Environmental Science and Pollution Research (2021) 28:24992–25013
https://doi.org/10.1007/s11356-021-13528-y

REVIEW ARTICLE

Carbon nitride-based photocatalysts for the mitigation of water pollution engendered by pharmaceutical compounds

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Received: 23 November 2020 / Accepted: 15 March 2021 / Published online: 27 March 2021

Abstract

In recent decades, the destructive impact of active pharmaceutical ingredients (API) present in surface and drinking water on aquatic and terrestrial life forms becomes a major concern of researchers. API like diclofenac (DCF), carbamazepine (CBZ), tetracycline (TC), and sulfamethoxazole (SME) found in water bodies cause antimicrobial resistance and are potent carcinogens and endocrine disruptors. Conventional wastewater treatment methods possess some drawbacks and were found to be insufficient for the effective removal of APIs. Visible light-assisted semiconductor photocatalysis has become an alternative choice for tackling this worse scenario. Graphitic carbon nitride, a metal-free visible light active semiconductor photocatalyst is an emerging hotspot nanomaterial whose practical utility in water purification is widely recognized. This review comes up with an insightful outlook on the panorama of recent progress in the field of g-C_3N_4-assisted photocatalytic systems for the eradication of APIs. In addition, the review summarizes various strategies adopted for the broad-spectrum utilization of visible light and the enhancement of charge separation of pristine g-C_3N_4. The mechanistic pathways followed by different pharmaceuticals during their photocatalytic degradation process were also briefly discussed.

Keywords Photocatalysis · g-C_3N_4 photocatalyst · Pollutant degradation · Pharmaceuticals · Solar light · Waste water treatment

Introduction

Active pharmaceutical ingredients (APIs) are fundamentally assorted class of emerging contaminants (Benotti et al. 2009) and the presence of pharmaceuticals in the environment resulted in the development of antimicrobial resistance (AMR) (UN Environment 2017) which is recognized as one of the biggest global public health concerns by the UN Environment. Advancements in the analytical method sensitivity (Siddiqui et al. 2017), expanded use of various pharmaceuticals, and improper disposal of medications by households, pharmaceutical companies, and hospitals have worsened the scenario. The highly soluble, persistent pharmaceutical compounds present in water bodies can act as potent carcinogens, and even low concentrations of pharmaceuticals in the environment can cause adverse effects on flora and fauna including renal malfunctioning in vultures (Swan et al. 2006), reproduction impairment in fish (Nash et al. 2004), and retardation and inhibition of growth in certain aquatic species (Ebert et al. 2011).

In order to tackle the problem, efficient wastewater treatment techniques should be utilized. Conventional methods involving filtration, adsorption, reverse osmosis (RO), activated sludge, etc. (Patel et al. 2019) are found inadequate for the efficient and complete removal of APIs from wastewater. Among various water treatment technologies, advanced oxidation processes (AOPs) (Kanakaraju et al. 2018) are promising choices for wastewater treatment as they can adequately debase watery contaminations, while essential ordinary procedures and actuated carbon-based adsorption process are just associated with the physical change of toxins without any degradation. Numerous AOPs, for example, UV/H_2O_2, photo-fenton, sonolysis, electrochemical oxidation, ozonation, and photocatalysis, are utilized for the effective degradation of organic pollutants, and the in situ generation of highly reactive oxygen species (ROS) such as hydroxyl radicals ($^{\bullet}OH$) and superoxide anion radicals ($^{\bullet}O_2^-$) in AOPs enables complete mineralization of pollutants into CO_2, H_2O, and inorganic ions or acids (Dalrymple et al. 2007). However, photocatalysis is recognized as ideal green, cost-effective, and sustainable technology (Xu et al. 2019a) for addressing worldwide ecological pollution and energy shortages.

Responsible editor: Sami Rtimi

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Researchers have attempted to explore novel semiconductor photocatalysts with high photo-response and real-world applications for the degradation of pollutants. As a result, several heterogeneous photocatalysts such as TiO_2 (Daghrir et al. 2013), ZnO (Lee et al. 2016), Fe_2O_3 (Mishra et al. 2019), CdS (Cheng et al. 2018), and ZnS (Lee and Wu 2017) are introduced in the field of photocatalysis for the removal of recalcitrant organic compounds. Among them, TiO_2 and ZnO nanophotocatalyst are widely explored by researchers due to its high reactivity, reduced toxicity and chemical stability. However, these photocatalysts essentially require UV light for the photocatalytic activity due to their wide band gap value, which impedes their practical utility as solar light active catalysts. Therefore, extensive research has been carried out to extend the photocatalytically active region of catalysts into visible range (400–700nm) for the degradation of pollutants with the direct utilization of sunlight (Dong et al. 2015).

Recently, visible light active catalysts, graphitic carbon nitride (g-C_3N_4) (Zhang et al. 2019b), have become hotspot nanomaterials and widely employed in the degradation of hazardous organic pollutants. Tunable band gap, porous layered structure, outstanding stability, as well as cost effective synthesis of graphitic carbon nitride pave new horizons in solar light-assisted photocatalytic degradation of pollutants. Nevertheless, bare g-C_3N_4 suffers limitations such as small specific surface area, photo corrosion, and low visible light utilization efficiency. Moreover, the high recombination rate of photo-induced charge carriers in single-component material significantly shades the photocatalytic as well as quantum efficiencies of g-C_3N_4.Various approaches have been exploited to overcome these problems such as heteroatom doping, metal and non-metal embedding (Bui et al. 2020; Zheng et al. 2020), and coupling with other semiconductors (Wu et al. 2020; Liu et al. 2020a). This review provides a comprehensive survey on the photocatalytic application of visible-light-responsive g-C_3N_4 photocatalyst for the effective eradication of different active pharmaceutical ingredients from water bodies. The work also outlines the recent advances in the enhancement of photocatalytic efficiencies of g-C_3N_4 photocatalysts along with their modification using various doping agents, heterostructure or composite formation, and exploration of multi-component oxides. Furthermore, we also focused on the mechanistic degradation pathway through which APIs are detoxified and give an insight into future furtherance in this field.

Graphitic carbon nitride-based photocatalysts for the eradication of pharmaceutical compounds

Graphitic carbon nitride (g-C_3N_4) is an environmentally benign, inexpensive metal-free semiconductor photocatalyst, having good physio-chemical stability as well as an appealing electronic structure with a medium band gap of 2.7 eV (Zhao et al. 2015b). The sole properties such as high mesoporous volume, high surface area, conjugated porous polymeric structure, visible light response, and high adsorption capacity enable g-C_3N_4 to be an ideal candidate for the catalytic removal of hazardous organic pollutants in aqueous medium (Dong and Zhang 2012; Zhu et al. 2014; Cao et al. 2020a).

It consists of 2D sheets of tris-s-triazines interconnected via tertiary amines and can be easily synthesized from richly available materials such as dicyandiamide, cyanamide, melamine, urea, and thiourea (Fig. 1) by calcinating at high temperatures (Cao et al. 2015).

Studies revealed that the precursor of graphitic carbon nitride has significant influence on its properties. In 2017, Panneri et al. investigated the role of precursors such as cyanamide, melamine, urea, and thiourea on the photophysical properties of carbon nitride for the degradation of tetracycline (TC) under visible light irradiation. The photocatalytic efficiency of g-C_3N_4 obtained from different precursors followed the trend; urea-derived g-C_3N_4 (U-CN) >thiourea-derived g-C_3N_4 (T-CN) > cyanamide-derived g-C_3N_4 (C-CN) > melamine (M-CN)-derived g-C_3N_4. The urea-derived graphitic carbon nitride showed excellent photocatalytic activity, whereas melamine-derived g-C_3N_4 showed the least activity towards tetracycline degradation. The increased TC degradation efficiency of U-CN is attributed to its high surface area values (BET surface area is 153 m^2g^{-1}) and reduced recombination rate of charge carriers. On visible light irradiation, photogenerated electrons in the conduction band of g-C_3N_4 react with molecular oxygen to form superoxide anion radical ($^{\bullet}O_2^-$). Studies on active species in U-CN with different radical scavengers (isopropanol, $AgNO_3$, benzoquinone, and triethanolamine) implied that these superoxide anion radicals as well as holes in the valence band triggered decomposition of the tetracycline molecules.

Several studies on the degradation of pharmaceutical pollutants by graphitic carbon nitride have been reported. Polymeric graphitic carbon nitride synthesized via polycondensation of melamine could successfully degrade different pharmaceutical products such as tetracycline, ciprofloxacin, salicylic acid, and ibuprofen under UV-visible light irradiation (Hernández-Uresti et al. 2016).The polymeric g-C_3N_4 showed a better degradation activity towards tetracycline (86%) and ciprofloxacin (60%) than salicylic acid (30%) and ibuprofen (20%) in acidic medium. The degree of mineralization of these drugs follows the order; tetracycline > salicylic acid > ciprofloxacin> ibuprofen. A recent study provides fundamental insights into enhanced photodegradation of pharmaceuticals such as naproxen (NPX),indomethacin (IDM), diclofenac (DCF), carbamazepine (CBZ), triclosan (TCS), ofloxacin (OFX), enrofloxacin (ENR), and sulfamethoxazole (SME), by improving the crystallinity of the pristine graphitic carbon nitride (Wang et al. 2020). The crystalline structure eases the

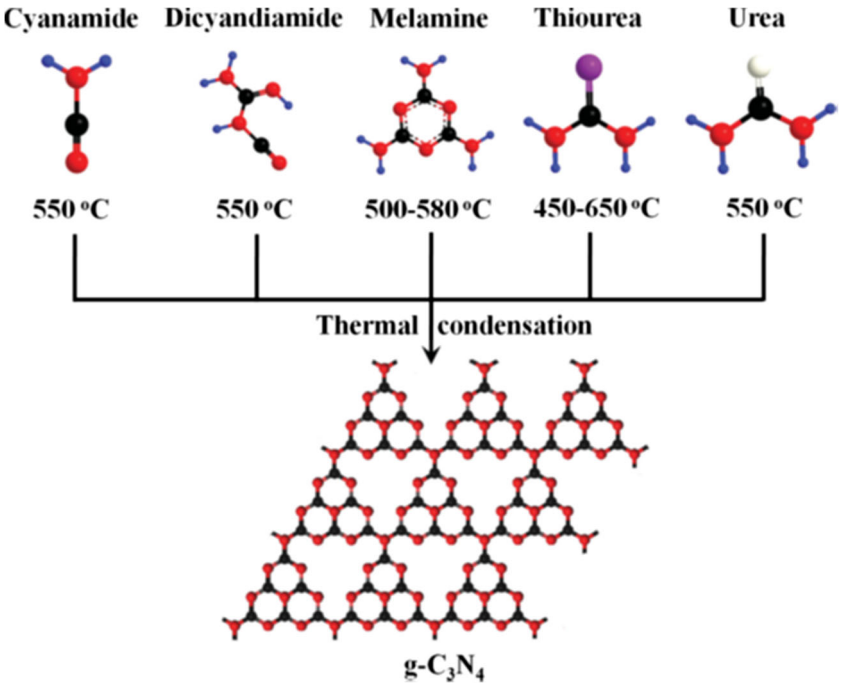


Fig. 1 Schematic illustration of synthetic routes of graphitic carbon nitride (reproduced from Ref. (Cao et al. 2015) with the permission of Wiley Inc.)

dissolved O_2 absorption and allows a direct oxygen reduction via one-step two-electron pathway. As an effect, the crystalline carbon nitride generates more H_2O_2 and thereby more hydroxy radicals for the decomposition of pharmaceuticals and was substantiated by experimental and computational analysis. Authors also proposed three major degradation pathways of naproxen (NPX) using crystalline carbon nitride, i.e. hydroxylation, decarboxylation, and demethylation reactions (Fig. 2). The hydroxylation pathway involves the electrophilic attack of hydroxyl radical on naphthalene ring in naproxen (NPX) and produce hydroxylated intermediate product (m/z=262).The cleavage of carboxylic groups (decarboxylation pathway) leads to the formation of carbon centred radicals (T1) which on subsequent reaction with $^{\bullet}O_2^{-}$. Hydroxyl radical ($^{\bullet}OH$) and holes (h^+) generate intermediate products like 2-(1-hydroperoxyethyl)-6-methoxynaphthalene (m/z=218), 2-methoxy-6-vinylnaphthalene (m/z =184), 1-(6-methoxynaphthalen-2-yl)ethanone (m/z =200), and 2-ethyl-6-methoxynaphthalene (m/z =186).The demethylation reaction of naproxen also produce the intermediates 2-(6-hydroxynaphthalen-2-yl)propanoic acid (m/z =216) and 6-vinylnaphthalen-2-ol (m/z=170). These intermediates on further oxidation converted into greener products, CO_2 and H_2O. The crystalline carbon nitride (CCN) achieved 98.4% of degradation of naproxen (NPX) upon 70 min visible light irradiation.

Even though g-C_3N_4 is a visible light active photocatalyst, high recombination rate of photogenerated charge carriers and low specific surface area significantly reduces its photocatalytic efficiency. Strategies like introducing vacancy defects and heteroatoms (Niu et al. 2012; Zhou et al. 2020; Zhang and Dai 2015), doping of metals/non-metals (Xu et al. 2013; Tonda et al. 2014; Thomas et al. 2018; Kavitha et al. 2020; Jiang et al. 2017; Hong et al. 2012; Liu et al. 2016), and coupling of narrow band gap semiconductors (Wei et al. 2017;Ye et al. 2016) have been adopted to overcome the drawbacks of g-C_3N_4. Some of the beneficial attempts in this regard for the degradation of pharmaceutical pollutants are discussed in this review.

Vacancies induced graphitic carbon nitride

Intrinsic point defects like cation vacancies, anion vacancies, and interstitial atoms can alter the electronic structure of photocatalyst and act as specific reaction sites for reactant molecules (Niu et al. 2012). Recently, Zhou and co-workers (Zhou et al. 2020) reported nitrogen vacancy installed carbon nitride nanosheets (g-C_3N_4-V_NNs) for efficient degradation of tetracycline antibiotic. In this study, modification of g-C_3N_4 sheets with nitrogen vacancy (g-C_3N_4-V_N Ns) was accomplished by gas reduction method. g-C_3N_4-V_N Ns displayed significant reduction in bandgap (2.45 eV) and forms energy disordered interfaces allowing good exciton dissociation for photogenerated electron-hole pairs (Fig. 3) which facilitate enhanced $^{\bullet}OH$ generation for the degradation of tetracycline.

Another study reported the degradation of carbamazepine (CBZ), using nitrogen vacancy induced graphitic carbon nitride (NV-g-C_3N_4) photocatalyst. Herein, NV-g-C_3N_4 was prepared via thermal condensation of melamine under N_2 flow (Cao et al. 2019). From photoluminescent spectra and transient photocurrent response, it is clear that introduction of nitrogen vacancies in the catalyst effectively traps photogenerated electrons. Thus, holes accumulating in the valence band produce sufficient sulphite radicals by activation of sulphite anions. They found that

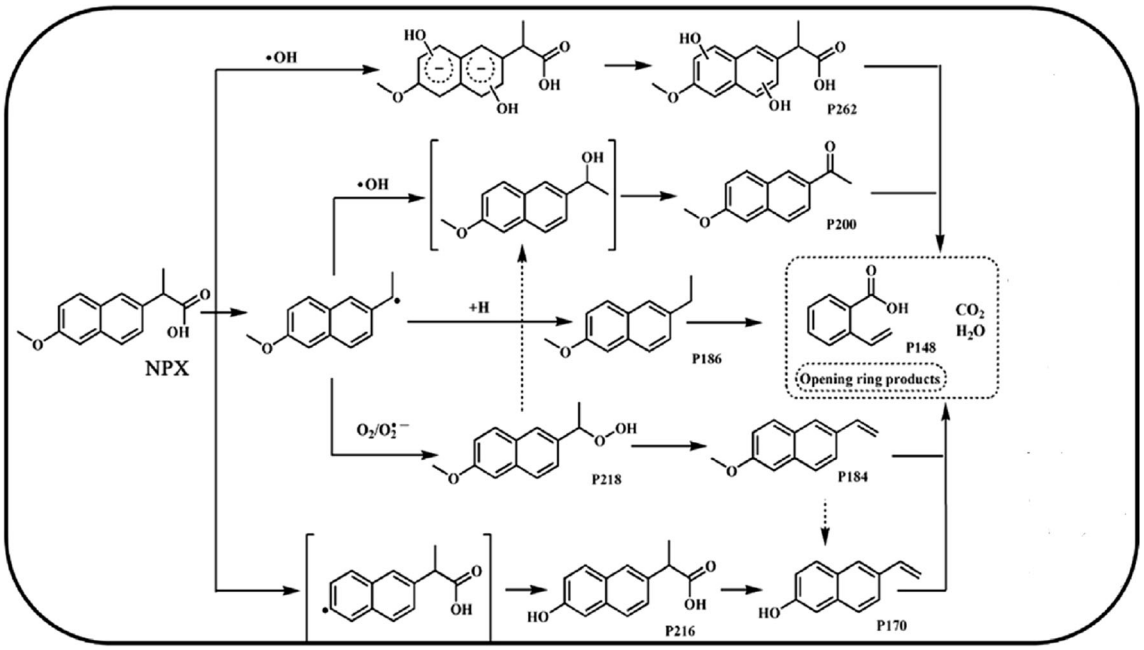


Fig. 2 Degradation mechanism of naproxen (NPX) by crystalline carbon nitride (Reproduced from Ref (Wang et al. 2020), with the permission of Elsevier publications)

NV-g C_3N_4/Na_2SO_3 catalytic system was able to degrade 97% (42 μmol L^{-1}) carbamazepine (CBZ) within 120 min, whereas bulk-g-C_3N_4/Na_2SO_3 system degrades only about 56% of carbamazepine. The intermediates formed during the degradation of carbamazepine (CBZ) were identified by LC-MS and given in Fig. 4. When sulphite radical attacks carbamazepine, it gets oxidized to epoxy carbamazepine which generates acridinium-9-carbaldehyde (via ring contraction) as well as di-hydroxylated carbamazepine as intermediates. These intermediates on further attack by sulphite radicals convert into carboxylic acids such as terephthalic acid, benzoic acid, succinic acid, and formic acid and finally decompose to non-toxic by-products.

Metal and non-metal doped graphitic carbon nitride

Studies revealed that metal/non-metal doping increases the photocatalytic activity of g-C_3N_4. Doping of metal or non-metal atoms has been widely recognized as an efficient and suitable approach, for tailoring the electronic structure and band gap of g-C_3N_4 for the improvement of its photocatalytic properties. These dopants help in trapping electrons and decrease the possibilities of electron-hole recombination that inactivates the photocatalytic system. Studies also revealed the utilization of broad-spectrum of solar light up on doping, whereas pristine g-C_3N_4 could absorb only blue light.

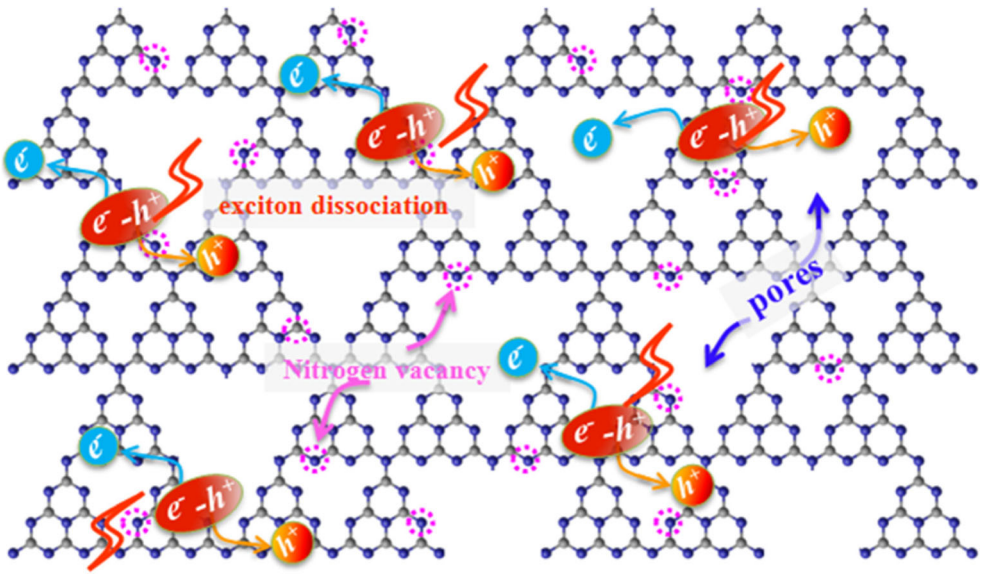


Fig. 3 Mechanism for vacancy mediated exciton dissociation in g-C_3N_4-V_NNs (reproduced fromRef. (Zhou et al. 2020), with the permission of Elsevier publications)

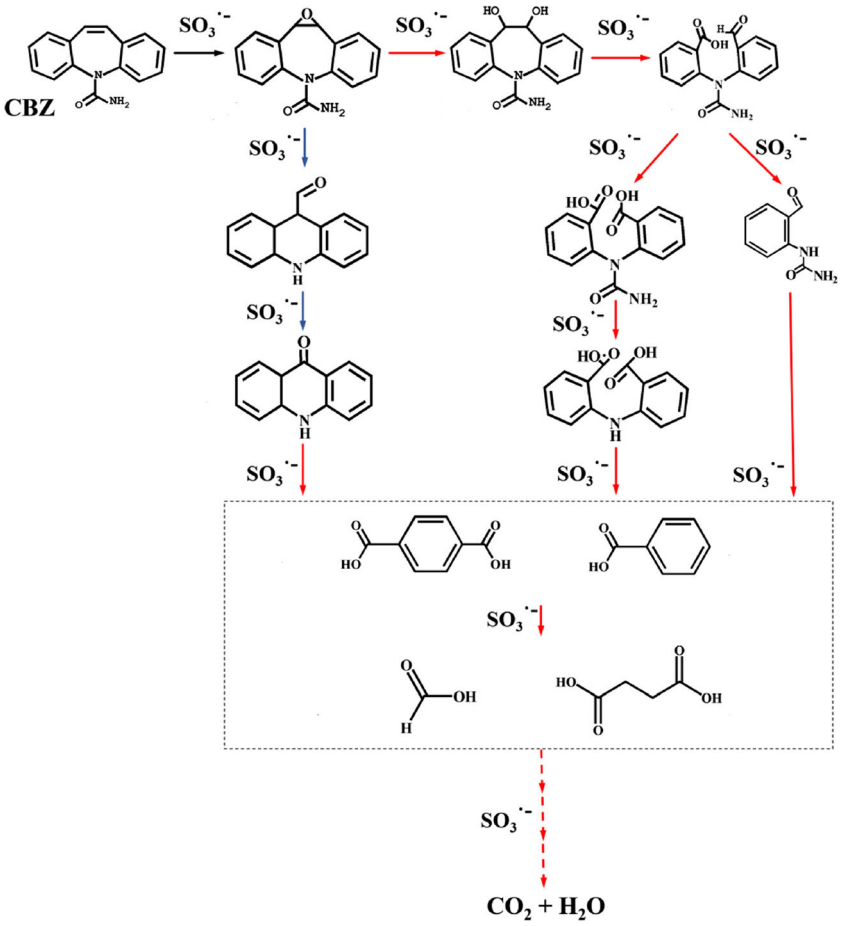


Fig. 4 Intermediates formed in the process of photodegradation of carbamazepine (CBZ) by sulphite radical in the NV-g-C_3N_4/Na_2SO_3 system (reproduced from Ref. (Cao et al. 2019) with the permission of Elsevier publications)

Graphitic carbon nitride serves as effective substrate for the fine distribution of metals without serious agglomeration on metal doping, and rich amine groups offer better compatibility for affixing the metal NPs by diminishing their size and improving the stability. The catalytic active sites offered by the metal atoms also enhance the efficiency of desired redox responses of graphitic carbon nitride (Kavitha et al. 2020). When noble metals like Ag and Au nanoparticles were used as dopants in g-C_3N_4, a significant enhancement in the photocatalytic efficiency was observed (Gondal et al. 2016; Azizi-Toupkanloo et al. 2019) and is due to the broadening of visible light absorption (surface plasmon effect (SPR). Minh Tri et al. (2019) developed Ag-doped g-C_3N_4 catalyst and applied towards toxic antibiotic contaminants, especially tetracycline (TC) in hospital wastewater under solar light. Ag-doped g-C_3N_4 could attain 96.8% degradation of tetracycline (TC) in 120 min solar light illumination by complete deterioration of TC into smaller intermediate molecules and finally to carbon dioxide and H_2O (Fig. 5).

Another study reports the increased activity of Ag doped g-C_3N_4 for the degradation of morphine, a hard-degradable pharmaceutical under sunlight (Azizi-Toupkanloo et al. 2019). Total organic carbon (TOC) analysis indicates that Ag@g-C_3N_4 attained 91% of mineralization of morphine. Ag ions in Ag@g-C_3N_4 matrix trap photoexcited electrons in the conduction band of g-C_3N_4 and reduce the recombination rate of charge carriers. These entrapped electrons react with molecular oxygen (O_2) and form superoxide radical anion. Studies on active species confirm that superoxide radical anion acts as major reactive species in the photocatalytic degradation of morphine.

H. Hori and his co-workers made use of graphitic carbon nitride for the degradation of monoethanolamine (MEA) which is a component of pharmaceuticals (Hori et al. 2018). Degradation of MEA has become inevitable as it gets converted into carcinogenic nitrosamines and nitramines in solution. Degradation studies showed that graphitic carbon nitride subjected to hydrothermal treatment with sodium hydroxide (HT-g-C_3N_4) gives significant decomposition of MEA. HPLC and ion chromatography analysis confirmed that HT-g-C_3N_4 successfully degraded MEA into HCOOH, NO_2^-, NO_3^-, and NH_3. Also, metals such as Ag and Pt, when incorporated with HT-g-C_3N_4, enhanced the efficiency of HT-g-C_3N_4 and accelerated the formation of NO_2^- and NO_3^-. Salicylic acid, a pharmaceutical secondary standard pollutant, was effectively degraded by Thomas et al. (2018) using samarium doped graphitic carbon nitride nanosheets. Sm^{3+} doping prevents the recombination of photoexcited electrons and holes and was

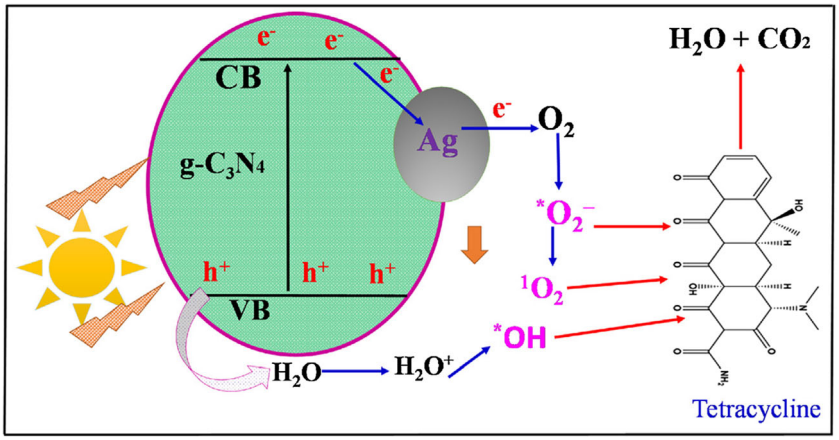


Fig. 5 Schematic diagram of mechanism involved in the photocatalytic degradation of tetracycline (TC) under visible light (reproduced from Ref. (Minh Tri et al. 2019) with the permission of Elsevier publications)

found to significantly enhance the photocatalytic activity under sunlight. Among the doped samples, g-C_3N_4-0.02 wt% Sm^{3+}doped sample showed highest photocatalytic efficiency and attained complete degradation of salicylic acid within 180 min under sunlight. Proposed degradation mechanism of pollutants by Sm^{3+}-doped g-$C_3N_4$is given in Fig. 6.

Recently, barium-doped graphitic carbon nitride (BCN) prepared via simple thermal polymerization method is found efficient in degrading tetracycline (TC) antibiotic (Bui et al. 2020). Two per cent barium-loaded BCN exhibited 91.94% degradation for TC at pH 10 upon 120-min visible light illumination. Incorporation of barium nanoparticles not only significantly decreased the band-gap energy of graphitic carbon nitride (2.71 to 2.56eV) but also increased the surface area which played key role in enhancing its photocatalytic performance. The active species studies indicate that photogenerated holes are the dominant oxidative species in degrading TC through different process including demethylation, deamination, and ring cleavage and converted TC into simpler products with m/z=102.10 (hexan-2-ol) and m/z=88.09 (pentan-3-ol). Bezafibrate (BZF), a persistent fibrate pharmaceutical having two aromatic rings and a fibrate chain, was successfully decomposed by palladium doped graphitic carbon nitride (Pd/g-C_3N_4) (Yin et al. 2020). One per cent Pd/g-C_3N_4 photocatalysts showed almost 100% BZF (3mg/L, pH=7) removal efficiency in 90 min of visible light irradiation with a rate constant 2.9 times higher than that of pure g-C_3N_4. Authors proposed three main possible photocatalytic degradation pathways of BZF including R-oxy substituent, $^{\bullet}$OH-addiction, and oxidative dechlorination using LC–MS/MS analysis (Fig. 7).Toxicity studies were also performed on BZF throughout the photocatalytic process which clearly indicates the reduction of genotoxicity of BZF solution along with the enhancement of photocatalytic efficiency upon Pd doping.

Non-metal doping is a viable and cost-effective technique which could enhance the visible-light absorption of g-C_3N_4, improve its carrier suppleness, and ease the separation of photogenerated electron-hole pairs, while maintaining its metal-free properties. Incorporation of non-metal such as sulphur (Cao et al. 2018a), phosphorus (Ran et al. 2015; Deng et al. 2017), oxygen (Qu et al. 2018), carbon (Li et al. 2014), nitrogen (Fang et al. 2015), and halogens (Zhang et al. 2013; Lan et al. 2016; Wang et al. 2010) into the g-C_3N_4 motifs has unaccountably improved the photocatalytic efficiency of graphitic carbon nitride for the effective removal of water pollutants. For instance, when phosphorus and oxygen is doped with g-C_3N_4 (POCN), an inexplicable enhancement in the photocatalytic degradation of fluoroquinolone antibiotics (enrofloxacin) (Huang et al. 2019) is detected. POCN was synthesized via one-step thermal polymerization method using guanidinium hydrochloride as g-C_3N_4 precursor, hexachlorocyclotriphosphazene, and polyvinylpyrrolidone reagent as phosphorus and oxygen dopants. The optimum concentration of phosphorus and oxygen in the POCN is about 15% and 0.01%, respectively. Electron spin resonance spectroscopy analysis which demonstrated phosphorus doping endorsed the generation of reactive oxygen species, i.e. superoxide anion radicals which played momentous roles in the photocatalytic decay of enrofloxacin (ENFX) under the visible light.

A broad-spectrum carbon- and oxygen-doped, porous g-C_3N_4 (COCN) found effective in the degradation of non-steroidal anti-inflammatory drug, indometacin (IDM). In this study, dicyandiamide and methylamine hydroiodide (CH_3NH_2·HI) were co-pyrolyzed for the synthesis of COCN photocatalyst. The utilization of CH_3NH_2·HI reagent as carbon dopant enables the introduction of −OH groups in the terminal resulted by the reaction between HI gas generated during thermal condensation and NH_3. The optimal sample 0.3COCN exhibited excellent photocatalytic degradation of IDM (5.9 times higher than pristine g-C_3N_4). The improved photocatalytic activity of COCN is attributed to the enhanced surface area and effective charge separation. Also, carbon and oxygen doping enabled the utilization of broad-spectrum of solar light such as yellow light (590 ± 5 nm), red light (655 ± 5 nm), and blue light (450 ± 5 nm). Active species studies

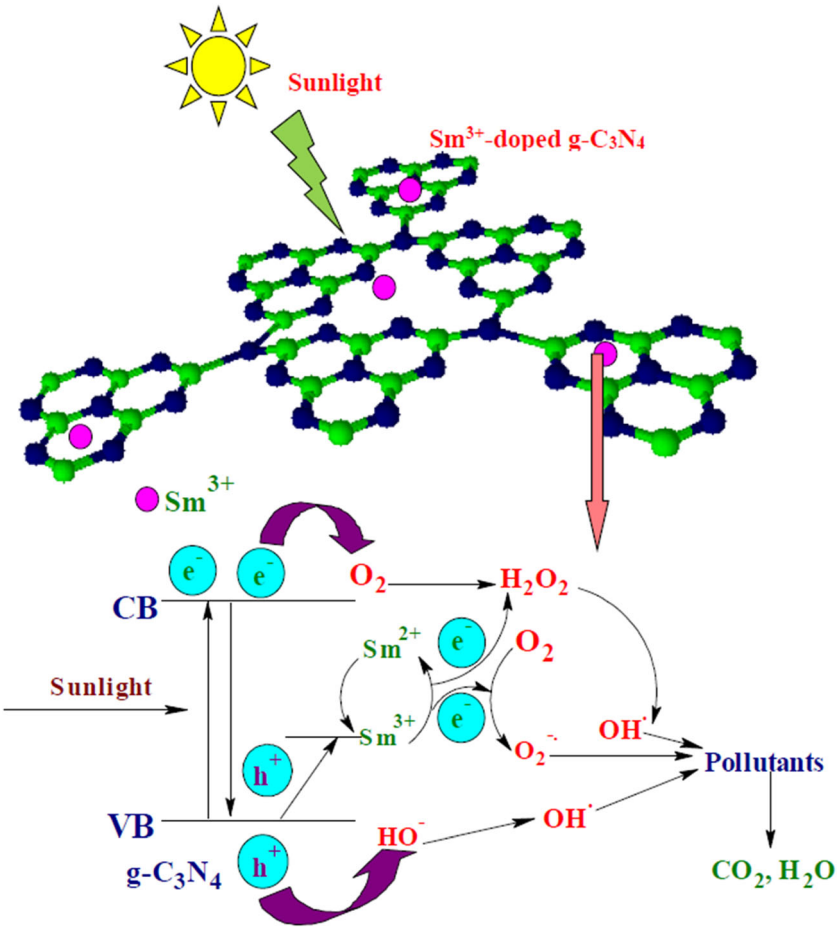


Fig. 6 Pollutant degradation mechanism using Sm^{3+}-doped g-C_3N_4 under sunlight (reproduced from Ref. (Thomas et al. 2018) with the permission of Elsevier publications)

indicate that superoxide anion radical, hydroxy radical, and singlet oxygen ($^1O_2$) played a major role in the degradation of IDM. Electron spin resonance (ESR) spectra evidence that COCN catalyst exhibited higher H_2O_2 generation leading to the formation of hydroxyl radicals. Generation of active species by COCN catalyst on visible light irradiation is as follows (Zheng et al. 2020).

$$\begin{aligned} \text{COCN} + h\nu &\rightarrow h^+ + e^- \\ OH^- + h^+ &\rightarrow {}^\bullet OH \\ O_2 + e^- &\rightarrow {}^\bullet O_2^- \\ {}^\bullet O_2^- + h^+ &\rightarrow {}^1O_2 \end{aligned}$$

$$\begin{aligned} 2H^+ + {}^\bullet O_2^- &\rightarrow HO_2^\bullet \\ 2HO_2^\bullet &\rightarrow H_2O_2 + {}^1O_2 \\ H_2O_2 + e^- &\rightarrow {}^\bullet OH \end{aligned}$$

The possible degradation pathway of IDM using COCN photocatalyst is shown in Fig. 8.

Dual doping/co-doping of non-metals and metals in graphitic carbon nitride is an attractive remedial approach to overcome the limitations of g-C_3N_4 including rapid recombination rate of photogenerated electrons and holes and low visible light absorption efficacy. Co-doping of non-metals and metal ions allows the unification of the merits of single dopants and imparts positive effects on the structural and photometric properties of g-C_3N_4 (Jiang et al. 2017). Literature reports that this dual doping appreciably enhances the photocatalytic efficiency of g-C_3N_4 for the degradation of organic pollutants present in water (Hu et al. 2014; Zhao et al. 2015a). Nguyen and his co-workers (Nguyen et al. 2020) co-doped silver and phosphorus on urea-derived graphitic carbon nitride (UCN) nanosheets (Ag/P/UCN). Ag/P/UCN composite with band gap 2.51eV could achieve 99% degradation of sulfamethoxazole (SMX) solution under basic conditions within 30 min. Uniformly distributed crystalline, nano-Ag particles on the surface of the catalyst improved light absorbance capacity and functioned as electron sink to capture photogenerated electrons and inhibited recombination of photo-induced charge carriers. Ag/P/UCN found to be stable and reusable up to six consecutive cycles without losing its photocatalytic activity. Paragas et al. (2018) reported about 99% degradation of sulfamethoxazole using iodine and potassium co-doped g-C_3N_4 (IK-g-C_3N_4) in a time span of 45 min visible light irradiation. Herein the catalyst was synthesized by the co-pyrolysis of urea and potassium iodate and showed

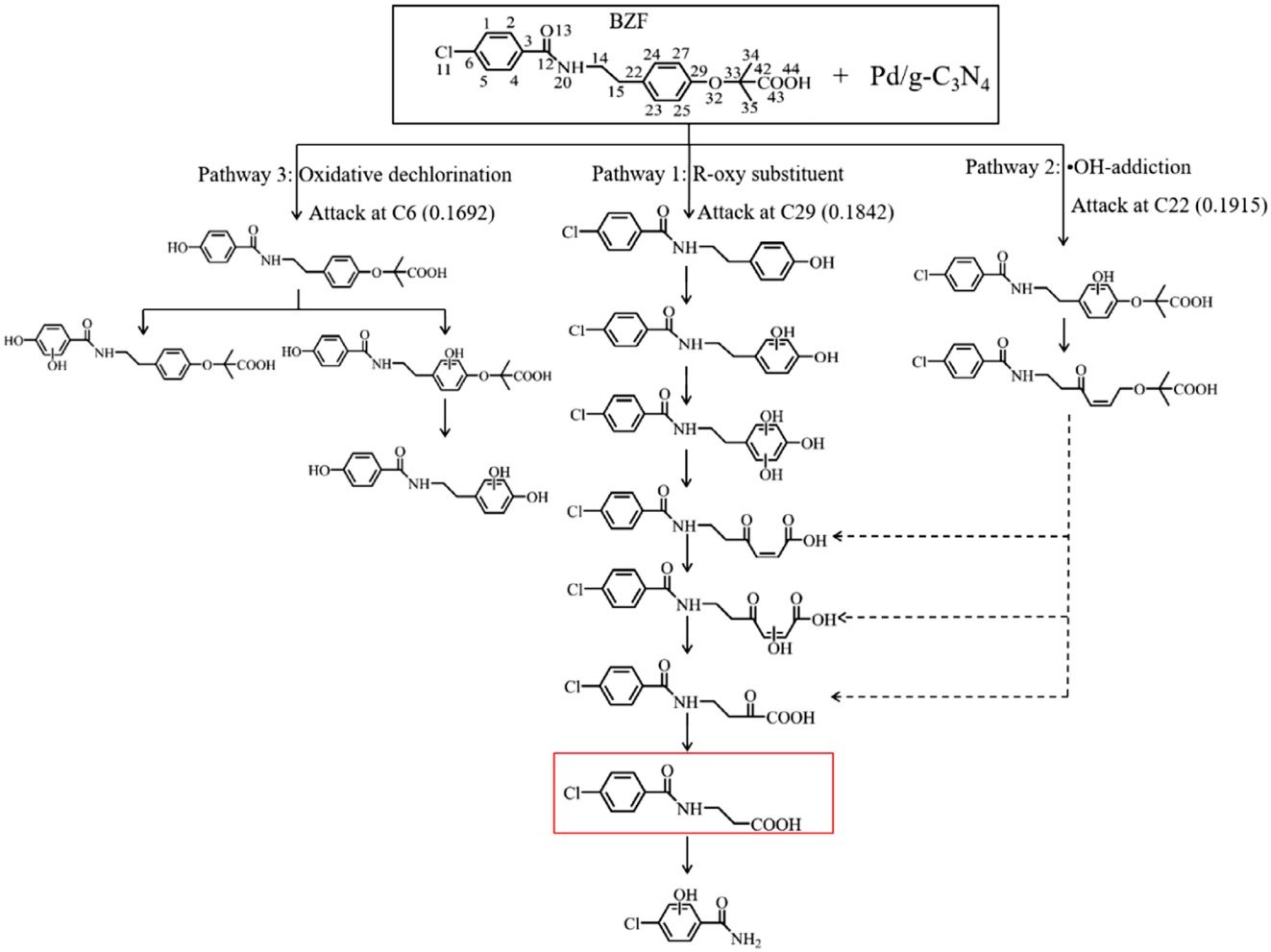


Fig. 7 Degradation pathway of bezafibrate by Pd/g-C_3N_4 (reproduced from Ref. (Yin et al. 2020) with the permission of Elsevier publications)

recyclability up to 3 runs. Iodine and potassium doping enhanced charge carrier transfer rate resulting in the rapid formation of excitons. These excitons react with oxygen species and water molecules to form superoxide anions radical ($^{\bullet}O_2^-$) and hydroxyl radical ($^{\bullet}OH$), respectively. These radicals played a vital role in the degradation of sulfamethoxazole. It was also observed that co-doping of Na and Cl into the g-C_3N_4 (CN-NaCl) framework strikingly enhanced the photocatalytic activity of g-C_3N_4 (Wang et al. 2019). CN-NaCl was developed via one-step thermal condensation of dicyanamide and sodium chloride. Doping of both Na and Cl causes narrowing of the band gap of g-C_3N_4 from 2.76 to 2.67 eV and enabled the rapid transfer of photogenerated electrons and holes to the surface of g-C_3N_4 via sodium ion and chlorine ion channels to achieve significant separation between electron-hole pairs. On 60 min exposure of visible light, the optimized sample CN-NaCl-0.5 degraded 66.6% of tetracycline hydrochloride. The Table 1 summarizes the studies on the degradation of different pharmaceutical compounds by metal and non-metal doped g-C_3N_4based photocatalysts.

Heterojunctions based on graphitic carbon nitride

Construction of heterostructures is a powerful method to boost the photocatalytic performance of g-C_3N_4 photocatalysts by promoting the separation of photo-induced electron-hole pairs and allows the transfer of charge carriers across the interface of the heterostructure to impede the recombination of charge carriers (Kong et al. 2016). The unique two-dimensional layered structure of g-C_3N_4 and its flexibility due to its polymeric feature favours the formation of heterojunctions with various semiconductors, including metal oxides (Le et al. 2017), metal chalcogenides (Chen et al. 2016), and multicomponent oxide (Wang et al. 2012). Recent studies on degradation of pharmaceutical compounds by graphitic carbon nitride-based heterojunctions (Du et al. 2020;Yashas et al. 2020; Liu et al. 2020b; Zhang et al. 2020a; Devi et al. 2019; Liu et al. 2020a, b; Lv et al. 2020; Zhang et al. 2020b;Liang et al. 2020; Zhang et al. 2020c;Cao et al. 2020a, b, c; Ma et al. 2019;Das et al. 2020;Wu et al. 2020) and their degradation efficacies are given in Table 2

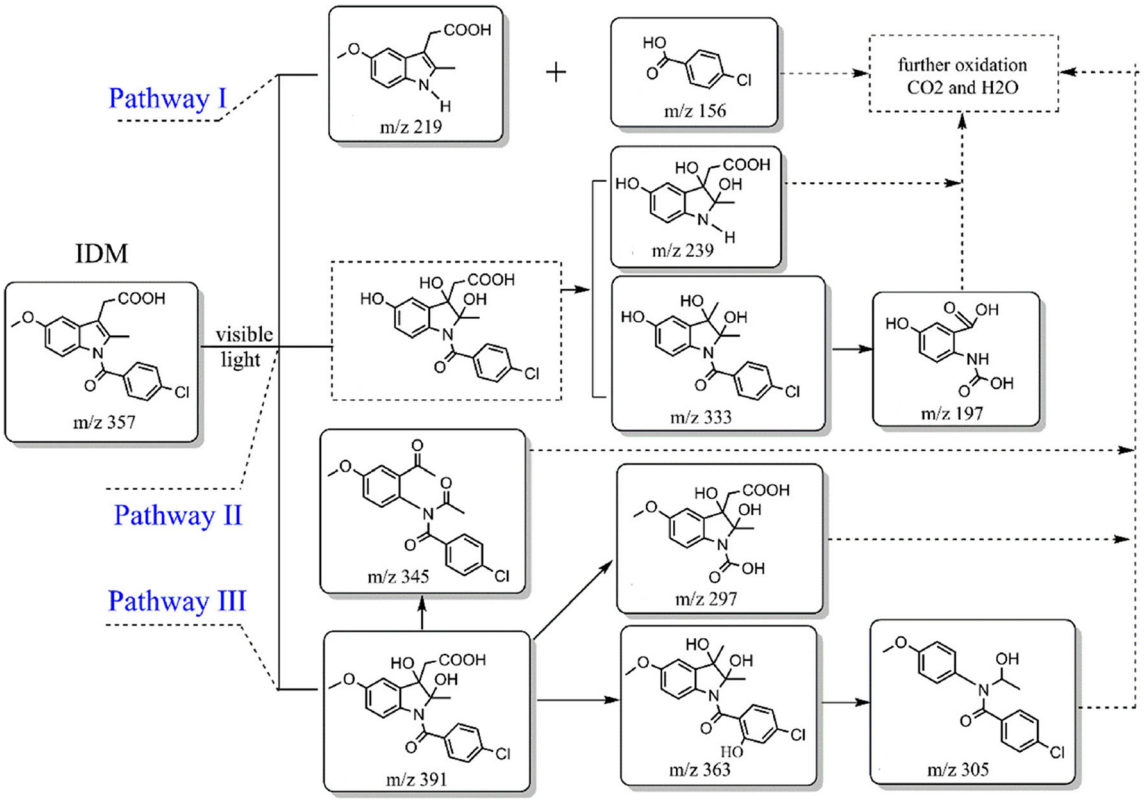


Fig. 8 Plausible degradation pathway of IDM using COCN photocatalyst (reproduced from Ref. (Zheng et al. 2020) with the permission of Elsevier publications)

Self-type heterojunction of graphitic carbon nitride is found effective for the degradation of tetracycline antibiotic (Muhmood et al. 2017). Self-type heterojunction was achieved by hydrothermal treatment of two different g-C_3N_4 derived from dicyanamide and melamine precursors. Photoelectrochemical analysis displayed that this self-type heterojunction possesses high photo-current density due to low recombination rate of charge carriers. Increased surface area, reduced band gap (1.2 eV), and prolonged lifetime of charge-carries enhanced its photocatalytic activity towards tetracycline and attained complete degradation after 70 min of visible light illumination. When metal oxides like cobalt oxide (CoO) form heterojunction with graphitic carbon nitride, both its photocatalytic activity and adsorption capacity increase. Niu et al. (2019) employed two-step impregnation-calcination method for the fabrication of CoO/g-C_3N_4 photocatalyst in which melamine was used as precursor for synthesis of g-C_3N_4. Incorporation of CoO nanoparticles fascinatingly enhanced tetracycline (TC) removal efficiency by adsorption. Even though CoO/g-C_3N_4 attained 73.12% of adsorptive removal of tetracycline (TC), only about 29.87% of photodegradation of tetracycline (TC) was observed. The study revealed that cobalt oxide (CoO) nanoparticles loaded on the surface of g-C_3N_4 act as adsorption sites, rather than cocatalyst for photocatalysis.

The efficiency of graphitic carbon nitride-based photocatalytic systems can be improved by the formation heterojunction between graphitic carbon nitride and metallic semiconductors with well-matched band gap and redox potential. Researchers are now focussing on the development of magnetically separable photocatalytically active g-C_3N_4 heterostructures by incorporating magnetic particles like Fe_3O_4 (Mousavi and Habibi-Yangjeh 2018) and $NiFe_2O_4$ (Sudhaik et al. 2018) which facile the easy recovery of catalyst. Magnetically recoverable g-C_3N_4 heterostructures with $NiFe_2O_4$ were constructed by Sudhaik and co-workers and were used for the photocatalytic removal of oxytetracycline (OTC) antibiotics from wastewater (Sudhaik et al. 2018). This ferromagnetic GCN/$NiFe_2O_4$ composite was synthesized by thermal condensation of urea followed by $NiFe_2O_4$ nanoparticles loading. SEM and TEM studies show a uniform dispersion of $NiFe_2O_4$ in the catalyst. GCN/$NiFe_2O_4$ composite displayed 60% of adsorptive removal oxytetracycline (OTC) in dark. The simultaneous adsorption and photocatalysis process of composite removed 94% of oxytetracycline (OTC) at pH 5 upon 60 min of irradiation of solar light. The mineralization studies on OTC showed 99% of COD removal by GCN/$NiFe_2O_4$ catalytic system. With the aid of magnetic separation, GCN/$NiFe_2O_4$ exhibited recycle efficacy of about 10 catalytic runs. Pantoprazole, a widely used drug for the treatment of gastrointestinal ailment was effectively degraded by

Table 1 Summary of studies on degradation of pharmaceutical compounds by metal- and non-metal-doped g-C_3N_4 based photocatalysts

Catalyst	Synthetic method	Irradiation time (min)	Targeted pharmaceuticals	Source	% of degradation	Reference/year
Fe^{3+}-g-C_3N_4	Thermal condensation	90	Sulfadiazine (2 mg/L)	White LED light (3W)	99.8%	Ou et al. 2020
Ag-g-C_3N_4	Thermal condensation	120	Oxytetracycline (30 mg/L)	Xenon lamp (300 W)	98.7%	Viet et al. 2019
Ag-g-C_3N_4	Thermal condensation	120	Tetracycline (20 mg/L)	Solar light	96.8%	Minh Tri et al. 2019
Sm^{3+}-g-C_3N_4	Thermal condensation	180	Salicylic acid (40 mg/L)	Sunlight	100%	Thomas et al. 2018
Ba-g-C_3N_4	Thermal condensation	120	Tetracycline (20mg/L)	Xenon lamp (150 W)	91.94%	Bui et al. 2020
Pd-g-C_3N_4	Thermal condensation	90	Bezafibrate (3mg/L)	Xenon lamp (500 W)	79.39%	Yin et al. 2020
Ag-P@UCN	Co-pyrolysis	30	Sulfamethoxazole (5 mg/L).	Visible lamps	99%	Nguyen et al. 2020
I-K-g-C_3N_4	Co-pyrolysis	45	Sulfamethoxazole (10 mg/L)	Visible light lamps	99%	Paragas et al. 2018
Na-Cl-g-C_3N_4	Co-pyrolysis	60	Tetracycline (10 mg/L)	Xe lamp (350 W)	66.1%	Wang et al. 2019

using Fe_3O_4/ZnO nanorods anchored g-C_3N_4 sheets (Raha and Ahmaruzzaman 2020). This photocatalyst achieved 97.09% degradation of pantoprazole on 90 min of LED irradiation (Philips 23 W white LED) with a TOC removal of 85.45%. Studies reported that the addition of H_2O_2 into the photocatalytic system enhanced the activity of the catalyst and facilitated 98.43% degradation of pantoprazole with a rate constant 0.04863 min^{-1} and attained 88.13% TOC removal. HRLCMS data depicts two possible degradation pathways for pantoprazole as shown in Fig. 9. The integration of Fe_3O_4 nanoparticles enabled ready retrieval of catalyst by magnetic separation and displayed constancy up to 4 cycles.

Metal chalcogenides like CdS, $ZnIn_2S_4$ incorporated graphitic carbon nitride heterojunctions exhibited significant enhancement in the photocatalytic activity and successfully degraded the pharmaceuticals like sulfamethazine and tetracycline (Cao et al. 2018b; Guo et al. 2017). Cadmium sulphide/graphitic carbon nitride (CdS-TGA/g-C_3N_4), isotype heterojunction was developed by the thermal polymerization of carboxylic acid-functionalized CdS nanoparticles and urea (Cao et al. 2018b). The interaction between acid groups on CdS-TGA NPs and amine groups on urea help to buildup well combined interface, which highly promoted the mobility of electron hole pairs. This also ensured the efficient separation of photogenerated charge carriers and stabilization of CdS. During photocatalytic degradation, photo-induced holes and the hydroxy radical attack the sulfamethazine and break sulfonate bonds to form intermediate products which on subsequent loss of amino groups mineralize to ammonia, carbon dioxide, and water. Major intermediates such as N-(4,6-dimethylpyrimidin-2-yl)benzene-1,4-diamine (m/z=215), 4-(4,6-dimethylpyrimidin-2-yl) aniline (m/z=199), and 2-phenylpyrimidine (m/z=156) formed during the photocatalytic degradation of sulfamethazine were examined by HPLC-MS given in Fig. 10

g-C_3N_4/$ZnIn_2S_4$ was another g-C_3N_4-based heterojunction introduced by Guo et al. (2017) for the decomposition of antibiotic tetracycline. g-C_3N_4/$ZnIn_2S_4$ heterojunction could reasonably enhance the charge carrier separation by promoting easy transfer of photogenerated electrons in the conduction band (−1.22eV) of g-C_3N_4 to the conduction band (−0.8eV) of $ZnIn_2S_4$. Simultaneously, holes in the valence band of$ZnIn_2S_4$ move to the valence band of g-C_3N_4. Further, these electrons in the conduction band of $ZnIn_2S_4$ convert molecular oxygen into $^{\bullet}O_2^-$. These active radicals as well as holes in the valence band of g-C_3N_4 directly oxidize tetracycline into non-hazardous by-products such as CO_2 and H_2O. The 50 wt.% g-C_3N_4/$ZnIn_2S_4$ displayed excellent photocatalytic degradation of tetracycline which was about 22.2% higher than pristine g-C_3N_4.

Reports are available for the enhancement of photocatalytic activity by quantum dot integration; Yuan et al. (2019) incorporated graphene quantum dots (GQDs) into g-C_3N_4 nanorods (g-CNNR) through hydrothermal method and used for the photocatalytic degradation of oxytetracycline (OTC). Characteristics studies of GQDs/g-CNNR photocatalyst indicate that it has a high crystallization level, enhanced visible light absorption, and a staggered band alignment. With the increase of GQDs content, the colour of GQDs/g-CNNR samples gradually changes from pale yellow to grey indicating the effective modification of g-CNNR with GQDs. The synthesized GQDs/g-CNNR photocatalyst showed much higher photocatalytic activity than g-C_3N_4 and g-CNNR under visible light and possesses enhanced transportation, separation, and migration rate of the photo-excited electrons and holes. Within 2 h, 0.75% GQDs/g-CNNR

Table 2 Some recent studies on degradation of pharmaceutical compounds by graphitic carbon nitride-based heterojunction

Catalyst	Synthetic method	Irradiation time (min)	Targeted pharmaceuticals	Source	% of degradation (mineralization efficiency)	Reference/year
g-C_3N_4/TiO_2 (persulfate 2 mM)	Calcination	30	Acetaminophen (5 mg/L)	Xenon lamp (300 W)	99.3% (80%)	Du et al. 2020
g-C_3N_4/MnO_2	Sonochemical synthesis	135	Tetracycline hydrochloride (20 mg/L)	LED irradiation (9W, 220 V)	93%	Yashas et al. 2020
CeO_2/gC_3N_4 (persulfate medium)	Thermal condensation	60	Norfloxacin (10 mg/L)	Xenon lamp (150 W, $\lambda > 420$ nm)	88.6% (63.8%)	Liu et al. 2020b
$NaNbO_3$/g-C_3N_4	Hydrothermal-thermal polymerization	30	Ofloxacin (50 μM)	Simulated solar (100 mW/cm^2)	99.55%	Zhang et al. 2020a
NiO/WO_3@g-C_3N_4	Ultra-sonication technique	90	Metronidazole (20 mg/L)	Sunlight	~100%	Devi et al. 2019
gC_3N_4/Bi_2WO_6/rGO	Microwave-hydrothermal treatment	200	Ibuprofen (5ppm in river water)	Sunlight	82.3% (59.2%)	Liu et al. 2020a, b
g-C_3N_4@$CoFe_2O_4$/Fe_2O_3 (20 mg of persulfate)	Thermal annealing Self-assembly procedure	80	Tetracycline Sulfamethoxazole Diclofenac Ibuprofen Ofloxacin (30 mg/L)	Xenon lamp (500 W, $\lambda > 400$ nm)	99.7% 94.8% 97.0% 96.1% 96.5%	Lv et al. 2020
g-C_3N_4@$CoFe_2O_4$/Fe_2O_3 (50mg persulfate)	Thermal annealing Self-assembly procedure	120	Tetracycline Sulfamethoxazole Diclofenac Ibuprofen Ofloxacin (30 mg/L)	Sunlight	Above 90%	Lv et al. 2020
MnO_2/Mn-modified alkalinized g-C_3N_4 (10mmol/L H_2O_2)	Calcination-impregnation method	120	Tetracycline (10 mg/L)	Xe lamp (300 W)	96.7% (74.9%)	Zhang et al. 2020b
P-g-C_3N_4/WC	Calcination	120	Tetracycline (20 mg/L) Ciprofloxacin (20 mg/L)	Xenon lamp (300W, $\lambda > 420$ nm)	93.76% (68.24%) 76.21% (51.73%)	Zhang et al. 2020c
g-C_3N_4/MIL-68(In)-NH_2	Solvothermal method	120	Ibuprofen (20 ppm)	Xenon lamp (300 W, $\lambda > 420$ nm)	93% (~70%)	Cao et al. 2020c
CTFNS/g-C_3N_4	Electrostatic self-assembly method	180	Sulfamethazine (10 ppm)	Xenon lamp (500W)	95.8 %.	Cao et al. 2020b
ZnTCPP/gC_3N_4	Thermal polycondensation	120	Tetracycline (30 mg/L)	Visible light irradiation ($\lambda \geq 400$ nm)	80.3%	Ma et al. 2019
Polypyrrole sensitized zinc ferrite/g-C_3N_4	In situ polymerization method	120	Ciprofloxacin (20ppm)	Visible light	92% (78%)	Das et al. 2020
Carbon dots/g-C_3N_4	Hard templating method	25	Naproxen		98.6 (~63.1%)	Wu et al. 2020

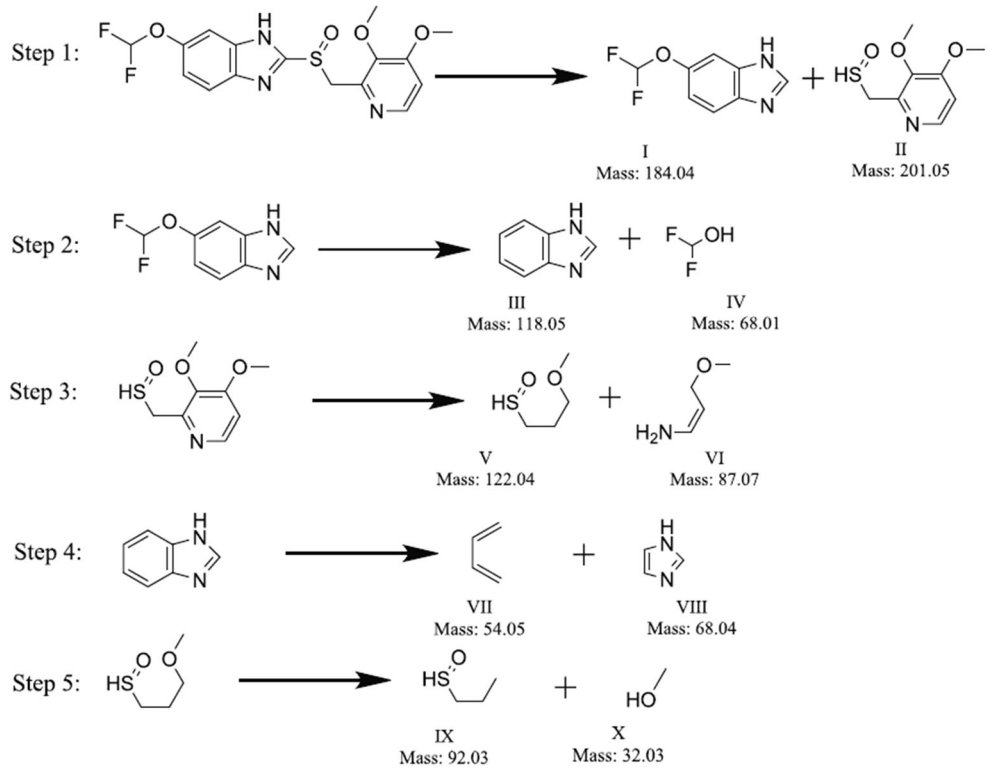
Table 2 (continued)

Catalyst	Synthetic method	Irradiation time (min)	Targeted pharmaceuticals (5 mg/L)	Source	% of degradation (mineralization efficiency)	Reference/year
Carbon dots/g-C_3N_4	Hard templating method	5	Naproxen (10 mg/L)	Xenon lamp (350 W, λ>420) Solar light (19.8 mw/cm^2)	~100%	Wu et al. 2020
g-C_3N_4/CQDs/$CdIn_2S_4$	Hydrothermal method	60	Ibuprofen (80 mg/L)	Xenon lamp (300W, λ>420 nm)	91.0% (85.0%)	Liang et al. 2020
BiOCl/g-C_3N_4	Hydrothermal method	60	Tetracycline (20 mg/L)	Xe lamp (300 W)	97.1%	Sun et al. 2020
BiOCl/g-C_3N_4	Microwave-assisted method	30	Nizatidine (0.4 mg/mL)	Mic-LED-365	96%	Al Marzouqi et al. 2019

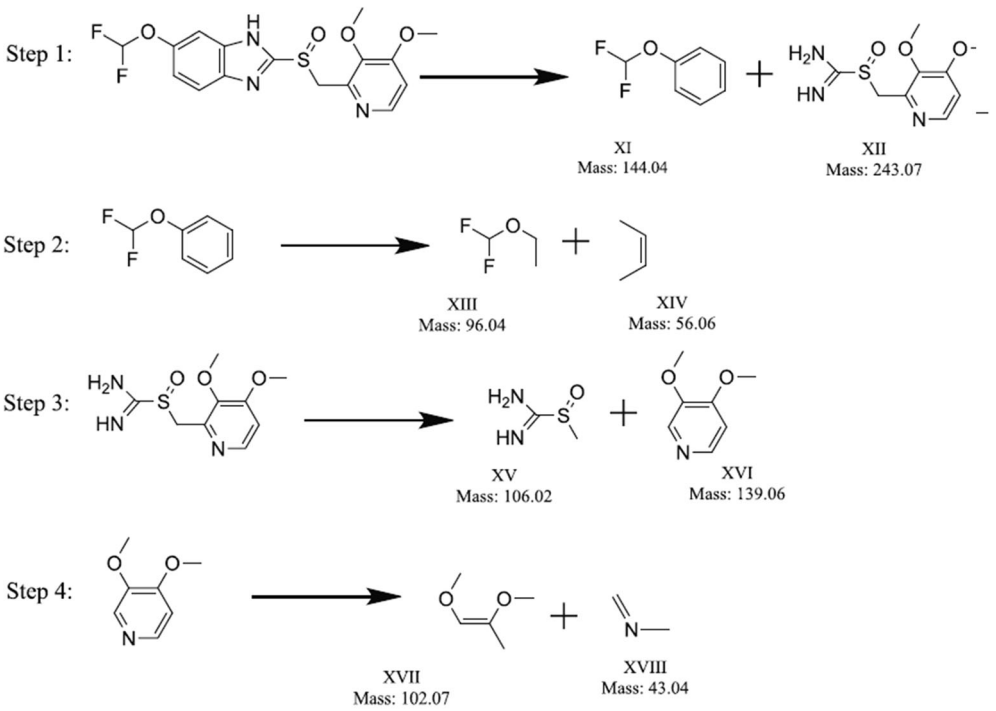
degraded 80% oxytetracycline (OTC). In another study, carbon quantum dots (CQDs) were combined with graphitic carbon nitride by facile thermal polymerization method (Liu et al. 2019). Decoration of CQDs significantly varied the optical properties of graphitic carbon nitride, without affecting its structural and morphological identity. X-ray photoelectron spectra analysis demonstrated that the characteristic peak at 286.3 eV corresponding to C-O species slightly shifted to 286.4 eV after the incorporation of CQDs, which indicates that CQDs are anchored to g-C_3N_4 surface through C-O bond. The C-O-C bond is formed between surface adsorbed hydroxyl groups of both g-C_3N_4 and CQDs by the elimination of one H_2O molecule. The CQDs modification greatly increased the photocatalytic activity of g-C_3N_4 and successfully degraded non-steroidal anti-inflammatory drug diclofenac (DCF) with a degradation rate ~15 times higher than that of pure g-C_3N_4. Degradation pathway demonstrates that ring hydroxylation, photocyclization, and C-N bond cleavage were the initial steps which led to the degradation of diclofenac (DCF) (Fig. 11). Photo-induced hydroxyl radicals hydroxylated the aromatic ring of DCF molecules and decomposed into quinone imine molecules and other intermediate products. The C-N cleavage followed by demethylation directly breakdown DCF molecules into small molecules (m/z=162,163) and these intermediates are finally mineralized into CO_2 and H_2O.

Construction of the Z-scheme photocatalytic system, enthused by the natural photosynthesis process, is an effective method to increase the light harvesting as well as to generate highly active oxidative and reductive species with strong redox ability (Xu et al. 2018). Carbon nitride-based Z-scheme photocatalyst g-C_3N_4/RGO/WO_3 with reduced graphene oxide (RGO) as the electron mediator found efficient in the degradation of antibiotic ciprofloxacin. Simple photo-reduction method was backed for the synthesis of this catalyst (Lu et al. 2019). The electron transfer properties of RGO strengthen the visible-light responsive range, absorption ability, and electronic mobility of g-C_3N_4/RGO/WO_3 than g-C_3N_4/WO_3, g-C_3N_4, and WO_3. Moreover, RGO acts as a special pathway for the inhibition of undesired charge carrier recombination in graphitic carbon nitride since photoexcited electrons of WO_3 nanoparticles were easily transferred via RGO to the valence band of g-C_3N_4.The electrons in conduction band of g-$C_3N_4$and holes in valence band of WO_3 generate reactive species like superoxide anion radical ($^{\bullet}O_2^-$) and hydroxyl radical ($^{\bullet}OH$) for the degradation of ciprofloxacin and is clearly illustrated in Fig. 12.

Zhang et al. (2019a) successfully synthesized Z-scheme heterojunction using Ag_3PO_4, nitrogen-doped graphene, g-C_3N_4 via in situ deposition method. Their studies revealed that wrinkled flake-like nitrogen-doped graphene (NG) act as bridging layer between Ag_3PO_4 and g-C_3N_4 which enhances facile mobility of electrons across the interface of the ternary photocatalyst. Herein, the NG could also stabilize the Ag_3PO_4 particles modified surface layer of g-C_3N_4 sheets and reduce the



Pathway 1



Pathway 2

Fig. 9 The two different degradation pathways of pantoprazole by Fe_3O_4/ZnO/g-C_3N_4 reproduced from Ref. (Raha and Ahmaruzzaman 2020) with the permission of Elsevier publications)

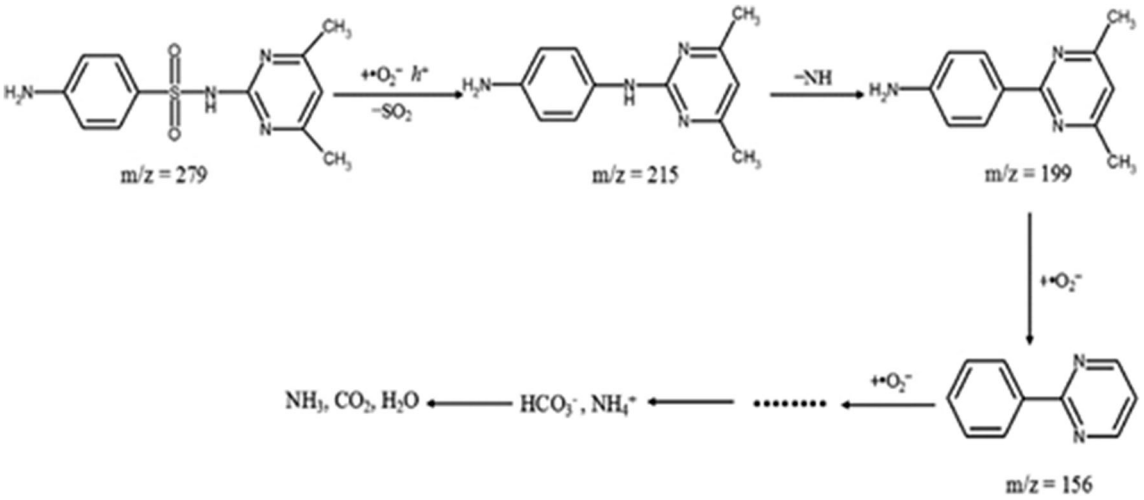


Fig. 10 Intermediates formed in the photocatalytic degradation of sulfamethazine (reproduced from Ref. (Cao et al. 2018a, b) with the permission of Elsevier publications

recombination rate of charge carriers. The lower photoluminescence spectral (PL) intensity of Ag_3PO_4 /NG/g-C_3N_4 indicated that synergistic effect of Ag_3PO_4, g-C_3N_4, and NG decreased the charge carrier recombination and verified the higher activity of ternary heterojunction. It was found that Ag_3PO_4 /NG/g-C_3N_4 can degrade 93.6% of tetracycline (TC) in 90 min with a rate constant 0.029 min^{-1} and achieved 72 % of mineralization of TC under visible light, also exhibited recyclability about four runs. Based on LC-MS analysis, authors proposed two degradation pathways for TC; one pathway involved the formation of intermediate of m/z =458 by the carbon-carbon double bond addition on TC; further, C–C and C–N bond cleavage resulted in the intermediates of m/z= 208 and m/z= 194. In another pathway, demethylation of TC lead to the generation of intermediate of m/z = 416 which on dehydroxylation converted to intermediate of m/z = 402. Finally, the oxidation reaction and ring opening process break it down into simpler products of m/z =178, 164, and 116 (Fig. 13).

Terephthalic acid functionalized g-C_3N_4/TiO_2 (TACN/TiO_2) heterojunction nano photocatalysts were found efficient in the degradation of pharmaceuticals like ibuprofen (IBU) and carbamazepine (CBZ) present in real sewage effluent (Kumar et al.

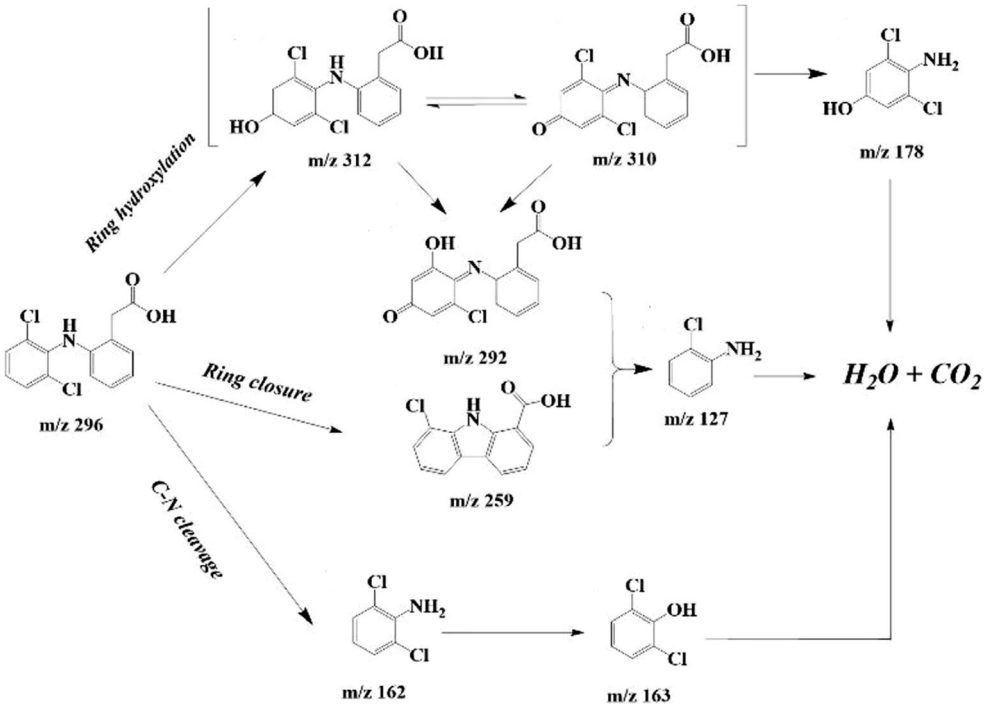


Fig. 11 Degradation pathway of diclofenac (DCF) (reproduced from Ref. (Liu et al. 2019) with the permission of Elsevier publications)

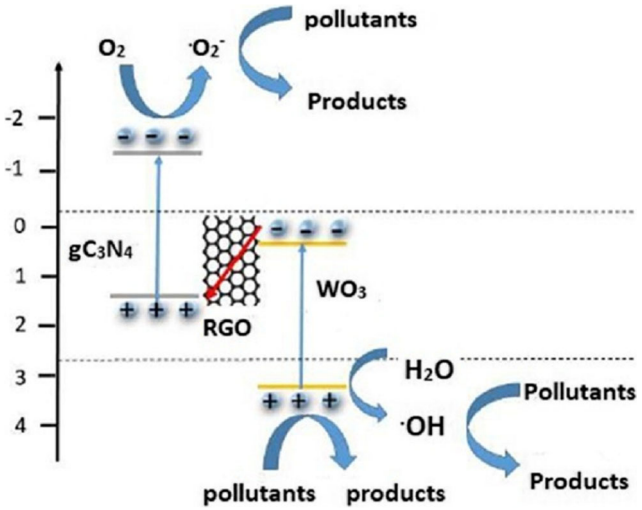


Fig. 12 Schematic illustration of the separation and transfer of photogenerated charges and the reactive species in the degradation process of Z-scheme photocatalyst g-C_3N_4/RGO/WO_3 (reproduced from Ref. (Lu et al. 2019) with the permission of Elsevier publications)

2020). TACN/TiO_2 catalyst was synthesized via sol-gel method wherein the TACN sheets were infused with titanium (IV) butoxide and subjected to hydrothermal treatment. The developed TACN/TiO_2 heterojunction with a high O/N ratio shows low recombination of charge carriers and enhanced the generation of hydroxyl radical, which finally ensued in the complete deterioration of pharmaceuticals (IBU, CBZ). Incorporation of superparamagnetic core-shell Fe_3O_4@SiO_2 nanoparticles into TACN/TiO_2 assured its magnetic separation from the reaction mixture. The SiO_2 shell forms an inert layer between Fe_3O_4 core and TACN/TiO_2 heterojunction and thus prevents photodissolution of the catalyst. On visible light irradiation, TACN/TiO_2/Fe_3O_4@SiO_2 (TTFS) achieved almost complete degradation of IBU and CBZ within 60 and 75 min, respectively. Mineralization studies indicate that TTFS Z–scheme heterojunction could mineralize 84.32% of 2 mg L^{-1} of IBU and 63.59% of the 2 mg $L^{-1}$of CBZ on 6 h of visible light illumination. Even though the presence of Na^+ and PO_4^{3-} ions in real sewage causes scavenging of hydroxyl radical and enhancement of recombination rate of charge carriers, TTFS could attain 97% degradation of 2 mg L^{-1} of IBU in 120 min and 94% degradation of 2 mg L^{-1} of CBZ in 240 min upon 330W m^{-2} of integrated visible light irradiance. The study demonstrates the competence of TTFS for real-world applications.

Another novel Z-scheme photocatalyst, BiOBr/reduced graphene oxide/protonated g-C_3N_4 (pg-C_3N_4), was developed by Bao and Chen (2018) for the degradation of tetracycline hydrochloride (TC-HCl) solution under visible light irradiation (λ >

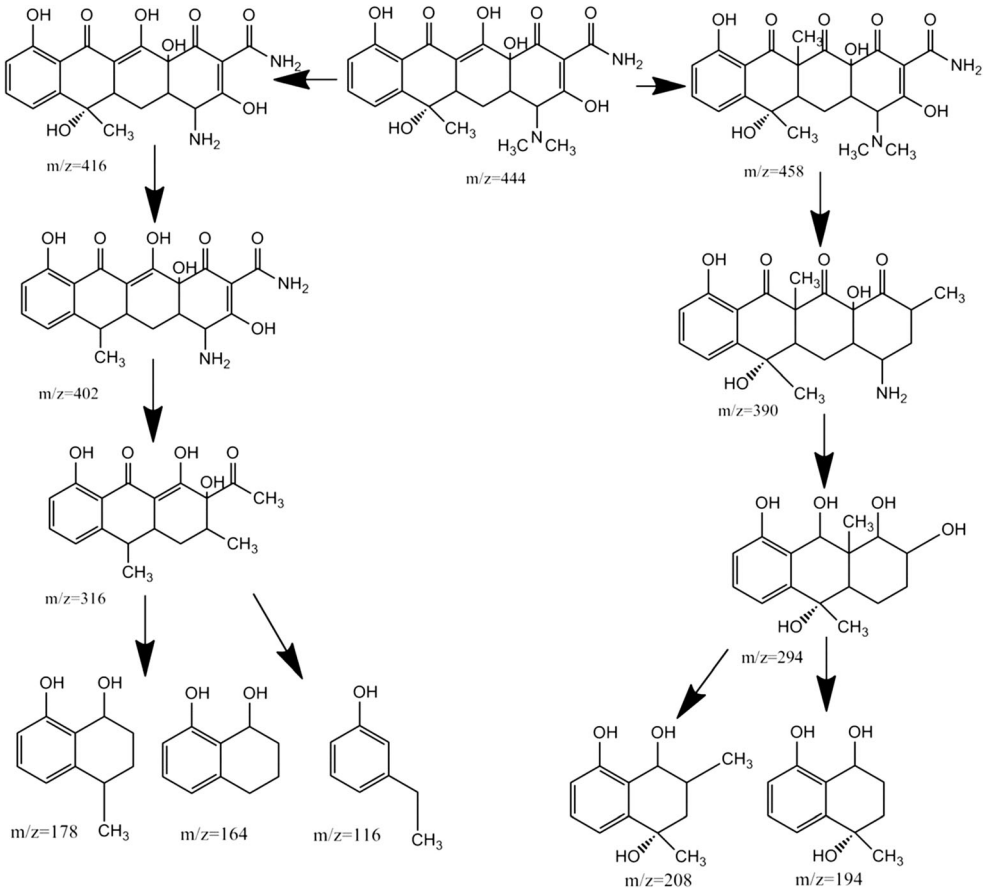


Fig. 13 The possible degradation pathway of TC during the photocatalytic process (reproduced from Ref. (Zhang et al. (2019a) with the permission of Elsevier publications)

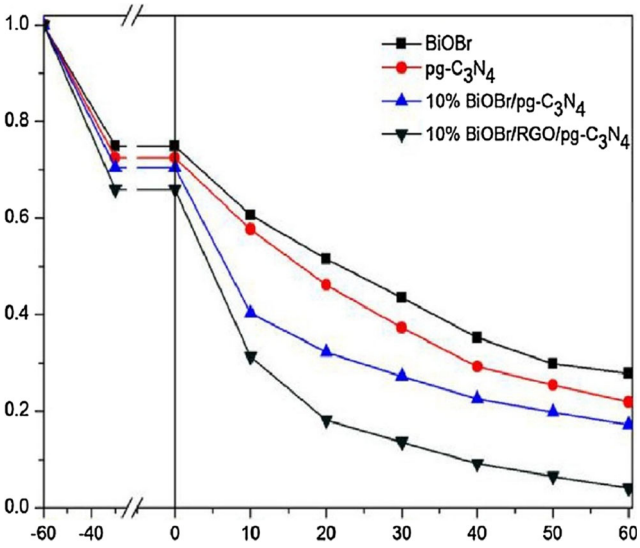


Fig. 14 Photodegradation curves tetracycline in the presence of BiOBr/RGO/pg-C_3N_4 photocatalysts under visible light irradiation (reproduced from Ref. (Bao and Chen 2018) with the permission of Elsevier publications)

420nm). RGO acts as interlayer between BiOBr nanosheets and pg-C_3N_4 nanosheets and provides a high-speed charge transfer channel, leading to greater charge separation efficiency. Thus, increases the reductive and oxidative capacities of photo-induced electrons in conduction band of pg-$C_3N_4$and holes in valence band of BiOBr. These photogenerated charge carriers produce active species like h^+, $^{\bullet}OH$ and $^{\bullet}O_2^-$. The ESR spin-trap with DMPO (5,5-dimethyl-1-pyrroline-*N*-oxide) and TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) techniques confirmed that$^{\bullet}O_2^-$ and h^+ played a chief role in mineralization of tetracycline hydrochloride intoCO_2 and H_2O. The optimal sample 10% BiOBr/RGO/pg-C_3N_4 removed 59% of TC-HCl in a period of 60-min visible light irradiation (Fig. 14).

Chen et al. (2019) introduced a direct Z-scheme photocatalyst without an electron mediator for the removal of pharmaceutical waste from wastewater. Z-scheme 2D $MnIn_2S_4$/g-C_3N_4 (MnISCN) nanocomposites were made-up by facile in situ deposition method, where $MnIn_2S_4$ (MnIS) nanoflakes were loaded on the surface of g-C_3N_4 nanosheets. The MnISCN-20 nanocomposites exhibited the highest photocatalytic activity towards tetracycline hydrochloride (TC-HCl) degradation. Photogenerated holes on valence band of g-C_3N_4 and electrons in the conduction band of MnIS react with OH^- and dissolved oxygen to generate hydroxyl radical as well as superoxide anion radical for the degradation of pollutants.

Organic compounds incorporated graphitic carbon nitride

Organic compounds when copolymerized with the precursors of graphitic carbon nitride such as melamine and urea (Shalom et al. 2013; Qiu et al. 2017), the photocatalytic activity of carbon nitride was found to be reasonably increased. Organic compounds like cyanuric acid and barbituric acid with melamine via supramolecular approach resulted in the formation of carbon-doped g-C_3N_4 (CCN) (Zhou et al. 2018). It is then further unified with $Bi_{12}O_{17}C_{l2}$ layers through an in situ deposition method. CCN/$Bi_{12}O_{17}Cl_2$ semiconductor photocatalyst showed excellent photocatalytic activity towards the degradation of tetracycline (TC) compared with pristine $Bi_{12}O_{17}Cl_2$. 20% CCN/$Bi_{12}O_{17}Cl_2$ photocatalytically removed tetracycline (TC) with an efficacy of 94% in 1h (degradation constant 0.0409 min^{-1}), whereas BiOCl, $Bi_{12}O_{17}Cl_2$, and CCN show only 8%, 54%, and 82% of degradation of sulfamethazine (SMZ), respectively. Zhou and his co-workers (Zhou et al. 2019b) found that copolymerization of urea with 2-thiobarbituric acid (TA) noticeably improved photocatalytic activity of resultant graphitic carbon nitride (TCN). The X-ray diffraction pattern, infrared spectroscopy, as well as X-ray photoelectron spectroscopy analysis clearly demonstrated that the incorporation of TA does not cause any deformation to the framework of g-C_3N_4. Electrochemical

Table 3 Comparative studies on degradation of different pharmaceutical compounds by organic compounds incorporated graphitic carbon nitride based photocatalysts

Catalyst	Synthetic method	Irradiation time (min)	Targeted pharmaceuticals	Source	% of degradation	Reference/year
CCN/$Bi_{12}O_{17}Cl_2$	Ultrasonic chemical method	60	Tetracycline (20 mg/L)	Xenon lamp (300 W)	94%	Zhou et al. 2018
Thiobarbituric acid/g-C_3N_4	Copolymerization	60	Sulfamethazine (10 mg/L)	Xenon lamp (300W)	-----	Zhou et al. 2019b
Salicylic acid/g-C_3N_4	Copolymerization	60	Tetracycline (100 μM)	Xenon lamp (300W)	86%	Zhou et al. 2019a
L-cysteine/g-C_3N_4	Copolymerization	60	Sulfamethazine (100 μM)	Xenon lamp (300W)	99.7 %	Zhou et al. 2019c
Naphthalene/g-C_3N_4	Co-thermalization	120	Trans-resveratrol (10 mg/L)	Visible light	100%	Khan et al. 2019

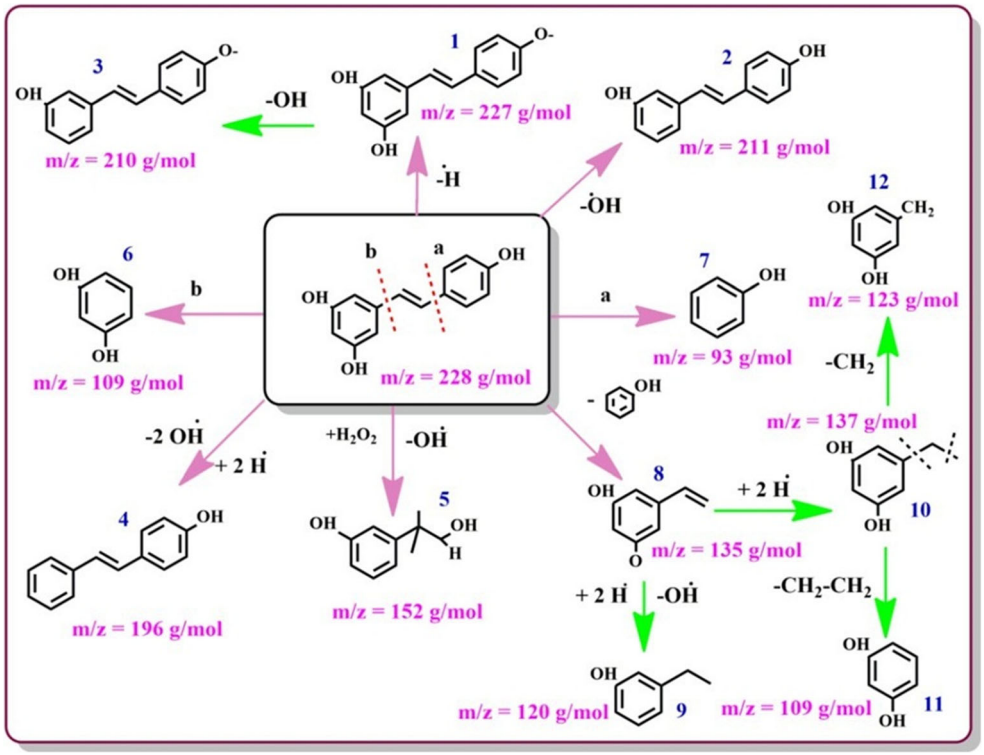


Fig. 15 Degradation pathway of trans-resveratrol by naphthalene modified g-C_3N_4 (reproduced from Ref. (Khan et al. 2019) with the permission of Elsevier publications)

impedance spectroscopy (EIS) analysis indicates the optimal sample, TCN-0.03, exhibited highest photocurrent density (0.85 μA cm^{-2}) than undoped g-C_3N_4 (0.21 μA cm^{-2}) which itself verified the enhanced degradation activity of TCN for the degradation of aqueous sulfamethazine (SMZ). TCN could breakdown sulfamethazine into small, harmless molecular organics and other inorganic species under visible light. On 60-min irradiation of visible light, the TCN-0.03 could decompose SMZ with a high reaction rate of 0.058 min^{-1} which was 4.2 times higher than undoped g-C_3N_4.

Studies show that both sulfamethazine and tetracycline were effectively decomposed by salicylic acid modified polymeric g-C_3N_4 (CN-SA), synthesized via copolymerization of urea and salicylic acid (Zhou et al. 2019a). Incorporation of salicylic acid (SA) destroyed the local symmetry and caused structural distortion in the graphically packed layered structure of g-C_3N_4 (nanosheets of g-C_3N_4 were broke-down into smaller ones and get curved) and thereby leads to enhanced charge carrier separation. Photocatalytic degradation studies indicated that CN-SA could degrade sulfamethazine (SMZ) with higher rate compared to tetracycline (TC) because -SO_2-NH-chemical bonds in sulfamethazine (SMZ) were easier to breakdown than benzene group in tetracycline (TC) with aid of sunlight. It was reported that naturally occurring amino acid (i.e. L-cysteine) when integrated with g-C_3N_4, its catalytic activity significantly enhanced and attained effective decomposition of sulfamethazine (SMZ) (Zhou et al. 2019c). L-cysteine on assimilation creates nitrogen vacancies and discrepancy in the structural framework of graphitic carbon nitride and induce the n-π* electronic transition. Photogenerated charge carriers with prolonged life generate $^{\bullet}OH$ and $^{\bullet}O_2^-$ active species which resulted in the decomposition of sulfamethazine into greener products. The degradation mechanism of an antioxidant stilbenoid drug, trans-resveratrol, was studied with naphthalene-modified g-C_3N_4 under sunlight (Khan et al. 2019). The LC-MS/MS analysis detects several by-products such as resorcinol (m/z=109), ethyl phenol (m/z=120), and phenol (m/z=93) which are formed upon the decomposition of trans-resveratrol by photo-induced holes and •OH and is given in Fig. 15. Table 3 gives the comparative study on the degradation of different pharmaceutical compounds by organic compounds incorporated graphitic carbon nitride based photocatalysts.

It is also observed that modification of graphitic carbon nitride by biomass is a novel method to increase its catalytic activity. Hydroxyapatite (HAp) ($Ca_{10}(PO_4)_6(OH)_2$ is a bioactive material with high thermal conductivity, high surface area, low water solubility, and low toxicity and have been widely used in cell imaging, tissue repair, and remodelling. Xu and colleagues were succeeded in manufacturing porous hollow hydroxyapatite (HAp) microspheres combined with small amounts of ultrathin graphitic carbon nitride (g-C_3N_4) by adopting a simple hydrothermal approach (Xu et al. 2019b). In comparison with ultrathin g-C_3N_4 and porous hollow HAp microspheres, g-C_3N_4/H Ap composite effectively decomposed tetracycline (TC) under 300W xenon lamp full spectrum irradiation. Tetracycline (TC) was almost completely degraded within 15min by g-C_3N_4 (1.5wt.%)/HAp composite. Photoexcited

holes in valence band (2.91eV) and electrons in conduction band (−2.2eV) of porous hollow hydroxyapatite microspheres transferred to valence band (1.56 eV) and conduction band (−1.37eV) of g-C_3N_4, respectively. This ensured effective separation of photogenerated electron-hole pairs in g-C_3N_4/HAp composite. Since the conduction band potential of HAp is more negative than standard reduction potential of $O_2/^{\bullet}O_2^-$ (−0.046 V), the excited electrons react with molecular oxygen to produce superoxide anion radicals. These superoxide anion radicals as well as holes in the valence band directly degrade tetracycline into simpler molecules.

Conclusion

Several investigations conducted over recent years propose g-C_3N_4-based photocatalysis as an effective method for the deterioration of pharmaceutical pollutants present in water bodies. This review broadly discusses on the recent advances in structural modification strategies and engineering of various materials based on g-C_3N_4 to develop efficient photocatalysts with extended visible light absorption, slow charge transfer efficiency, enhanced surface area, and increased adsorption rate. Metallic impurities like Ag, Au, Pd, as well as nonmetal dopants inflict additional binding functions which help in lowering the band gap and boost up the visible light adsorption capability of graphitic carbon nitride. Among various improvement strategies, semiconductor-semiconductor coupling method for the construction of heterojunctions encourages the band bending and the development of internal electrical field for the enhancement of overall catalytic performance of graphitic carbon nitride. Z-scheme heterostructures accelerate the separation of photo-induced electron-hole pairs and provide higher redox potential for the excitons. Studies reveal that carbonaceous materials such as graphene and its derivatives serve as good adsorbents as well as suitable electron mediator in g-C_3N_4 heterojunctions which significantly enhance the activity of the catalyst for the effective removal of active pharmaceutical compounds. Integration of carbon dots with g-C_3N_4 could achieve remarkable activity in degrading pharmaceuticals under direct solar irradiation. Recently researchers are now focused on the synthesis of graphitic carbon nitride hybrids with metal organic frame works (MOF) as well as covalent triazine-based frameworks (CTFs) due to their exceptional ability in establishing strong interface contact with graphitic carbon nitride and significant influence in charge-carrier transfer and separation owing to its intense physical and electronic coupling effects. Degradation pathways adopted by several pharmaceuticals on reaction with these nanohybrids under visible light demonstrate that most of the studies could achieve almost complete degradation of pharmaceutical pollutants into nontoxic product, carbon dioxide, and water at laboratory scale.

However practical implication of this technique requires more efficient, stable, as well as easily reproducible photocatalyst. Various template-free and green synthetic methodologies for better functionalized and cost-effective g-C_3N_4 composites are needed to adopt large-scale application of photocatalysts. Retrieval and catalyst loss during the photodegradation process is a challenging issue confronted by researchers in this field. Therefore, more studies are required in designing and developing immobilized g-C_3N_4 composites or for the fabrication of thin films of developed g-C_3N_4 catalyst. Besides, deep research on the applications of various g-C_3N_4 nanocomposites in treating in real wastewater by completely assessing their photocatalytic ability, cost, energy consumption, and reusability is vital to make wastewater treatment at industrial scale more feasible and economical. Wide applicability of these catalysts against different types of pharmaceutical pollutants and cleansing action of developed catalyst with effluent directly released from pharmaceutical companies under direct solar irradiation need to be explored more.

Acknowledgements The authors are grateful to the management of Kuriakose Elias College, Mannanam Kottayam for the support and encouragement.

Availability of data and materials Not applicable.

Author contribution All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Anju John, Mekha Susan Rajan, and Dr. Jesty Thomas. All authors read and approved final manuscript.

Declaration

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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