Functionalization of graphitic carbon nitride/ZnO heterojunctions with zinc cyanamide groups: A powerful approach for photocatalytic degradation of anticancer drugs

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#### Abstract

Graphitic carbon nitride/zinc oxide composites (CN/ZnO) were innovatively synthesized via a one-pot thermal treatment of a mixture of melamine and different zinc salts (zinc acetate, zinc nitrate, zinc sulfate, and zinc chloride) as the precursor of CN and ZnO, respectively. Composites derived from acetate, nitrate or sulfate showcased hexagonal ZnO wurtzite phase, while those prepared with zinc chloride revealed a unique secondary phase identified as tetragonal zinc cyanamide (ZnNCN). This novel phase formation was fine-tuned by optimizing synthesis conditions, including temperature ranging from 450 to 650 °C and metal salt loading between 25 and 75 wt.%. Photocatalytic testing for the degradation of cyclophosphamide (CP) and 5-fluorouracil (5-FU) under near UV-Vis irradiation, highlighted the standout performance of the composite synthesized with 75 wt.% zinc chloride at 550 °C, labelled C-75-550. This composite delivered superior activity, attributed to enhanced pollutant adsorption and the suppression of electron-hole recombination due to the synergistic interplay of CN, ZnO, and ZnNCN. Furthermore, C-75-550 exhibited remarkable stability across multiple cycles, bolstered by Zn–N bond stabilization. Advanced analysis using UHPLC-MS, coupled with reactive species scavenger studies, allow to propose several pathways for the photodegradation of 5-FU, underscoring the composite transformative potential in environmental remediation.

Keywords: Graphitic carbon nitride; Zinc oxide; Zinc cyanamide; Photocatalysis; Water treatment.

# 1. Introduction

Medicines are one of the major groups of emerging pollutants, increasing in both number and concentration. Thus, more drugs become available for treating a wider range of diseases and progressively reach more sectors of society. However, their presence in water reservoirs poses potential hazards to human health and ecosystems [1, 2]. Cytostatic drugs are used in cancer therapy to inhibit the growth and division of tumor cells [3]. Recent studies have detected several cytostatic drugs in hospital wastewater (HWW), wastewater treatment plant (WWTP) influents and effluents, and even in surface water, such as rivers and lakes across countries in Europe, America and Asia. These drugs have been found in concentrations of up to hundreds of ng  $L^{-1}$ , because they are discharged directly into the sewage system and are not efficiently removed by conventional WWTP treatments [4-6]. Exposure to cytostatic drugs can cause acute and chronic toxicological effects, including carcinogenic, cytotoxic, mutagenic, teratogenic, embryotoxic and genotoxic effects in humans and wildlife. Therefore, their removal from surface waters, groundwater and the environment are essential. Both 5-fluorouracil (5-FU) and cyclophosphamide (CP) have been used as chemotherapy drugs since the 1950s and are classified as antimetabolite and alkylating agent, respectively, according to World Health Organization (WHO) [7, 8]. 5-FU is a pyrimidine-based molecule commonly used to treat, among others, colorectal and pancreatic cancers; it exhibits a low biodegradability and adsorption into active sludge [3, 9]. As note, 5-FU is one of the most prescribed cytostatic drugs in Europe [10] and detected in HWWs worldwide [11-13]. On the other hand, CP exhibits a chemical structure analogous to mustard gas and is widely employed for the treatment of leukemia and non-Hodgkin's lymphoma [3, 11]. Recent studies demonstrated the occurrence of CP in rivers from Europe and Asia at concentrations from 0.2 to 500 ng  $L^{-1}$  [14-17]. which possesses significant threat to aquatic environment and human health due to its established ecotoxicity and mutagenic effects [8, 18].

Over the past decades, advanced oxidation processes (AOPs) have proven to be effective in removing cytostatic drugs from water transforming them into more biodegradable organic compounds [19, 20]. In particular, heterogeneous photocatalysis has gained significant attention for their effectiveness in degrading a wide range of pharmaceutical compounds even from real HWW and utilizing sustainable

energy sources like sunlight and non-toxic catalysts [21, 22]. To date, zinc oxide (ZnO) is one of the most studied photocatalysts, together with TiO<sub>2</sub>, for environmental applications. Both materials share similar band gaps (approximately 3.2 eV) and exhibit properties such as strong oxidation ability, photostability, non-toxicity, and biodegradability [23, 24]. The response of ZnO under visible irradiation can be improved by forming composites with other semiconductors, as well as inhibiting the rapid recombination of the photogenerated electron-hole pairs [24, 25]. The photo-response of ZnO in the solar range is higher than TiO<sub>2</sub>, which may be attributed to its greater quantum efficiency. However, like other metal oxides, it has some drawbacks such as the rapid recombination of the photogenerated by forming composites with other semiconductors [24-28].

The excellent properties of carbon materials render them suitable for their use in heterogeneous photocatalysis, either as catalysts or as effective catalyst supports. These materials offer a substantial number of active sites for the adsorption of pollutants. Furthermore, the photogenerated electrons produced during the photocatalytic reaction can be stored and delocalized into the carbon structure, thereby generating more oxidizing radicals which contribute to the degradation process [29-31].

Graphitic carbon nitride (CN) is an n-type semiconductor known for its efficient visible light absorption and excellent photocatalytic properties. It features a narrow band gap (approximately 2.7 eV), nontoxicity and strong corrosion resistance [32, 33]. The structure of CN shares similarities with graphene, as both are two-dimensional (2D) materials with a structure of hybridized conjugated carbon atoms. Additionally, the presence of nitrogen atoms within the carbon structure provides electron donor sites, enhancing charge mobility [34]. Several effective methods have been developed to enhance photon conversion efficiency and improve photogenerated charge separation, addressing the main practical limitations of CN. These methods include the optimization of synthesis parameters (e.g., precursor, temperature, time, atmosphere, etc.) [35-37], mechanical, thermal or chemical exfoliation , heteroatom doping [38, 39], structural defects [40] and heterojunction formation [41], among others. The ideal polymeric structure of CN consists of a two-dimensional (2-D) material formed by triazine or heptazine rings linked and terminated only by amino groups [36, 42]. The functionalization of CN by generating defects, oxygenated or nitrogenated groups such as amino, cyano, and cyanamide, as well as aromatic ring motifs, has been studied [43], leading to enhance both catalytic performance and electronic properties. Cyano-functionalized groups ( $-C\equiv N$ ) are incorporated into the network by breaking the C–N bonds, and consequently, forming N–vacancies, while cyanamide groups ( $-N-C\equiv N$ ) are formed by incomplete cyclization and/or thermal depolymerization of heptazine aromatic rings [44, 45]. Additionally, cyanamide defects offer better coordination sites for cationic species compared to amino groups, further improving the photocatalytic performance of the material [40, 44, 45].

The formation of heterojunctions between semiconductors during thermal treatment is of particular interest due to the development of a synergistic effect between phases. The introduction of functional groups such as cyanamides, associated with the 2-D network of CN and bonded with the metals (i.e., Zn) seems to favor the catalytic activity of the composites in various photocatalytic applications including nitrogen fixation, supercapacitors, water splitting, NO removal, CO<sub>2</sub> reduction and H<sub>2</sub>O<sub>2</sub> production [46-50]. To the best of our knowledge, several references concerning the formation of this functionalization (ZnNCN) have been reported in the literature. For instance, Zhang et al. [51] developed a synthesis method from melamine and zinc metal using a thermal method at 900 °C for 2 h under Ar atmosphere, resulting in N-rich organics into graphene coordinated with zinc cyanamide (ZnNCN) groups. The prepared materials demonstrated high catalytic activity for peroxymonosulphate activation. Gunawan et al. [46] reported Ni-photodeposition on cyanamide functionalized carbon nitride for the photoproduction of acetaldehyde and  $H_2$ . In this method, defects are introduced into CN by thermal treatment with KSCN. Kaye et al. [52] described the synthesis of ZnNCN thin films using chemical vapour deposition (CVD) at 450 °C, where the introduction of precursors (i.e., urea and zinc acetate) into the reaction chamber was supplied in aerosol form rather than vapour form. Similarly, a spray pyrolysis method was described for preparing ZnS thin film with traces of ZnNCN, where the precursors are sprayed onto a substrate composed of commercial glass and n-type Si (100) at temperatures between 200-600 °C [53]. Chen et al. [47] developed a synthesis method to add cyano/cyanamide groups to CN edges using monodisperse SiO<sub>2</sub> as templates. The functionalized CN exhibited approximately 70%

higher photoactivity than bare CN in the photocatalytic degradation of Bisphenol A under near UV-Vis irradiation. Fu et al. [48] observed the formation of ZnNCN groups during the synthesis of accordionlike active carbons (AC) by chemical activation, using lignin as the organic precursor and KOH and ZnCl<sub>2</sub> as activating agents. The AC-based materials demonstrated high performance as supercapacitor. Other authors have studied various methods of thermal polymerization from melamine or its derivatives for the photocatalytic production of H<sub>2</sub>O<sub>2</sub> and aldehydes from the oxidation of benzyl alcohol or as a catalyst for Minisci reaction [54, 55]. Zhou et al. [49] developed a photocatalytic system for microbial nitrate photoreduction, using cyano/cyanamide functionalized CN as photocatalyst, and solar irradiation as energy source. A method for preparing ZnNCN at high temperatures from the metal-organic framework (MOF) [ZnF(AmTAZ)] has been also reported [56]. When thermal treatment is conducted under an inert atmosphere, ZnNCN is formed. Conversely, if the treatment occurs in air atmosphere, zinc oxide (ZnO) is produced instead. Xie et al. [50] prepared a ternary photocatalyst consisting of CN/ZnNCN/ZIF-8 for CO<sub>2</sub> photoreduction, where ZnNCN was formed by *in-situ* growth on the surface of CN through solid-solid synthesis using zinc acetate as the precursor.

In the present work, we introduce an innovative, cost-effective and straightforward strategy to engineer cutting-edge CN/ZnO/ZnNCN photocatalysts. This approach uses melamine as the CN precursor and various zinc-containing salts—including zinc acetate, zinc nitrate, zinc sulfate, and zinc chloride—as precursors for both ZnO and ZnNCN phases. By varying the molar ratio of CN to zinc salts and fine-tuning the synthesis temperature, the method enabled precise control over the proportions of ZnO and ZnNCN phases in the resulting composites. The photocatalytic potential of these materials was tested for the degradation of pharmaceutical contaminants, 5-FU and CP under near UV-Vis irradiation. Comprehensive characterization of physicochemical properties, including textural, optical and crystallographic characteristics provided a deep understanding of their functionality. Furthermore, the investigation into reactive species using scavenger agents revealed mechanistic insights, while reusability tests confirmed the stability and robustness of these novel photocatalysts, marking a significant step towards practical and sustainable applications in environmental remediation.

## 2. Experimental

## 2.1. Synthesis of carbon nitride-based composites

CN—ZnO composites were synthetized by a one-step thermal polymerization process using a mixture of melamine (C<sub>3</sub>H<sub>2</sub>N<sub>6</sub>, 99%, Acros Organics) and different zinc-containing salts, namely zinc nitrate tetrahydrate (Zn(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O, 98.5 %, Merck), zinc acetate dihydrate (Zn(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> · 2H<sub>2</sub>O, 99%, VWR Chemicals), zinc sulfate heptahydrate (ZnSO<sub>4</sub> · 7H<sub>2</sub>O, 99%, Probus) and zinc chloride (ZnCl<sub>2</sub>, 98+%, Alfa Aesar) in a 25:75 mass ratio as precursors of CN and ZnO, respectively. For the synthesis, a mechanical mixture of precursors was placed in a semi-closed alumina crucible and treated at 450 °C for 2 h, followed by 550 °C for 4 h at a heating rate of 2 °C min<sup>-1</sup> inside a muffle furnace (Nabertherm mod. L9/11/B510) under static air atmosphere. To enhance charge separation efficiency and porosity, a thermal post-treatment was performed in a semi-open crucible at 500 °C for 2 h under the same conditions [57]. The obtained catalysts were washed with distilled water to remove impurities and then dried at room temperature. A schematic representation of the synthesis procedure was added in the supporting information (Fig. S1).

Sample	Zn precursor	Melamine:Zn salt ratio	Temperature (°C)
A-75-550	Zinc acetate (A)	25:75	550
C-75-550	Zinc chloride (C)	25:75	550
N-75-550	Zinc nitrate (N)	25:75	550
S-75-550	Zinc sulfate (S)	25:75	550
C-50-550	Zinc chloride (C)	50:50	550
C-25-550	Zinc chloride (C)	75:25	550
C-75-450	Zinc chloride (C)	25:75	450
C-75-650	Zinc chloride (C)	25:75	650

Table 1. Nomenclature and synthesis conditions of prepared carbon nitride-based composites.

This salt screening allowed to select  $ZnCl_2$  as the zinc precursor to optimize the organic/inorganic precursor ratio (melamine:Zn salt with mass ratio of 75:25, 50:50 and 25:75) and the synthesis

temperature (450, 550 and 650 °C). The prepared materials were labelled according to the zinc salt used, precursor ratio and synthesis temperature as shown in Table 1. Reference samples of pristine ZnO and bare g-C<sub>3</sub>N<sub>4</sub> (CN) were also synthetized following the same procedure but without adding melamine and a zinc precursor, respectively.

### 2.2. Characterization techniques

Textural characterization was performed using the N<sub>2</sub> adsorption-desoprtion isotherms obtained at -196 °C using a Quadrasorb SI equipment from Quantachrome. All samples were outgassed for 8 h at 120 °C prior to the analysis. Brunauer-Emmet-Teller (BET) equation was applied to adsorption isotherms to determinate the apparent surface area (S<sub>BET</sub>) [58, 59]. Barret-Joyner-Halenda (BJH) method was applied to the desorption branch to calculate the total pore volume ( $V_{total}$ ) and mesopore volume (V<sub>meso</sub>) [60]. Crystalline phases were determined by powder X-ray diffraction (XRD) using a Philips PW 1710 diffractometer with CuK $\alpha$  radiation and a Ni filter to remove the  $\kappa\beta$  radiation. The average crystallite sizes were estimated using the Scherrer equation for the highest diffraction peaks corresponding to the (101) lattice plane of the ZnO hexagonal wurtzite phase (JCPDS 36-1451) and the (220) lattice plane of the zinc cyanamide phase (JCPDS 70-4898). The crystalline phase percentage of ZnNCN ( $\eta_{ZnNCN}$ ) was determined by normalizing the intensities of the most prominent diffraction peak  $(I_{100})$  for each phase, ensuring an accurate comparison of their relative contributions. Scanning electron microscopy (SEM) was used to determine the morphology of materials, employing a GEMINI-1430VP microscope from LEO (Carl Zeiss). Thermogravimetric analysis (TGA) of the prepared materials was conducted by heating up to 950 °C at a rate of 20 °C min<sup>-1</sup> under air flow, using a SHIMADZU TGA-50H thermobalance. The chemical properties of composites were studied by infrared spectroscopy (ATR-IR) using a ThermoFisher NICOLET 510P spectrometer equipped with an attenuated total reflection accessory and a ZeSn as ATR crystal. The surface chemistry was evaluated by X-ray photoelectron spectroscopy (XPS). The spectra were obtained on a Physical Electronics VersaProbe II equipment with a hemispherical electron analyzer and a MgK $\alpha$  X-ray source (hv = 1486.6 eV) operating at 1.3 eV and 20 mA. Survey and multi-region spectra were measured for C1s, N1s, O1s and Zn2p photoelectron peaks. The point of zero charge (pH<sub>PZC</sub>) was analyzed following the methodology

described in the literature [57, 61]. The optical properties of materials were evaluated using a VARIAN CARY 5E UV-Vis spectrophotometer equipped with a diffuse reflectance accessory (DRA). The band gap ( $E_g$ ) was determined from the corresponding Tauc's plots using Kubelka-Munk units ( $K \cdot M \cdot E$ )<sup>1/2</sup> as a function of energy (eV) [62].

### 2.3. Photocatalytic experiments

The photocatalytic performance of the synthetized catalysts was evaluated for the degradation of 5-FU (C<sub>4</sub>H<sub>3</sub>FN<sub>2</sub>O<sub>2</sub>, >99%, Tokyo Chemical Industry) and CP (C<sub>7</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>P, >98%, Tokyo Chemical Industry) in aqueous solutions under near UV-Vis irradiation. The reactions were conducted using a medium-pressure mercury lamp (125 W, mod. 3010/PX0686) from Photochemical Reactors LTD., which was located axially in a glass water-cooling jacket to achieve irradiation in the near UV-Vis range  $(\lambda > 350 \text{ nm})$  and to maintain the temperature stable. Photocatalytic experiments were carried out in a glass immersion photochemical reactor (with a diameter and length of 4.4 and 13.7 cm, respectively), charged with 100 mL of a 5-FU solution (76.9  $\mu$ mol L<sup>-1</sup>) and CP (38.3  $\mu$ mol L<sup>-1</sup>) and with a photocatalyst load of 1 g  $L^{-1}$ . The distance between the irradiation source and solution was approximately 1 cm. The suspension was purged with an O<sub>2</sub> flow and magnetically stirred. In order to saturate the surface of catalysts, the suspension was kept in the dark for 30 min before starting the photocatalytic reaction. A control reaction without any photocatalysts, referred to as photolysis, was performed under the same conditions. Moreover, adsorption kinetics were determined by placing the suspension in a thermostatic shaking bath at 25 °C. However, concentration changes occurred only during the first few minutes, as equilibrium was reached quickly due to the low porosity (Table 2) and 2D structure (without internal pores) of CN. Based on these observations, 30 min in the dark were selected to standardize the reaction protocol.

Samples taken from the reaction mixture were analyzed by ultra-high performance liquid chromatography (UHPLC) using a Shimadzu Corporation equipment (Nexera model), equipped with a diode array detector (SPD-M20A). Chromatographic separation was performed using a Shim-pack GISS-HP C18, 3 µm column (100 x 3.0 mm ID) from Shimadzu Corporation. The temperature of the

autosampler and the column oven was set at 15 and 30 °C, respectively. The mobile phase consisted of a mixture of water/methanol (97:3 v/v) in isocratic mode with a flow rate of 0.2 mL min<sup>-1</sup>.

The reaction kinetics were described using a pseudo-first order model according to the equation (1):

$$[C] = [C]_0 \times e^{-k_{app} \times t} \tag{1}$$

where [C] and [C]<sub>0</sub> denote the pollutant concentration at t = 0 and t = t, respectively,  $k_{app}$  is the apparent first order kinetic constant, t is the reaction time. The values of  $k_{app}$  were obtained by non-linear regression.

The possible reactive oxygen species (ROS) involved in the photodegradation process were evaluated with the addition of different scavengers, such as MeOH, NaN<sub>3</sub> and ethylenediaminetetraacetic acid (EDTA) for radical species, non-radical species (as singlet oxygen,  ${}^{1}O_{2}$ ) and holes, respectively. Transformation products (TPs) were identified by an ultra-high performance liquid chromatography coupled with mass spectroscopy (UPLC-MS), Acquity H class model from Waters, equipped with an electrospray ionization mass (ESI), a Positive Water Xevo TQ detector and a column of Acquity UPLCr HSS T3 (1.8  $\mu$ m,100 mm x 2.1 mm). The mobile phase consisted in acidic H<sub>2</sub>O (0.1% formic acid) and methanol (97:3  $\nu/\nu$ ) at isocratic mode, the flow rate was 0.2 mL min<sup>-1</sup> and the injection volume was 10  $\mu$ L.

#### 3. Results and discussion

#### 3.1. Photocatalyst characterization

Physisorption of  $N_2$  at –196 °C was performed to evaluate the textural properties of the synthetized photocatalysts. The N<sub>2</sub>-adsorption isotherms (Fig. S1, Supplementary Material) classified as type-II according to the IUPAC classification indicated that the prepared composites exhibited null microporosity, while mesoporosity was formed mainly as interparticle spaces [63, 64]. Thus, N<sub>2</sub> adsorption was negligible at low relative pressures (P/P<sub>0</sub>), capillary condensation occurring at high P/P<sub>0</sub>

as displayed by the hysteresis loop (type-H3), typical of slit-shaped pores or aggregates formed by platelike particles [57, 65].

Sample	$\frac{S_{BET}}{(m^2 g^{-1})}$	$\begin{array}{c} V_{total} \\ (cm^3 \ g^{-1}) \end{array}$	d (ZnO) (nm)	d (ZnNCN) (nm)	η <sub>ZnNCN</sub> (%)	pH <sub>PZC</sub>	Eg (eV)
A-75-550	14	0.15	23.9	-	-	7.6	3.10
N-75-550	21	0.26	26.3	-	-	7.2	3.10
S-75-550	14	0.17	13.4	-	-	6.9	3.10
C-75-550	48	0.27	24.6	29.5	85.0	6.5	3.18
C-50-550	22	0.05	26.7	31.7	77.6	6.5	3.10
C-25-550	11	0.12	28.4	34.5	70.0	6.4	2.83
C-75-450	50	0.12	-	-	-	6.4	2.95
C-75-650	10	0.08	22.6	30.0	52.6	6.8	3.08
CN	18	0.07	-	-	-	6.3	2.68
ZnO	< 5	-	32.3	-	-	7.5	3.20

**Table 2.** Textural characteristics, crystallite sizes, point of zero charge ( $pH_{PZC}$ ) and band gap energy ( $E_g$ ) of the prepared photocatalysts.

 $S_{BET}$  = BET surface area;  $V_{total}$  = total pore volume; d(ZnO) and d(ZnNCN) = average crystallite size of ZnO and zinc cyanamide, respectively;  $\eta_{ZnNCN}$  = percentage of tetragonal ZnNCN phase;  $pH_{PZC}$  = point zero of charge;  $E_g$  = band gap energy.

In general, carbon nitride-based composites exhibited low apparent surface areas ( $S_{BET}$ ) of around 10-50 m<sup>2</sup> g<sup>-1</sup> (Table 2), likely due to the presence of large mesopores. Composites prepared from zinc acetate and zinc sulfate, i.e. A-75-550 and S-75-550, respectively, showed slightly lower  $S_{BET}$  values than bare CN (e.g., 14 and 18 m<sup>2</sup> g<sup>-1</sup> for S-75-550 and bare CN, respectively). However, composites synthetized from zinc nitrate and zinc chloride displayed higher  $S_{BET}$  values compared with bare CN (e.g., 21 and 48 m<sup>2</sup> g<sup>-1</sup> for N-75-550 and C-75-550, respectively). Therefore, N-75-550 and C-75-550 materials should have larger mesopore volumes than bare CN and the catalysts prepared from zinc nitrate and zinc chloride. This phenomenon was evidenced by the high N<sub>2</sub> volume adsorbed at high P/P<sub>0</sub>, resulting from capillary condensation in mesopores [66]. Additionally, their total pore volume ( $V_{total}$ ) was higher than bare CN (e.g., 0.05 and 0.27 cm<sup>3</sup> g<sup>-1</sup> for CN and C-75-550, respectively). A trend was observed in CNbased composites synthetized with ZnCl<sub>2</sub> and different organic/inorganic precursor ratios, whereby an increase in the metal phase corresponded to a higher  $S_{BET}$  (e.g., 11 and 48 m<sup>2</sup> g<sup>-1</sup> for C-25-550 and C-75-550, respectively). Conversely, the surface area of materials synthetized at varying temperatures exhibited an inverse relationship with temperature, showing a lower surface area with an increased temperature (e.g., 10 and 50 m<sup>2</sup> g<sup>-1</sup> for C-75-650 and C-75-450, respectively, Table 2).

The crystalline phases of prepared composites were evaluated by XRD. Figure 1a shows the XRD patterns of the composites prepared with different zinc salts and treated at 550 °C (N-75-550, A-75-550, S-75-550 and C-75-550). For reference, the diffraction peaks of hexagonal ZnO wurtzite (JCPDS 36-1451) and tetragonal ZnNCN (JCPDS 70-4898) phases are also included. It is noteworthy that a higher intensity of diffraction peaks associated with the inorganic structures (ZnNCN and ZnO phases) and the low CN content in the composites, cause the disappearance of the corresponding peaks to the CN phase [57, 66]. In general, XRD patterns of all the prepared materials (Fig. 1a) displayed main diffraction peaks at 31.8°, 34.4°, 36.3°, 47.5°, 56.6°, 62.9°, 66.2°, 67.9° and 69.0°, associated to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) diffraction planes, respectively, evidencing the presence of the hexagonal ZnO wurtzite phase [67-69]. Furthermore, the sample prepared from melamine and zinc chloride as precursors (i.e., C-75-550) also showed diffraction peaks at 19.2°, 28.0°, 28.7°, 36.2°, 38.9°, 40.5°, 45.6° and 54.8°, corresponding to the planes of (101), (211), (220), (112), (202), (321), (411) and (431), respectively, denoting the formation of the zinc cyanamide (ZnNCN) crystalline structure [50] . In fact, except for the catalyst synthetized at 450 °C, which exhibited an amorphous structure (Fig. 1b), all the materials prepared with ZnCl<sub>2</sub> salt present a mixture of XRD peaks corresponding to the tetragonal ZnNCN and hexagonal ZnO wurtzite phases in a proportion that varies according the precursor ratio (i.e. C-50-550 and C-25-550) or the synthesis temperature (i.e., C-75-450 and C-75-650).

The percentage of tetragonal ZnNCN phase and the average crystalline size of both ZnO and ZnNCN phases were determined and listed in Table 2. All composites synthetized with ZnCl<sub>2</sub> exhibited percentages greater than 50% of the zinc cyanamide phase but this percentage increased with the amount of the ZnCl<sub>2</sub> precursor, i.e., varies between 85.0 and 70.0% for C-75-550 and C-25-550, respectively. Conversely, an increase in the synthesis temperature led to a significant reduction in the ZnNCN phase

(i.e., 85.0 and 52.6 % for C-75-550 and C-75-650, respectively), thereby promoting the formation of ZnO in the composites.



Fig. 1. XRD patterns of composites prepared with different Zn salts (a) and composites prepared with  $ZnCl_2$  and different synthesis parameters (b).

Additionally, the zinc content of carbon nitride-based composites had a discernible impact on the crystalline size of both ZnNCN and ZnO phases. In general, a higher amount of metallic phase resulted in a smaller crystalline size (e.g., 24.6 and 29.5 nm for C-75-550 and 28.4 and 34.5 nm for C-25-550, for ZnO and ZnNCN phases, respectively). The same trend was observed for the crystalline phase of ZnO when synthesis temperature increased (e.g., 24.6 and 22.6 nm for C-75-550 and C-75-650, respectively). However, the crystallite size of ZnNCN remained constant, i.e., 29.5 and 30.0 nm for C-75-550 and C-75-650, respectively.

The morphology of materials was determined by SEM. Micrographs of selected carbon nitride-based composites are depicted in Figure 2. It has been previously demonstrated that the synthesis conditions can significantly influence on the morphology of ZnO, leading to a diverse range of structures, including

flowers, rods, wires, tubes, and others [26, 70]. The morphology of A-75-550 and N-75-550 samples (Figs. 2a and b, respectively) consisted of large structures of CN coated by sphere-like particles associated with the ZnO phase. In contrast, the S-75-550 micrograph (Fig. 2c) showed clusters of petal-like ZnO particles. This structure is probably formed by the generation of sulfur-containing gases during the synthesis, acting as templates. On the other hand, the C-75-550 composite exhibited small particles of ZnNCN/ZnO covering CN flakes. The presence of CN is more notable in composites with a higher amount of CN (C-50-550 and C-25-550, Figs. 2e and f, respectively), consisting of pillar-shaped aggregates composed of irregular flakes. Bare CN (Fig. S3a) showed a typical morphology of irregular flake aggregates, while the structure of pristine ZnO (Fig. S3b) consisted of large clusters of hexagonal pyramid-like particles.

The thermal stability of CN in air was determined by TG (Fig. 3). Combustion of bare CN started at around 600 °C, where the heptazine rings become unstable, leading to the breakdown of the CN polymeric structure [36]. The burn-off percentage increased linearly up to the complete removal of CN at around 750 °C. A similar procedure was used to analyze the stability and content of CN in the composites prepared with ZnCl<sub>2</sub>. The composite prepared at 450 °C using ZnCl<sub>2</sub> as a precursor (C-75-450) exhibited lower thermal stability, with a weight loss (WL) progressively increased from 150 °C, but a more significant rise in the TG slope was observed from 750 °C. This fact may be attributed to that the CN polymerization occurs at around 520 °C, suggesting that the formation of graphitic CN is not favored at 450 °C [36, 71].



Fig. 2. SEM micrographs of A-75-550 (a), N-75-550 (b), S-75-550 (c), C-75-550 (d), C-50-550 (e) and C-25-550 (f).

The sample with the lowest Zn content (C-25-550) also showed a reduced thermal stability compared to other samples obtained at 550 °C, where combustion started at a similar temperature range to bare CN (around 600 °C). As commented, WL increased linearly with temperature. The profile obtained for the composites, regardless of the synthesis conditions and composition, showed different changes in the slope, which normally decreased, indicating the formation of more stable species by interaction between phases (Fig. 3). Previous studies have reported the different thermal stability of ZnNCN in both air and

nitrogen atmospheres. Under inert conditions, ZnNCN begins to decompose at 800 °C, but it retains its crystalline structure and chemical composition until 1100 °C [72]. However, when heated to 400 °C in an air atmosphere, the ZnNCN structure transforms into ZnO [73]. As previously mentioned, at 400 °C, the WL in our composites is negligible, except for the case of C-75-450, where the reaction progress is limited and ZnNCN is not formed. As the treatment temperature increases, the TG profile also changes in accordance with the ZnO content. The slope gradually decreases with higher ZnO content, suggesting the formation of more stable phases. Therefore, this behavior is not only induced by the temperature effect but also likely catalysed by the oxide phase.



Fig. 3. Thermogravimetric analysis under air flow of composites prepared with zinc chloride.

These experiments also provide information about the real composition of composites. The WL observed for C-75-550, C-50-550 and C-25-550 were 22.3, 41.1 and 59.2 wt.%, respectively. Considering that WL should correspond to the theoretical CN content in the composites (i.e., 25, 50 and 75 wt.%, respectively), it is clear that the difference in percentage progressively increased (i.e., 10.8, 17.8, and 21.1%, respectively), as the expected CN ratio increased. Regarding the influence of temperature, the WL obtained for sample C-75-450 was 53.4 wt.%, significantly higher than the programmed 25%, which confirms the scarce development of the CN formation. Conversely, the mass losses observed for the samples synthetized at 550 and 650 °C were similar between then, being 22.3% and 24.8%, respectively in this case, in good agreement with the expected CN content.

The formation of the CN polymeric network and its different functional groups were evaluated by ATR-IR. Figure 4 shows the spectra of bare CN, the composited prepared with zinc nitrate (N-75-550), zinc acetate (A-75-550), zinc sulphate (S-75-550) and those obtained with ZnCl<sub>2</sub> at different molar ratios and temperatures (i.e., C-25-550, C-50-550, C-75-550, C-75-450 and C-75-650). The main absorption bands of CN are attributed to the bending vibration of heptazine aromatic rings located at 806 and 887 cm<sup>-1</sup>, whereas the bands at 1240, 1330 and 1562 cm<sup>-1</sup> are associated to stretching vibrations of C-N-C and *sp*<sup>2</sup> aromatic C=N bonds [74, 75]. In general, all prepared composites exhibited main bands characteristic of the CN structure and a band at around 500-550 cm<sup>-1</sup> ascribed to the stretching vibration of ZnO bonds [76], as shown for S-75-550 as an example (Fig. 4). Moreover, the S-75-550 catalyst showed a band at around 1090 cm<sup>-1</sup>, which was associated with the vibration of C-S-C bonds . Regarding the ATR-FTIR spectra of the composites synthetized from ZnCl<sub>2</sub>, they exhibited a band at 463 cm<sup>-1</sup> assigned to the stretching vibration of Zn-N bonds [50]. Moreover, the peaks located around 671 and 2046 cm<sup>-1</sup> are indicative of the symmetric and asymmetric vibration modes of N=C=N<sup>2</sup> groups, respectively [51, 52]. These results also support the zinc cyanamide functionalization within the CN polymeric network, as observed by XRD (Fig. 1b).



Fig. 4. ATR-FTIR spectra of CN and CN/zinc composites.

Raman spectroscopy was also used to study the prepared materials (Fig. S4, Supplementary Material). Bare CN exhibited several peaks between 1300 and 200 cm<sup>-1</sup>, corresponding to the typical vibrations of CN heterocycles. The sharp peak at 1230 cm<sup>-1</sup> is associated with the stretching vibrations of C–N and C=N bonds in the heterocycles [77]. The strong peaks at 750 and 704 cm<sup>-1</sup> correspond to the bending vibrations of melon oligomers, while the bands at 977, 586, and 470 cm<sup>-1</sup> are attributed to heptazine ring vibrations [74, 78]. The broad band at 290 cm<sup>-1</sup> is primarily associated with nitrogen ion vibrations [79]. In contrast, pristine ZnO displayed a peak at 437 cm<sup>-1</sup>, corresponding to the typical vibrational modes of wurtzite ZnO [80]. The Raman spectra of the prepared photocatalysts showed peaks associated with both phases; however, no significant differences were observed between the composites with and without ZnNCN functionalities.

The pH<sub>PZC</sub> of pure phases varies around neutral pH, with CN and ZnO being slightly acid (6.3) and basic (7.5), respectively. Consequently, composites showed pH<sub>PZC</sub> values between these values. Nevertheless, there are some clear tendencies that should be highlighted. The pH<sub>PZC</sub> of composites prepared at 550 °C with 75% of ZnO varies significantly according to their respective precursor salt, following the trend: A > N > S > C, with pH<sub>PZC</sub> values ranging from 7.6 to 6.9 (Table 2), similar to the value obtained for pristine ZnO (i.e., 7.5). In contrast, the photocatalysts synthetized from ZnCl<sub>2</sub> exhibited a slightly acid character, with pH<sub>PZC</sub> values between 6.4 and 6.8, like bare CN (i.e., 6.3). These results suggest that the incorporation of ZnNCN groups leads to the formation of composites with a slightly acidic surface. Composites prepared under different synthesis conditions showed comparable results, although the acid character increased as decreased both proportion of Zn and synthesis temperature.

The surface chemistry composition of bare CN and CN-based composites with different content in ZnCl<sub>2</sub> salt and synthesis temperatures was characterized by XPS. Figures 5a and b illustrate the deconvoluted C1s and N1s regions, respectively, while the percentage of each chemical species are shown in Figures 5c and d, respectively. Carbon, nitrogen, oxygen and zinc atomic contents are also listed in Table 3. XPS survey spectra are included in Figure S5.

Sample	C <sub>XPS</sub> (%)	N <sub>XPS</sub> (%)	O <sub>XPS</sub> (%)	Zn <sub>XPS</sub> (%)	C/N <sub>XPS</sub> ratio	Zn/O <sub>XPS</sub> ratio
C-25-550	48.4	33.8	8.1	7.7	1.43	0.95
C-50-550	48.4	24.9	12.1	14.6	1.94	1.21
C-75-550	41.4	20.0	16.6	22.0	2.08	1.33
C-75-450	43.8	23.7	17.4	15.1	1.85	0.87
C-75-650	32.7	9.4	35.7	22.2	3.47	0.62
CN	41.6	56.1	2.3	-	0.74	-
ZnO	-	-	52.4	47.6	-	0.91

Table 3. Atomic surface content (wt.%) obtained by XPS analysis.

The results showed that the surface Zn-content increased three times from C-25-550 to C-75-550, indicating a uniform distribution of ZnO on the surface regardless of the ZnO content, the surface C-content remained practically unaffected by changing the proportion of the phases (Table 3). However, the surface N-content associated to the CN phase progressively decreased, while the O-content increased as the ZnO ratio in the composite. Furthermore, both C/N and Zn/O ratios increased with increasing ZnO content. The C-75-550 composite displayed the lowest C, N and O contents, suggesting that ZnO effectively interacts with cyanamide structures, potentially facilitating their linkage.

High resolution spectra of C1s and N1s (Figs. 5a and b, respectively) were investigated to determinate the presence and amount of zinc cyanamide functionalities. In general, the C1s spectral region (Fig. 5a) for all photocatalysts, except for C-75-650, was deconvoluted into four main components located at approximately 284.6, 285.9, 287.2, and 288.4 eV, corresponding to adventitious carbon (i.e., defects in sp<sup>2</sup>-C atoms or carbon impurities), C–(N)<sub>3</sub> bonds from sp<sup>3</sup>-C atoms, C=N bonds, and N–C=N bonds from sp<sup>2</sup>-C in heptazine rings, respectively [35, 66]. The C1s region for all composites showed a higher presence of N–C=N bonds compared to pure CN, which may be attributed to the increased aromaticity in the CN network [57]. The C-75-650 composite, however, exhibited a fourth component at 289.4 eV, attributed to residual carbonates. These carbonates may have formed due to the breakdown of the CN polymeric network during the synthesis at the higher temperature (650 °C), favouring the oxidation for the formation of these carbonate groups.



Fig. 5. High resolution XPS spectra and deconvolution of (a) C1s and (b) N1s regions of synthetized CN and composites. Components percentages for the synthetized photocatalysts calculated from the deconvolution (c) C1s and (d) N1s regions.

Regarding the N1s region (Fig. 5b), the spectrum was deconvoluted into three main contributions. The first component, located at approximately 397.7 eV, was attributed to N–Zn bonds of sp<sup>2</sup>-N atoms bonded to zinc atoms in cyanamide groups [51]. The second and third components, at around 398.5 and 399.6 eV, were associated with C–N=C bonds in the heptazine rings and N–(C)<sub>3</sub> bonds from tertiary

nitrogen atoms, respectively [81]. The N1s deconvolution of the C75-550 composite showed a higher presence of N–Zn bonds compared to C-25-550 and C-50-550 composites (Fig. 5d), which can be explained by the formation of a less condensed CN network with a higher content of zinc cyanamide terminal groups (NCN–Zn). For the C-75-450 composite, the spectrum was deconvoluted similarly; however, the expected peak corresponding to N–Zn bonds was not observed, suggesting that zinc cyanamide was not formed at low temperature. Bare CN exhibited a component at 401.2 e, assigned to residual amino groups. Finally, the deconvolution of the Zn2p spectral region (Fig. S2) exhibited characteristic peaks attributed to Zn2p<sub>3/2</sub> and Zn2p<sub>1/2</sub>, assigned to Zn<sup>2+</sup> species at ~1021.2 and 1044.2 eV, with a binding energy difference between the two peaks maintained at 23.0 eV. With exception of C-75-450, all materials with N-Zn bonds presented a shift of the Zn2p peak towards lower binding energy, as consequence less electron-rich regions.

UV-Vis diffuse reflectance spectroscopy was used to evaluate the optical properties of the prepared materials. Figures 6a and c show the UV-Vis absorption spectra, expressed in Kubelka-Munk absorption units, for the synthesized photocatalysts and pure CN, while Figures 6b and d depicted Tauc's plots versus the energy (eV). The N-75-550, A-75-550, and S-75-550 composites (Fig. 6a) displayed a strong absorption band at wavelengths below 400 nm in the UV range, corresponding to the typical UV-Vis absorption of pristine ZnO [57, 76]. Figure 6c showed the UV-Vis absorption spectra of photocatalysts prepared from melamine and zinc chloride at different synthesis temperature and metal loading. The calculated band gaps of prepared composites ranged from 2.83 to 3.18 eV (Table 2). The results indicate that the composite with the lowest metal content and highest CN content (C-25-550) presented the highest absorption in the visible spectrum. This finding is consistent with previous studies on CN/ZnO composites [57].



**Fig. 6.** UV-Vis spectra (a, c) and Tauc's plots versus energy expressed in eV (b, d) of pure CN, pristine ZnO and carbon nitride-based composites.

The strong absorption band in the visible range and the narrow band gap of CN are associated with the  $\pi$ - $\pi$ \* transitions of the CN conjugated aromatic system [74]. In contrast, the band gap of ZnNCN (~ 4.8 eV) [72, 82] is considerably higher than that of ZnO (~3.2 eV), which may be attributed to differences in the energy band structures, specifically the linear combination of atomic orbitals. The valence band (VB) of ZnNCN is predominantly composed of N2p orbitals, while the conduction band (CB) is largely made up of Zn4s orbitals. However, because energy bands in solids are formed only from units with the same symmetry, the varying crystal orientations of neighbouring zinc cyanamide units lead to an increased effective distance between the interacting units [72, 83, 84]. Moreover, the

high band gap of ZnNCN can contribute to the higher band gap energy of the C-75-550 composite in comparison to the other materials (Table 2).



**Fig. 7.** Band gap, valence and conduction band positions of CN, ZnO and composites (expressed in terms of redox potential at pH 7 in aqueous solution vs NHE).

The VB edge position was estimated using XPS by locating the intersection of the linear VB region (i.e., -2.0 to 9.0 eV) with the binding energy axis (i.e., X axis). The CB position was then calculated as the difference between the VB and band gap energy, providing the complete band structure (Fig. 7). All the prepared photocatalysts showed favorable band positions for the formation of oxygen radical species. Previous studies have reported the edge band position of ZnNCN at 0.24 and -4.44 eV for VB and CB, respectively [50]. Bare CN have exhibited a VB at approximately 1.5 eV and a CB at -1.2 eV, while pristine ZnO showed VB and CB at 3.1 and -0.1 eV, respectively [50, 85, 86]. The band positions of the C-25-550 and C-75-450 composites were found to closely resemble those previously reported for CN, likely due to higher proportion of CN (ca. 60 %) for C-25-550 and the absence of ZnNCN crystalline phase in the case of C-75-450, as observed by TG and XRD, respectively. In contrast, a shift toward more positive edge band positions was observed for C-75-550 and C-50-500. Therefore, the formation of composites resulted in a more positive edge band position, which may be attributed to the formation

of a Z-scheme heterojunction, which facilitates the migration of charge from ZnNCN to CN surface, as previously reported in literature [50], leading to an excellent charge separation. It is important to highlight that C-75-550 is the only material aligned with the redox potentials for a strong oxidation ability for pollutants degradation and formation of HO<sup>•</sup> radicals, as well as the formation of superoxide radicals  $(O_2^{\bullet-})$ .

#### 3.2. Photocatalytic degradation of cytostatic drugs under UV-Vis irradiation

The photocatalytic efficiency of the prepared materials was evaluated for the degradation of both 5-FU and CP in aqueous solution under near UV-Vis irradiation (Fig. 8). Pollutant conversion (X), kinetic rate constant  $(k_{app})$  and regression coefficient  $(r^2)$  are gathered in Table 4. The reaction in absence of catalyst, i.e., photolysis, showed the resistance of these cytostatic drugs to be degraded under near UV-Vis light, with a 5-FU conversion of 15% and CP conversion of 1% after 30 and 60 min of irradiation, respectively. The adsorption-desorption equilibrium was established for all composites in absence of light after 30 min. The calculated adsorption capacities (Ads) of both pollutants are shown in Table 4. The 5-FU removal by adsorption of the composites prepared from different Zn salts varied widely, ranging from 9.6% for N-75-550 to 43.4% for C-75-550 composite. The results indicated that increasing the temperature or reducing the metal phase in composites prepared with ZnCl<sub>2</sub> (C samples) led to a significant decrease in adsorption efficiency, with values reaching 18.8% and 30.1% for C-25-550 and C-75-450, respectively (Table 4). The results of the adsorption experiments conducted with CP demonstrate a similar pattern to that observed with 5-FU, with the adsorption values ranging from 4.4% to 18.3% for C-25-550 and C-75-550, respectively. The adsorption capacity of the catalysts can be correlated with their textural properties, such as the surface area ( $S_{BET}$ , Table 2). It is important to note that at the working pH (6.3 for 5-FU and 5.2 for CP), both molecules remain neutral. Additionally, the catalyst surfaces are either neutral or slightly acidic, so electrostatic interactions are expected to be negligible in both cases.

Initially, the composites prepared from different Zn salts and pristine phases were evaluated for the photocatalytic degradation of 5-FU (Fig. 8a). As expected, the presence of Zn phase in the composites

leads to a higher pollutant degradation than that observed for the bare CN material. For the 5-FU degradation, the photocatalytic activity of the catalysts follows the order (Fig. 8a): C-75-550 > S-75-550 > A-75-550 > N-75-550 > CN. Thus, the composite prepared with ZnCl<sub>2</sub> salt, specifically C-75-550, showed the highest photocatalytic efficiency, achieving nearly 100% degradation after just 5 min of reaction under the specified conditions. This sample presented not only the highest BET surface area (Table 2) and adsorption capacity (Table 4), but also the larger presence of cyanamide functionalities (indicated by the high Zn content and proportion of cyanamide groups in Table 2), which contributed to enhanced charge separation due to the heterojunction structure and the favorable positions of the VB and CB bands for radical formation (Fig. 7).

**Table 4.** Cytostatic drugs adsorption (Ads), conversion ( $X_{Xmin}$ ), pseudo-first order kinetic rate ( $k_{app}$ ), and regression coefficient ( $r^2$ ) under near UV-Vis irradiation.

Sample	5-FU					СР			
~~~ <b>F</b> ~~	Ads (%)	X <sub>30 min</sub> (%)	k <sub>app</sub> (10 <sup>-2</sup> min <sup>-1</sup> )	$r^2$	Ads (%)	X <sub>60 min</sub> (%)	k <sub>app</sub> (10 <sup>-3</sup> min <sup>-1</sup> )	$r^2$	
Photolysis	-	15.0	-	-	-	6.7	-	-	
CN	6.1	85.1	6.1	0.999	13.7	30.0	6.0	0.984	
N-75-550	9.6	96.2	12.3	0.992	-	-	-	-	
A-75-550	14.3	100.0	15.5	0.992	-	-	-	-	
S-75-550	26.2	100.0	20.3	0.996	-	-	-	-	
C-75-550	43.4	100.0	88.4	0.999	18.3	100.0	59.5	0.993	
C-50-550	30.8	95.3	73.9	0.999	6.5	59.7	17.7	0.992	
C-25-550	18.1	95.7	12.0	0.996	4.4	21.6	6.0	0.983	
C-75-450	30.1	100.0	24.4	0.974	12.5	94.3	38.7	0.979	
C-75-650	36.8	100.0	27.3	0.980	13.1	93.2	40.7	0.990	



**Fig. 8.** Normalized concentration of 5-FU as a function of time for composites prepared with different Zn salts (a) and CN-ZnNCN based composites (b). Normalized concentration of CP as a function of time for CN/ZnO/ZnNCN based composites (c).

Figure 8b illustrates the influence of synthesis temperature and metal loading in ZnCl<sub>2</sub>-prepared composites on the photocatalytic degradation of 5-FU. The results indicate that activity increased with the Zn-content, although even the composite with the lowest Zn content (C-25-550) achieved around 85% degradation, while C-75-550 showed a complete degradation (100%). The composites prepared at different temperatures achieved a high 5-FU removal, although at a slower rate compared to those synthesized at 550 °C, underscoring the significant influence of synthesis temperature on photocatalytic efficiency. The catalyst prepared at 550 °C demonstrated the highest photocatalytic performance, while those prepared at 450 °C and 650 °C showed similar photodegradation rates, with degradation constants of 27.3×10<sup>-2</sup> and 24.4×10<sup>-2</sup> min<sup>-1</sup> for C-75-650 and C-75-450, respectively. This could be because the C-75-450 catalyst does not form the ZnNCN phase, while at higher temperatures in the C-75-650 catalyst partially degrade the ZnNCN phase, reducing its presence from approximately 80 to 50% (Table 2). This degradation results in a decrease in photocatalytic activity. The incorporation of ZnNCN into the composites enhanced their photocatalytic efficiency for the 5-FU removal under near UV-Vis irradiation compared to bare phases, highlighting the significant impact of synergistic interactions between the phases.

The photocatalytic degradation of CP was also studied with this series of samples under near-UV-Vis irradiation (Fig. 8c). Similar to the degradation of 5-FU, both catalysts prepared at 450 °C and 650 °C exhibited comparable photocatalytic performance, with photodegradation rates of  $38.7 \times 10^{-3}$  and  $40.7 \times 10^{-3}$  min<sup>-1</sup> for C-75-450 and C-75-650, respectively, as detailed in Table 4. On the other hand, the photocatalysts prepared with varying Zn contents showed similar trends to those observed in 5-FU degradation. However, significant differences in activity were found between composites synthesized with 50% and 75% of ZnCl<sub>2</sub>. The C-75-550 composite exhibited a photodegradation rate approximately three times higher than that of C-50-550 (59.5×10<sup>-3</sup> vs 17.7×10<sup>-3</sup> min<sup>-1</sup>, respectively). These results highlight the importance of precisely controlling composition and physicochemical properties throughout the synthesis process.

#### 3.3. Influence of reactive oxygen species (ROS) and reaction mechanism

The possible ROS involved in the photodegradation process were evaluated with the addition of scavengers, such as MeOH, NaN<sub>3</sub> and EDTA for radical species, non-radical species (as singlet oxygen,  ${}^{1}O_{2}$ ) and holes, respectively as indicated in literature [57, 87]. Figure 9 shows the 5-FU degradation (%) under near-UV/Vis irradiation in the presence of the selected scavengers for the most active composite, i.e., C-75-550. The results show that the presence of MeOH led to a decrease of the pseudo-first order rate constants for the catalysts tested. This decrease was much deeper in the presence of EDTA. The calculated kinetic ratio for the 5-FU degradation was  $62.8 \times 10^{-2}$ ,  $25.9 \times 10^{-2}$  and  $1.1 \times 10^{-2}$  min<sup>-1</sup>, respectively, compared to the kinetic degradation rate of  $88.4 \times 10^{-2}$  min<sup>-1</sup> obtained without the addition of any scavengers.



**Fig. 9.** Effect of radical/non-radicals/holes scavengers (MeOH/NaN<sub>3</sub>/EDTA) on the photocatalytic degradation of 5-FU using C-75-550 composite.

The quenching effect observed with MeOH and EDTA suggests that photogenerated holes ( $h^+$ ) and radical species are the main responsible to the photocatalytic process. Thus, VB and CB positions of C-75-550 composite (Fig. 7) support the formation of HO<sup>•</sup> radicals and superoxide radicals ( $O_2^{\bullet-}$ ). However, the more significant decrease in the rate constant when EDTA indicates that photogenerated holes play the main role. Conversely, non-radical species with the quenching effect from NaN<sub>3</sub> play a negligible role, as degradation remained similar to that observed in absence of scavengers [88-90].

Taking into consideration the ROS involved in the photocatalytic process, the analysis of the band structure, the physicochemical properties of the composites and the reported literature, a tentative photocatalytic mechanism is proposed in Figure 10. The photogenerated electrons in CN (Eg ~ 2.68 eV) can migrate to the CB of ZnO (Eg ~3.20 eV) enabling the reduction of oxygen molecules dissolved in water to generate superoxide radicals (-0.33 eV) for ZnO. Moreover, the corresponding holes generated in the VB of ZnO are able to form hydroxyl radicals. On the other hand, considering unfavourable energy band gap of ZnNCN ( $E_g \sim 4.8 \text{ eV}$ ) for harvesting photon energies, electrons in CB cannot be generated under UV/vis irradiation. The photogenerated holes in the VB of ZnO could be transferred to the corresponding VB of CN and also to ZnNCN, realizing spatial separation between photogenerated electron-hole pairs. However, the generated holes into ZnNCN and CN are not able to oxidize HO-(1.99 eV) and  $H_2O$  (2.74 eV) molecules into HO<sup>•</sup> radicals, indicating that the degradation of the contaminants is mainly due to the direct oxidation by photogenerated holes [91-94]. This mechanism agrees with the results obtained from the scavenger study (Fig. 9) revealing that direct oxidation by photogenerated holes in ZnNCN plays a decisive role in the degradation of the contaminants. Oxidation by reactive radicals (such as O2<sup>-</sup>) formed from photoexcited electrons can also participate in the degradation mechanism although they are not the main active species involved in the photodegradation.



Fig. 10. Scheme of the propose photocatalytic mechanism with CN/ZnO/ZnNCN composites.

#### 3.4 Study of reusability

The photocatalytic stability of both C-75-550 (25% of ZnO and 85% of ZnNCN) and S-75-550 (100% ZnO) composites was evaluated over several consecutive reuse cycles under near-UV/Vis irradiation (Figs. 11a and b, respectively). The experiments followed the methodology described in section 2.3. After each experiment, the composite was rinsed with water and dried in an oven at 90 °C for 5 hours before being reused in two additional photocatalytic experiments. Subsequently, the composite was reused with a fresh 5-FU solution. The results for C-75-550 showed a slight decrease in photocatalytic activity between the initial and subsequent cycles, with a reduction from 100% to 96.4%. However, the photocatalytic performance between the second and fifth runs remained practically constant, ranging from 96.4% to 94.6%. Notably, the composite demonstrated remarkable stability, with only a 5.4% reduction in activity after five consecutive cycles. The slight deactivation observed can likely be attributed to the surface chemisorption of 5-FU or its degradation intermediates, which block active sites after repeated catalytic reactions (Fig. 11a).

Regarding the S-75-550 composite (Fig. 11b), the results exhibited a progressive decrease in photoactivity over the course of five consecutive reaction cycles, with a reduction from nearly 100% in the first run to approximately 70% by the fifth run. This significant decline in photocatalytic performance suggests that while the S-75-550 composite initially performs well, it suffers from instability during an extended use. This deactivation can be linked to photocorrosion, a process in which the photocatalyst undergoes structural or chemical degradation upon exposure to light over time. In contrast, the CN/ZnO/ZnNCN composite (i.e., C-75-550) demonstrated exceptional photostability, with minimal loss in photocatalytic efficiency even after multiple reuse cycles. This stability is attributed to the strong Zn-N bonding present within the CN-ZnO/ZnNCN structure, which effectively stabilizes the composite and prevents significant degradation of its photocatalytic properties. These results point out the importance of the structural integrity and bonding within photocatalytic materials, particularly for applications requiring long-term stability [40, 45].



**Fig. 11.** Reusability of C-75-550 (a) and S-75-550 (b) photocatalysts for the 5-FU degradation during five consecutive cycles.

For comparison purposes, Table 4 provides a summary of recently published studies on different materials for the photocatalytic degradation of cytostatic drugs. Some experimental details are included, such as the synthesis method, irradiation source, selected cytostatic drug, pollutant concentration and the degradation achieved at a given time. It should be noted that the composites reported in the referenced studies were generally prepared through complex synthesis procedures. For example, Garg et al. [95] reported a CN/NiFe<sub>2</sub>O<sub>4</sub> composite for the photocatalytic degradation of doxorubicin (DOX). In the initial stage, pure phases of CN and NiFe<sub>2</sub>O<sub>4</sub> were prepared via thermal polymerization and solgel process, respectively. The CN/NiFe<sub>2</sub>O<sub>4</sub> composite was then formed using a sonication-calcination strategy. In contrast, the photocatalysts presented in our work were prepared using a simple one-pot thermal method with common and low-cost precursors. Of note, the accurate comparison of the photocatalytic activity of the materials prepared in this work with those listed in Table 4 is challenging due to differences in reaction parameters, such as the irradiation source, pollutant concentration, and catalyst loading. For instance, almost complete degradation of 5-FU and CP was achieved in 30 and 120 min under near-UV-Vis irradiation using  $g-C_3N_4$ -based photocatalysts with a band gap energy around 2.7 eV [74]. Wang et al. [96] reported that Fe<sub>3</sub>O<sub>4</sub> hollow microspheres decorated with Ag and CN quantum dots achieved total degradation of 5-FU and capecitabine (CAP) in 60 min using a Xe lamp ( $\lambda$ > 420 nm), as the irradiation source. In comparison, the composites prepared in this work demonstrated

excellent photocatalytic performance for the degradation of both 5-FU and CP under near-UV-Vis irradiation, outperforming the catalysts described in the literature.

**Table 4.** Compilation of recently published studies regarding photocatalysts for the degradation of cytostatic drugs

Catalyst	Synthesis methods	Irradiation source	Cytostatic drugs	Degradation (%) / time (min)	Ref.
TiO <sub>2</sub>	IL-assisted solvothermal	Medium Pressure Hg lamp $(\lambda > 366 \text{ nm})$	5-FU (15 mg L <sup>-1</sup> )	92 / 120	[97]
Bi/B–TiO <sub>2</sub>	Sol-gel	Xe lamp $(\lambda > 420 \text{ nm})$	5-FU (50 mg L <sup>-1</sup> ) IMA (50 mg L <sup>-1</sup> ) CP (50 mg L <sup>-1</sup> ) IFO	~95 / 240 ~50 / 240 ~70 / 240	[98]
N-TiO <sub>2</sub>	Calcination + Microwave	Blue light lamp $(\lambda_{max} = 430 \text{ nm})$	(50 mg L <sup>-1</sup> ) CP (20 mg L <sup>-1</sup> ) 5-FU (20 mg L <sup>-1</sup> )	100 / 60	[99]
BiOCl <sub>1.3</sub> Br <sub>0.7</sub>	Solvothermal	Xe lamp ( $\lambda > 290 \text{ nm}$ ) Xe lamp ( $\lambda > 420 \text{ nm}$ )	$\begin{array}{c} (20 \text{ mg } \text{L}^{-1}) \\ 5\text{-FU} \\ (15 \text{ mg } \text{L}^{-1}) \\ 100 \text{ IMA} \\ (15 \text{ mg } \text{L}^{-1}) \\ 5\text{-FU} \\ (15 \text{ mg } \text{L}^{-1}) \\ 100 \text{ IMA} \\ (15 \text{ mg } \text{L}^{-1}) \end{array}$	100 / 120 100 / 180 ~98 / 180 100 / 180	[100]
B/DGNW- (BiO <sub>2</sub> )OHCl/BiOBr	CVD + Solvothermal	Xe lamp $(\lambda > 290 \text{ nm})$	5-FU (15 mg L <sup>-1</sup> )	100 / 120	[101]
CN	Thermal	Medium Pressure Hg lamp $(\lambda > 350 \text{ nm})$	5-FU (10 mg L <sup>-1</sup> ) CP (10 mg L <sup>-1</sup> )	99 / 30 90 / 120	[74]
		Solar-LED $(\lambda > 410 \text{ nm})$	(10  mg L) 5-FU $(10 \text{ mg L}^{-1})$	46 / 420	
CN/ZnO	Thermal	$UV-LED (\lambda_{max} = 385 \text{ nm})$	5-FU (20 mg L <sup>-1</sup> )	100 / 180	[57]
CN/NiFe <sub>2</sub> O <sub>4</sub>	Thermal + Sol- gel + Calcination	Hg lamp	DOX (9.5 mg L <sup>-1</sup> )	94 / 15	[95]
CNQD/CuFe <sub>2</sub> O <sub>4</sub> /Cu <sup>0</sup>	Solvothermal + Calcination	Xe lamp $(\lambda > 420 \text{ nm})$	5-FU (3.9 mg L <sup>-1</sup> )	100 / 60	[102]
Ag-CNQD/Fe <sub>3</sub> O <sub>4</sub>	Impregnation + Calcination	Xe lamp $(\lambda > 420 \text{ nm})$	5-FU (10 mg L <sup>-1</sup> )	100 / 60	[96]

				CAP (10 mg L <sup>-1</sup> )	98 / 60	
	CN/Ni <sub>3</sub> (VO <sub>4</sub> ) <sub>2</sub> /ZnCr <sub>2</sub> O <sub>4</sub>	Thermal + Hydrothermal + Co-precipitation	Halogen lamp $(\lambda > 200 \text{ nm})$	5-FU (20 mg L <sup>-1</sup> )	100 / 200	[103]
	CN/ZnO/ZnNCN	Thermal	Medium Pressure Hg lamp	5-FU (10 mg L <sup>-1</sup> )	100 / 15	This
(C-75-550)	Therman	$(\lambda > 350 \text{ nm})$	CP (10 mg L <sup>-1</sup> )	100 / 60	work	

B/DGNW: Boron doped diamond/graphene nanowalls; QD: Quantum dots; IL: Ionic liquids; CVD: Chemical vapor deposition; 5-FU: 5–Fluorouracil; IMA: Imatinib; CP: Cyclophosphamide; IFO: Ifosfamide; DOX: Doxorubicin; CAP: Capecitabine.

#### 3.5 Photodegradation pathway of 5-fluorouracil

The transformation products (TPs) of 5-FU were identified using UHPLC-MS in both negative and positive ion modes to elucidate the potential photocatalytic degradation pathway. A total of ten intermediate transformation products (Table S1) were detected when using the C-75-550 photocatalyst under near UV-Vis irradiation. The 5-FU transformation products were designed as TPX-Y, wherein "X" denotes to the degradation pathway (i.e., Pathway I, II, III or IV) and "Y" represents the position within the pathway (1, 2 or 3).

Figure 12 illustrates the various proposed photodegradation pathways for 5-FU. In the first pathway, degradation begins with the hydrogenation and subsequent hydroxylation of 5-FU, leading to the formation of TPI-1. Further hydroxylation results in the creation of TPI-2, which has an empirical formula of  $C_4H_4N_2O_5$ . Through a series of oxidation and hydroxylation steps, the ring structure is cleaved, resulting in the formation of TPI-3, a derivative of carbamic acid. This degradation pathway was previously proposed using the heterostructure CN quantum dots/CuFe<sub>2</sub>O<sub>4</sub>/Cu *via* a photooxidation process [102]. In the second pathway (Pathway II), 5-FU undergoes degradation through the loss of fluorine ions and ketonization, resulting in the formation of TPII-1. TPI-4 is subsequently formed from TII-1 by the cleavage of the C-N bond, which leads to ring opening [104-106]. In the third pathway, the initial transformation product, TPIII-1, is generated through the hydrogenation and lactam hydrolysis of the uracil ring, resulting in 3-(carboxyamino)-2-fluoropropanoic acid. Further oxidation leads to the cleavage of the pyrimidine ring and the formation of smaller molecules such as TPIII-2 and TPIII-3, identified as 3-amino-2-fluoroacrylic acid ( $C_3H_4FNO_2$ ) and 2-fluoro-3-oxopropanoic acid ( $C_3H_3FO_3$ ),

respectively [102, 103]. It is interest to note that intermediate TPIII-2 is one of the most frequently reported transformation products in the literature [103, 107]. Finally, the fourth degradation pathway, previously reported by Mazierski et al. [104], involves the defluorination and ketonization of the 5-FU pyrimidine ring, leading to the formation of TPIV-1. Subsequent ring opening, likely caused by the cleavage of C-N bonds due to nitrogen atom hydrogenation, results in TPIV-2, identified as 1-(3-oxopropyl)urea, with an empirical formula of  $C_4H_8N_2O_2$ . Theoretical predictions of acute and chronic toxicity of 5-FU and its TPs have been studied in previous works, based on half-maximum effective concentration (EC<sub>50</sub>) and half-maximum inhibition concentration (IC<sub>50</sub>) values for fish, daphnids, and green algae. Generally, the transformation products exhibit lower acute and chronic toxicity compared to 5-FU. Finally, most of the intermediates would be further degraded to CO<sub>2</sub> and H<sub>2</sub>O.



**Fig. 12.** Proposed photocatalytic oxidation pathway of 5-fluorouracil using C-75-550 under near UV-Vis irradiation.

# 4. Conclusions

This study successfully developed a series of composites based on graphitic carbon nitride (CN) and ZnO using melamine as the precursor for CN and zinc acetate, zinc nitrate, zinc sulfate or zinc chloride as precursors for ZnO. The composites prepared with zinc chloride were found to form CN/ZnO composites functionalized by zinc cyanamide (ZnNCN). The ZnNCN content incorporated into the composite was precisely controlled by varying the melamine to zinc salt ratio and the synthesis temperature, achieving a remarkable 85% ZnNCN incorporation in the optimal catalyst, C-75-550, synthesized using a melamine:salt ratio of 25:75 at 550 °C. This composite exhibited exceptional pollutant adsorption capacity and superior photocatalytic performance, making it highly effective for environmental remediation applications.

The enhanced catalytic efficiency of the composites, particularly C-75-550, is attributed to a synergistic interplay among g-C<sub>3</sub>N<sub>4</sub>, ZnO, and ZnNCN. This synergy facilitated efficient charge transfer processes, significantly suppressing electron-hole recombination and amplifying photocatalytic degradation activity. Mechanistic studies highlighted the pivotal role of photogenerated holes in the degradation of 5-FU, as evidenced by the substantial reduction in the reaction rate constant upon EDTA addition.

Notably, C-75-550 demonstrated outstanding stability over multiple catalytic cycles, driven by Zn–N bond stabilization, ensuring long-term durability under UV-Vis irradiation. These findings position the C-75-550 composite as a cutting-edge photocatalyst, merging high efficiency and robust stability, and underscore its potential for real-world applications in advanced pollutant degradation and sustainable environmental remediation.

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# **CRediT** authorship contribution statement

**A. Pérez-Molina:** Investigation, Conceptualization, Formal analysis, Methodology, Writing - original draft. **S. Morales-Torres:** Conceptualization, Data curation, Resources, Writing - review & editing, Supervision. **L.M. Pastrana-Martínez:** Conceptualization, Data curation, Resources, Writing - review & editing, Supervision, Funding acquisition. **F.J. Maldonado Hódar**: Conceptualization, Resources, Project administration, Funding acquisition, Writing - review & editing, Supervision.

# **Declaration of Competing Interest**

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

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