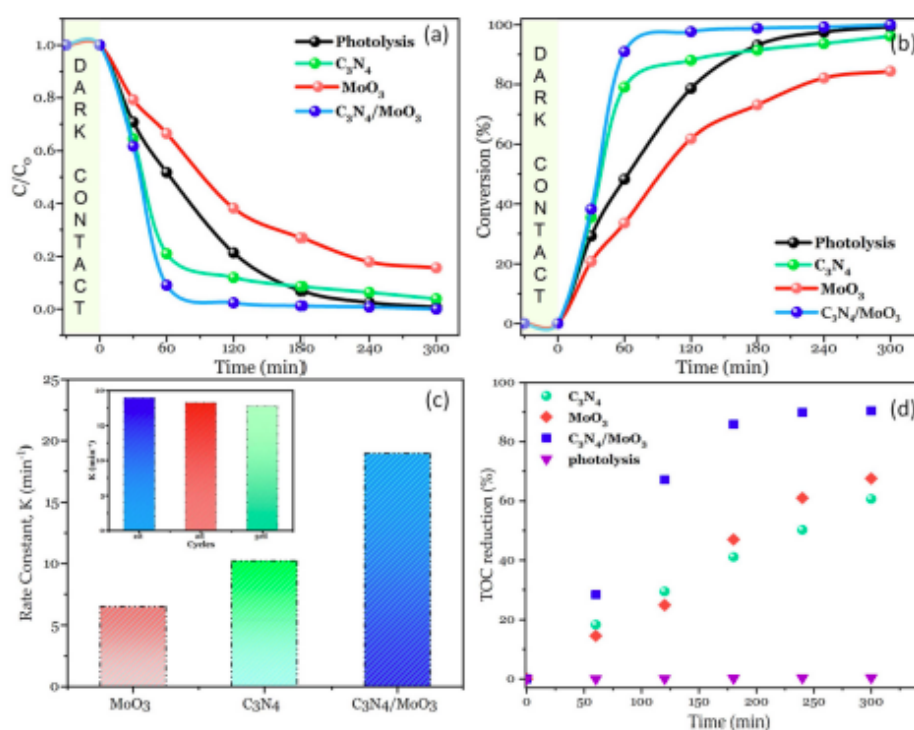


Figure 4. Concentration decay curves (a) and conversion (b) of methylparaben upon illumination of the studied materials; (c) methylparaben degradation rate constants; (d) TOC reduction.

Figure 4 shows the concentration decay curves of MPB for all three studied photocatalysts, compared to the photolytic reaction (in the absence of a catalyst). For comparison purposes, the data are also plotted as the conversion of methylparaben. Note that under our experimental conditions the decay in MPB contribution can be directly related to its photooxidative degradation (disregarding adsorption effects as discussed above).

With the exception of sample MoO_3 , the photocatalytic degradation of MPB was more efficient than the photolytic reaction (in the absence of a catalyst). Even though the decay in MPB concentration during the photolytic degradation was relatively high (ca. 40% and 90% decay after 1 and 4 h respectively), the photolytic reaction was quite inefficient for the complete mineralization of MPB. The evolution of the Total Organic Carbon (Figure 5) showed that only ca. 0.4% of complete degradation of MPB was achieved after 5 h of irradiation in the absence of a catalyst. This evidences the low conversion of the degradation intermediates of MPB in the photolytic reaction. The relatively large decay of methylparaben concentration on the photolytic reaction under our experimental conditions may be due to the low concentration (ca. 5 ppm) of the pollutant in the solution. Indeed, most studies reported in the literature on the photocatalytic degradation of methylparaben typically use higher initial concentrations of the pollutant (Table 1).

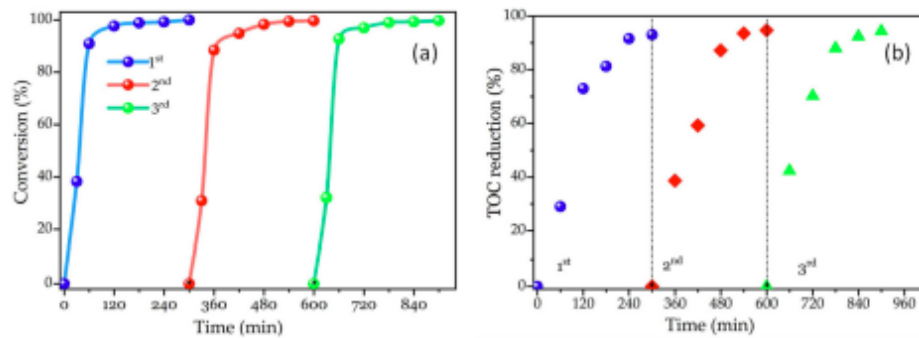


Figure 5. Photocatalytic performance of the $\text{g-C}_3\text{N}_4/\text{MoO}_3$ heterojunction upon several consecutive cycles (1st, 2nd, 3rd): (a) concentration decay curves of methylparaben and (b) TOC reduction.

Table 1. Comparison of the photocatalytic degradation studies of parabens with $\text{g-C}_3\text{N}_4$ semiconductor and heterojunctions with other semiconductors.

Catalyst	Synthesis	Paraben Concentration, Catalyst Loading	Irradiation Source	Photodegradation Efficiency (%)	Ref.
$\text{g-C}_3\text{N}_4/\text{MoO}_3$	Solid state dispersion	Methylparaben 5 ppm, 0.5 g/L catalyst	125 W lamp (UV-vis)	100% after 120 min; TOC reduction of 93%	This work
$\text{g-C}_3\text{N}_4$ and $\text{WO}_3/\text{g-C}_3\text{N}_4$	hydrothermal treatment	Methylparaben 10 ppm, 1 g/L catalyst	Xe lamp (300 W)	36% after 60 min ($\text{g-C}_3\text{N}_4$) 44–98% ($\text{WO}_3/\text{g-C}_3\text{N}_4$)	[31]
$\text{g-C}_3\text{N}_4$	calcination	Methylparaben 0.1–1 ppm, 0.05–0.5 g/L catalyst	100 W Xe lamp	100% after 90 min of irradiation	[33]
$\text{g-C}_3\text{N}_4/\text{BiVO}_4$	hydrothermal treatment	benzyl paraben 10 ppm, 1 g/L catalyst	300 W Xe lamp	86% after 150 min	[34]
$\text{g-C}_3\text{N}_4$ (nanosheets, bulk)	Thermal exfoliation	methyl-, ethyl- and propyl paraben 10 ppm, 0.2 g/L catalyst	300 W Xe lamp	Nanosheets > 95% Bulk < 30%	[35]
$\text{g-C}_3\text{N}_4/\text{BiVO}_4$	hydrothermal treatment	benzyl-paraben 20 ppm, 1 g/L catalyst	300 W Xe lamp	62% after 150 min 5% composite	[36]

Table 1. Cont.

Catalyst	Synthesis	Paraben Concentration, Catalyst Loading	Irradiation Source	Photodegradation Efficiency (%)	Ref.
N-vacancies on g-C ₃ N ₄	N ₂ etching method	Propylparaben (no details)	70 W metal halide lamp	94%	[37]
g-C ₃ N ₄ (various precursors)	Thermal polymerization method	Mixture of methyl-, ethyl-, propyl-paraben, 1 ppm each, 0.2 g/L catalyst	ultraviolet-A, visible LED, natural sunlight	28–32% under UV light	[38]
P25 (TiO ₂)	Commercial	methylparaben 10 ppm, 2 g/L catalyst	125 W UV lamp (365 nm)	99% after 120 min	[39]
P25 (TiO ₂)	Commercial	methylparaben 30 ppm, 2.5 g/L catalyst	15 W UV lamp (350–410 nm)	20% after 100 min	[40]

To better compare the performance of the studied materials, the rate constant values of the photocatalytic assays were determined from the concentration decay curves using a first-order reaction model. The data are shown in Figure 4c. The rate constant of methylparaben conversion was twice as large for sample g-C₃N₄/MoO₃ than that of bare g-C₃N₄ and almost three times larger than that of bare MoO₃. This demonstrates the faster degradation rate of the heterojunction.

The extent of MPB mineralization (i.e., complete conversion to CO₂ and water) was monitored by observing the evolution of the total organic carbon of the solutions (Figure 4d) and the analysis of the degradation subproducts in the reaction by HPLC (Figure S4). For g-C₃N₄/MoO₃, a TOC abatement of ca. 93% was achieved after 300 min of illumination, demonstrating the capacity of this photocatalyst to degrade both MPB and its reaction intermediates. The extent of mineralization was higher for the heterojunction than that observed for the bare semiconductors, with TOC abatements ranging between 55–75% for g-C₃N₄ and MoO₃, respectively. This is in agreement with the low amounts of intermediates detected in the solution by HPLC (Figure S4). A preliminary screening of the degradation subproducts pointed out the presence of small amounts of polyhydroxylated intermediates (e.g., trihydroxybenzoic acid isomers and tri- and di-hydroxybenzene isomers) in the first 60 min of irradiation for the heterojunction. These intermediates were not detected after longer periods of the reaction in the heterojunction, but were still seen when the bare semiconductors were used as photocatalysts.

The good photocatalytic performance of g-C₃N₄/MoO₃ in terms of methylparaben conversion, degradation of intermediates, and TOC abatement was maintained after three consecutive illumination assays (ca. 15 h) (Figures 5 and S4). The stability of the heterojunction during the cycles was further confirmed by the post-mortem analysis of the composition by XPS (Figure 3) after the consecutive photocatalytic assays. The C1s and N1s core level spectra of the heterojunction after the consecutive runs were similar to those of the initial material. Small differences were observed in the O1s signal; after the photocatalytic cycles, the heterojunction displayed a slightly higher oxygen content (ca. from 3 at.% to 6 at.%). While the O1s core level spectrum in the as-prepared material was deconvoluted in one peak at 532.2 eV (adsorbed oxygen/water), an additional contribution to the O1s signal appeared after the cycles. A small peak featuring at 533.21 eV was observed, assigned to surface hydroxyl radicals [41]. The relative abundance of the O1s peaks was still relatively low after the cycles (ca. 6.7 at.%), confirming the stability of the catalysts upon three consecutive cycles. The peaks attributed to Mo-O bonds (either O1s or Mo 3d signals) were still not present in the heterojunction, as discussed above for the initial sample before the subsequent photocatalytic runs.

According to the literature, such enhanced photocatalytic activity of the heterojunction may be attributed to an efficient charge separation via the charge migration between the two semiconductors [13,42]. To corroborate this hypothesis, a photoelectrochemical characterization of the materials was carried out. The cyclic voltammograms of ITO/semiconductor electrodes under on/off illumination obtained in 0.1 M Na₂SO₄ are presented in Figure 6.

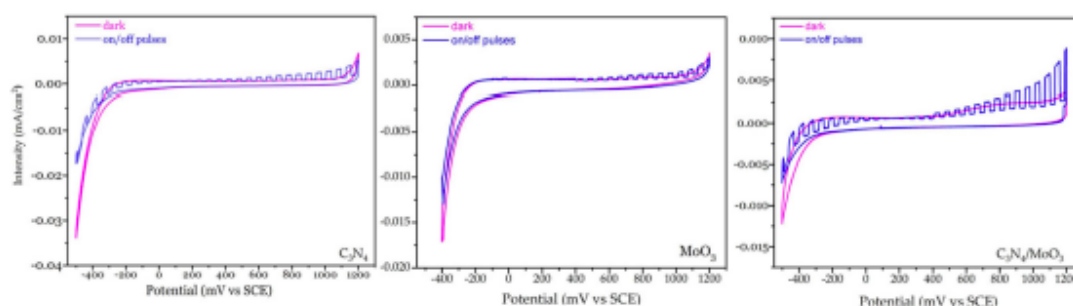


Figure 6. Cyclic voltammograms recorded at 20 mV/s of ITO/semiconductor electrodes in 0.5 M Na₂SO₄ (pH 6.10) under dark conditions and illumination using a 340 nm LED. Before the measurements, the electrodes were stabilized for 20 cycles in the dark (last cycle shown).

In dark conditions, the profiles of bare g-C₃N₄ and MoO₃ showed the characteristic shape of n-type semiconductors with two distinctive regions in the voltammograms. A first region between +200 and +1200 mV is characterized by a flat small current at anodic potentials and corresponds to the depletion region where electrons cannot move (the material behaves like a diode). The second region (accumulation region) between −400 and +200 mV is characterized by a cathodic current indicating a flux of electrons. (Note that the average cathodic current in this region is slightly higher than that in the depletion region.) The dark currents were slightly more intense in the g-C₃N₄/MoO₃ heterojunction, compared to the pristine semiconductors, which could be attributed to the small differences in capacitive contribution (in agreement with the porous features, Figure S2). Upon illumination, cathodic and anodic photocurrents were observed at potentials below −100 mV and above +200 mV, respectively, due to the migration of the majority charge carriers, indicating the formation of hole-electron pairs (recombination is not dominant at these bias potentials). In an aqueous inert supporting electrolyte, the anodic photocurrent is related to water oxidation by the photoholes (through the formation of •OH radicals). In the anodic sweep, the photocurrent gradually increased with the potential bias; this is characteristic of systems governed by a photohole capture regime [43].

Figure 7 shows the transient chronoamperometric curves upon on-off illumination at +600 mV of the three studied materials. All the catalysts showed a similar qualitative response, with an initial sharp current spike on switching on the light followed by a gradual decrease in the photocurrent (the pulses were very fast). The current returned to the original values almost instantaneously upon switching off the light. The photocurrent response was reproducible during repeated on/off illumination cycles, reaching a steady state regime after the second cycle (this cycle was used for the semi-quantitative analysis of the photoelectrochemical response). This confirms that the initial current decay is due to fast recombination of the charge carriers, rather than to photocorrosion of the electrode. For the second cycles and so forth, the photocurrent decay would be most likely associated with the trapping of electrons in deep states, resulting in the redistribution of interfacial potential [43].

The photocurrent intensity of the g-C₃N₄/MoO₃ electrode was much larger (ca. 3 times) than that of pristine g-C₃N₄, demonstrating the reduced recombination of the charge carriers in the heterojunction. The estimated photocurrent rate constants using a simple first-order kinetic approach also demonstrated the slower photocurrent decay for g-C₃N₄/MoO₃, compared to the bare semiconductor (Figure S3). This is in line with the matched band alignment reported in the literature for both semiconductors [19,44,45]. It also confirms that the preparation of the heterojunction via a solid-state dispersion of both phases is adequate to provide a close interfacial contact between them and to facilitate the flow of the charge carriers in the solid state without the need of a mediator in solution.

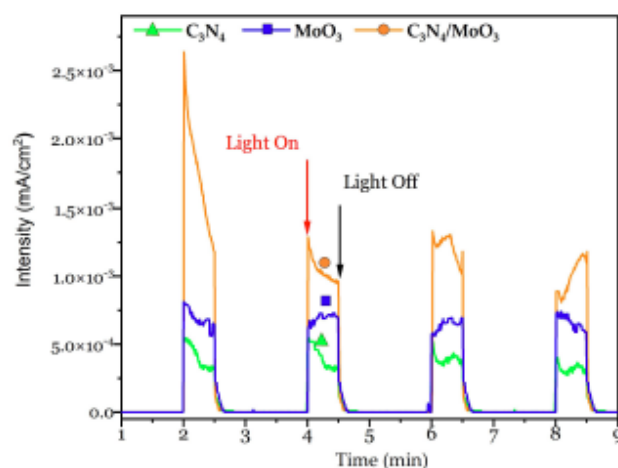


Figure 7. Transient photocurrent response of ITO/semiconductor electrodes recorded at a bias potential of +600 mV vs. SCE in 0.5 M Na₂SO₄ (pH 6.10). Illumination source is an LED at 340 nm; on/off cycles of 2 min were recorded.

2.3. Photocatalytic Mechanism

To explore the photoactivity mechanism of the g-C₃N₄/MoO₃ heterojunction system, we estimated the alignment of the conduction and valence band edges of the semiconductors used in the heterojunction using the Butler and Ginley method [46]. (The complete dataset and equations are compiled in Table S2.) The calculated energy levels for the valence band (VB) and conduction band (CB) of MoO₃ are 0.47 and 3.32 eV, respectively. Those calculated for g-C₃N₄ are 1.63 eV (VB) and -1.07 eV (CB). The proximity of the CB of MoO₃ to the VB of g-C₃N₄ makes possible a charge transfer upon a Z-scheme, as illustrated in Figure 8.

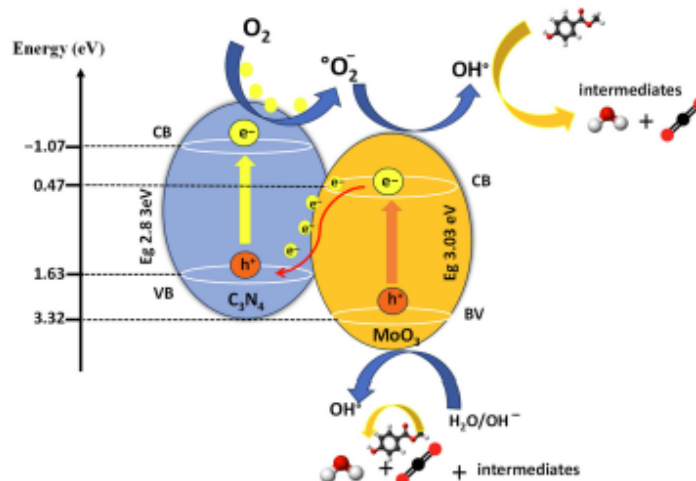


Figure 8. Schematic illustration of the photocatalytic activity on methylparaben following the direct Z-scheme in the g-C₃N₄/MoO₃ heterojunction.

g-C₃N₄ is a metal-free n-type indirect semiconductor that can be synthesized from earth-abundant organic precursors. Its structure is based on triazine or heptazine units

polymerized in a layered structure. It has a high visible light absorption capacity, which makes it attractive in photocatalytic applications, with an optical bandgap of ~ 2.7 eV. The energy levels of the CB of $g\text{-C}_3\text{N}_4$ enable the reduction of water into hydrogen and the reduction of oxygen into superoxide radicals (via the photoelectrons' reactivity). Still, they cannot promote the oxidation of water (via photoholes reactivity) into hydroxyl radicals [13,14]. However, owing to its 2D layered structure, this semiconductor presents a rapid surface charge recombination. Similarly, orthorhombic MoO_3 is a *n*-type indirect semiconductor, with the orthorhombic polymorph presenting a lamellar structure consisting of edge- and corner-sharing distorted MoO_6 octahedra in an ABA arrangement. It has a band gap of 2.8–3.6 eV, depending on the oxygen vacancies. The relatively low VB edge level of MoO_3 has a strong oxidation ability (i.e., the high oxidation power of photoholes), but the electrons in the CB edge are unable to reduce water to hydrogen due to slow electron mobility [45–48]. This causes the surface accumulation of electrons in the CB upon illumination of MoO_3 , increasing the recombination rate and ultimately reducing the photocatalytic performance.

The Z-scheme heterojunction $g\text{-C}_3\text{N}_4/\text{MoO}_3$ compensates for this limitation of both semiconductors, as observed in their enhanced photocatalytic performance (Figure 4). Upon light excitation of the heterojunction, the photoelectron injected in the CB of MoO_3 (a semiconductor with a low reduction potential) can be easily transferred to the VB of $g\text{-C}_3\text{N}_4$ due to the alignment of the energetic levels, then recombine with the low oxidation potential photoholes in the VB of $g\text{-C}_3\text{N}_4$ [19,44], forming a direct Z-scheme photocatalytic system without an electron mediator. As a result, isolated photoholes and photoelectrons formed in the heterojunction show a higher redox ability than those in the individual semiconductors. This would account for a higher capacity to generate radical reactive species (hydroxyl, superoxide) and ultimately promote the photodegradation of methylparaben and its intermediates to reach a high mineralization extent (Figure 6).

3. Materials and Methods

3.1. Catalysts Preparation

Bulk $g\text{-C}_3\text{N}_4$ was obtained upon calcination of melamine powders at 550°C during three hours in a muffle. MoO_3 powders were prepared by solid-state decomposition of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ at 500°C for 4 h under an air atmosphere. The resulting products were thoroughly washed in ultrapure water and dried at 70°C for 12 h. The $g\text{-C}_3\text{N}_4/\text{MoO}_3$ heterojunction (composition fixed to 10:90 wt.%) was prepared by dispersion of the solids under mild sonication. Briefly, 90 g. of $g\text{-C}_3\text{N}_4$ were dispersed in 20 mL of a mixture of ethanol:water (3:1 *v/v*) and sonicated for 30 min. Likewise, 10 g. of MoO_3 were dispersed in 20 mL of ethanol:water and sonicated for 30 min. Then, the MoO_3 dispersion was gradually added to the $g\text{-C}_3\text{N}_4$ one under constant stirring. The mixture was stirred for 2 h at room temperature, and then placed in a hot water bath at 100°C for 1 h, followed by cooling to room temperature. The resulting catalyst powders were washed, filtered and dried for 6 h at 70°C . They were finally calcined in a muffle furnace at 300°C for 3 h. For comparison purposes, the bare semiconductors were sonicated and calcined in the same conditions.

3.2. Characterization

The porosity of the catalysts was evaluated by N_2 adsorption at -196°C in a volumetric analyzer (Tristar, Micromeritics, Norcross, GA, USA). The samples were previously outgassed at 120°C overnight under primary vacuum. The gas adsorption isotherms were used to calculate the specific surface area, total pore volume, and micropore volume using the Dubinin-Radushkevich equation [49]. X-ray diffraction (XRD) patterns were recorded in a Bruker instrument (D8 Advance, Billerica, MA, USA) operating at 40 kV and 40 mA and using $\text{CuK}\alpha$ (0.15406 nm) radiation. The optical band gap of the photocatalysts was determined by UV-Vis diffuse reflectance spectroscopy in a spectrophotometer (Shimadzu UV-2501, Kyoto, Japan) equipped with an integrating sphere. Powders of the catalysts were pressed in holders of ca. 3 cm diameter and 5 mm depth. The measurements were recorded

between 220–700 nm in the diffuse reflectance mode, using BaSO_4 as reference. Spectra were collected at 1 nm intervals with a spectral bandwidth of 2 nm. Data were transformed to a magnitude proportional to the extinction coefficient through the Kubelka-Munk function, $F(R_\infty)$. The graphical representation of the Tauc method was used to evaluate the optical band gap, using a double linear fitting approach [50]. The morphology of the catalysts was determined by scanning electron microscopy (SEM) using a microscope (JEOL JSM-IT200, JEOL Ltd., Akishima, Japan) coupled with energy dispersive X-ray spectrometry (EDS) analysis. X-ray photoelectronic spectroscopy (XPS) experiments were collected in a K-Alpha ThermoScientific spectrometer (ThermoScientific, Waltham, MA, USA) using monochromatic $\text{AlK}\alpha$ (1486.6 eV) radiation at $3 \text{ mA} \times 12 \text{ kV}$. The spectra of dried samples were recorded using a $400 \mu\text{m}$ diameter analysis area. Processing of the XPS spectra was performed in Avantage software (v5), with energy values referenced to the C1s peak of adventitious carbon located at 284.6 eV, and a Shirley-type background.

3.3. Photoelectrochemical Measurements

The photoelectrochemical properties of the prepared photocatalysts were evaluated at room temperature in a conventional three-electrode electrochemical using an electrochemical workstation (Biologic VMP3, Seyssinet-Pariset, France). The working electrodes were prepared by spin-coating ca. 200 μL of inks containing the active material (ca. 90:10 photocatalyst:nafion 5 wt.% dispersed in dimethylformamide) onto conductive ITO substrates. A saturated calomel (SCE) and a graphite rod were used as reference and counter electrodes, respectively. A monochromatic 340 nm LED (Thorlabs Inc., Newton, NJ, USA) was used as irradiation source. The electrodes were immersed in 0.5 M Na_2SO_4 (pH 6) inert electrolyte, placed in front of the irradiation source and allowed to equilibrate for at least 3 h before recording any measurements. The photoelectrochemical response of the prepared electrodes was recorded by cyclic voltammetry under on/off illumination in a potential sweep from -400 to $+1200 \text{ mV}$ vs. SCE (scan rate 20 mV/s). The transient photocurrent response of the electrodes upon on/off illumination at a fixed bias potential was recorded to evaluate the electron transfer mechanism upon calculation of the rate of photocurrent decay from the transient profiles using a first-order kinetic approach [51]. (See details in Supplementary Materials File).

3.4. Photocatalytic Performance Assays

Methylparaben (98% purity) was purchased from Sigma Aldrich (St. Louis, MO, USA). Photodegradation experiments were performed at room temperature in a 500 mL batch reactor using an immersion photoreactor of cylindrical configuration (125W, Helios ItalQuarz (Cambiago, Italy), photon flux 900 W/m^2). The lamp was provided with a double-walled cylindrical quartz jacket cooled by flowing water (to prevent overheating of the treated solution during the photocatalytic assays), and vertically immersed in the solution. Before the photocatalytic assays, the catalyst was stirred in the dark in contact with the pollutant solution for 30 min. An excess of oxygen was provided during the photocatalytic assays by supplying a continuous air flow. Aliquots of the solution were periodically removed and filtered (0.45 μm nylon filter), then analyzed by reverse-phase HPLC (C18 column $125 \text{ mm} \times 4 \text{ mm}$; 45:55 methanol: phosphate buffer at pH 2.5 as mobile phase; 40°C ; flow rate of 0.7 mL/min ; injection volume $10 \mu\text{L}$; photodiode array detector). The degradation of MPB in the absence of catalysts and with the bare semiconductors was also carried out. All photodegradation experiments were performed with a catalyst loading at 1 g/L at least in duplicate; average data is herein presented (accuracy of ca. 5%). For total organic carbon (TOC) analysis, samples were filtered with $0.45 \mu\text{m}$ filters (Whatman, Maidston, UK) and measured in a Shimadzu VCSN TOC analyzer.

4. Conclusions

This study focused on the synthesis of a $\text{g-C}_3\text{N}_4/\text{MoO}_3$ heterojunction via a fast solid-state dispersion of the individual semiconductors. This simple synthetic route allowed us

to obtain a good interfacial contact between both semiconductor phases, favoring a direct solid-based Z-scheme photocatalytic mechanism (i.e., an interfacial electric field across the semiconductors enabling the flow of the photogenerated charge carriers). The reduced recombination rate of the e^-h^+ pairs upon illumination of the heterojunction was demonstrated by the increased photocurrent intensities and rates, as well as the increased oxidation performance for the photooxidation of methylparaben (a recalcitrant pollutant) and its derivatives. The reduction in overall total organic content increased by two times in the heterojunction compared to the isolated bare semiconductors. The heterojunction showed a stable performance through 3 consecutive cycles, with no modifications of the composition of the heterojunction. These results point out that matching the optical bandgap and the energy levels of the conduction and valence bands of semiconductors becomes more important for achieving efficient photocatalytic Z-schemes in solid state heterojunctions, than the synthetic route for the preparation of the heterojunction itself. A good interfacial contact can be achieved using a solid dispersion of powdered semiconductors, leading to efficient photocatalytic performance if the energy levels are adequately matched. Hence, efforts to synthesize new semiconductor formulations and make advances in the field of photocatalysis for environmental remediation should be focused in this direction.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal14030170/s1>, Figure S1: N_2 adsorption/desorption isotherms at -196°C of the studied catalysts. Inset: main textural parameters evaluated from the isotherms; Figure S2: SEM micrographs and EDX elemental spectrum of the $g\text{-C}_3\text{N}_4/\text{MoO}_3$ heterojunction; Figure S3: Photocurrent decay rate constant (s^{-1}) of the studied catalysts evaluated from the transient photocurrent responses of ITO/semiconductor electrodes at +600 mV vs. SCE in 0.5 M Na_2SO_4 (pH 6.10); Figure S4: Evolution of methylparaben degradation intermediates detected by HPLC for the studied catalysts, assigned to isomers of trihydroxybenzoic acid and/or tri- and di-hydroxybenzene derivatives. Note that the photolytic reaction has been plotted in the second axis for clarity purposes (due to the high intensity of the peaks); Table S1: Crystallite size (D) calculated by Scherrer equation from the X-ray diffraction data; Table S2: Electronegativity (eV) of the semiconductors used for the estimation of the energy levels of the conduction and valence bands [52–55].

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Photocatalytic activity of NiZnAl hydrotalcite-like compound/carbon nitride composites for the degradation of methylparaben

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ABSTRACT

The scope of this study is to improve the photocatalytic performance of C_3N_4 for the degradation of methylparaben in solution, upon the immobilization of the semiconductor in the interlayer spacing of a NiZnAl-hydrotalcite like compound (LDH). The growth of LDH in the presence of a homogenous dispersion of increasing amounts of carbon nitride allowed the incorporation of this carbon-based semiconductor in the interlayer space of the LDH. The prepared photocatalysts exhibited light absorption features similar to those of the pristine semiconductor and displayed better photocatalytic performance for the degradation of methylparaben and intermediates (higher conversions and degradation rates). This is attributed to the improved separation of the photogenerated charge carriers boosted by the interfacial contact between the carbon nitride confined in the lamellar structure of the hydrotalcite-like compound. The best performing material containing 15 wt% of carbon nitride showed good cycling stability over 20 h of illumination. The confinement of C_3N_4 affects the photodegradation mechanisms of methylparaben, with a hydroxylation-mediated reaction through the photogenerated holes as the main oxidation pathway and a minor impact of dissolved oxygen formed upon reaction of the photogenerated electrons.

1. Introduction

Parabens are natural compounds found in many fruits and vegetables and are widely used in the formulation of highly consumed products due to their antimicrobial activity (e.g., preservation of food, cosmetics beverages and personal care products) [1]. Due to the extensive utilization and an improper disposal of products containing parabens, their presence in the environment has increased in the last years. Their presence in water courses (natural and wastewater discharges) has become a critical environmental issue due to their toxicity to aquatic ecosystems and potential risks to human health as they can bio-accumulate [2]. Like many other pollutants of emerging concerns, parabens can cause estrogenic activity and have been associated with various types of cancer, as well as reproductive and immunological complications [3].

Conventional wastewater treatment methods based on biological sludge have proven to be poorly efficient for removing parabens [4]. As a result, research into more effective processes has gained interest in

water remediation. Among different options, solar-driven photocatalytic processes have attracted significant attention for the degradation of recalcitrant organic pollutants in wastewater, as parabens [5–8]. Owing to the poor activity of benchmark TiO_2 powders under solar light, significant efforts are being directed towards exploring alternative photocatalysts with enhanced activity under natural solar light.

In this context, carbon nitride derivatives (C_3N_4) have received considerable attention in numerous photocatalytic applications (e.g., water splitting for hydrogen production, degradation of a variety of pollutants) due to their favorable band gap structure, good chemical stability, low toxicity and abundance of precursors [9–13]. However, the main limitation of carbon nitride photocatalysts is the high recombination rate of the photogenerated electrons/holes. An effective approach to overcome this drawback is the use of mixed photocatalysts with distinct phases. In this regard, heterojunctions of semiconductors with two-dimensional materials have recently attracted the attention as a means to improve the lifetime of the photogenerated charge carriers due to the reduced distances within the 2D structures [14–16].

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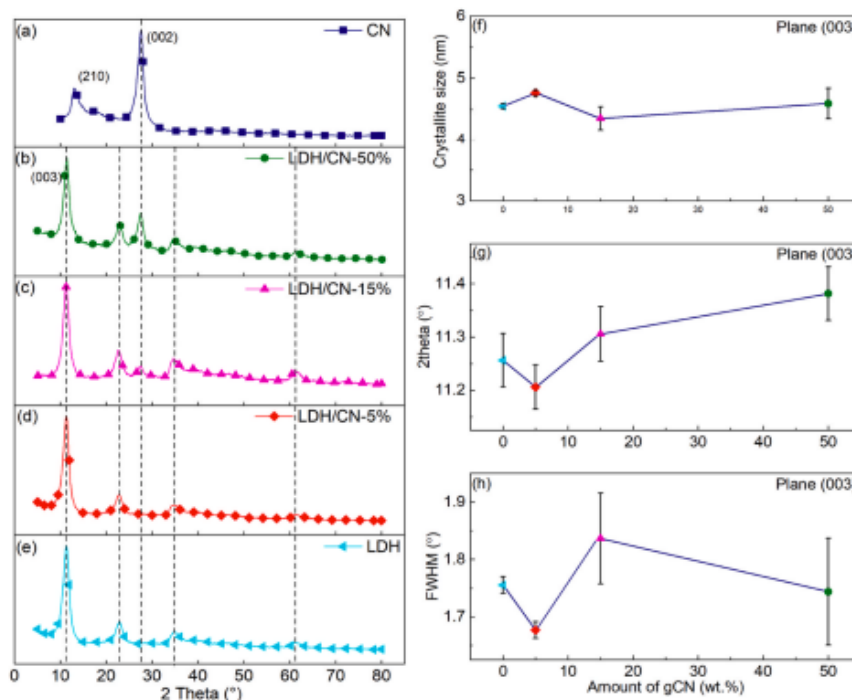


Fig. 1. (a-f) X-ray diffraction patterns, (g) crystallite size, (h) position and (i) FWHM of the (003) reflection plane of the prepared samples. Average patterns are presented (accuracy is ca. 5 % in all cases). Error bars of crystallographic indicators are shown for clarity.

Among these two-dimensional materials, hydrotalcite-like compounds -also known as layered double hydroxides (LDHs)- are promising candidates to improve the performance of semiconductors in photocatalytic applications. LDH are characterized by lamellar arrangements composed of positively charged layers formed by divalent and trivalent metal cations coordinated with hydroxyl groups and anions to compensate the surface charge [17,18]. The layered structure of LDHs is expected to facilitate the separation and migration of the charge carriers, while the ability to host diverse cations and anions within the interlayer space can enhance the light absorption in the visible range [16,19–21]. The synergistic effect of photocatalytic heterostructures based on LDH and C_3N_4 has been reported for the degradation of pollutants and the generation of hydrogen from water splitting [16,20–26]. As an example, C_3N_4 supported on ZnAl-LDH has been reported display better photocatalytic activity under visible light due to a red shift in the optical absorption edge of immobilized carbon nitride [20,24,26]. Similarly, Sherry et al. reported the synthesis of a trimetallic C_3N_4 /NiCoAl-LDH heterojunction with excellent structural stability and improved activity for hydrogen production due to optimized charge transfer pathways [27]. Feng et al. [28] have also described the synthesis of a C_3N_4 /NiZnAl-LDH heterojunction with good performance for the photocatalytic degradation of methyl orange and tetracycline. Despite the favorable results reported in the literature for LDH/carbon nitride heterojunctions [16], the challenge remains in the control of the incorporation of the semiconductor in the interlayer spacing of the 2D structure of the LDH and in the understanding of the charge transfer mechanisms occurring at the interface between both phases.

Considering all the above, in this study we report the preparation of a

hybrid photocatalyst by immobilizing C_3N_4 in the interlayer space of a trimetallic NiZnAl-LDH. Our results demonstrate that the growth of the crystallites of the LDH in the presence of a homogenous dispersion of carbon nitride particles allows the incorporation of the carbon nitride phase in the interlayer space of the LDH. The C_3N_4 /NiZnAl-LDH photocatalyst displayed better photocatalytic performance towards the degradation of a recalcitrant organic pollutant (i.e., methylparaben) and its intermediates, demonstrating the benefits of the confinement of the semiconductor. The photocatalyst prepared with 15 wt% of C_3N_4 showed faster degradation rates for methylparaben and its intermediates, as well as a stable photocatalytic activity after 20 h of consecutive illumination. Through an extensive characterization of the heterostructures and a deep analysis of the photocatalytic performance for the degradation of the selected pollutant and its intermediates in the presence of chemical scavengers, our study demonstrates that the confinement of the semiconductor nitride in the interlayer space of the LDH allows modifying the degradation mechanism of methylparaben, favoring the reactivity of the photogenerated holes.

2. Experimental

2.1. Synthesis of the photocatalysts

NiZnAl-LDH was synthesized via the co-precipitation method adjusting the chemical composition to a Ni:Zn:Al molar ratio of 2:1:1 [29,30]. Briefly, 12.36 g of $NiCl_2 \cdot 6 H_2O$, 3.54 g of $ZnCl_2$ and 9.75 g of $Al(NO_3)_3 \cdot 9 H_2O$ were dissolved in 50 mL of deionized water. A second solution was prepared by dissolved 4.68 g of Na_2CO_3 and 3.18 g of NaOH

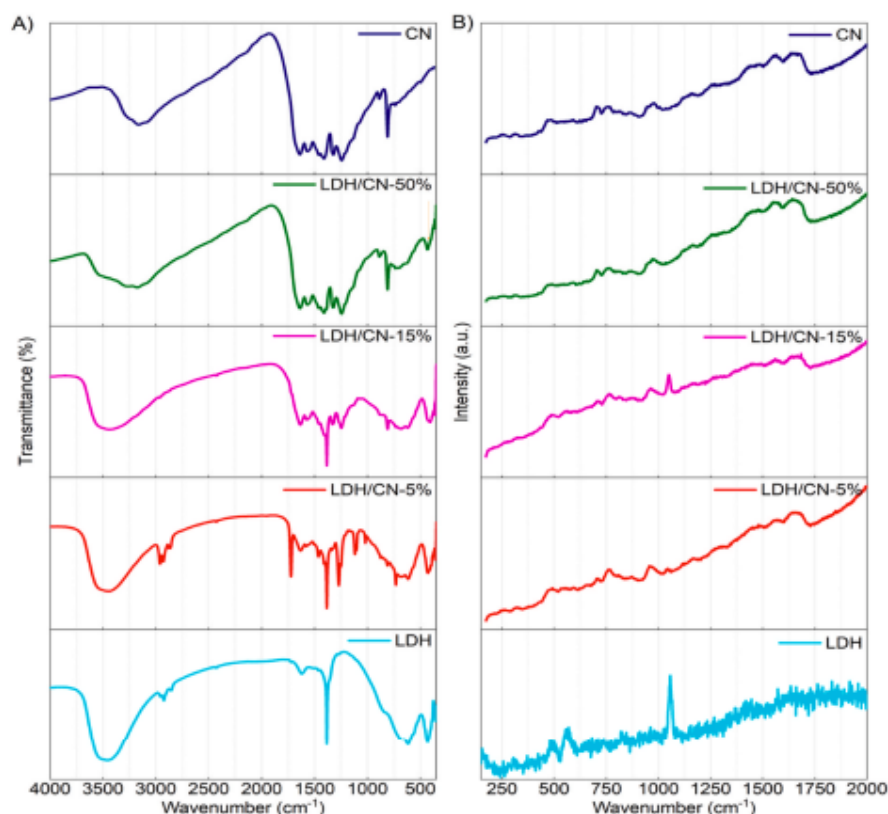


Fig. 2. (A) IR and (B) Raman spectra of the prepared LDH/CN composites and the pristine components. Average spectra are presented (accuracy is below 5 % in all cases).

in 50 mL of deionized water (to adjust the pH of the synthesis). Both solutions were mixed dropwise into an Erlenmeyer flask under vigorous stirring at 25 °C, and allowed to age in an oven at 80 °C for 24 h. After cooling, the solid was recovered by filtration, washed with distilled water, and dried overnight at 100 °C. The sample was labeled as LDH-NiZnAl. The LDH/carbon nitride composites were prepared by dispersing the carbon nitride powders (between 5 and 50 wt%) to a freshly prepared solution containing the LDH precursors upon sonication for 3 h to ensure a uniform dispersion, followed by the aging step at 80 °C for 24 h. This allows the growth of the crystallites of the LDH in the presence of the carbon nitride particles during the aging process, assuring a good interaction between both phases in the final composites. Those composites were labelled as LDH/CN-Y%, where Y refers to the amount of carbon nitride powders dispersed in the suspensions. Bulk graphitic carbon nitride powders were prepared by thermal decomposition of melamine at 520 °C for 4 h in a muffle furnace (heating rate of 10 °C/min) under air atmosphere (sample labeled as CN) [13]. All the synthesis were in triplicate; a high reproducibility was obtained for all the synthesis, with dispersion yields below 5 % in all the cases and similar characterization of different batches (see error bars in the presented characterization data).

2.2. Characterization techniques

X-ray diffraction (XRD) patterns were recorded in a Bruker instrument (D8 Advance) operating at 40 kV and 40 mA and using CuK α radiation (1.5418 Å). A zero-diffraction silicon substrate with a 5 mm diameter cavity was used for recording XRD on dried samples. The porosity of the materials was evaluated by high resolution N₂ adsorption/desorption at -196 °C in a 3Flex volumetric analyzer (Micromeritics) provided with a turbomolecular vacuum pump and three pressure transducers to assure sensitivity in the low-pressure range. The materials were outgassed under dynamic vacuum (ca. 10⁻⁵ torr) at 120 °C for 12 h. Ultrahigh purity nitrogen gas was used (Air Liquid, 99.9992 %). Strict analysis conditions were programmed during the gas adsorption measurements to assure equilibrium data, with over 100 equilibrium points recorded for each sample. The gas adsorption isotherms were used to calculate the specific surface area -using BETSI computational approach for an accurate determination [31]-, total pore volumes and mesopore volume. IR spectra were recorded under vacuum in a Nicolet spectrometer equipped with a DTGS detector. Dried powders of the materials were pressed into KBr pellets (dilution 1:250). Each spectrum resulted from the accumulation of 128 scans, recorded with a spectral resolution of 2 cm in the mid-IR range (4000–400 cm⁻¹) spectral domain. Raman spectra were recorded in ambient conditions in a Renishaw InVia Qontor spectrometer using 350 and 532 nm lasers. The

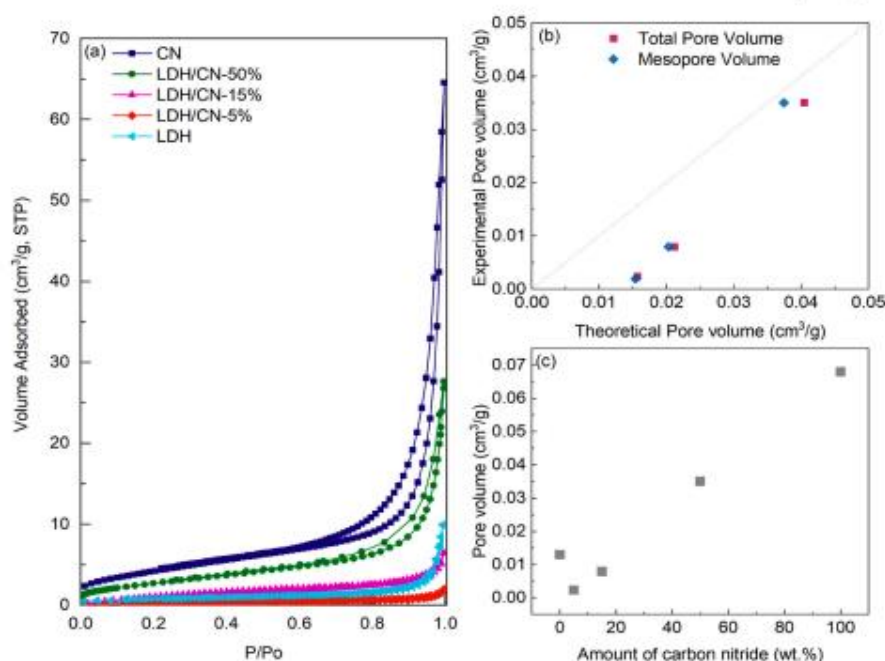


Fig. 3. (a) N₂ adsorption/desorption isotherms at -196 °C of the studied samples; (b) correlation between the theoretical and experimental pore volumes; (c) correlation between the total pore volume and the amount of carbon nitride in the LDH/CN composites. All isotherms were run in duplicate; accuracy is below 2 %.

Table 1

Summary of main textural parameters (specific surface area - S_{BET} -, total pore volume and mesopore volume) of the samples evaluated from the nitrogen adsorption isotherms at -196 °C.

	S_{BET} (m ² /g)	Total Pore Volume (cm ³ /g)	Mesopore Volume (cm ³ /g)
LDH-NiZnAl	3 ± 0.1	0.013 ± 0.001	0.013 ± 0.001
LDH/CN-5 %	1 ± 0.1	0.002 ± 0.001	0.002 ± 0.001
LDH/CN-15 %	6 ± 0.2	0.008 ± 0.001	0.008 ± 0.001
LDH/CN-50 %	9 ± 0.2	0.035 ± 0.001	0.034 ± 0.001
CN	16 ± 0.5	0.068 ± 0.001	0.062 ± 0.001

Average values and standard deviation of three determinations are presented.

spectra were collected under a Leica DM2500 optical microscope with a x50 long working distance objective (ca. 10 mm). Each spectrum was recorded with an integration time of 120 s; data presented represent the average of three measurements. The optical features of the catalysts were analyzed by UV-Vis diffuse reflectance spectroscopy using an integrating sphere (Shimadzu UV-2501). Powders of the samples were mixed in a mortar with BaSO₄ at a mass ratio 0.05:1, and pressed in a 3 cm diameter holder (5 mm depth). Reflectance values were recorded in the range 220–700 nm at 1 nm intervals and a spectral bandwidth of 2 nm. The collected reflectance data (R_{∞}) was transformed to a magnitude proportional to the extinction coefficient using the Kubelka-Munk function $F(R_{\infty})$ using the expression $F(R_{\infty}) = (1 - R_{\infty})^2 / 2R_{\infty}$. The energy bandgap of the catalysts was evaluated from the Tauc method:

$$\alpha h\nu = B (h\nu - E_g)^n \text{ or } F(R_{\infty}) h\nu = B (h\nu - E_g)^n$$

where h is Planck's constant (4.136 1015 eVs⁻¹), B is an energy independent constant, $h\nu$ is the photon energy (eV), E_g is the optical bandgap energy (eV), and n is a constant refers to the type of optical transitions (direct/indirect, allowed/forbidden).

The E_g values were obtained from the extrapolation of the linear least squares fit of the representation $[F(R_{\infty}) h\nu]^{1/n}$ vs $h\nu$, using a double-linear fitting approach [32]. The steady state fluorescence emission spectra of the samples upon excitation at 300 nm were recorded in a Horiba Fluoromax 4 P spectrofluorometer. For these measurements the photocatalysts were dispersed in water using a solid concentration of 0.1 g L⁻¹.

2.3. Photocatalytic assays

The methylparaben photocatalytic degradation (98 % purity, Sigma Aldrich) was carried out in a 500 mL immersion photoreactor, using a high-pressure mercury lamp (125 W UV-vis light; photon flux 900 W/m²) vertically immersed in the solution as an illumination source. The lamp was equipped with a double-walled cylindrical quartz jacket cooled by flowing water to maintain the temperature of the solution at 25 °C during the photocatalytic runs. A continuous air flow was maintained during the photocatalytic assays to assure the supply of oxygen. Before starting the illumination, the photocatalyst powders were put in contact with the methylparaben solution for 30 min (dark conditions), to achieve equilibrium conditions before the irradiation. The initial concentration of methylparaben was adjusted in every case considering the adsorption capacity of the catalysts at dark conditions, to assure that the concentration of the pollutant after the 30 min in the dark (before irradiating) is 10 ± 1 mg/L for all the catalysts. This allows a straightforward comparison of the photodegradation conversion and rates. For selected catalysts, photocatalytic runs were also carried out in the

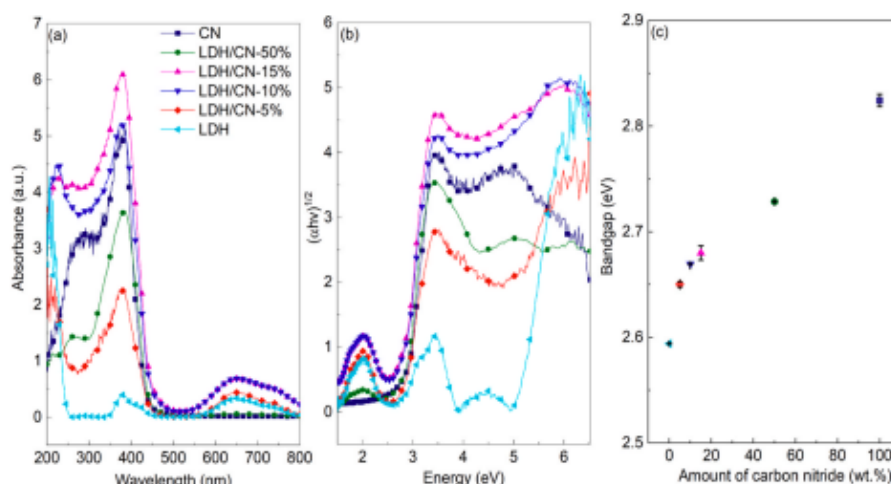


Fig. 4. (a) Absorption spectra and (b) Tauc graphical representation of the synthesized LDH/CN composites; (c) correlation between the optical band gap and the amount of carbon nitride in the composites. Average values of duplicate measurements (a,b) and error bars (c) are presented (accuracy below 5 %).

presence of an excess of isopropyl alcohol (ca. 10 mL added to the solution before irradiation) and in an oxygen-free atmosphere (bubbling helium as inert gas to prevent the formation of superoxide radicals by charge transfer). Aliquots of ca. 1.5 mL of the solution were periodically extracted and analyzed by reverse-phase HPLC using a C18 column (125 x 4 mm), 45:55 methanol:28 mM phosphate adjusted to pH 2.5 with phosphoric acid as mobile phase; 40 °C; flow rate of 0.7 mL/min; injection volume 10 μ L. The degradation assays were performed with a photocatalyst loading at 0.25 g/L at least in duplicate (average data is presented; accuracy was ca. 5 % in all cases; absolute error bars of each measurement are plotted). Consecutive photocatalytic tests were also carried out on the prepared materials. For this, an adequate volume of a concentrated methylparaben solution was added to the dispersions of the photocatalysts after the illumination for 6 h, so as to reestablish the initial concentration of the pollutant. Total organic carbon (TOC) analysis of aliquots of the solutions was measured in a Shimadzu VCSN TOC analyzer.

3. Results and discussion

3.1. Characterization of the photocatalysts

Fig. 1 (a-e) depicts the XRD patterns of the prepared LDH/CN composites, compared to those of the pristine components LDH-NiZnAl and carbon nitride. The diffraction pattern of the synthesized NiZnAl double layered hydroxide displayed the characteristic peaks corresponding to the LDH structure, indexed to JCPDS-ICDD files of nickel oxide hydroxide (01-089-7111), nickel aluminum hydroxide (04-025-1941), zinc hydroxide (04-013-9365) and zinc hydroxide dehydrate (01-091-1676). The well-defined peaks at -11° (003) -23° (006) and -34° (009) planes indicate a crystalline layered structure with rhombohedral symmetry. The basal spacing distance of the (003) peak was 0.786 nm, which is consistent with values reported for similar LDH materials in the literature [18,27–30].

For CN (00-066-0813), the characteristic diffraction peak at 27.46° (002) associated to the interlayer stacking of aromatic structures with a graphitic-like structure [33] was clearly observed, along with an ill-defined peak at 12.93° (210) associated to parallel chains of tri-s-triazine units [34]. The XRD patterns of the LDH/CN composites

displayed the typical characteristic diffraction peaks of both components NiZnAl-LDH and g-C₃N₄, without evidences of additional peaks corresponding to different phases. Similar observations have been reported for LDH/CN composites prepared by different methods [25–28, 35]. A detailed analysis of the crystallinity parameters (position, FWHM, crystallites size) corresponding to the main reflection peak of the LDH shows a correlation with the amount of carbon nitride (Fig. 1f-h). As a general trend, the peak at -11° (003, LDH) became slightly broader and shifted towards higher 2θ values with the increase in the amount of CN in the composites (Fig. 1f-h). This indicates a subtle distortion of the structure of the LDH, confirming the incorporation of the CN particles in the interlayer spacing (although differences are minor). The increase in the amount of CN brought about an increase in the intensity of the diffraction peak at 27.46° corresponding to the (002) reflection of CN. The basal spacing distance of the (003) peak decreased gradually with the amount of CN (from 0.78 nm for LDH/CN-5 % up to 0.77 nm for LDH/CN-50 %), which confirms the incorporation of the carbon nitride in the interlayer space of the LDH.

The composition of the photocatalysts was further investigated by IR and Raman (Fig. 2). Both bare components (LDH and CN) showed the characteristic bands widely reported in the literature for both materials [25,28,35–37]. The spectrum of carbon nitride showed the characteristic bands at ca. 3200, 1640–1200 and 810 cm, ascribed to the vibrations of terminal uncondensed amino groups, C–N and C=N heterocycles, and triazine rings, respectively [36,37]. For LDH, a broad band centered at 3400 cm (vibrations of surface -OH groups), the intense peak at 1384 cm (vibrations of O–C–O groups), and the peaks at 617 and 432 cm (vibrations of metal-oxygen and metal-oxygen-metal bonds) were observed.

The LDH/CN composites showed the coexistence of the characteristic bands of LDH and CN, with a decrease in the intensities of the bands assigned to LDH (particularly 1384 and between 3000 and 2800 cm⁻¹) with the amount of CN. Similar observations have been reported for LDH/CN composites prepared by mixing both components [36,37] -compared to the coprecipitation method used in this study-, and have been interpreted as the evidence of specific interactions between both phases. Raman spectra of the photocatalysts are shown in Fig. 2B. For pristine LDH, the characteristic bands at 480 cm (Al–OH stretching), 600 cm (Co–O bonds) and 1050 cm (C–O stretching of carbonate ions)

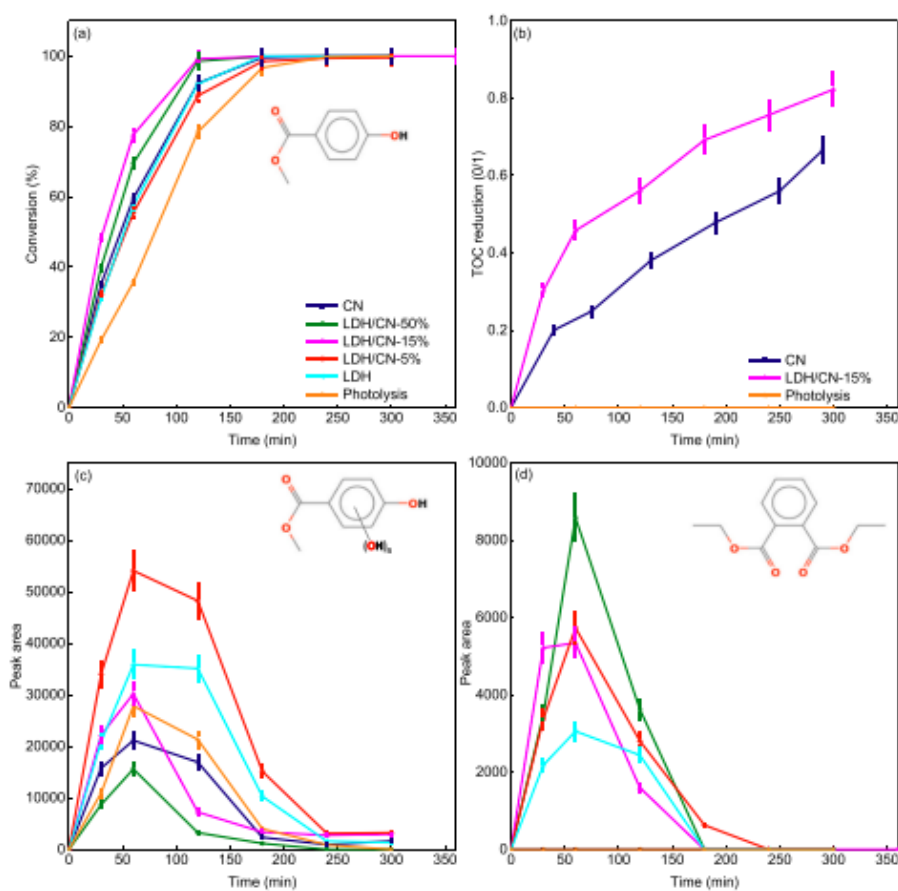


Fig. 5. (a) Conversion of methylparaben; (b) Total Organic carbon (TOC) reduction; (c,d) evolution of the degradation intermediates detected in solution for the studied photocatalysts. Average values and actual error bars of each measurement are presented (accuracy below 5 %).

were observed, in agreement with IR observations. Due to fluorescence interference (Fig. S1), the resolution of the Raman spectra of carbon nitride and all the LDH/CN composites was rather poor (for both 532 and 350 nm lasers), although several weak peaks were observed at 1642, 1558, 1465, 1258, 980, 753, 707, and 486 cm corresponding to vibration modes of CN heterocycles [38,39]. The peak at 1050 cm assigned to carbonate ions in the LDH was particularly pronounced in sample LDH/CN-15%. The similarities in the Raman spectra in the LDH/CN composites than in bare CN suggests that the confinement in the interlayer space of the LDH does not cause any significant modification in the structural skeleton of the carbon nitride. However, a distinct spectral feature was observed: a small blue shift in the peaks at 980, 753 and 707 cm in the composites, which could be attributed to phonon confinement effects in the interlayer of the LDH. Similar observations have been reported for exfoliated CN nanosheets [38,39].

The porosity of the LDH/CN composites was determined by gas adsorption and analyzed in terms of the composition and the expected trend considering the rule of the mixtures (Fig. 3). The main textural parameters evaluated from the gas adsorption isotherms are compiled in Table 1.

The pristine LDH displayed a type II nitrogen adsorption isotherm

characteristic of materials with low surface area (ca. 3 m²/g). It is well known that several factors (e.g., molar ratio of precursors, synthesis temperature and aging time) influence the porosity of LDH materials obtained from coprecipitation methods [25,28,40,41]. The low porosity of the pristine LDH compared to some of the studies in the literature [24, 27,35,41] is attributed to the shorter time and lower temperature of the aging step during the synthesis. On the other hand, the pristine carbon nitride also displayed a type II isotherm but showed a larger amount of gas adsorbed in the whole range of relative pressures. This effect was more pronounced above 0.8, indicating a marked mesoporous/macroporous character in this material.

The LDH/CN composites also displayed low surface areas and pore volumes, as expected based on the porosity of the pristine components. Note that the low porosity of all the samples discourages the calculation of average pore sizes and the analysis of pore size distributions to avoid the large error associated to those calculations. Clear correlations were observed between the textural parameters of the composites and the amount of carbon nitride (Fig. 3b, 3c). The experimental pore volumes (total pore volume and mesopore volume) of the LDH/CN samples were found to be lower than the expected theoretical values calculated considering the composition of the LDH/CN samples and the rule of the

Table 2
Rate constants (k_{app}) for the degradation of methylparaben degradation and the degradation intermediates at consecutive photocatalytic assays.

	assay 01	assay 02	assay 03	assay 04
Methylparaben				
LDH-NiZnAl	0.021	0.022	0.024	0.011
photolysis	0.007	0.009	0.011	0.013
LDH/CN-5 %	0.023	–	–	–
LDH/CN-15 %	0.044	0.037	0.034	0.026
LDH/CN-50 %	0.031	0.035	0.029	0.021
CN	0.022	0.027	0.027	0.023
Polyhydroxylated intermediates				
LDH-NiZnAl	0.018	0.021	0.020	0.017
photolysis	0.020	0.008	0.015	0.012
LDH/CN-5 %	0.016	–	–	–
LDH/CN-15 %	0.018	0.021	0.016	0.017
LDH/CN-50 %	0.017	0.021	0.018	0.017
CN	0.018	0.022	0.023	0.019
Diethyl phthalate intermediate				
LDH-NiZnAl	0.004	0.007	–	–
photolysis	n.d.	n.d.	n.d.	n.d.
LDH/CN-5 %	0.018	–	–	–
LDH/CN-15 %	0.020	0.022	0.005	0.005
LDH/CN-50 %	0.014	0.014	0.002	0.001
CN	n.d.	n.d.	n.d.	n.d.

n.d. not detected intermediate

mixtures (Fig. 3b). This demonstrates that the pores of the carbon nitride phase in the composites are not accessible to the nitrogen probe, and suggests that the carbon nitride is confined in the lamellar structure of the LDH (in agreement with the XRD data). Indeed, the porosity of composites prepared by a simple physical mixture of LDH and CN with similar composition followed the trend based on the rule of the mixtures.

The optical bandgap and the light harvesting properties of the obtained catalysts were evaluated from diffuse reflectance spectroscopy. Fig. 4 shows the absorption edge spectra and the Tauc graphical representation of the diffuse reflectance data of the prepared materials. The pristine LDH-NiZnAl showed three low-intensity broad absorption bands that can be ascribed to several transitions of the metals. The band in the 200–300 nm range is assigned to transitions between oxygen atoms and Ni(II) ions; the two bands in the visible range between 350 and 500 nm and 600–800 nm correspond to spin-allowed (380, 740 nm) and spin-forbidden (420, 640 nm) transitions of Ni(II) ions [42,43]. No electronic transitions involving Zn(II) ions are expected due to their d10 configuration. For pristine CN, the characteristic sharp absorption edge between 400 and 500 nm commonly reported for this material was observed [11–14], corresponding to a bandgap energy of 2.83 eV.

For the LDH/CN composites, the absorption profiles showed the distinct bands of both components, regardless of the composition: the absorption edge of CN around 430 nm and the band at 600–800 nm of the transitions of the LDH. The position of the absorption edge of CN in the LDH/CN composites showed a slight redshift, indicating an increased light absorption in the visible region owing to the confinement in the layered structure of the LDH. As a result, a slight decrease was observed in the optical band gap values of the composites with the amount of carbon nitride (Fig. 4c). Similar optical redshifts have been reported for LDH/CN heterostructures with different composition [42,43]. On the other hand, the absorption in the 600–800 nm region was enhanced in the composites with 5 and 15 wt% of CN, and negligible in the composite with 50 wt% of CN. This can be attributed to oxygen vacancies in the LDH phase, pointing out differences in the interfacial interactions between both phases upon the amount of carbon nitride.

3.2. Photocatalytic assays

As described in the experimental section, the photocatalytic assays were initiated after the equilibration of the materials with the solution of methylparaben in the dark for 30 min. All the catalysts showed similar

uptakes and adsorption kinetics of methylparaben from solution (Fig. S2), thus the initial concentration of methylparaben in solution when the illumination of the catalyst started was similar for all the studied materials. This is important given the rather high conversion of methylparaben in the photolytic reaction (see discussion below), to avoid misinterpretations of the degradation rates that would be related to differences in the initial concentration of the pollutant in solution rather than to the different photocatalytic activity of the materials [44].

Fig. 5 shows the conversion of methylparaben during the photocatalytic degradation using the composites prepared with 5, 15 and 50 wt%. Data corresponding to the photolytic degradation in solution (absence of a catalyst), and the corresponding control assays for carbon nitride and the LDH are also shown for comparison purposes. As seen, the conversion methylparaben is high in all the cases, reaching 100 % after 180 min of illumination for the composites and after 240 min for the photolytic reaction. This was expected due to the low initial concentration of the pollutant. Despite the high conversion, the mineralization of methylparaben is not complete, as inferred from the total organic carbon values of the solution (Fig. 5b) and the evolution of the concentration of intermediates. Indeed, the reduction in the total organic carbon of the solution after 2 h of photolysis represented only 0.4 %, due to a low conversion of the intermediates. Similar values were obtained for the control of the LDH, indicating the poor photocatalytic activity of the bare material.

On the contrary, the fall in the total organic carbon for the photocatalytic degradation using carbon nitride was 30 % after 2 h of irradiation, and ca. 47 % for the composite LDH/CN-15 % (the one showing the best performance). The HPLC analysis of the solutions revealed that the photocatalytic degradation of methylparaben rendered the formation of polyhydroxylated intermediates (e.g., di-hydroxymethylparaben, tri-hydroxymethylparaben, dihydroxybenzoic acid; m/z 167, 183, 199) for all the studied catalysts. The intermediates accumulated at short illumination times, and started to decrease after ca. 100 min of irradiation for the studied photocatalysts, confirming the complete degradation of the intermediates. A second degradation intermediate featuring at a higher elution times was assigned to diethyl phthalate (m/z 222). This intermediate was only observed for the LDH/carbon nitride composites (not been detected for the photolytic reaction or carbon nitride alone), and it disappeared after 200 min of illumination in all the assays. Similar degradation intermediates for methylparaben using advanced oxidation processes have been reported in the literature with different catalysts [45–47].

To compare the photocatalytic performance of the materials, the apparent rate constants (k_{app}) of methylparaben and its intermediates were calculated, assuming a first-order reaction-rate mechanism. The use of rate constant as metric indicators is a common practice (compared to turnover numbers in homogenous phase) in heterogeneous photocatalysis due to the difficulty to determine (and quantify) the active sites of a photocatalyst [48–51]. Fitted data corresponded to 99 % of methylparaben conversion; the rate constants for the degradation of the intermediate compounds were also calculated (Table 2).

Data shows that the rate constants of methylparaben degradation of the LDH/CN composites were higher than those of the photolytic reaction and the controls with LDH and carbon nitride alone, demonstrating the faster degradation of the pollutant. The trend was maintained over several consecutive photocatalytic cycles. The highest rate constants of the degradation of both methylparaben and its intermediates were obtained for sample LDH/CN-15 % (ca. twice the value of bare carbon nitride and 1.5 times that of LDH/CN-50 %), and decreased with the amount of carbon nitride in the composites (Fig. 6). As discussed above, the second intermediate was not detected for carbon nitride or for the photolytic reaction, thus rate constants were not calculated.

Fig. 7 shows the photocatalytic performance of the materials under consecutive illumination assays. The cyclic performance was evaluated by adding a small volume of methylparaben to the dispersions of the photocatalysts after each cycle, so as to increase the concentration of the

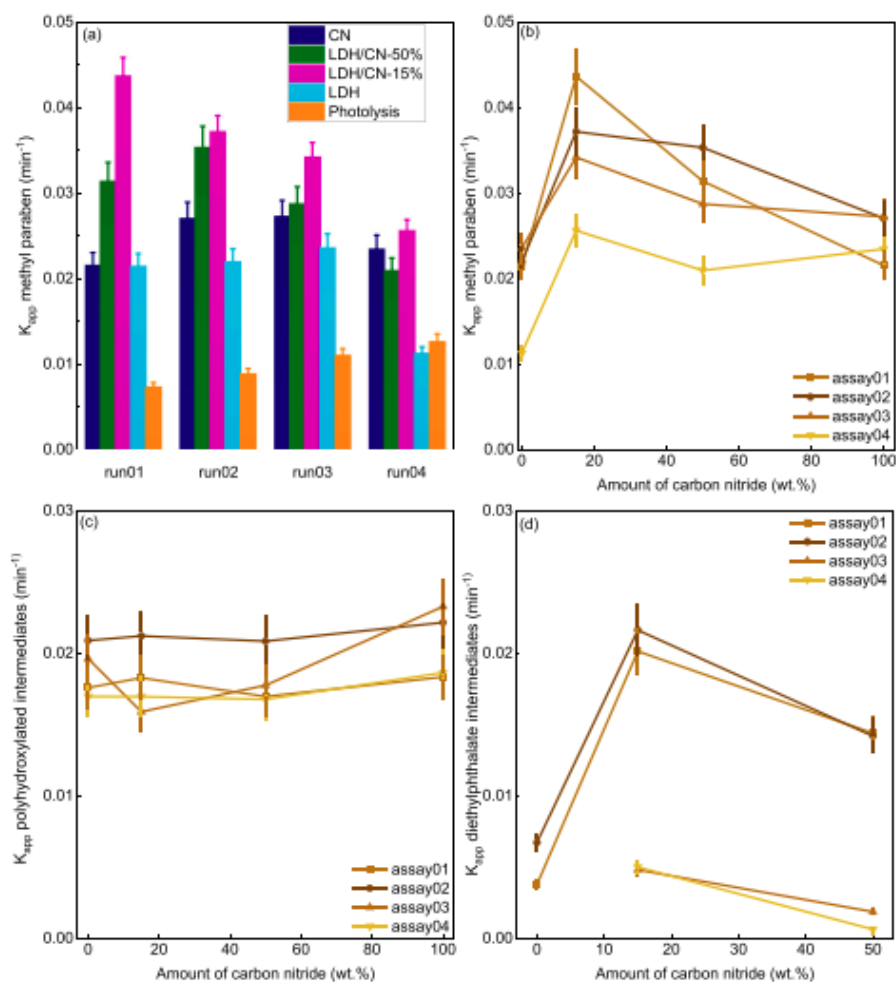


Fig. 6. (a) Apparent rate constants for the degradation of methylparaben for the investigated photocatalysts during the consecutive photocatalytic assays; (b,c,d) correlation between the apparent rate constants of degradation of methylparaben (b) and its detected intermediates (c,d) with the amount of carbon nitride in the composites. Average values and actual error bars of each measurement are presented (accuracy below 5 %).

pollutant up to 10 ppm (ca. the initial concentration used in the first cycle). It is important to note that by doing this, any un-degraded intermediate from the previous cycles remains in the dispersion. This allows finding out if there is an accumulation of intermediates during the consecutive photocatalytic assays.

The high conversion of methylparaben was well maintained during the consecutive cycles, with full conversion after 180 min in all the cycles. Differences are visible when analyzing the intermediates from the solution and the degradation rate constants. The rate constant of methylparaben degradation with the LDH/CN composites decreased slightly with the number of photocatalytic cycles (Fig. 7), although the values were still higher than those of the individual components and the photolytic reaction after the fourth cycle.

The amount of degradation intermediates was rather similar for the consecutive cycles (Fig. 8), with the exception for the photolytic reaction and the control with the LDH where an accumulation of the

intermediates is observed. This indicates that both methylparaben and its intermediates are degraded in the consecutive photocatalytic cycles, thus confirming that the activity of the materials is maintained. Interestingly, the apparent rate constant for the degradation of the polyhydroxylated intermediates remained rather constant over the cycles for all the samples (Fig. 7b), while the values for the degradation of the second intermediate (Fig. 7c) showed a decrease with the number of cycles and the amount of the carbon nitride in the composites.

To explore the degradation mechanism of methylparaben, the photocatalytic assays for the best performing composite (LDH/CN-15 %) and the bare components (LDH and CN) were carried out in the presence of scavengers of hydroxyl and superoxide radicals (Fig. 8).

The conversion of methylparaben was largely slowed down for sample LDH/CN-15 % in the presence of hydroxyl radical scavenger, indicating that the hydroxylation-mediated oxidation reaction is the predominant pathway in the degradation of this compound, and that the

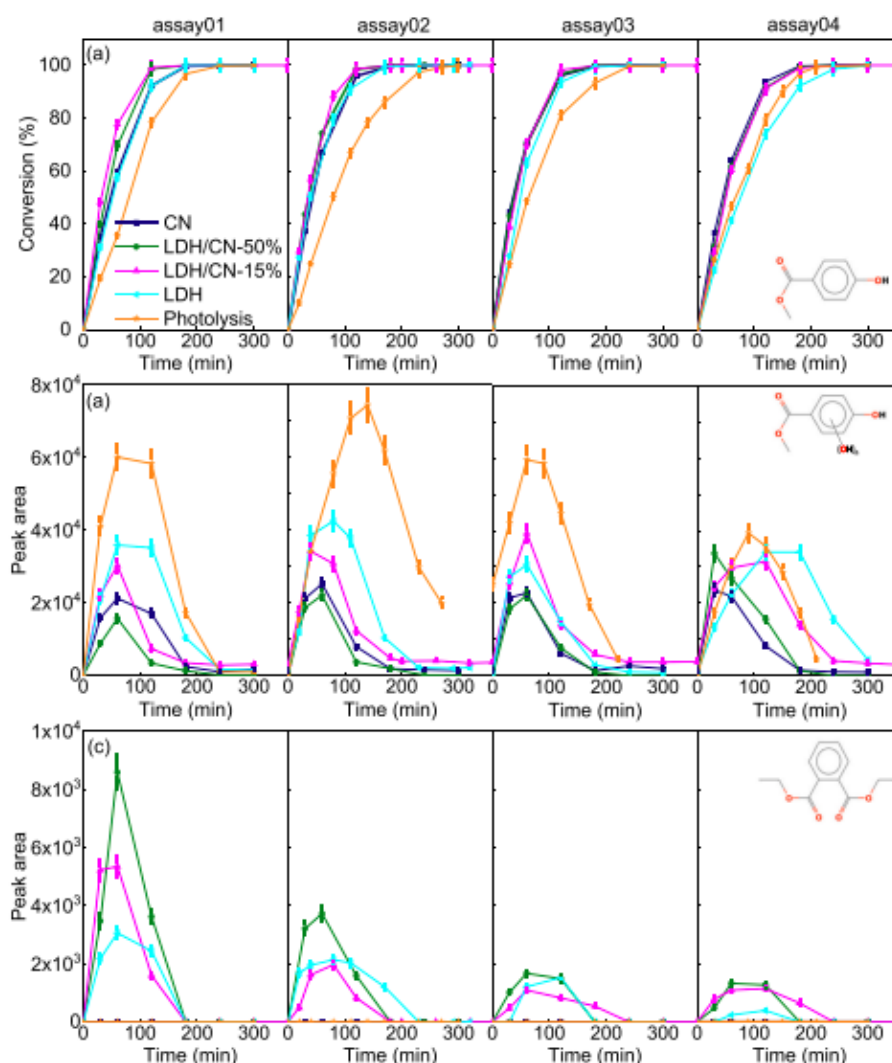


Fig. 7. (a) Conversion of methylparaben and (b,c) evolution of the degradation intermediates for the studied photocatalysts during several consecutive catalytic assays. Average values and actual error bars of each measurement are presented (accuracy below 5 %).

photogenerated holes are indispensable for the hydroxylation of methylparaben (see also the trends of the degradation apparent rate constants in the presence of the scavengers in Fig. S3). The use of a superoxide radical scavenger also decreased the conversion of methylparaben although to a smaller extent, indicating that the hydroxylation can also occur from the reaction of the photogenerated electrons with dissolved oxygen in solution, as frequently reported for TiO_2 [52]. The intermediates tended to accumulate for longer times when the photocatalytic assays are carried out in the presence of the scavengers, being the effect more pronounced for scavenging the hydroxyl radicals and for the polyhydroxylated intermediate. When carbon nitride or LDH were used alone as photocatalysts, a rather similar performance was obtained for the assays scavenging of hydroxyl and superoxide radicals. This

corroborates that water oxidation by the photoholes is a critical step for the degradation of methylparaben with sample LDH/CN-15 %, and that in the bare materials (carbon nitride and LDH) the activation of oxygen upon reaction with the photogenerated electron is also important.

Photoluminescence emission spectra of the photocatalysts in water were recorded to further probing the optical properties of the prepared photocatalysts (Fig. 9). Colloidal aqueous suspensions of the materials were used to record the photoluminescence emission spectra, with the same loading than the photocatalytic assays to assure similar environmental conditions -as this may affect surface reactions leading/quenching the radiative recombination of the photogenerated species-. As seen in Fig. 9, all the samples displayed a broad emission spectrum upon excitation at 300 nm spanning from 400 to 570 nm.

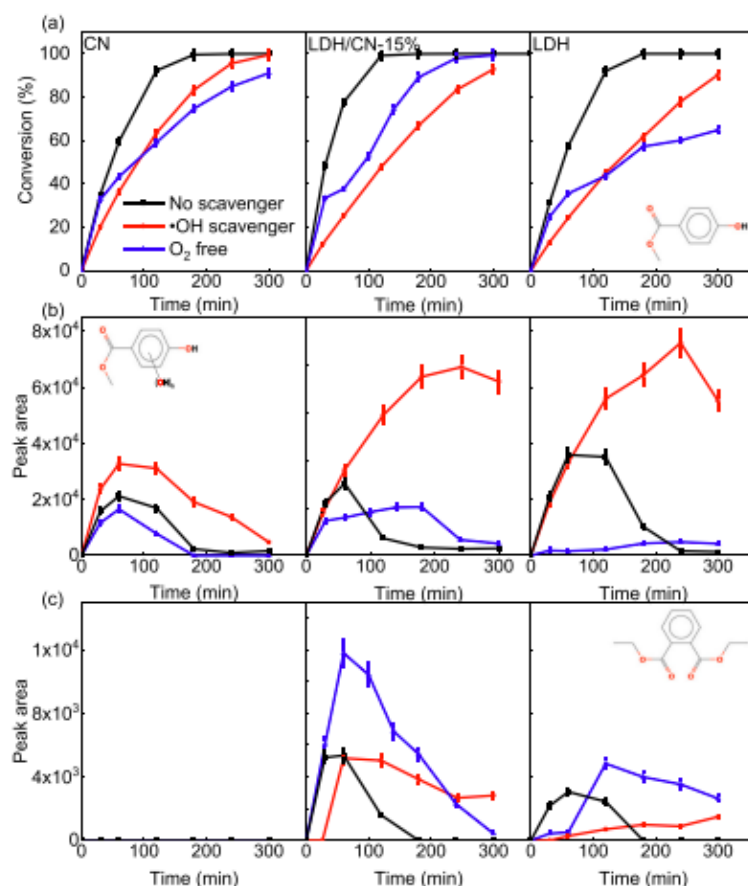


Fig. 8. Conversion of (a) methylparaben and (b,c) evolution of its degradation intermediates in the presence of hydroxyl radical scavenger and in oxygen-free conditions for samples LDH, CN and LDH/CN-15 %. Average values and actual error bars of each measurement are presented (accuracy below 5 %).

The emission band showed a maximum at ca. 440 nm (2.96 eV) and a shoulder at 455 nm (2.87 eV), with a similar shape for all the samples. Upon excitation at 375 nm, the profiles are rather similar, but the emission band is centered between 400 and 650 nm, with a maximum at 450 nm. According to the literature, the emission at 440 nm is associated with different transitions between lone pair state in the valence band and the π^* antibonding state in the conduction band (e.g., $\pi^*-\pi$, $\pi^*-\text{lone pair}$, $\sigma^*-\text{lone pair}$ state transitions) [53,54]. The photoluminescence emission of carbon nitride was substantially quenched in the LDH/carbon nitride composites, as inferred from the lower intensity of the signal, showing that the immobilization of the semiconductor in the layered structure of the hydrotalcite-like compound suppressed the radiative recombination of the electron-hole pairs.

This strongly suggests an effective separation of the photogenerated charge carriers in the composites, likely due to an adequate matching of the energy levels of both materials (e.g., midgap energy levels in LDH matching the defect states in carbon nitride responsible for the radiative emission). The decrease in the intensity of the photoluminescence emission was more noticeable for sample LDH/CN-15 %, which agrees with the better photocatalytic performance of this material and the strong impact of water oxidation by the photoholes as a critical step for

the degradation of methylparaben.

4. Conclusions

A series of hybrid photocatalysts have been synthesized by the coprecipitation of a NiZnAl hydrotalcite-like compound in the presence of increasing amounts of carbon nitride powders, and used for the degradation of methylparaben in aqueous solution. The incorporation of CN particles inside the interlayer spacing of the LDH through our synthetic approach was confirmed by XRD by the gradual decrease in the basal spacing distance with the CN content. The blue shift in the Raman spectra of the peaks assigned to the semiconductor in the LDH/CN composites also confirmed the confinement of former. Our data has shown that the photocatalytic activity the hybrid LDH/carbon nitride materials increased compared to that of pristine CN, owing to its immobilization in the layered structure of the LDH. The synthesized hybrid photocatalysts showed faster degradation rates for both methylparaben (the main pollutant) and its degradation intermediates, and displayed better photocatalytic performance upon consecutive assays (after 20 h of consecutive illumination), than bare carbon nitride and the NiZnAl hydrotalcite-like compound alone. The improved

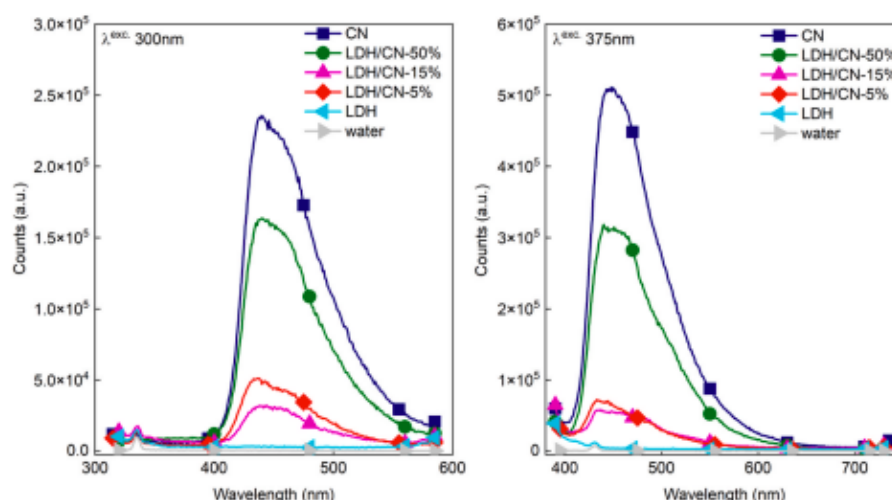


Fig. 9. Photoluminescence emission spectra of aqueous suspensions of the synthesized photocatalysts (loading is similar to that used in the photocatalytic assays) upon excitation at 300 nm and 375 nm. Average values of duplicate measurements are presented (accuracy below 5 %).

photocatalytic performance confirmed that our synthetic route allowed a good interfacial contact between the carbon nitride confined in the lamellar structure of the hydrotalcite-like compound. The reduced recombination via radiative emission in the synthesized LDH/CN composites points out to an adequate matching of the energy levels of both materials owing to the confinement of the semiconductor. This enables a more efficient exploitation of the photogenerated charge carriers (hence increased photocatalytic performance). Furthermore, the photocatalytic assays carried out in the presence of selective scavengers of hydroxyl radicals, and in an oxygen-free environment to prevent the formation of superoxide radicals demonstrated that the degradation mechanism of methylparaben is modified upon the confinement of carbon nitride. The degradation pathway of methylparaben proceeds mainly through a hydroxylation-mediated reaction with radical species generated by the photoholes and the photoelectrons; in the LDH/CN composites, the reactivity of the photoholes is accelerated and becomes predominant over the pathway involving the photoelectrons.

CRediT authorship contribution statement

Conchi Ania: Writing – review & editing, Writing – original draft, Funding acquisition, Formal analysis, Data curation, Conceptualization. **German P. Benedictto:** Writing – review & editing, Investigation. **Tingwei Sun:** Writing – review & editing, Writing – original draft, Investigation. **María S. Legnoverde:** Writing – review & editing, Investigation. **Maximiliano R. Gonzalez:** Writing – review & editing, Investigation. **Elena I. Basaldella:** Writing – review & editing, Funding acquisition, Conceptualization. **Encarnacion Raymundo-Piñero:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2025.115432

Data availability

Data will be made available on request.

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Annex III. Communications in conferences

Oral presentations:

T. Sun (presenter), Encarnacion Raymundo-Piñero, Conchi O. Ania, The role of carbon materials as scavengers of photogenerated reactive species upon irradiation of semiconductor/carbon photocatalysts. Carbon 2025, Saint-Malo, 29 June – 4 July 2025.

T. Sun (presenter), Encarnacion Raymundo-Piñero, Conchi O. Ania, Investigating the photocatalytic mechanism of C₃N₄/carbon heterojunctions for the degradation of aqueous pollutants. Journées des Doctorants (JDD) 2024, Orleans, 06 June 2024.

T. Sun (presenter), Encarnacion Raymundo-Piñero, Conchi O. Ania, Insights on the photocatalytic activity of carbon-semiconductor heterojunctions. SFEC-2024 (Société francophone d'études du carbone), Saint-Die-des-Vosges, 13-16 May 2024.

T. Sun (presenter), Encarnacion Raymundo-Piñero, Conchi O. Ania, Carbon-semiconductor photocatalysts for the degradation of emerging water pollutants. Journées des Doctorants (JDD) 2023, Orleans, 21 September 2023.

T. Sun (presenter), Raymundo-Pinero E, Ania CO, Photocatalytic activity of carbon/carbon heterojunctions for the degradation of emerging pollutants, C'NANO 2023, Poitiers, 15-17 March 2023.

Imgharn A, **T. Sun**, Albourine A, Ania CO (presenter), Carbon nitride/semiconductor heterojunctions for the photocatalytic degradation of parabens from solution, International Material Conference, Lille, 24-28 October. 2022.

Posters:

T. Sun (presenter), Encarnacion Raymundo-Piñero, Conchi O. Ania, Carbon-semiconductor heterojunctions as charge carriers stabilizers in photocatalytic systems. Journées de la section régionale Centre-Ouest in Orleans 2023, June 15-16 2023

T. Sun (presenter), Raymundo-Pinero E, Ania CO, Optimization of semiconductor/carbon materials heterojunctions for heterogeneous photocatalysis: application to the degradation of emerging pollutants, International Material Conference, Lille, 24-28 October 2022.

T. Sun, Raymundo-Pinero E, Ania CO (presenter), Exploring the photocatalytic activity of solid-state carbon/carbon heterojunctions, International Carbon

Annex III. Communications in conference

Conference, London, 3-8 July 2022.

T. Sun (presenter), Imgharn A, Albourine A, Ania CO, Evaluating the optical and electronic energy band gaps of semiconductor/carbon composites, SFEC-2022 (Société francophone d'études du carbone), Orléans, 4-8 Avril 2022.

Étude de la dégradation photocatalytique de methylparaben avec catalyseurs semi-conducteur/matériaux carboné

Résumé :

L'application de procédés d'oxydation avancés est une technologie prometteuse pour améliorer l'assainissement des eaux usées en raison de l'apparition de polluants émergents récalcitrants qui ne sont pas complètement éliminés par les traitements conventionnels. La photocatalyse hétérogène à base de semi-conducteurs a été beaucoup étudiée pour le traitement de l'eau (TiO_2 est le photocatalyseur de référence). Même si des avancées notables ont été réalisées dans les dernières années, son utilisation dans les stations d'eaux usées présente encore de nombreux verrous liés notamment à la séparation et à l'aggrégation des catalyseurs, le génie des photo-réacteurs, le contrôle des propriétés optiques et l'augmentation du rendement de photoconversion des matériaux photocatalytiques dans le spectre visible. Différentes stratégies sont étudiées à ce jour afin de surmonter les principales limitations des semi-conducteurs utilisés comme matériaux photocatalytiques. Parmi elles, la formation d'hétérojonctions entre divers semi-conducteurs et le couplage avec des nanomatériaux carbonés représente une approche d'intérêt. Dans ce travail, nous traiterons l'optimisation de hétérojonctions semi-conducteur/matériaux carbonés à partir des différentes voies de synthèse (hydrothermal et méthode de co-précipitation) afin d'améliorer les propriétés optiques des photocatalyseurs résultants, ainsi que l'efficacité de séparation de charge des paires électron-trou photogénérées sous illumination visible. Une série d'hétérojonctions binaires a été préparée en mélangeant des semi-conducteurs BWO et hydrotalcite double en couches, avec des matériaux carbonés avec des nanostructures 2D et 3D ($\text{g-C}_3\text{N}_4$ et charbons actifs). Les photocatalyseurs seront utilisés pour la dégradation des micropolluants de l'eau, notamment des parabènes méthyliques, sous diverses conditions d'illumination.

Mots clés : parabène méthylique, photocatalyse, carbone nanoporeux, lumière UV-visible, semi-conducteur, mécanisme

Photocatalytic Degradation of Methylparaben using semiconductor/carbon catalysts

Summary :

The application of advanced oxidation processes is a promising technology for improving wastewater treatment due to the appearance of recalcitrant emerging pollutants that are not completely eliminated by conventional treatments. Heterogeneous semiconductor-based photocatalysis has been extensively studied for water treatment (TiO_2 is the reference photocatalyst). Although significant progress has been made in recent years, its use in wastewater treatment plants still presents a number of challenges, particularly in terms of catalyst separation and aggregation, photoreactor engineering, control of optical properties and increasing the photoconversion efficiency of photocatalytic materials in the visible spectrum. Various strategies are currently being studied to overcome the main limitations of semiconductors used as photocatalytic materials. Among them, the formation of heterojunctions between various semiconductors and coupling with carbonaceous nanomaterials represents an approach of interest. In this work, we will address the optimisation of semiconductor/carbon nanomaterial heterojunctions from different synthesis routes (hydrothermal and co-precipitation method) in order to improve the optical properties of the resulting photocatalysts, as well as the charge separation efficiency of the electron-hole pairs photogenerated under visible illumination. A series of binary heterojunctions were prepared by mixing semiconductors BWO and layered double hydrotalcite with carbonaceous materials with 2D and 3D nanostructures (e.g. $\text{g-C}_3\text{N}_4$ and activated carbons). Photocatalysts will be used for the degradation of water micropollutants, in particular methyl paraben, under various illumination conditions.

Keywords : methyl paraben, photocatalysis, nanoporous carbons, UV-visible light, semiconductor, mechanism



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