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Recent advances in removal of pharmaceutical pollutants in wastewater using metal oxides and carbonaceous materials as photocatalysts: a review[†]

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The pharmaceuticals industry has played an important role in developing medicines for improving health and quality of life in treating humans and animals around the world. But it is also considered to be one of the sources of pollutants entering deliberately or accidentally into global water bodies causing toxicity that eventually threatens human health, aquatic organisms and environments even at low concentrations. These contaminants are non-biodegradable and cannot be completely removed from various water matrices following conventional treatment methods. In this regard, photodegradation techniques involving modified/unmodified semiconducting materials have attracted a lot of attention as a promising solution in achieving complete antibiotic degradation with the generation of non-toxic by-products. In view of this, the present review article summarizes current research progress in the removal of several emerging contaminants, such as acetaminophen, amoxicillin, sulfamethoxazole, norfloxacin, ibuprofen, ciprofloxacin, tetracycline, diclofenac and atenolol in water. Considerable emphasis has been placed on metal oxides and carbon-based photocatalysts following their modification through doping with metals and non-metals, metal loading, the formation of composites, immobilization and heterostructure/heterojunction approaches. Finally, the review ends with future prospects for nanomaterial-based heterogeneous photocatalysts in the removal of pharmaceutical contaminants from water.

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1 Introduction

Water plays an essential role in sustaining a cherished healthy life for living organisms as well as ecosystems. Therefore, the purity of water remains of utmost concern for the survival of human beings, plants, animals and several other living species in the world. A report presented by UNESCO at the UN 2023 Water Conference revealed the nonavailability of safe drinking water for 26% of the global population.¹ This problem is also compounded by the presence of several pollutants in water bodies. This contributes to the depletion of fresh water, resulting in an overall water crisis worldwide.² This adversely affects human health, several other living organisms and sustainable social development. According to an estimate, about 80% of wastewater is discharged globally into the environment without any prior treatment, jeopardizing human health, the ecosystem, and the environment.3 In this regard, dye effluents, heavy metals and pesticides discharged as wastewater from different industries contribute significantly to water pollution.⁴⁻¹²

In addition, the wide application of pharmaceuticals in daily life for the treatment of complex diseases is also the major contributor of emerging contaminants, with potential adverse effects on humans and the aquatic environment.^{13–22} The presence of these pharmaceutical pollutants could lead to cancers, severe bleeding, organ damage, birth defects, reproductive disorders, endocrine disorders, and mild to severe toxic effects in human beings in the global population.¹⁴ The toxic effects are also threats to mammals, other organisms, and the ecosystem. Fig. 1 shows the effect of pharmaceuticals in reducing the quality of water.¹⁴ The presence of these pharmaceutical pollutants in water through improper disposal, irrigation of crops, and consumption by agriculture, humans, and animals seriously affects the ecosystem.

Further, the accumulation of antibiotic drugs in water can result in the development of antibiotic-resistant bacteria and the dissemination of antibiotic-resistant genes in humans and other living organisms.^{15,16} According to a recent report, urban wastewater treatment plants are

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Fig. 1 Routes of pharmaceutical contaminants (PCs). Reproduced from ref. 14 with permission from Elsevier (2022).

recognized sources for the dissemination of antibiotic resistance in the environment.¹⁷ In view of the rising effects of this antibiotic resistance on the global population, the removal of these bioactive molecules from the environment is important to slow down the growth of resistant microorganisms. In addition, antibiotic residues absorbed by plants could interfere with physiological processes, leading to potential ecotoxicological effects.¹⁸ These contaminants cannot be completely removed from various water matrices by conventional chemical, physical, flocculation, reverse osmosis or a few other processes, due to the formation of secondary pollutants, high cost, and

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Leibniz Institute of Polymer Research, Dresden (2013) Germany, and University of Nantes, France (2003, 2007). His research interests are in the field of nondimensional nanomaterials for their application in the fields of energy, environments and polymer nanocomposites. Dr Srivastava has guided 23 Ph.Ds, published about 200 research papers in referred journals, contributed to 16 chapters in books and edited 2 books. operational time.¹⁹ Therefore, the development of costeffective, eco-friendly, economical, and effective technologies is urgently needed to remove these emerging contaminants, due to the rising effects of antibiotic resistance in aquatic environments.

Design of the surface and interface plays a promising role in the performance of photocatalysts through maximizing the efficacy of catalysts. Therefore, heterogeneous photocatalysis has been receiving considerable attention as one of the most attractive, low-cost, efficient and outstanding approaches in the degradation of pharmaceutical pollutants.¹⁹⁻⁵⁵ In this regard, a considerable amount of research interest has focused mostly on TiO₂ and to some extent on other semiconducting materials and transition metal oxides as photocatalysts in the degradation of pharmaceutical pollutants in water.²³⁻³⁹ The choice of semiconducting metal oxides as photocatalysts is motivated by the availability of a renewable energy source (solar energy) and the generation of non-toxic degradation products (chemicals and gases). They can be commonly prepared by sol-gel, hydrothermal, solvo-thermal, microwave heating, wet chemical, physical vapour deposition and chemical vapour deposition methods.³⁰ However, the potential of TiO₂ and other semiconducting metal oxides could not be harnessed due to the higher rate of recombination of electron-hole pairs and its limited photocatalytic activity under visible light exposure.

Recently, carbonaceous materials have also been reported as promising materials for use in the photocatalytic degradation of antibiotics in water.⁴⁰⁻⁵⁰ This is facilitated by combining these carbon-based materials with other semiconductors, which is considered to be an outstanding approach to enhancing photocatalytic performance. In order to facilitate this, carbonaceous materials with different structures and properties are used as additives in semiconductor materials. This invariably results in enhanced charge separation and visible light activity and is considered the best solution. In addition, semiconducting metal oxides and carbonaceous materials are subjected to doping with metals, non-metals, metal oxides, coupling with noble metal nanoparticles and the formation of composites.36,39,49 Other approaches involving immobilization and the formation of a heterojunction are reported as imperative alternative strategies for achieving enhanced photocatalytic efficiency for these photocatalysts in water treatment.51

According to the available literature, several reviews have been published focusing on metal oxides,23-30 TiO2,31-33 ZnO-based photocatalysts,³⁴ semiconductors,³⁵ doped TiO₂,³⁶ hybrids,³⁷ TiO₂-carbon dot nanocomposites,³⁸ plasmonic composites,39 metal-TiO₂ carbonaceous/carbon-based materials,40,41 carbon dots,^{38,44} $g-C_3N_4$,⁴² MWCNT,⁴³ carbon,⁴⁵ graphene-based composites,46-48 activated graphene-TiO₂ and doped graphene-TiO₂ nanocomposites,⁴⁹ materials,⁵⁰ graphene-based and nanomaterial-based heterogeneous photocatalysts⁵¹ as photocatalysts for the

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Table 1 Structure and uses of different pharmaceutical pollutants. Adopted from PubChem⁵⁵



treatment of wastewater containing pharmaceuticals. Alternatively, several review articles have reported on the photodegradation of antibiotic contaminants in water, such as amoxicillin,²¹ ibuprofen,²² tetracycline,^{52,54} ciprofloxacin,^{53,54} and norfloxacin⁵⁴ antibiotics in wastewater

and several others, which are referred to in section 3. However, there is still a need for an extensive review article in this field, covering in a single window a larger number of pharmaceutical pollutant photocatalysts for their photocatalytic performance.

The present review is focused primarily on the photocatalytic degradation of acetaminophen, amoxicillin, sulfamethoxazole, ibuprofen, norfloxacin, ciprofloxacin, tetracycline, diclofenac, etc. The structure and uses as well as the solubility of these antibiotics in water are provided in Table 1 (ref. 55) and ESI,[†] respectively. In view of this, the describes fundamental article the properties of semiconducting materials as photocatalysts as well as role of metal oxides, carbon-based materials, and heterojunctions and the immobilization approaches employed and the mechanisms involved in the removal of these pharmaceutical pollutants. Subsequently, the article deals with the removal of the above-mentioned drugs from contaminated water using semiconducting TiO₂, ZnO, and many other oxides, their combination with graphitic-carbon nitride $(g-C_3N_4)$, carbon nanotubes (CNTs), activated carbon (AC), graphene oxide, graphene and graphene quantum dots, doping with metals and nonmetals, the formation of composites, semiconducting materials deposited on certain supports as photocatalysts and a heterojunction approach. It is anticipated that, in the light of this, the current review could be of immense help in identifying cost-effective and efficient photocatalytic methods for the remediation of these pharmaceutical pollutants. In addition, various research gaps, their possible solutions and several future prospects are also provided at the end of this article for the possible enhancement of environmental conservation.

2 Important photocatalysts and their role in the removal of pharmaceutical pollutants

The primary mechanism for the degradation of organic pollutants by a semiconducting material involves irradiating it with light energy in the form of photons ($h\nu$) sufficiently greater than the band gap energy of the photocatalyst (Fig. 2 (ref. 37)). Holes (h_{VB}^+) and electrons (e_{CB}^-) are generated in this manner in the valence band (VB) and the conduction band (CB), respectively. The separated holes reacts with



Fig. 2 Photocatalytic processes over a heterogeneous photocatalyst. Reproduced from ref. 37 with permission from MDPI (2021).

hydroxyl ions (OH⁻) or water molecules (H₂O) to produce hydroxyl radicals (·OH). In addition, the separated electrons reacts with dissolved O₂ in water to produce superoxide radicals (·O₂⁻), which upon further reaction, produce ·OH.^{37,51} Subsequently, the active species generated in this manner react with pharmaceutical pollutants on the surface of the semiconductor catalyst to give H₂O, CO₂ and other byproducts.

> Semiconductor + $h\nu \rightarrow h_{VB}^{+} + e_{CB}^{-}$ $h_{VB}^{+} + H_2O \rightarrow H^+ + \cdot OH$ $e_{CB}^{-} + O_2 \rightarrow \cdot O_2^{-}$ $\cdot O_2^{-} + H^+ \rightarrow HO_2 \cdot$ $HO_2 \cdot + HO_2 \cdot \rightarrow H_2O_2 + O_2$ $H_2O_2 + \cdot O_2^{-} \rightarrow \cdot OH + OH^- + O_2$ $H_2O + h_{VB}^{+} \rightarrow \cdot OH + H^+$ $h_{VB}^{+} + OH^- \rightarrow \cdot OH$

It should be mentioned that the efficiency of a photocatalytic reaction depends on the capability of the photocatalyst to generate longer-lived e^- and h^+ that lead to the formation of reactive free radicals. In addition, photodegradation efficiency also depends on catalyst loading, contaminant concentration, pH, the presence of ions in the water, hydrogen peroxide, ultrasound irradiation, bubbling of O_2 and N_2 into the solution and irradiation time.^{13,26,34}

2.1 Metal oxides

Several semiconductor metal oxides have been used as photocatalysts in the abatement of aqueous pollution due to organic pollutants. From this point of view, TiO₂ has received a considerable amount of attention and its choice is mainly guided by its superior photocatalytic degradation efficiency, low processing cost, high environmental stability, nontoxicity, chemical stability, and high oxidizing ability.^{31–33} However, its wide band gap ($\sim 3-3.2 \text{ eV}$),³² and the fast e⁻-h⁺ recombination rate of photogenerated electron-hole pairs in TiO₂ limit its applications. Semiconducting ZnO (band gap: 3.37 eV) has been used as another photocatalyst in water treatment as an alternative to TiO₂.⁵⁶ Several other metal oxides (ZrO₂, Fe₂O₃, γ -Fe₃O₄, SnO₂, Mn₂O₃, WO₃, CeO₂, CuO,

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and NiO) have also been investigated as alternatives to TiO₂ ZnO.²⁶ Nano-engineered and metal-oxide-based photocatalysts have also attracted a lot of attention in wastewater treatment.⁵⁷ However, metal oxide catalysts experience similar drawbacks to TiO2. As a consequence, significant developments have taken place in recent years in tailoring these metal oxide photocatalysts. This is achieved by reducing their band gap by the addition of dopants that include both metals and non-metals, such as iron, copper, carbon, nitrogen, platinum and sulfur. In addition, metal sulfides,⁵⁸ metal ferrites,⁵⁹ and oxychlorides⁶⁰ have also been explored as emerging photocatalysts for the removal of pharmaceutical pollutants.

Photocatalytic studies have been reported on the performance of semiconductor-metal composites in the removal of several pollutants from water. In this regard, plasmonic composites in combination with various semiconducting photocatalysts have been widely studied for enhancing overall photocatalytic performance.^{61,62} The improved photocatalytic efficiency is attributed to the surface plasmon resonance effect. In addition, metal nanoparticles can decrease the recombination rate of the photo-induced e⁻-h⁺ pairs of the semiconductor material by effective electron trapping in the conduction band. Metal oxide nanocomposites derived from a mixture of two or more oxides or between these oxides and other functional semiconductor materials have also been found to be efficient, economical, and environmentally friendly photocatalysts in water pollutant remediation.63,64

2.2 Carbonaceous materials

The photocatalytic performance of various carbonaceous materials has been receiving more attention for antibiotic removal owing to their intriguing properties and good stability.40,41 The choice of these carbonaceous materials in removing antibiotics is mainly guided by simple and costeffective synthesis methods, the easy availability of raw materials and their unique physiochemical properties, such as the presence of micropores, mesopores, and macropores, the large number of oxygen-functional groups, high porosity, and high surface area, coupled with good visible-light adsorption ability, chemical stability, excellent electrical conductivity and high intrinsic electron mobility.40 The carbonaceous materials explored for this purpose include carbon dots,³⁸ g-C₃N₄,^{42,65} activated carbon^{45,66} and carbon nanotubes (CNTs).67 Graphene is another carbon-based material composed of a one-atom-thick layer of carbon atoms arranged in a hexagonal lattice.68 It is a semimetal with a small degree of overlap between the valency band and the conduction band.⁶⁹ This makes graphene a promising candidate for application in photocatalysis. However, the photocatalytic performances and practical applications of carbon-based materials have not been encouraging, due to poor solar-light absorption and the rapid recombination of pairs.⁴¹ photogenerated electron-hole Interestingly,

combinations of these carbon-based materials with other semiconductor metal oxides have been utilized as promising photocatalysts owing to their notable properties like stability, conductivity, durability and high absorptivity. In addition, carbon-based materials-metal oxide nanocomposites have also enhanced the degradation efficiency of pharmaceuticals by improving the generation of radical species, through improved surface area and light absorption, and reducing the recombination of generated charge carriers.^{48,69}

2.3 Heterojunction nanocomposites as photocatalysts

A heterojunction is defined as the interface between two layers or regions of different semiconductors with unequal band structures that can result in band alignments. Based on semiconductor-semiconductor-based this concept, heterojunction composites showed excellent improvements in photocatalytic efficiency. This is ascribed to minimized charge carrier recombination, the interface of the heterojunction, superior charge transfer, prolonged charge carrier lifetime, separate active sites, and extended light characteristics.51 absorbance These semiconductor heterojunction photocatalysts are classified into several types: i.e., conventional heterojunctions (type-I, type-II, and type-III), p-n heterojunctions, direct Z-scheme heterojunctions, and S-scheme heterojunctions.⁷⁰⁻⁷³ The schematic separation of charges via electron migration from one semiconductor to another in various heterojunction mechanisms is represented in Fig. 3.⁵¹ Among these, in a type-I heterojunction, the VB and CB of semiconductor-1 are respectively lower and higher those of semiconductor-2 (Fig. 3(a)). than The photogenerated holes migrate from the VB of semiconductor-1 to the VB of semiconductor-2 accompanied by the transfer of photoelectrons from the CB of semiconductor-1 to the CB of semiconductor-2.52 However, this type-I heterojunction cannot spatially separate e^-h^+ pairs and this leads to the accumulation of charge carriers and their accelerated recombination rate. A type-II heterojunction (Fig. 3(b)) involves the transfer of photogenerated holes generated in semiconductor-2 to semiconductor-1, considering the VB of semiconductor-1 to be lower than that of semiconductor-2 on irradiating with light.52 In contrast, photogenerated electrons in the CB of semiconductor-1 can migrate to that of semiconductor-2, if the level of the CB in semiconductor-1 is higher than that of semiconductor-2. It should be noted that the spatial separation of electron-hole pairs can occur in a type-II heterojunction. Furthermore, the structure of a type-III heterojunction is similar to that of a type-II heterojunction; however, charge-carrier separation cannot occur in a type-III heterojunction because the band gaps of both semiconductors do not overlap, since the levels of the VB and CB of both semiconductors are very far apart (Fig. 3(c)). When p-type and n-type semiconductors are combined, a p-n heterojunction can be formed. A spacecharge region could be formed at the interface before light irradiation due to diffusion of the majority of charge carriers,



Fig. 3 Schematic illustration of various types of heterojunction: (a) straddling bandgap (type I), (b) staggered bandgap (type II), (c) broken bandgap (type III), (d) p-n type, (e) direct Z-scheme, and (f) S-scheme. Reproduced from ref. 51 with permission from Amer Sci Publ (2023).

leading to a built-in electric field, as shown in Fig. 3(d). In the Z-scheme heterojunction system, the band structure is quite analogous to that of a type-II heterojunction, but the direction of charge transfer is the opposite. The photogenerated electrons from the second semiconductor migrate aggressively to the VB of the first semiconductor and occupy the available holes, while the strongly oxidative holes in the VB of the second semiconductor take part in the redox reaction (Fig. 3(e)). In a step-scheme (S-scheme) heterojunction, two n-type semiconductors are combined with a staggered band structure similar to a type-II heterojunction (Fig. 3(f)).

2.4 Immobilized photocatalysts

The immobilization of photocatalysts on supports (Fig. 4)⁵¹ can maximize the activity of semiconductors by offering a greater number of active sites. The high photocatalytic activity of such immobilized semiconductor photocatalysts is guided by the properties of their semiconductor-active species and the kind of support employed.⁵¹ The high catalytic performance of these immobilized photocatalysts originates from impeding the rate of electron-hole pair recombination. The recovery, reusability, and stability issues of a photocatalyst remain challenging after several reaction runs. In this regard, the immobilization of a catalyst on a support facilitates the rapid separation and efficient recycling

of the catalyst. This reduces production costs as well as minimizing waste generation, especially in industrial applications compared to conventional pure photocatalysts.⁷⁴

3 Removal of pharmaceutical components using different Photocatalysts

In this review article, we present the use of photocatalysts based on bare metal oxides (TiO_2 , ZnO and other oxides) and carbon-based materials (graphitic carbon nitride, g- C_3N_4 , carbon nanotubes CNTs, activated carbon AC, and graphene) in the removal of pharmaceutical pollutants from water. In addition, several modification approaches are also highlighted and those involving metal loading, doping with metals and nonmetals, the formation of composites, immobilization and the formation of heterojunctions for this purpose are described below for pharmaceutical pollutants.

3.1 Acetaminophen

Acetaminophen (ACT), also known as paracetamol is commonly used all over the world as a painkilling, antiinflammatory, analgesic, and antipyretic drug.^{75–78} It is available both as a single-entity formulation and in combination with other medications. The presence of acetaminophen in wastewater, surface water and groundwater can have an adverse effect on living organisms



Fig. 4 Supporting materials used for the immobilization of photocatalysts. Reproduced from ref. 51 with permission from Amer Sci Publ (2023).

and environmental ecology owing to its oxidative transformation to toxic *N*-acetyl-*p*-benzoquinone imine. The stable chemical structure of acetaminophen remains one of the major constraints to its removal through conventional wastewater treatment. Therefore, attention has focused on its removal from aqueous media following a photocatalysis approach, as described below.^{79–147}

3.1.1 Metal oxides. Two titania photocatalysts prepared by a sol-gel method showed higher photocatalytic activity than commercial TiO₂-P25 when tested for the photodegradation of paracetamol in aqueous solution.⁷⁹ Marizcal-Barba et al.⁸⁰ studied the photocatalytic degradation of acetaminophen in the presence of TiO₂ synthesized by a sol-gel method and observed its 99% degradation of acetaminophen corresponding to a pH of 10, acetaminophen concentration of 35 mg L^{-1} and a catalyst dose of 0.15 g of $TiO_2.$ Hollow mesoporous TiO₂ microspheres have also been investigated as a photocatalyst to study the degradation of acetaminophen in water owing to its large surface area and the possibility of efficient light harvesting capability.81 These findings showed an increase in the conversion fraction of the drug to 94% in

60 min following a 25% increase in the initial reaction rate and good photodegradation activity even after 10 repeated runs.

Zhang et al.⁸² reported about 95% photocatalytic degradation of acetaminophen in an aqueous solution of TiO₂ (1.0 g L⁻¹) after 100 min of irradiation under a 250 W metal halide lamp. This is attributed to direct hole (h⁺) oxidation and ipso-substitution comprising the main initial steps in the degradation. The photodegradation of paracetamol (20 mg L⁻¹) has been investigated in the presence of nanostructured TiO₂ catalysts with a nanotube-type morphology using ultraviolet radiation (λ : 254 nm) and the removal efficiency was found to be 99% after 100 min.⁸³ The photocatalytic degradation of acetaminophen in water has also been reported using ZnO,⁸⁴ faceted-TiO₂⁸⁵ and molecularly imprinted ZnO nanonuts.⁸⁶

3.1.2 Metal-incorporated metal oxides. The introduction of metal species into TiO_2 and other metal oxides could modify their structural, electronic, optical and morphological properties. In view of this, several studies have been reported on the photodegradation of pharmaceutical pollutants in

metal-loaded metal oxides. Jiménez-Salcedo *et al.*⁸⁷ applied an organometallic approach for the preparation of Au–TiO₂ nanohybrids and studied the degradation of paracetamol (0.3 mg L⁻¹) under UVA light. These studies revealed 100% degradation of paracetamol in 30 min for Au–TiO₂ photocatalysts compared to TiO₂ (40 min). The kinetic studies also supported these findings as being inevitable from the higher rate constant of Au–TiO₂ photocatalysts (0.14 min⁻¹) compared to TiO₂ photocatalysts (0.12 min⁻¹) in the degradation of paracetamol. In addition, Ag-, Au- and Ptloaded TiO₂ (Ag/TiO₂, Au/TiO₂ and Pt/TiO₂) have shown significant enhancement in the photocatalytic degradation (>90%) of acetaminophen in water over a wide pH range (4.2–8.0) under solar light.⁸⁸

Pd-decorated CuO nanostructured thin film showed enhanced visible-light degradation of acetaminophen.⁸⁹ The influence of radical trappers revealed no role for $\cdot OH$, $\cdot O_2^-$ (or 1O2) radicals on the photocatalytic degradation of acetaminophen. The photocatalyst possessed good stability, as indicated by the observed insignificant change in photodegradation even after 5 cycles. According to the available literature, ZnFe₂O₄ (bandgap: 1.9 eV) is non-toxic and exhibits good photostability.90 Its photocatalytic behaviour is guided by several factors, such as its preparative method, morphology, and the presence of impurities. In view of this, Huerta-Aguilar et al.91 reported the efficient degradation of paracetamol during water treatment using Au nanoparticles grown on ZnFe₂O₄ as a visible light (200 W halogen lamp, C-type R7s, $\lambda > 400$ nm) assisted photocatalyst. TiO₂/BN/Pd nanofibers showed significantly enhanced degradation of ACT (>90%), compared to pure TiO₂ (20%) after 4 h under visible-light irradiation.⁹² This was explained on the basis of the good dispersion of Pd nanoparticles on TiO2-BN nanofibers to facilitate the transfer of photoexcited hole carriers and a decrease in photogenerated electron-charge recombination. Reusability studies and recycling tests on the $TiO_2/BN/Pd$ photocatalyst indicated its good stability over 5 cycles under UV and visible light.

3.1.3 Doped metal oxides. C,N-co-doped TiO₂ (20 mg) degraded 69.31% paracetamol (4 mg L^{-1}) under UV light and 70.39% under solar light in 120 min.⁹³ According to Shaban and Fallata,⁹⁴ carbon-doped TiO₂ nanoparticles (2.0 g L^{-1}) successfully photocatalytically degraded acetaminophen (2 ppm) in aqueous solution, seawater, and real polluted seawater on irradiation with UV and natural sunlight. This enhancement could be attributed to the lowering of its bandgap as a result of carbon doping in TiO₂. In addition, Mg-doped TiO₂ has also been reported in the photodegradation of paracetamol.⁹⁵ Accordingly, 25 wt% Mgdoped TiO₂ produced 60% and 48.3% degradation of paracetamol under UV and visible light, respectively. In all likelihood, the Mg dopant in TiO2 acts as a photosensitizer for photocatalysts and hinders the recombination of electron-hole pairs. In another study, TiO₂ and Ta-doped TiO₂ nanomaterials showed 70-80% degradation of paracetamol in 2 h in UV-irradiated aqueous suspensions, which was attributed to surface acidity as a key parameter.96 Mn-doped TiO₂ exhibited 53% degradation of an aqueous solution of acetaminophen in 3 h under ultrasound and UV irradiation owing to the reduced band gap (1.6 eV) and the high surface area (158 m² g⁻¹).⁹⁷ Fe-doped TiO_2 ,⁹⁸ KAl(SO₄)₂ and NaAlO₂-doped TiO₂,⁹⁹ N-doped halloysite (HNT)/TiO₂,¹⁰⁰ carbon-self-doped TiO₂,¹⁰¹ Bi³⁺-doped TiO₂¹⁰² and Ba_{0.95}- $Bi_{0.05}Fe_{0.95}Cu_{0.05}O_3^{103}$ have also been prepared and examined for the photocatalytic degradation of acetaminophen and paracetamol.

The degradation of acetaminophen and its reaction mechanism have been investigated in presence of Ag–ZnO¹⁰⁴ and La-doped ZnO¹⁰⁵ photocatalysts under visible-light



Fig. 5 (a) Photocatalytic degradation of pharmaceuticals over (a) ZnO (1:6) and (b) 1% Ce–ZnO nanostructured photocatalysts [experimental conditions: catalyst dosage: 1 mg mL⁻¹; concentration of pharmaceutical: 5 mg L⁻¹]. Reproduced from ref. 106 with permission from Elsevier (2019).

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irradiation. Abri *et al.*¹⁰⁶ studied the photocatalytic degradation of nizatidine, acetaminophen and levofloxacin over ZnO (1:6) nanostructured photocatalysts under UVB light for 240 min and the findings are displayed in Fig. 5(a). Similar studies on using 1% Ce-doped ZnO produced almost no change in the degradation of acetaminophen and levofloxacin compared to that observed for nizatidine (~95%), as evidenced from Fig. 5(b). Such different photocatalytic degradation of these pharmaceuticals in the presence of ZnO and 1% Ce-ZnO photocatalysts could be attributed to their chemical structures.

Kumar *et al.*¹⁰⁷ investigated the photocatalytic degradation of acetophenone by irradiating nitrogen-implanted ZnO nanorod arrays (NRAs) with visible light. It should be noted that an N ion (1×10^{16} ions per cm²) doped ZnO NRA sample (referred to as N–ZnO₄) showed maximum degradation efficiency (98.46%) of acetaminophen (20 ppm) in the presence of sunlight under 120 minute duration. The linear variation in $\ln(C_0/C)$ versus irradiation time followed pseudofirst-order degradation kinetics for acetaminophen. Furthermore, the superior photocatalytic activity of the N– ZnO₄ catalyst was inevitable from the high value of its rate constant (0.038 min⁻¹) compared to pristine ZnO NRAs (0.0045 min⁻¹). In addition, further investigations also revealed a more or less unaltered degradation efficiency (98.46% to 97.63%) of N–ZnO₄ after five repeated cycles. The findings of the effect of scavengers on the photocatalytic degradation of acetaminophen in the presence of N–ZnO₄ showed a decrease in degradation efficiency for acetaminophen (98.4%) in the presence of benzoquinone (BQ 28.52%), EDTA (65.6%) and methanol (98.4%) due to the major role played by O₂. The mechanism of acetaminophen degradation on subjecting N-ion-implanted ZnO NRAs to visible light suggested a shifting of the band gap to the visible region.

3.1.4 Metal oxide composites. Nanosized Fe₂O₃-TiO₂ nanocomposites exhibited higher degradation (95.85%) of acetaminophen compared to bare TiO₂ under stimulated solar radiation (optimal conditions: initial concentration of ACT: 30 mg L⁻¹; catalyst loading: 1.25 g L⁻¹; initial pH: 11).¹⁰⁸ Khasawneh *et al.*¹⁰⁹ synthesized a hematite (α -Fe₂O₃)-doped TiO₂ nanocomposite *via* a sol-gel method and investigated the role of UV light on the degradation of paracetamol. The photocatalytic degradation of acetaminophen has also been



Fig. 6 (a) Schematic of the possible charge separation and photocatalytic mechanism of $TiO_2-Bi_4O_5I_2$ composite under visible-light irradiation. Reproduced from ref. 114 with permission from Elsevier (2020). (b) Schematic diagram of charge transfer in the photoexcited TiO_2/Fe_2O_3 coreshell photocatalyst. Reproduced from ref. 117 with permission from Elsevier (2017).

investigated using montmorillonite nanosheets modified with TiO_2 under UV radiation.¹¹⁰ These findings revealed 100% removal efficiency for acetaminophen in aqueous solution corresponding to pH 7, catalyst dose of 0.75 g L⁻¹, acetaminophen concentration of 2 mg L⁻¹ and contact time within 120 min.

Magnetic TiO₂/Fe₃O₄ (1.16 g L⁻¹) and TiO₂/SiO₂/Fe₃O₄ $(1.34 \text{ g } \text{L}^{-1})$ nanoparticles degraded acetaminophen, antipyrine, caffeine, and metoprolol pharmaceuticals on illuminating its aqueous solution (pH: 7, ACT concentration: 30 mg L⁻¹).¹¹¹ TiO₂/SiO₂/Fe₃O₄ nanoparticles also showed good reusability, as evidenced within four repeated experiments. Czech and Tyszczuk-Rotko¹¹² explored the visible-light (centered at 500-550 nm) driven photocatalytic removal of acetaminophen from water using MWCNT (1.72 wt%)-TiO2-SiO2 nanocomposites and observed ~82% efficiency due to the key role played by photogenerated holes. In another study, Fernandes et al.¹¹³ selected combinations of Fe_2O_3 and Fe_3O_4 nanoparticles due to their easy availability and used them in the photodegradation of acetaminophen under UV-vis irradiation. The total acetaminophen (and caffeine) degradation (20 ppm/150 mL) took place by means of 0.13 g catalyst L⁻¹ solution in 45 min (and 60 min) and it remained almost unaltered over five cycles. A ternary heterogeneous anatase-TiO₂ (B) biphasic nanowires/Bi4O5I2 composite exhibited 95% degradation of acetaminophen in 6 min under visible-light irradiation.¹¹⁴ This is ascribed to the multiphase structure, including the synergistic effect of anatase TiO₂ and Bi₄O₅I₂. A schematic of the possible charge separation and photocatalytic mechanism of the TiO₂-Bi₄O₅I₂ composite under visible-light irradiation is displayed in Fig. 6(a).

Chau et al.¹¹⁵ synthesized a Cu₂O/WO₃/TiO₂ ternary composite in view of the narrow band gaps of Cu₂O (2.20 eV) and 2.70 eV (WO₃) guided by their low cost, nontoxicity, chemical stability and strong absorption ability towards visible light. The composite fabricated in this manner produced 92.50% photodegradation of ACT (1 mg L^{-1}) compared to pure TiO2 under 60 min of solar irradiation. This is attributed to the effective separation and low recombination rate of the charge carriers. The produced composite exhibited high reusability for photodegradation with 83% at the fifth cycle of ACT photodegradation. Nanostructured titania supported on activated carbon (AC) has been used to study the effects of photocatalyst dosage, initial solution pH and irradiation (UV) time on the photocatalytic degradation of aqueous acetaminophen.¹¹⁶ Abdel-Wahab et al.¹¹⁷ prepared flower-like core-shell TiO₂/ Fe₂O₃ photocatalysts instead of TiO₂/Fe₃O₄ due to the photostability of Fe₂O₃ compared to Fe₃O₄ and investigated its activity in the degradation of paracetamol in aqueous solution using a medium-pressure mercury lamp (450 W). These findings indicated increases in the photocatalytic degradation of paracetamol (52.5%) to 87.8% for 50% content of TiO2. This is ascribed to the separation of the photogenerated electron-hole pairs accomplished by coupling the narrow band gap with the wide band gaps of Fe_2O_3 and TiO_2 , respectively. A schematic diagram of charge transfer in the photoexcited TiO_2/Fe_2O_3 core-shell photocatalyst is displayed in Fig. 6(b). Jallouli *et al.*¹¹⁸ used TiO_2 nanoparticles and TiO_2 /cellulosic fiber to carry out the photocatalytic degradation of paracetamol under UV and sunlight irradiation. $WO_3/TiO_2/SiO_2^{119}$ and $TiO_2/ZSM-5$ (ref. 120) also exhibited enhanced photocatalytic degradation of acetaminophen in contaminated wastewater.

TiO₂ immobilized on glass spheres (sunlight)¹²¹ and ZnO– polystyrene (UV-LED)¹²² photocatalysts effectively removed acetaminophen and paracetamol, respectively. The photodegradation of acetaminophen is also reported with zeolite-supported TiO₂ and ZnO under UV and sunlight,¹²³ bi-modified titanate nanomaterials (visible light),¹²⁴ BaTiO₃/ TiO₂ composite (UV-vis),¹²⁵ and Ag/AgCl@ZIF-8 (visible light).¹²⁶

3.1.5 C₃N₄ and C-dot-based composites. The rapid (and photocatalytic degradation of acetaminophen levofloxacin) targeted by modifying g-C₃N₄ bulk material to g-C₃N₄ nanosheets under solar-light irradiation reached 99% in 60 min compared to bulk g-C₃N₄ (38% in 240 min).¹²⁷ Such performance of g-C₃N₄ nanosheets could be assigned to multiple contributions, such as smaller particle size, rich carbon surface and lower band gap. Contemporary studies on exfoliated g-C₃N₄ have also been reported for the degradation of paracetamol (and ibuprofen) in an aqueous environment under visible light.¹²⁸ A ZnO/Ph-g-C₃N₄ nanocomposite acted an efficient visible-light-active catalyst for the as photodegradation of paracetamol in aqueous suspension.¹²⁹ The findings revealed hydroxyl and superoxide radical anions to be responsible for the degradation process.

Heterostructures comprising α -Fe₂O₃/g-C₃N₄¹³⁰ have been the photocatalytic degradation examined for of acetaminophen. The photocatalytic activity of g-C₃N₄ combined with UiO-66-NH₂ in different proportions (25%-g-C₃N₄/UiO-66-NH₂, 50%-g-C₃N₄/UiO-66-NH₂, 75%-g-C₃N₄/UiO-66-NH₂) was tested for the removal of acetaminophen from an aqueous solution under given experimental conditions ([ACT]: 5 mg L^{-1} , [Cat]: 0.5 g L^{-1} , V: 350 mL).¹³¹ The corresponding findings on the temporal evolution of acetaminophen with the different samples and their pseudofirst-order rate constants (k_{obs}) are displayed in Fig. 7(a) and (b). These findings depict complete removal of acetaminophens by the 75%-g-C₃N₄/UiO-66-NH₂ heterostructure in 120 min with a pseudo-first-order rate constant of 2 h⁻¹. It is suggested that incorporation of UiO-66-NH₂ in g-C₃N₄ enhanced the separation of the photogenerated charges. Silica-carbon quantum dots (1 wt%) decorated TiO₂ as a sunlight-driven photocatalyst completely removed acetaminophen 33.3% faster than pure TiO2.75 Gupta et al.132 studied the augmented photocatalytic degradation of acetaminophen using hydrothermally treated g-C₃N₄ and persulfate under LED irradiation.

3.1.6 Graphene and its composites. Khavar *et al.*¹³³ observed the complete degradation of acetaminophen (pH



Fig. 7 (a) Photocatalytic degradation of acetaminophen with different $g-C_3N_4/UiO-66-NH_2$ samples. (b) Pseudo-first-order rate constant (k_{obs}) of different $g-C_3N_4/UiO-66-NH_2$ samples. Experimental conditions: V = 350 mL; T = 20 °C, $C_{ACE} = 5$ mg L⁻¹; $C_{CAT} = 0.5$ g L⁻¹. Reproduced from ref. 131 with permission from MDPI (2022). (c) Schematic illustration of the TiNiW NPs decorating the surface of the graphene composites and (d) TiNiW nanoparticle showing the possible chemical reactions for the formation of reactive oxygen species that degrade the ACT contaminant. Reproduced from ref. 138 with permission from Elsevier (2021).

5.4) for 3 wt% rGO@TiO2 under visible UVA-LED irradiation within 50 min. A graphene-oxide-supported bioinspired CuO photocatalyst (50 wt%) showed 96.2% acetaminophen degradation.134 A calcined ZnFe-layered double hydroxide (CLDH)/rGO (for initial wt. of GO: 30 mg) exhibited the highest degradation of about 95% of paracetamol in 420 min, owing to the synergistic effect between Zn-Fe calcined LDH and rGO.¹³⁵ Tao et al.¹³⁶ synthesized nanocomposites comprising 5% graphene/TiO₂ nanotubes by a hydrothermal method and observed a 96% degradation rate for acetaminophen (5 mg L^{-1}) under UV-light irradiation for 3 h. Further investigations indicated holes to be the main oxidation species in the photocatalytic process. According to Umejuru et al.,¹³⁷ coal fly ash (CFA) decorated with graphene oxide nanorods with Pb2+-ion-loaded spent adsorbent exhibited 93% degradation of acetaminophen on subjection to photocatalysis. Ni@TiO2:W nanoparticles (TiNiW) and TiNiW immobilized on the surface of a flexible graphene (FG) composite on subjection to natural solar irradiation (3 h) achieved acetaminophen degradation efficiencies of 100% and 86%, respectively.138 Subsequent findings suggested that acetaminophen degradation was mainly caused by reactive oxygen species, such as $\cdot OH$ radicals and h⁺. Reusability

experiments confirmed the stability of TiNiW and FG/TiNiW composite for the degradation of acetaminophen. Fig. 7(c) schematically represents the TiNiW nanoparticles decorated on the flexible graphene support and a proposed use in the mechanism of acetaminophen degradation. It is suggested that on subjecting it to solar excitation, photogenerated electrons could be rapidly trapped by the graphene layers, as evident through the scheme displayed in Fig. 7(d). Core/shell rGO/BiOBr¹³⁹ and vitamin-C-assisted synthesis of rGO-Ag/ PANI¹⁴⁰ have also been reported to successfully achieve the improved photocatalytic degradation of acetaminophen.

3.1.7 Heterojunctions and Z-scheme-based photocatalysts. Recently, Parida et al.²⁰ fabricated a Bi₂O₃/MnO₂ Z-scheme heterojunction and achieved 94.3% photocatalytic degradation efficiency (0.0202 min⁻¹) for acetaminophen in 120 min. This was found to be about 3.5 and 3.8 times higher than MnO₂ and Bi₂O₃, respectively, in deionized water. Their studies on real water systems further revealed relatively inferior degradation efficiency in tapwater (88.7%), municipal (75.5%), hospital (63.6%) and pharmaceutical industry (55.4%) wastewater compared to that in deionized water (94.3%). The assembly of Sr@TiO2 with UiO-66-NH2 in different ratios was used to construct Sr@TiO₂/UiO-66-NH₂

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Table 2 Performance data on removal of acetaminophen in water using variety of photocatalysts

| Photocatalyst | Preparative method | ACT | Catalyst dose | рН | Light source | Degradation and time | Rate constant |
|--|--|--------------------------------------|---|---------|---|-----------------------|-----------------------------|
| TiO ₂ -rutile ⁷⁶ | Precipitation | 20 ppm | 0.1 g (50 mL) | 9 | Tungsten halogen lamp $(400 \text{ W}) = 0.0146 \text{ W cm}^{-2}$ | 68% (60 min) | |
| TiO ₂ -anatase ⁷⁶ | Thermal precipitation | 20 ppm | 0.1 g | 9 | Tungsten halogen lamp (400 W) , 0.0146 W cm ⁻² | 60% | _ |
| ZnO ⁷⁶ | Thermal precipitation | 20 ppm | (50 mL) 0.1 g (50 mL) | 9 | (400 W), 0.0146 W cm ^{-2}) | $\sim 100\%$ | _ |
| $T_{10} + 2006$ apatasa + 2006 | Commercial | 40 mg I ⁻¹ | (30 mL) | | (400 W), (0.0140 W Chi) | in 1 h | |
| rutile (Degussa P25) ⁷⁷ TiO $(4\pi)(590)^{78}$ | Dhata dan asiti an mathad | (250 mL) | 2 g L | | UV radiation (265 mm) | (300 min) | _ |
| $11O_2/Ag (5\%)$ | Photoaeposition methoa | $(O_2: 100)$ cm^3 min^{-1} | 1 g L | _ | UV radiation (365 nm) | 94.50% (240 min) | _ |
| TiO ₂ ⁷⁹ | Sol-gel method | 50 ppm (750 mL) | 1.33 g L^{-1} | — | TQ159-ZO lamp (150 W) | ~50% (180 min) | 0.0056 min^{-1} |
| $\mathrm{TiO_2}^{80}$ | Sol-gel method | 35 mg L^{-1} | 0.15 g | 10 | UV lamp with a wavelength of 256 nm, 1 mW cm ⁻² | 99% (180 min) | — |
| Solid TiO ₂ spheres ⁸¹ | Template-free solvothermal route | 50 mg L^{-1} | $0.1 \mathrm{~g~L^{-1}}$ | — | Mercury lamp (500 W) | 90% (60 min) | 0.075 min^{-1} |
| Mesoporous TiO ₂ microspheres ⁸¹ | Template-free solvothermal route | 50 mg L^{-1} | $0.1~g~L^{-1}$ | — | Mercury lamp (500 W) | 94% (60 min) | 0.043 min ⁻¹ |
| TiO_2 (High Techn. Nano | Commercial | 50 µM | $1.0~g~L^{-1}$ | 9 | Metal halide lamp $(250 \text{ W}), \lambda \ge 365 \text{ nm}$ | $\sim 95\%$ (100 min) | _ |
| ZnO powders (Fluka) ⁸⁴ | Commercial (thermally calcined at 100 °C) | 50 mg L^{-1} | 0.25 g (0.25 L) | — | UV-lamp (315–400 nm), P.D: 0.66 mW cm^{-2} | $\sim 97\%$ (240 min) | 0.0136 min ⁻¹ |
| ZnO nanonuts ⁸⁶ | Chemical method | $5 	imes 10^{-5}$ M | ~1.0 mg | 7.2 | UV lamp: 4 mW cm ^{-2} , 368 nm | $\sim 92\%$ (180 min) | 1.32×10^{-2} |
| TiO_2 (Degussa P25) ⁸⁷ | Commercial | 0.3 mg | 40.5 mg | Neutral | LED lamp – UVA light | 100% | \min^{-1} 0.12 |
| Au-TiO ₂ ⁸⁷ | Mixing tempered | L^{-1} 0.3 mg | (70 mL) 40.5 mg | Neutral | (15 W), 365 nm LED lamp – UVA light | (40 min) 100% | min^{-1} 0.14 |
| - | colloidal solution of au and TiO ₂ in water | L^{-1} | (70 mL) | | (15 W), 365 nm | (32 min) | min ⁻¹ |
| $Au-g-C_3N_4^{87}$ | Reflex method | 0.3 mg L^{-1} | 40.5 mg (70 mL) | 5.9 | Visible light | 100% (25 min) | 0.17 min ⁻¹ |
| Ag(1 wt%)/TiO ₂ ⁸⁸ | Sonicating mixture of TiO ₂ and aqueous AgNO ₃ , stirring and irradiating with 450-W ACE lamp for 1 h | 20 mg L^{-1} | 0.4 g L ⁻¹ | 6.3 | Simulated solar light xenon lamp (1000 W), 50.0 mW cm ⁻² | ~98% (180 min) | 0.019 min ⁻¹ |
| Au(1 wt%)/TiO ₂ ⁸⁸ | Sonicating mixture of TiO ₂ and aqueous H ₂ AuCl ₆ , stirring and irradiating with 450 W ACE lamp for 1 h | 20 mg L^{-1} | 0.4 g L^{-1} | 6.3 | Simulated solar light xenon lamp (1000 W), 50.0 mW cm ⁻² | ~93% (180 min) | 0.016 min ⁻¹ |
| Pt(1 wt%)//TiO ₂ ⁸⁸ | Sonicating mixture of TiO ₂ and aqueous H ₂ AuCl ₆ , stirring and irradiating with 450 W ACE lamp for 1 h | 20 mg L^{-1} | $0.4 \mathrm{g L}^{-1}$ | 4.2 | Simulated solar light xenon lamp (1000 W), 50.0 mW cm ⁻² | ~100% (180 min) | 0.020 min ⁻¹ |
| Pd/CuO ⁸⁹ | Deposition and sputtering | 10 mg L^{-1} (20 mL) | $15 (l) \times 15 (w) \times 1 (t) mm film$ | — | Xenon arc lamp: 150 W, $\lambda > 420 \text{ nm}$ | ~90% (240 min) | $0.796 h^{-1}$ |
| TiO ₂ /BN/Pd ⁹² | Electrospinning and atomic layer deposition | 1 mg L^{-1} (250 mL) | $0.5~g~L^{-1}$ | 6.8 | Medium-pressure metal halide UV lamp (400 W) | 100% (10 min) | 0.019 min ⁻¹ |
| TiO ₂ /BN100/Pd100 ⁹² | Electrospinning and atomic layer deposition | 1 mg L^{-1} (250 mL) | $0.5 \mathrm{g L}^{-1}$ | 6.8 | 400 W halogen linear lamp (visible irradiation) | 98% (180 min) | 0.28 min ⁻¹ |
| C,N-co-doped ${\rm TiO_2}^{93}$ | Peroxo-gel method | 4 mg L^{-1} | 20 mg | — | UV-light (10 W), λ: 365 nm | 69.31% (120 min) | — |
| C-doped TiO ₂ ⁹⁴ | Sol–gel method | 2.0 ppm | $2.0~g~L^{-1}$ | 7 | Low UV lamp pressure (15 W), 365 nm, 65 W m ⁻² | 100% (90 min) | $0.0817 \ { m min}^{-1}$ |
| Supported titania-based catalysts (25 wt% mg | Industrial petrochemical (source) | 20 mg L^{-1} | 0.7 g L^{-1} (25 mL) | 4.3 | UV lamp: 365 nm , 30 W m^{-2} | 60% (60 min) | — |

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Table 2 (continued)

| Photocatalyst | Preparative method | ACT | Catalyst dose | pН | Light source | Degradation and time | Rate constant |
|--|--|-------------------------------------|-------------------------------------|-------------------|---|-------------------------------|---|
| doping) ⁹⁵ | | | | | Mercury vapour lamp | 48.3% | _ |
| TiO ₂ ⁹⁶ | Hydrolysis of Ti isopropoxide (sol–gel method) | 35 mg L^{-1} | $0.5 \mathrm{~g~L}^{-1}$ | 5.5 | (125 W), (202 W m ⁻²) UV irradiation: HG500 lamp (30 mW cm ⁻²) | (60 min) ~84% (120 min) | $12.4 \pm 0.2 \times 10^{-3}$ min ⁻¹ |
| Ta-doped TiO ₂ (Ti/Ta molar ratio: 1%) ⁹⁶ | Hydrolysis of Ti isopropoxide (sol–gel method) followed by Ta doping through | 35 mg L^{-1} | $0.5 \mathrm{g L}^{-1}$ | 5.5 | UV irradiation: HG500 lamp (30 mW cm ⁻²) | ~70% (120 min) | 9.4 ± 0.1 × 10^{-3} min ⁻¹ |
| TiO ₂ ⁹⁶ | impregnation method Hydrolysis of Ti isopropoxide in presence of CH ₂ COOH | 35 mg L^{-1} | $0.5~g~L^{-1}$ | 5.5 | UV irradiation: HG500 lamp (30 mW cm $^{-2}$) | ~70% (120 min) | 9.3 ± 0.1 × 10^{-3} min ⁻¹ |
| Ta-doped TiO ₂ (Ti/Ta molar ratio: 1%) ⁹⁶ | Hydrolysis of Ti isopropoxide in presence of CH_3COOH followed by ta doping through imprometion method | 35 mg L^{-1} | $0.5 {\rm ~g~L^{-1}}$ | 5.5 | UV irradiation: HG500 lamp (30 mW cm ⁻²) | ~73% (60 min) | $10.4 \pm 0.1 \times 10^{3} \text{ min}^{-1}$ |
| Mesoporous MnO _x -TiO ₂ ⁹⁷ | Sol-gel method | 25 ppm (150 mL) | $0.1 {\rm g L}^{-1}$ | _ | Continuous sonication (20 W) and UVA radiation (160 W m^{-2}) | 26% (180 min) | _ |
| IL-Fe-doped TiO ₂ with Fe to Ti molar ratios (%): 2^{98} | Sol-gel method | 10 mg L^{-1} (200 mL) | $0.65~g~L^{-1}$ | 7 | UV lamps | 90.35% (90 min) | 0.25 min ⁻¹ |
| Synthetic TiO ₂ doped with $(KAl(SO_4)_2)^{99}$ | Sol-gel method | 0.10 mM | $1.0~g~L^{-1}$ | 6.9 | Visible light: source (light emitting diodes) with $\lambda > 440$ nm | 95% (540 min) | 5.20×10^{-3} min ⁻¹ |
| Carbon-self-doped TiO ₂ ¹⁰¹ | Sol–gel method (product calcined at 300 °C) | 0.1 mM (500 mL) | $1.0 \mathrm{g L}^{-1}$ | 6.9 | LEDs ($\lambda > 440 \text{ nm}$) | ~96% (540 min) | 5.0×10^{-3} min ⁻¹ |
| $\operatorname{Bi}^{3+}(10\%)$ -doped anatase TiO ₂ ¹⁰² | Hydrolysis method | 10 ⁴ M (100 mL) | $0.1~g~L^{^{-1}}$ | 5 | Source: UV-vis, (4 W cm ⁻²) | ~100% (240 min) | 0.97 h^{-1} |
| $Ba_{1-x}BiFe_{1-x}Cu_{x}O_{3}$ (x = 0.05) ¹⁰³ | Pechini method | 50 mg L^{-1} | 0.75 g L^{-1} | 9 | Metal halide efficacy lamp | 98.1% (120 min) | — |
| Ag/ZnO ¹⁰⁴ | Chemical method | 5 mg L^{-1} (500 mL) | $1 \mathrm{g L}^{-1}$ | 8.5 | Tungsten halogen lamp (300 W) | 90.8% (120 min) | 0.020 min ⁻¹ |
| 1.0 wt% La-doped ZnO ¹⁰⁵ | Precipitation method | 100 mg L^{-1} (500 mL) | 0.1 g | — | Compact fluorescent lamps: 20 W | 99% (3 h) | _ |
| 1% Ce-doped ZnO ¹⁰⁶ | Hydrothermal method | 5 mg L^{-1} | 1 mg mL^{-1} | 6.8 | UV-B mercury lamp (8 W) | 68% (240 min) | $0.0058 \ { m min}^{-1}$ |
| N-Implanted ZnO nanorod array $(NRA)^{107}$ | ZnO NRAs by two-step process followed by N implantation by low energy ion beam | 20 ppm (5 mL) | 10 × 10 mm aligned ZnO NRA | _ | Visible-light irradiation | 98.46% (120 min) | 0.038 min ⁻¹ |
| $\mathrm{TiO_2/SiO_2/Fe_3O_4}^{111}$ | Ultrasonic-assisted sol–gel method | 30 mg L^{-1} (400 mL) | 1.34 g L^{-1} | 7 | Low-pressure mercury lamp: λ : 254 nm, 3.8 × 10 ⁻⁶ Ein L ⁻¹ s ⁻¹ | ~97% (300 min) | $1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ |
| $\begin{array}{l} \text{MWCNT} (1.72 \text{ wt\%}) \\ \text{TiO}_2\text{-}\text{SiO}_2^{-112} \end{array}$ | Sol–gel method | 10 mg L^{-1} | _ | Nearly neutral | High-pressure mercury lamp, 500–550 nm, 7.31-7.53 mW m ⁻² | 81.6% (60 min) | 0.0113 min^{-1} |
| Magnetite-hematite ¹¹³ | Hydrothermal | 20 mg | 0.13 g L^{-1} | _ | Medium-pressure hg | ~100% (45 min) | _ |
| TiO_2 (438 mg)- $Bi_4O_5I_2^{114}$ | <i>In situ</i> calcination method | 3 ppm | 25 mg | — | Xenon lamp with a light filter of 400 nm | ~95% (6 min) | 0.425 min ⁻¹ |
| $\mathrm{Cu_2O/WO_3/TiO_2}^{115}$ | Hydrothermal | 1 mg L^{-1} (80 mL) | 20 mg | 9 | Solar-light irradiation (source) | 92.5% (60 mL) | 4.42×10^{-2} min ⁻¹ |
| Flower-like 50% TiO ₂ /Fe ₂ O ₃ ¹¹⁷ | Modified ultrasonic assisted sol-gel method | 50 mg L^{-1} (50 mL) | 0.1 g L^{-1} | _ | Medium-pressure Hg lamp (450 W) Venon Jamp (500 W) | 87.8% (90 min) | 0.0219 min ⁻¹ |
| 570 WO3/11O2/3IO2 | | 10 IIIS F | 1.0 g L | 7 | without cut-off filter 800 nm cut-off filter (800 nm $> \lambda$ > 200 nm) | (240 min) | 0.70 11 |

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Table 2 (continued)

| Photocatalyst | Preparative method | ACT | Catalyst dose | рН | Light source | Degradation and time | Rate constant |
|--|---|---|-------------------------------------|---------|--|-------------------------|--|
| TiO_2 (40 wt%) /ZSM-5 ¹²⁰ | Sol-gel method | 15 mg L^{-1} (500 mL) | $1.0 \mathrm{g L}^{-1}$ | 6.8 | UV lamp (14 W), 254 nm, 0.97 mW cm ⁻² | 96.6% (180 min) | _ |
| 1.1% ZnO/polystyrene ¹²² | Solvent casting method | 12.5 mg L ⁻¹ | 25 g (50 mL) | 6.5 | UV light (13 W m^{-2}) | 77% (240 min) | _ |
| Bi modified titanate ¹²⁴ | Hydrothermal method | $_{L^{-1}}^{0.7}$ mg | $1.0 {\rm g}{\rm L}^{-1}$ | 7 | Metal halogen lamp with UV and IR cut-off filters | 88% (180 min) | 12.61×10^{-3} min ⁻¹ |
| BaTiO ₃ /TiO ₂ ratio of $3:1$ (w/w) ¹²⁵ | Grounding followed by drying and calcination | 5 mg L^{-1} | $1~g~L^{-1}$ | 7 | Xenon lamp: 500 W (200 nm $< \lambda < 800$ nm) | 95% (240 min) | 0.5529 h^{-1} |
| Ag/AgCl@ZiF-8 ¹²⁶ | Stirring method | 1 mg L^{-1} | $0.5~g~L^{-1}$ | 5 | Metal halogen lamp (500 W) combined with UV and IR cut-off wave length | 99% (90 min) | 0.0579 min ⁻¹ |
| g-C ₃ N ₄ ¹²⁷ | Thermal oxidation | 5 mg L^{-1} | 0.1 g (250 mL) | — | Solar irradiation (source) | 99% (60 min) | — |
| Exfoliated g-C ₃ N ₄ ¹²⁸ | Thermal synthesis | 25 g dm ⁻³ | 0.9 g | _ | UVA lamp: 368 nm, 0.96 mW cm ⁻² | 41% (120 min) | 4.5×10^{-3} Mol dm ⁻³ min ⁻¹ |
| Exfoliated $g - C_3 N_4^{-128}$ | Thermal synthesis | 25 g dm ⁻³ | 0.9 g | — | Visible light lamp (446 nm), an intensity of 8.5 mW cm ^{-2} | 54% (120 min) | _ |
| 0.05% ZnO/Ph-g-C ₃ N ₄ ¹²⁹ | Single-step calcination and combustion process | 20 mg L^{-1} | $1 \mathrm{g L}^{-1}$ | _ | Halogen lamp (500 W) | 90.8% (120 min) | _ |
| α -Fe ₂ O ₃ /g-C ₃ N ₄ ¹³⁰ | Dispersion under sonication followed by heating in air | 2.0 mg L^{-1} (H ₂ O ₂ : 5.0 mM) | $0.1 \mathrm{~g~L}^{-1}$ | 5.0 | Xenon lamp: 35.0 W $(\lambda > 420 \text{ nm})$ | 100% (25 min) | 0.134 min ⁻¹ |
| $g-C_3N_4(75\%)/UiO-66-NH_2^{-131}$ | Hydrothermal method | 5 mg L^{-1} (350 mL) | $0.5~{\rm g~L}^{-1}$ | 4-5 | 9 W lamps, 365 nm | 100% (120 min) | 2.0 h^{-1} |
| Bi_2O_3/MnO_2^{-20} | Room temperature solution phase synthesis | 5 mg L^{-1} | $1 \mathrm{g L}^{-1}$ | 6.8 | 200 W LED strip $(\lambda > 420 \text{ nm})$ | 94.3% (120 min) | 0.0202 min ⁻¹ |
| TiO ₂ @rGO prepared by using 3 wt% GO^{133} | Sol-gel method | 50 mg L ⁻¹ (25 mL) | 2.0 g L^{-1} | 5.4 | LED lamps (18 no.) and each of l3 W, λ : 365 nm, 95 μ W cm ⁻² | 100% (50 min) | 0.061 min ⁻¹ |
| Calcined ZnFe-LDH/rGO (using 30 mg of GO) ¹³⁵ | Hydrothermal calcined method (using 30 mg GO) | 5 mg L^{-1} (50 mL) | 25 mg | — | Xenon lamp (500 W), 300 nm cut-off filter | 95% (420 min) | 0.00737 min ⁻¹ |
| 5% graphene/TiO ₂ nanotubes ¹³⁶ | Hydrothermal | 5 mg L^{-1} (500 mL) | $0.1 { m g L}^{-1}$ | 7 | UV lamp (14 W), 254 nm | 96% (180 min) | 00197 min ⁻¹ |
| Coal fly ash (CFA)/GO/WO ₃ NRs ¹³⁷ | Hydrothermal | 5 mg L^{-1} | 100 mg | — | 250 HW lamp | 86% (180 min) | -0.0116 min ⁻¹ |
| $Ni@TiO_2:W^{138}$ | Hydrothermal treatment immobilizing | 25 mg L^{-1} | 30 mg (100 mL) | 7 | Solar natural irradiation $(754 \pm 13 \text{ W m}^{-2})$ | 100% (180 min) | 10.7×10^{-3} min ⁻¹ |
| Flexible graphene/Ni@TiO ₂ :W ¹³⁸ | TiNiW grown on the surface of graphene | 25 mg L^{-1} | 30 mg (100 mL) | 7 | Solar natural irradiation $(754 \pm 13 \text{ W m}^{-2})$ | 86% (180 min) | 8.8×10^{-3} min ⁻¹ |
| 1% rGO/BiOBr core/shell ¹³⁹ | Hydrothermal | 5 mg L^{-1} (30 mL) | _ | 5.5-9.5 | Hg/xenon lamp (visible light irradiated with 400 nm cut-off filter), 20 mW cm ⁻² | 93% (105 min) | 0.006 min ⁻¹ |
| rGO-Ag/PANI ¹⁴⁰ | Mixing reduced GO with polyaniline AgNO ₃ by vitamin C | 25 mg L^{-1} | 50 mg | 5 | Visible light | 99.6% (100 min) | _ |
| Sr@TiO ₂ with UiO-66-NH $_2^{141}$ | By carrying out growth of UiO-66-NH ₂ on SrTiO ₃ | 5 mg L^{-1} | 250 mg L^{-1} (150 mL) | — | Xenon lamp: 600 W m ⁻² (λ cut-off filter: 320 nm) | ~94% (240 min) | $0.67 \ h^{-1}$ |
| $15 \text{ wt}\% CeO_2/IK-g-C_3N_4^{-142}$ | Mixing method | 10 mg L^{-1} (20 mL) | 2.0 g L^{-1} | 9 | Visible light lamps (8 W), 465 ± 40 nm | 98% (90 min) | $0.0386 \ { m min}^{-1}$ |
| 5% g-C ₃ N ₄ /TiO ₂ /persulfate ¹⁴³ | Ultrasonic mixing | 5 mg L ⁻¹ (100 mL) and PS: 2 mM | 0.331 g L^{-1} | 7 | Xenon lamp (300 W) with 400 nm cut-off filter | 99.3% (30 min) | 0.181 min ⁻¹ |

(cc)

Table 2 (continued)

| Photocatalyst | Preparative method | ACT | Catalyst dose | рН | Light source | Degradation and time | Rate constant |
|---|---------------------------------|------------------------|------------------------|------|---|-------------------------|--|
| CdO–ZnO (0.1:0.2 mole ratio) ¹⁴⁴ | Homogeneous co-precipitation | 12 ppm | 1 g L^{-1} | 6.15 | Halogen lamp (500 W) | 96% (160 min) | 0.05 min ⁻¹ |
| magnetic mesoporous carbon ¹⁴⁶ | co-precipitation method | L^{-1} , PMS: 0.6 mM | 0.12 g L - | 6 | with 254 nm cut-off filter | 97.4% (40 min) | _ |
| $TiO_2/graphene/g-C_3N_4$ (60 : 10 : 30) ¹⁴⁷ | Hydrothermal method | 50 mg L ⁻¹ | 0.6 g L^{-1} | 9 | Xenon lamp (SSL irradiation): 300 W, λ cut-off filter: 420 nm | 100% (120 min) | 2.7×10^{-2} min ⁻¹ |

heterostructures and achieved more than 90% conversion of acetaminophen under solar light.¹⁴¹ A visible-light-driven CeO₂/I,K-co-doped C_3N_4 wt% heterojunction 15 photocatalyst removed about 98% acetaminophen from aqueous solution after 120 min of irradiation compared to pure g-C₃N₄ (47%) and doped IK-C₃N₄ (75%).¹⁴² In another study, a g-C₃N₄/TiO₂ (weight ratio: 5%)-persulfate (PS) almost photocatalytic system showed complete photodegradation ability and stability for acetaminophen under visible-light irradiation.¹⁴³ Visible-light-mediated CdO-ZnO demonstrated efficient photocatalytic performance as a heterogeneous photocatalyst in the decomposition of paracetamol in an aqueous solution.¹⁴⁴ Radical scavenger tests established the dominance of ·OH and h^+ for this photocatalytic process.

A heterojunction magnetic ternary g-C₃N₄/TiO₂-MnFe₂O₄ halloysite photocatalyst showed about 79.1% removal of acetaminophen (10 ppm) within 90 min under visible light.145 The ternary photocatalyst could be easily recovered by applying an external magnetic field and reused several times without any significant reduction in its catalytic activity. The removal efficiency for acetaminophen under optimum conditions in the presence of a magnetic carbon coupled heterojunction with UV light and peroxymonosulfate was insignificantly reduced from 97.4% even after five consecutive cycles.¹⁴⁶ Moradi et al.¹⁴⁷ used 0.6 g L^{-1} of TiO₂/graphene/g-C₃N₄ (60:10:30) Z-type photocatalyst and observed complete degradation of acetaminophen (50 mg L⁻¹) at a pH of 9.0 in 120 min due to a synergistic effect. Their investigations also showed HOand O_2 . radicals to be the dominant species in the degradation of acetaminophen.

Table 2 records the performance data of different photocatalysts on the removal of acetaminophen from wastewater.

3.2 Amoxicillin

Amoxicillin (AMX) is a widely used semi-synthetic β -lactam and broad-spectrum antibiotic in the treatment of different types of infection for treating both human and animal diseases.¹⁴⁸ Therefore, it is possible to find traces of this drug or its degradation products in various aquatic environments in the treated discharge from wastewater treatment plants. Its presence in aquatic animals and humans contributes to toxic effects though the aquatic system due to its structure, high polarity, and water solubility. However, amoxicillin in water is not easy to remove by conventional wastewater treatment processes due to its resistance to biodegradation. Hence, it is necessary to conduct a large amount of research on the treatment and removal of amoxicillin from wastewater using a variety of photocatalysts before discharging it into the natural aquatic environment.^{149–216}

3.2.1 Metal oxides

3.2.1.1 TiO₂. Radosavljević et al.¹⁴⁹ applied TiO₂ in a nanocrystalline form and compared it with commercial TiO₂ to study the photocatalytic degradation of amoxicillin using an Osram Ultra-Vitalux® lamp as the light source. Their findings indicated almost complete degradation of AMX after 210 min for catalyst and AMX concentrations of 2 g dm⁻³ and 100 mg dm⁻³, respectively. The UV-mediated photocatalytic degradation of amoxicillin was found to be low (27.6%) in the presence of TiO2 (10-25 nm) compared to cephalexin (63.5%) and tetracycline (100%) under optimal conditions.¹⁵⁰ Pereira et al.¹⁵¹ used photoreactors and studied the degradation of amoxicillin in aqueous solution (pH: 7.5) by subjecting it to a solar-driven TiO_2 (0.5 g L⁻¹) assisted photocatalytic process. According to this, TiO₂/solar UV radiation was able to reduce the antibiotic concentration from 40 to 3.1 mg L^{-1} after 4.6 kJ_{UV} of UV accumulated energy per liter of solution.

The degradation of amoxicillin (10 mg L^{-1}) was also examined under UV and visible irradiation (15 min) and found to be nearly 100% for TiO_2 and ZnO (both 0.01 g), respectively.¹⁵² Amoxicillin (104 mg L⁻¹) in aqueous solution (pH \sim 5) was completely degraded under TiO₂/ UVA (365 nm) in 30 min in the presence of H_2O_2 (100 mg L⁻¹).¹⁵³ TiO₂-catalyzed photodegradation of amoxicillin (10 mg L^{-1}) was found to be ~100% under UV irradiation of 30 min duration.¹⁵⁴ According to Klauson et al.,¹⁵⁵ Degussa P25 TiO₂ showed about 83% degradation of AMX (pH: 6.0) after 2 h under solar radiation. Moosavi and Tavakoli¹⁵⁶ studied degradation amoxicillin in contaminated water using TiO2 in solar photocatalysis, considering variations in pH, catalyst dose and initial concentration of amoxicillin. These studies showed 84.12% degradation of amoxicillin after 240 min under optimum conditions of pH 9.5, catalyst dose of 1.5 g L^{-1}

and initial concentration of amoxicillin of 17 mg L⁻¹ under 240 min of solar irradiation due to a synergistic effect. In addition, several other studies have also been reported using TiO_2 ,^{157–159} and supported TiO_2^{160} on the photocatalytic remediation of amoxicillin.

3.2.1.2 ZnO and other metal oxides. The effect of operating variables has been studied on the degradation of amoxicillin (104 mg L^{-1}) in aqueous solution driven by a UV/ZnO photocatalyst prepared by a microwave-assisted gel combustion method, which achieved complete degradation corresponding to a zinc oxide concentration of 0.5 g L^{-1} , irradiation time of 180 min and pH 11.¹⁶¹ The photocatalytic reactions followed pseudo-first-order kinetics with a rate constant of 0.018 min⁻¹. In another study, the photocatalytic removal of amoxicillin (and sulfamethoxazole) was achieved in 6 h from aqueous solutions using ZnO nanoparticles irradiated with UVC irradiation.¹⁶² Al-zobai et al.¹⁶³ reported the recovery of 72.3%, 85.3%, and 100% of amoxicillin under optimum conditions using UV/TiO₂, UV/ZnO/TiO₂ and UV/ ZnO.¹⁶³ Bi₂O₃/Fe (3 wt%), successfully synthesized by a microwave-assisted precipitation method, exhibited a degradation efficiency of 76.34% and a degradation rate for amoxicillin of 0.0079 min⁻¹.¹⁶⁴

The effect of AMX concentration, WO₃ dosage, and pH was studied for the photocatalytic degradation of amoxicillin by solar-driven simulated irradiation.¹⁶⁵ These findings revealed the complete removal of AMX under optimal conditions corresponding to an initial AMX concentration of 1.0 μ M, catalyst dosage of 0.104 g L⁻¹ and pH 4. Sol-gel-synthesized nano-NiO under optimal conditions efficiently degraded 96% of amoxicillin from pharmaceutical wastewater.¹⁶⁶ The photodegradation process was found to follow pseudo-first-order kinetics (*k*: 0.084 min⁻¹) for an amoxicillin concentration of 25 mg L⁻¹.

3.2.2 Doped metal oxides. According to Klauson et al.,¹⁵⁵ TiO₂ doped with C (32 at%) and Fe (2.2 at%) under identical conditions of solar radiation in 2 h of treatment and pH 6.0 TiO₂ showed about 83%, 73% and 75% degradation of amoxicillin, respectively. Mohammadi et al.¹⁶⁷ used Sn (1.5 mol%) doped/TiO₂ nanoparticles to carry out the photocatalytic decomposition of amoxicillin trihydrate in aqueous solutions under UV light. It showed high photocatalytic activity during the mineralization of AMX due to hydroxyl radicals and band gap energy. Sol-gel-synthesized Sn,Zn-co-doped TiO₂ showed marked improvement in the photocatalytic degradation of amoxicillin trihydrate due to the synergistic actions of the dopants.¹⁶⁸ According to Wahyuni et al.,169 doping of Cu in TiO2 shifts the light absorption into the visible region. Furthermore, doping of Cu in TiO₂ increased the degradation of amoxicillin under visible light. Amoxicillin (10 mg L⁻¹) exhibited about 90% photodegradation using 0.40 g L^{-1} of a Cu (4.56 mg g^{-1}) doped TiO₂ photocatalyst in 24 h at pH 6 under visible-light irradiation. In another study, the removal of amoxicillin from aquatic and pharmaceutical wastewater solution was studied using Fe³⁺-doped TiO₂ under UVA radiation.¹⁷⁰ These

findings revealed removal efficiencies of 99.14% and 88.92% under the optimum conditions (pH: 11, initial concertation of amoxicillin: 10 mg L^{-1} , catalyst: 90 mg L^{-1} , contact time: 120 min) for synthetic and pharmaceutical water, respectively.

A Ce^{3+} -doped TiO₂ thin film, prepared using polyethylene glycol as the templating agent, acting as a catalyst succeeded in the removal of amoxicillin under UVA radiation from aqueous solution (pH 6.0).¹⁷¹ It was noted that the removal of amoxicillin increased from 28% to 67% (2 h) in the presence of Ce^{3+} (a)TiO₂, corresponding to a decrease in the initial concentration of amoxicillin from 15.0 to 0.5 mg L^{-1} , respectively. The Ce³⁺(a)TiO₂ thin film retained its photocatalytic stability more or less unaltered even after 6 cycles. It was suggested that cerium ions trapped the electron and hole pairs in the TiO₂ catalyst to form hydroxyl and peroxy radicals that play a significant role in the degradation of amoxicillin. Mn-doped Cu₂O nanoparticles synthesized using aloe vera leaf extract exhibited 92% degradation of amoxicillin under sunlight irradiation at pH 9, an initial concentration of amoxicillin of 15 mg L⁻¹, and a photocatalyst dosage of 1 g L^{-1.172} In all likelihood, Mn doping in Cu₂O delays rapid recombination by trapping the photogenerated electrons, accounting for its enhanced photocatalytic performance in amoxicillin degradation.

3.2.3 Metal dispersed on metal oxides. The photocatalytic degradation of amoxicillin antibiotic was investigated in the presence of La and Ce nanoparticles as co-catalysts dispersed on the surface of TiO₂.¹⁷³ These findings showed it had more than twice the activity of pure TiO2 in the removal of amoxicillin, which was attributed to the synergistic interaction between La and Ce nanoparticles loaded on TiO₂. However, more work still needs to be carried out to explore the effect of different metals on the surface of TiO₂ and ZnO for the photodegradation of antibiotics. UV-visible or visible illuminated TiO₂ nanowire arrays (TNAs), TiO₂ nanowires (TNWs)/TNAs, Au-TNAs and Au-TNWs/TNAs degraded amoxicillin completely in aqueous solution within 20 min due to the surface plasmonic effect and synergistic effects.¹⁷⁴ The photodegradation of amoxicillin (and levofloxacin) was performed using an Ag/ZnO photocatalyst in aqueous solution under A-type ultraviolet irradiation (UVA 365 nm) to study its variation with solution pH, initial concentration of amoxicillin, catalyst dosage, and reaction time.¹⁷⁵ According to this, maximum removal (93.7%) of amoxicillin was achieved under optimum conditions corresponding to Ag/ ZnO concentration of 0.15 g L⁻¹, pH 5, amoxicillin concentration of 5 mg L^{-1} and contact time of 120 min.

3.2.4 Metal oxide nanocomposites

3.2.4.1 TiO_2 nanocomposites. Bergamonti *et al.*¹⁷⁶ studied the photocatalytic activity of TiO_2 immobilized on a chitosan scaffold under UV/vis irradiation to examine the degradation of amoxicillin in wastewater under UV-vis irradiation. These findings showed high photodegradation efficiency compared to the direct photolysis of amoxicillin. A TiO_2 /PAC (powdered activated carbon) mixture in suspension removed 95% amoxicillin in 60 min owing to significant synergy.¹⁷⁷ TiO₂/ zeolite-photocatalysis also presented a feasible methodology for the degradation of the AMX under UV radiation.¹⁷⁸ It was noted that a material obtained by acid-alkaline pretreatment and calcination (300 °C) showed the best performance due to its favorable surface structure and TiO₂ content.

Pastrana-Martínez and others¹⁷⁹ prepared nanodiamond (ND) composites of pristine TiO₂ (NDDT) to study its oxidative degradation of amoxicillin soluble in water under near-UV/vis irradiation. Their findings clearly revealed the complete degradation of amoxicillin by NDDT, owing to the generation of holes and better charge separation. In addition, specific surface area, functional groups introduced in ND and the porosity of NDDT compared to bare TiO₂ also play an important role in the photocatalytic degradation efficiency of amoxicillin. Li and coworkers180 investigated the effect of Fe₃O₄ loading in TiO₂-Fe₃O₄ composites, H2O2 concentration, different initial pH and light intensity on the degradation of amoxicillin. The separation showed the following trend towards the degradation of amoxicillin in 100 min under optimum conditions (amoxicillin: 30 mg L⁻¹, UV irradiation: 200 W, $[H_2O_2]$: 4.24 mM, pH: 2.84): TiO₂/15 wt% Fe₃O₄ + H₂O₂ > $TiO_2/20 \text{ wt\% } Fe_3O_4 + H_2O_2 > TiO_2/25 \text{ wt\% } Fe_3O_4 + H_2O_2$ $TiO_2/10$ wt% $Fe_3O_4 + H_2O_2 > TiO_2 + H_2O_2$. It was noted that the presence of H₂O₂ contributed to oxidation in a photo-Fenton process while the choice of the optimum pH of 2.84 is guided by the scrambling of Fe^{3+} between OH and H_2O_2 . Furthermore, the reaction rate below 200 W increased remarkably with increasing light intensity due to the generation of electrons and holes. As a consequence, maximum AMX removal efficiency (~88% in 100 min) was achieved for 0.4 g L⁻¹ of TiO₂/15 wt% Fe₃O₄/H₂O₂ (6 mM) under optimum conditions corresponding to an initial concentration of amoxicillin of 30 mg L⁻¹ and catalyst loading of $0.4 \text{ g } \text{L}^{-1}$. The highest performance for amoxicillin in the presence of TiO₂/15 wt% Fe₃O₄ could be ascribed to the generation of more active ·OH. The proposed mechanism involved the rapid transfer of excited electrons from TiO_2 to Fe_3O_4 , reducing h^+/e^- pair recombination and providing an additional ·OH generation pathway for amoxicillin degradation.

dela Rosa *et al.*¹⁸¹ studied the degradation and kinetic profiles of amoxicillin using solar/TiO₂/Fe₂O₃/persulfate and the corresponding findings are displayed in Fig. 8(A) and (B), respectively. It was observed that AMX degradation was reduced from 70% (no scavengers) to 39%, 54% and 64% (50 min) in the presence of methanol (MeOH), *tert*-butanol (*t*-BuOH) and 1,4-benzoquinone, respectively. Based on the overall findings, arrangements of reactive oxygen species (ROS) for AMX degradation by a solar/TiO₂–Fe₂O₃/PS process follows the order: $h^+ > SO_4 \cdot - > HO \cdot > O_2 \cdot -$. The overall amoxicillin degradation can be accounted for by considering the suppression of recombination of charges by the presence of PS as well as the generation of ROS at h^+ .

TiO₂ immobilized on activated carbon fabricated by a impregnation high-temperature method degraded amoxicillin, diclofenac and paracetamol by 100% (120 min), 85% (180 min) and 70% (180 min) in aqueous solution under solar irradiation.¹⁸² Li et al.¹⁸³ reported the photocatalytic degradation of amoxicillin using TiO₂ nanoparticles submerged on a porous ceramic membrane. TiO2 immobilized on sand has been used as a catalyst in a solar photocatalytic process for the removal of amoxicillin residues from aqueous solution.¹⁸⁴ These findings showed 93.12% degradation of amoxicillin under the optimal conditions of pH 5, 7 5 mg L^{-1} of TiO₂, 400 mg L^{-1} of H₂O₂, and 10 mg L^{-1} of AMX concentration at 150 min irradiation time. Furthermore, the removal of undesirable compounds follows a pseudo-second-order kinetic model. In addition, TiO₂/Mg-Al-layered double hydroxide (LDH),¹⁸⁵ Ag-ion-exchanged zeolite/TiO₂,¹⁸⁶ Fe-8-hydroxyquinoline-7-carboxylic/TiO₂ flowers¹⁸⁷ and TiO₂-SiO₂¹⁸⁸ composites have also been used to remove amoxicillin from aqueous solutions.



Fig. 8 (A) Photocatalytic degradation of AMX under solar irradiation in the presence of scavengers; and (B) corresponding zero-order rate constants (k_{obs}) (experimental conditions: [AMX] = 50 μ m; initial pH = 4; [PS] = 334 μ m, treatment time, t = 50 min). Reproduced from ref. 181 with permission from Wiley (2021).

3.2.4.2 ZnO-based nanocomposites. Thi *et al.*¹⁸⁹ observed the enhanced photocatalytic activity of ZnO–TiO₂ (10%) for the ozonation and perozone degradation of amoxicillin in water under visible-light irradiation. The visible-light-driven MIL-53(Al)/ZnO hierarchical photocatalyst produced 100% removal of amoxicillin corresponding to an initial amoxicillin concentration of 10 mg L⁻¹, solution pH 4.5 and catalyst dose of 1.0 g L⁻¹.¹⁹⁰ Recently, Liu and others¹⁹¹ reported significantly high degradation efficiency of amoxicillin (93.10%) in wastewater using Bi₂WO₆/nano-ZnO (1:3) after 120 min in comparison to ZnO and Bi₂WO₆. It is anticipated that the reduction in band gap energy of Bi₂WO₆/nano-ZnO (1:3) could prevent the recombination of photogenerated charge carriers.

3.2.5 Graphitic-carbon-based nanocomposites

3.2.5.1 g-C₃N₄-based nanocomposites. Carbon-rich g-C₃N₄ nanosheet samples were prepared by a combination of 20 g of urea and 60 mg, 90 mg and 120 mg of 1,3,5cyclohexanetriol as starting materials (referred to as C-CN60, C-CN90 and C-CN120, respectively).¹⁹² They included plenty of carbon-rich functionalities and were examined for their photocatalytic activity for amoxicillin degradation under solar and visible light in the aqueous phase and the results are displayed in Fig. 9. The degradation of amoxicillin was found to follow the order: C-CN90 > C-CN60 > C-CN120 > g-C₃N₄. Photocatalyst C-CN90 showed nearly complete photocatalytic degradation of amoxicillin under solar light and visible light after 150 and 300 minutes, respectively. This has been attributed to the interaction between g-C₃N₄ and graphited conjugated construction narrowing the band gap and separating photogenerated electron-hole pairs.

Silva *et al.*¹⁹³ synthesized metal-free polymeric carbon nitrides using melamine (CN-M), thiourea (CN-T) and their 1:1 mixture (CN-1M:1T) as precursors in a Teflon reactor comprising 25 mL of deionized water followed by heating of the products at 550 °C for 30 min. Their investigations revealed 100% degradation of AMX for CN-T followed by CN-M (65%) and CN-1M:1T (56%) after 48 h of visible-light exposure. The superior performance of CN-T was found to be directly related to the greater number of defects present in its structure, that can help in the separation of electron–hole

pairs. An Ag/g-C₃N₄/ZnO nanorod (0.08 g L^{-1}) nanocomposite has also acted as an efficient photocatalyst in the photocatalytic degradation of amoxicillin of high concentration (40 mg L^{-1}) irradiated by visible light.¹⁹⁴ V₂O₅nanodot-decorated laminar C3N4 degraded amoxicillin under solar light, exhibiting 91.3% removal efficiency.¹⁹⁵ It is suggested that such a V₂O₅/C₃N₄ S-scheme structure provides an internal electron channel at the interface and maintains the active sites with high potentials for the photodegradation of amoxicillin. Mesoporous g-C₃N₄/persulfate exhibited 99% degradation of AMX under visible-light irradiation within 60 min at pH 7 due to a synergistic effect.¹⁹⁶ Graphitic-carbon-CuO-ZnO nanocomposites exhibited 49% efficiency in the photocatalytic degradation of amoxicillin under direct sunlight and followed pseudo-first-order kinetics.¹⁹⁷ α-Fe₂O₃/ g-C₃N₄,¹⁹⁸ mesoporous g-C₃N₄,¹⁹⁹ and CQDs/K₂Ti₆O₁₃²⁰⁰ photocatalysts have also been reported in the photocatalytic degradation of amoxicillin.

3.2.5.2 Graphene-based nanocomposites. Changotra et al.²⁰¹ prepared nanocomposites of varying FeS₂ to GO weight to study the degradation of amoxicillin as a function of different parameters, such as solution pH value, optimal doses of H₂O₂ and catalyst, stability of the catalyst, and leaching effect of the catalyst, under optimal solar-Fenton treatment. These investigations showed the complete degradation of amoxicillin (~99%) by FeS₂/GO (4:3) in 180 min owing to the synergistic coupling of FeS₂ and GO under the optimal conditions of $[amoxicillin]_{init conc}$ 25 mg L⁻¹, [FeS/GO] 0.75 g L^{-1} , 12 mM [H₂O₂] and pH 5. Further, HO· acted as dominant reactive species and no toxic secondary products were produced in the amoxicillin degradation. The photocatalytic degradation efficiency for amoxicillin by TiO₂ nanoparticles loaded on graphene oxide under UV light was found to be >99% at pH 6, catalyst dose of 0.4 g L^{-1} , amoxicillin concentration of 50 mg L⁻¹ and intensity of 36 W (Fig. 10(a-d)).²⁰²

According to Song and others,²⁰³ KBrO₃ added to graphene–TiO₂ nanotubes achieved 100% photodegradation of amoxicillin under UVA-light irradiation. It is suggested that KBrO₃ prevents electron–hole recombination and has a direct role as an oxidant in the degradation of amoxicillin. A



Fig. 9 Photocatalytic degradation kinetics of AMX by the synthesized materials under (a) simulated solar light, (b) visible light, and (c) AMX degradation rate constants under solar and visible light. Reproduced from ref. 192 with permission from Elsevier (2021).



Fig. 10 The effect of different operational factors on AMX photocatalytic degradation and kinetic constant (a–d). Reproduced from ref. 202 with permission from Springer (2021).

visible-light-driven MIL-68(In)–NH₂/graphene oxide (GO) composite photocatalyst (0.6 g L⁻¹) exhibited 93% degradation (120 min) of amoxicillin in aqueous solution of pH 5 compared to pure MIL-68(In)–NH₂.²⁰⁴ It is suggested that MIL-68(In)–NH₂/GO acted as an electron transporter for suppressing photogenerated carrier recombination and also acted as a sensitizer for enhancing visible-light absorption. The proposed mechanism suggested that h⁺ and \cdot O₂⁻ are active species. In another study, a 2D/3D g-C₃N₄/BiVO₄ hybrid photocatalyst decorated with rGO (1.2 wt%) degraded amoxicillin by 91.9% under optimized conditions with visible-light illumination.²⁰⁵

3.2.6 Heterostructures, heterojunctions and Z-schemebased photocatalysts. Thuan *et al.*²⁰⁶ compared the superior performance of an InVO₄@Ag@g-C₃N₄ ternary heterojunction in the photocatalytic degradation of amoxicillin in an aqueous environment at an initial AMX concentration of 10 ppm and catalyst dose of 0.5 g L⁻¹ under visible light for 420 min: InVO₄@Ag@g-C₃N₄ (~99%) > InVO₄@Ag@g-C₃N₄ (~80%) > InVO₄@ (~43%) > g-C₃N₄ (~37%). The choice of Ag in this work is mainly guided by its two-fold contribution in the InVO₄@Ag@g-C₃N₄ ternary heterojunction. It accounts for the enhanced electron-hole separation of both g-C₃N₄ and InVO₄ components. In addition, silver also acts as an electron mediator to improve electron transfer from the InVO₄ conduction band to the g-C₃N₄ valence band. A CuI/ FePO₄ heterojunction nanocomposite showed p–n photodegradation efficiency of 90% for the elimination of under simulated sunlight radiation.²⁰⁷ amoxicillin A mesoporous $SnO_2/g-C_3N_4$ nanocomposite exhibited degradation to the extent of 92.1% against amoxicillin and 90.8% for pharmaceutical effluent in 80 min.208 Such excellent performance is ascribed to the presence of a heterojunction, effective separation, good band structure and good light absorption.

El-Fawal et al.²⁰⁹ observed the better performance of an AgFeO₂-graphene/Cu₂(BTC)₃ MOF heterojunction compared to AgFeO₂/graphene and $AgFeO_2/Cu_2(BTC)_3$ binary photocatalysts in achieving about 97% removal of amoxicillin and diclofenac after 150 min under sunlight irradiation, which exhibited excellent stability up to four cycles. Based on these findings, a direct Z-scheme heterojunction mechanism has been proposed for the separation of photo-induced charge carriers at the interface of these photocatalysts. The enhanced photocatalytic activity of the tertiary heterojunction photocatalyst was mainly attributed to its superiority for light absorption (up to 650 nm) with high photostability, accelerated e⁻/h⁺ pair separation and increased lifetime of photogenerated charges. The heterojunction p-ZnO/CuO (50: 50 wt%) assisted photocatalytic process removed amoxicillin (initial concentration: 50 mg L⁻¹) from water (pH: 11) almost completely on exposure to solar irradiation for 4 h.210 The

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degradation of amoxicillin followed pseudo-first-order kinetics (k: 9.95 × 10⁻³ min⁻¹).

Gao et al.²¹¹ deposited Ag nanoparticles on the surface of a TiO₂/mesoporous g-C₃N₄ heterojunction and used it in the photocatalytic removal of amoxicillin under visible light. A photocatalyst fabricated in this manner achieved higher degradation efficiency for amoxicillin than a TiO₂/ mesoporous- $g-C_3N_4$ heterojunction, mesoporous- C_3N_4 , or bulk-g-C₃N₄. Such photoactivity of an Ag/TiO₂/M-g-C₃N₄ catalyst has been assigned to the synergistic effect accounting for the effective transfer of electrons and inhibition of electron-hole recombination. The effectiveness of this photocatalyst was also tested for the removal of amoxicillin in real situations. A WO₃/Ag₃VO₄ Z-scheme heterojunction with enhanced separation efficiency of electron-hole and surface area was deposited on rGO and used as a photocatalyst in the degradation of amoxicillin under irradiation by visible light.²¹² The amoxicillin photocatalytic degradation followed the following order on irradiating it with visible light: $Ag_3VO_4/WO_3/r$ -GO (~96%) > Ag_3VO_4/WO_3 $(\sim 37\%) > WO_3 > Ag_3VO_4$ ($\sim 32\%$). It is suggested that the presence of rGO, by increasing the surface area in Ag₃VO₄/ WO₃/rGO, facilitates amoxicillin adsorption and electron transfer for charge separation of Ag₃VO₄/WO₃.

Investigations have also been the made on photodegradation of amoxicillin via a magnetic TiO2graphene oxide-Fe₃O₄ composite²¹³ and Pd nanoparticles anchored to anatase TiO2.²¹⁴ Hajipour et al.²¹⁵ fabricated heterojunctions of TiO2/CuO, adopting the surface modification of TiO2 with CuO, and investigated its application in the photocatalytic degradation of amoxicillin in wastewater. It should be noted that TiO₂/CuO (7.5%) showed reduced photo-activity compared to a TiO₂/CuO (10%) photocatalyst, which could be attributed to the partial blockage of the active sites in the TiO₂ nanoparticles, In another study, a novel nanophotocatalyst of CuO nanoparticles and ZnO nanorods anchored on thermallyexfoliated g-C₃N₄ nanosheets established the complete removal of amoxicillin corresponding to a catalytic dosage of 0.9 g L^{-1} and pH 7.0 within 120 min under simulated sunlight illumination.²¹⁶ Subsequently, a double Z-scheme mechanism as well as a tentative pathway were proposed in detail.

Table 3 records the performance data of different photocatalysts on the removal of amoxicillin from wastewater.

3.3 Sulfamethoxazole

Sulfamethoxazole is used to treat a wide variety of bacterial infections, including those of the urinary, respiratory, and gastrointestinal tracts.²¹⁷ However, it has been frequently detected in wastewater and surface water in aquatic environments due to its extensive consumption, excretion and disposal. Therefore, several investigations have been made by many researchers focusing on the biodegradation of

sulfamethoxazole during wastewater treatment following photocatalytic degradation of sulfamethoxazole in water using a variety of photocatalysts.^{218–291}

3.3.1 Metal oxides

3.3.1.1 TiO2. The photodegradation of sulfonamides has been studied in the UV/TiO₂ system to study the effects of pH and salinity on sulfamethoxazole concentration and total organic carbon (TOC) during the removal of sulfonamides in UV/TiO₂ system.²¹⁹ The a photodegradation and mineralization rates of sulfonamides in the UV/TiO₂ system satisfied pseudo-first-order kinetics. A TiO₂ suspension has been used as a catalyst in a sunset solar simulator to examine the degradation of sulfamethoxazole in real municipal wastewater treatment plant effluent.²²⁰ It was inferred that hydrogen peroxide can be highly recommended for working with TiO₂ at low concentrations. The photocatalytic degradation of sulfamethoxazole in surface and drinking water in the absence and presence of UV (265 nm) involving TiO₂ nanoparticles after 60 minutes follow the order: UV $(\sim 100\%)$ > anatase TiO₂ $(\sim 92\%)$ > rutile and commercial TiO_2 (~90%).²²¹ The effects of different UV-LED (UVA, UVB, and UVC) wavelengths were studied in carrying out the photocatalytic decomposition of sulfamethoxazole by TiO2.222 These findings showed complete decomposition within 1 h by TiO₂/UVC under the conditions of TiO₂: 0.5 g L^{-1} , natural pH, and initial concentration of sulfamethoxazole: 20 mg L^{-1} . Sulfamethoxazole in an aqueous suspension of TiO_2 (0.5 g L⁻¹) showed 82% degradation of sulfamethoxazole under UV irradiation.²²³ In another study, the removal efficiency for the photocatalytic degradation of sulfamethoxazole (20 mg L^{-1}) in aqueous solution (pH: 3) by TiO_2 (0.08 g L⁻¹) as a photocatalyst was found to be 96.5% in 60 min under UV light.²²⁴ In addition, investigations have also been reported on the degradation of sulfamethoxazole using TiO2,²²⁵⁻²²⁷ biochar-supported TiO2²²⁸ and immobilized TiO2²²⁹⁻²³¹ as photocatalysts.

3.3.1.2 ZnO. ZnO nanoparticles prepared by a microwaveassisted gel combustion synthesis method showed complete removal of amoxicillin (and sulfamethoxazole) from contaminated water in six hours under UVC irradiation.¹⁶² It was inferred that the photocatalytic removal followed the Langmuir-Hinshelwood model in the range of concentration of 5-20 mg L⁻¹. Mirzaei et al.²³² achieved ~97% removal of sulfamethoxazole by a zinc oxide photocatalyst in the presence of fluoride ions (F-ZnO) after 30 min of reaction illuminated by UV irradiation under optimum conditions and followed pseudo-first-order kinetics (k: 0.099 min^{-1}). The hydrothermally synthesized ZnO at 200 °C for 8 h at pH 7.5 reached 84% removal of sulfamethoxazole after 60 min under UVA irradiation.²³³ In addition, TiO₂ and WO₃ nanoparticles have also been utilized in the removal of sulfamethoxazole by its photocatalytic degradation.234

3.3.2 Metal-modified metal oxide and mixed metal oxides. Tiwari *et al.*²³⁵ studied the removal of sulfamethoxazole aqueous solutions by means of $Ag^{0}(NP)/TiO_{2}$ thin film irradiated under UVA light (λ_{max} : 330 nm) for 2 h by varying

Table 3 The performance data on removal of amoxicillin in water using variety of photocatalysts

| Photocatalyst | Method of preparation | AMX | Catalyst dose | pН | Light source details | Degradation (time) | Rate constant |
|--|------------------------------------|--|--|------|---|---|---|
| TiO_2 nanoparticles | Commercial | 15 mg L^{-1} | 2 g L^{-1} | 5 | UV lamp | 27.6% | _ |
| ZnO nanoparticles | Commercial | 15 mg L^{-1} | $2~g~L^{-1}$ | 5 | UV lamp | (15 min) 48.6% (15 min) | — |
| $GO-Fe_3O_4^{150}$ | Ultrasonic mixing | 15 mg L^{-1} | $2~g~L^{-1}$ | _ | Lamp (UV): 1 | (15 min) 87.1% (15 min) | _ |
| $TiO_2 (P25 Degussa)^{152}$ | Commercial | 10 mg L^{-1} (20 mL) | 0.01 g | — | UV | (13 min) 100% (15 min) | 4.33×10^{-1} |
| $TiO_2 (P25 Degussa)^{152}$ | Commercial | 10 mg L^{-1} | 0.01 g | _ | Visible | 99% (15 min) | |
| ZnO (Hoechst) ¹⁵² | Commercial | 10 mg L^{-1} (20 mL) | 0.01 g | — | UV | (15 min) 98% (15 min) | 3.03×10^{-1} |
| ZnO (Hoechst) ¹⁵² | Commercial | 10 mg L^{-1} | 0.01 g | — | Visible | 99% (15 min) | |
| TiO_2 (Fluka) ¹⁵³ | Commercial | (20 mL) 104 mg L ⁻¹ (500 mL) | $1.0~g~L^{-1}$ | 11 | UV lamp: | (15 mm) ~71% (200 min) | 0.007 |
| $TiO_2 (H_2O_2: 100 \text{ m L}^{-1})^{153}$ | Commercial | (500 mL) 104 mg L ⁻¹ | $1.0~g~L^{-1}$ | 5 | UV lamp: | (300 mm) 100% | |
| $TiO_2 (P25 Degussa)^{154}$ | Commercial | (500 mL) 0.01 g | 10 mg L^{-1} (20 | _ | 6 W (365 hm) UV lamp | (20 min) 100% | 0.433 |
| TiO_2 (Degussa P25) ¹⁵⁵ | Commercial | $25~{\rm mg}~{\rm L}^{-1}$ | mL) 1 g L^{-1} , slurry | 6 | Solar light (16 mW sm^{-2}) | (30 min) ~83% (120 min) | min — |
| Carbon (32%) doped TiO (Decuses $P25$) ¹⁵⁵ | Commercial | $25~{\rm mg~L}^{-1}$ | 1 g L^{-1} , slurry | 6 | (16 mW cm ^{-2}) Solar light | (120 mm) ~73% (120 min) | — |
| Fe (2.2%) doped TiO ₂ (Deguese P25) ¹⁵⁵ | Commercial | $25~{ m mg~L}^{-1}$ | 1 g L^{-1} , slurry | 6 | (16 mW cm ^{-2}) Solar light | (120 mm) ~75% (120 min) | _ |
| TiO_2 (sigma Aldrich) ¹⁵⁶ | Commercial | $1.5~g~L^{-1}$ | 17 mg L^{-1} | 9.5 | Solar irradiation | (120 mm) 84.12% (240 min) | — |
| ZnO ¹⁶² | Microwave assisted gel | 10 mg L^{-1} | $0.25~g~L^{-1}$ | 10 | UVC lamp | (240 mm) 100% (5 b) | 0.014 |
| $\mathrm{WO}_3 (\mathrm{sigma} \; \mathrm{Aldrich})^{165}$ | Commercial | 1.0 μM | 0.104 g L^{-1} | 4 | (30 W) Xenon lamp (300 W) | (3 ff) 99.99% (180 min) | 2.908×10^{-2} min ⁻¹ |
| NiO ¹⁶⁶ | Sol-gel method | $25~{ m mg~L}^{-1}$ | $0.2~g~L^{-1}$ | _ | Low mercury | ~96% (120 min) | 0.084 min ⁻¹ |
| Cu (4.54 mg g ⁻¹) doped TiO ₂ ¹⁶⁹ | Photoreduction | $10 \text{ mg } \mathrm{L}^{-1}$ | 40 mg | 6 | Wolfram lamp as | $\sim 90\%$ (24 h) | 4×10^{-4} min ⁻¹ |
| Fe ³⁺ doped TiO ₂ ¹⁷⁰ | Sol-gel method | 10 mg L^{-1} | 90 mg L^{-1} | 11 | UV lamp of C type, 125 W, 247 nm | Synthetic water: 99.14% (120 min), pharmaceutical water: 88.92% (120 min) | |
| Mn-doped Cu ₂ O ¹⁷² | Green synthesis | 15 mg L^{-1} (100 mL) | 1 g L^{-1} | 9 | Sunlight irradiation (900 W m ⁻²) | 92% (180 min) | 0.073 min^{-1} |
| La–Ce (1 wt%) TiO_{2}^{173} | Sonochemical-assisted synthesis | 10 mg L^{-1} (100 mL) | Appropriate | — | Halogen lamp | 75.7% (?) | — |
| Ag/ZnO ¹⁷⁵ | Conventional method | 5 mg L^{-1} | 0.15 g L^{-1} | 5 | UVA, 365 nm | 93.76% (120 min) | 0.073 min ⁻¹ |
| TiO ₂ /chitosan ¹⁷⁶ | 3D printing | 0.1 mM (40 mL) | 15 layers (AMX/TiO ₂ molar ratio: 1/100) | 6.7 | Medium-pressure Hg vapour water jacket lamp (UV-vis), 125 W, 300–800 nm, 3.5 mW cm ⁻² | ~95% (2 h) | 0.57×10^{-2} min ⁻¹ |
| TiO ₂ /PAC ¹⁷⁷ | Suspension method | 15 mg L^{-1} | TiO ₂ : 1 g L ^{-1} , PAC: 0.1 \circ L ^{-1} | 6.5 | UV-vis (540 W m ⁻²) | 90–97% (60 min) | 0.034 min ⁻¹ |
| TiO ₂ /zeolite ¹⁷⁸ | Modified reported method | 30 mg L^{-1} (100 mL) | 2 g L^{-1} | 4.05 | Medium-pressure Hg lamp (47 W) with $\lambda \le 290$ nm cut-off | 88% (240 min) | |
| Functionalized nanodiamond-TiO ₂ ¹⁷⁹ | Liquid phase deposition | 0.1 mM (7.5 mL) | $1 \mathrm{g L}^{-1}$ | _ | Medium-pressure hg vapor lamp | 100% (60 min) | 83.3×10^{-3} min ⁻¹ |

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Table 3 (continued)

| Photocatalyst | Method of preparation | AMX | Catalyst dose | рН | Light source details | Degradation (time) | Rate constant |
|--|---|---|---------------------------------|---------|---|-------------------------------|---|
| TiO ₂ -15 wt% Fe ₃ O ₄ ¹⁸⁰ | Hydrothermal | 30 mg L^{-1} , (H ₂ O ₂ : 24 mM) | $0.4 \mathrm{g L}^{-1}$ | 2.84 | Low-pressure mercury vapor lamp: 100 W, 1200 mW cm ^{-2} | ~88% (100 min) | |
| TiO ₂ (a) α -Fe ₂ O ₃ film (PS: 334 μ m) ¹⁸¹ | Spin coating | 50 µm | _ | 4 | Xenon lamp (450 W) | 70% (50 min) | $7.4 \times 10^{-7} M$ min ⁻¹ |
| TiO_2 immobilized on activated carbon ¹⁸² | High-temperature impregnation method | 50 mg L^{-1} (4 L) | $1.2~{\rm g~L}^{-1}$ | 10 | Solar irradiation | 100% (120 min) | 0.037 min ⁻¹ |
| TiO ₂ -sand ¹⁸⁴ | Sol-gel dip-coating | 10 mg L^{-1} , H ₂ O ₂ , 400 mg L^{-1} | 75 mg L^{-1} | 5 | Solar irradiation | 93.12% (150 min) | $\begin{array}{c} 0.0175\\ \text{min}^{-1} \end{array}$ |
| TiO ₂ /Mg–Fe-LDH ¹⁸⁵ | Direct co-precipitation method | 30 mg L^{-1} | $2~g~L^{-1}$ | 11 | UVA light | ~100% (240 min) | — |
| TiO ₂ /Mg–Al-LDH ¹⁸⁵ | Direct co-precipitation | 30 mg L^{-1} | $2~g~L^{-1}$ | 5.5 | $(\lambda_{\text{max}}^{2}, 365 \text{ mm})$ | $\sim 95\%$ (240 min) | — |
| Ag/zeolite/TiO2 ¹⁸⁶ | Liquid ion-exchange method | One g L^{-1} (15 mL) | 0.01 g | 6.7 | High-pressure Hg lamp (400 W), 120 mW cm^{-2} | ~25% (75 min) | _ |
| $TiO_2(80\%)$ -SiO_2(20\%) ¹⁸⁸ | Sol-gel method | 20 mg L^{-1} (100 mL) | 4 g L^{-1} | 5 | Hg lamp – UVA (15 W), 365 nm | 88% (150 min) | 0.0014 min ⁻¹ |
| MIL-53 (Al)/ZnO ¹⁹⁰ | Hydrothermal/chemical conditions followed | 10 mg L^{-1} | $1.0 \mathrm{g L}^{-1}$ | 4.5 | Metal halide lamp: 400 W. 510 nm | 100% (60 min) | _ |
| g-C ₃ N ₄ ¹⁹³ | Heating of aq. Thiourea in Teflon reactor | 30 mg | 50 mg L^{-1} (10 mL) | pH ~ 6 | Visible light: 150 W, 16 mW cm ⁻² | (100%) (48 h) | $0.088 h^{-1}$ |
| Ag/g-C ₃ N ₄ /ZnO nanorods ¹⁹⁴ | Dispersion method | 40 mg L^{-1} | 0.08 g L^{-1} (60 mL) | — | Solar simulator lamp: 300 W ($\lambda > 420$ nm) | 41.36% (180 min) | 0.01017 min ⁻¹ |
| $V_2O_5/C_3N_4^{-195}$ | Heating powdered NH ₄ VO ₃ /g-C ₃ N ₄ mixture | 20 mg L^{-1} | 0.5 g L^{-1} | 7 | Simulated sunlight | ~91% (120 min) | 0.0268 min^{-1} |
| $\alpha \text{-} Fe_2O_3 \text{ (5\%)/g-}C_3N_4 \text{^{198}}$ | Solution method | 20 mg L^{-1} | 0.02 g (60 mL) | Neutral | Solar simulator (300 W) with cut-off filter ($\lambda > 420 \text{ nm}$) | 46% (180 min) | 40.20×10^{-4} min ⁻¹ |
| Mesoporous g-C ₃ N ₄ ¹⁹⁹ | Template-free method | $2~mg~L^{-1}$ | 100 g L^{-1} (100 mL) | 9 | Xenon lamp: 300 W $(\lambda > 420 \text{ nm})$ | 90% (60 min) | 0.036 min ⁻¹ |
| CQDs modified $K_2 Ti_6 O_{13}$ nanotubes ²⁰⁰ | Hydrothermal method combined with calcination | $1 \text{ mg } L^{-1}$ (50 mL) | 0.2 g L^{-1} | 6 | Light-emitting diode, 10 mW cm ^{-2} , 365 nm | (90 min) (90 min) | 0.0495 min^{-1} |
| $\mathrm{GO/TiO_2}^{202}$ | Chemical hydrothermal method | 50 mg L^{-1} (100 mL) | $0.4 \mathrm{g L}^{-1}$ | 6 | UV light (36 W) | 99.84% (60 min) | $0.105 \ { m min}^{-1}$ |
| Graphene@TiO ₂ nanotube/KBrO ₃ $(0.20 \text{ g L}^{-1})^{203}$ | Reaction under autoclave | 5 mg L^{-1} | _ | — | Light: UVA lamp: 19 W, λ = 369 nm | (180 min) (180 min) | 0.0186 min ⁻¹ |
| MIL-68(In)-NH ₂ /GrO ²⁰⁴ | Dispersion method | 20 ppm (200 mL) | $0.6 \mathrm{g L}^{-1}$ | 5 | Xenon lamp (300 W) with 420 nm cut-off filter | 93% (120 min) | $0.0187 \ { m min}^{-1}$ |
| 1.2 wt% rGO@g- C_3N_4 / | Wet impregnation | 10 mg L^{-1} | 0.1 g | — | Halogen lamp | 91.9% | 0.0023 |
| $InVO_4/Ag/g-C_3N_4^{206}$ | Hydrothermal | 10 ppm | 0.5 g L^{-1} | — | Visible light | (130 min) >99% | |
| CuI/FePO ₄ ²⁰⁷ | Reflux-assisted co-precipitation | 20 mg L^{-1} (50 mL) | 50 mg | — | Visible light (400 W) | (420 min) 90% (120 min) | _ |
| Mesoporous $SnO_2/g-C_3N_4^{208}$ | Green modified technique | 10 ppm (40 mL) | 10 mg | _ | Xenon lamp: 300 W with a cut-off filter | 92.1% (80 min) | _ |
| AgFeO ₂ -graphene/Cu ₂ (BTC) ₃ MOF ²⁰⁹ | <i>In situ</i> solvothermal impregnation | 5 mg L^{-1} | 5 g L^{-1} (50 mL) | 8 | $(\lambda > 400 \text{ mm})$ Halogen lamp 500 W, 420–600 nm | 97% (150 min) | (6.4-8.7) × 10 ⁻² |
| p-CuO/n-ZnO (50:50 wt%) ²¹⁰ | Chemical route | 50 mg L^{-1} | $0.5~g~L^{-1}$ | 11 | Sunlight (109 mW cm $^{-2}$) | >87% (240 min) | 100^{-3} min ⁻¹ |
| 1.94 wt% Ag/TiO ₂ / | Photodeposition means | 5 ppm | 0.1 g | _ | Xe lamp: 300 W | 99% | 0.0614 |
| mesoporous $g-C_3N_4$ ²¹² WO ₃ /Ag ₃ VO ₄ /rGO ²¹² | Multiple steps | (0.1 L) 20 ppm | 0.5 g L^{-1} | — | $(\lambda > 420 \text{ nm})$ LED lamp (220 V, 30 W) | (60 min) ~96% (420 min) | min * — |

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Table 3 (continued)

| Photocatalyst | Method of preparation | AMX | Catalyst dose | рН | Light source details | Degradation (time) | Rate constant |
|--|---|------------------------|------------------------|-----|--|-----------------------|-----------------------------|
| CuO and ZnO co-anchored on g- $C_3N_4^{216}$ | <i>Via</i> isoelectric point-mediated annealing | 60 mg L^{-1} | 0.9 g L^{-1} | 7.0 | Xenon lamp (250 W) simulated sunlight | 100% (120 min) | 0.0269 min ⁻¹ |

of

the solution pH (4.0-8.0) with an initial sulfamethoxazole concentration of 1.0 mg L⁻¹. A decreasing trend in the removal (%) of sulfamethoxazole was noted from 59% to 50% with a variation in pH from 4 to 10. The percentage removal of sulfamethoxazole as a function of pollutant concentration of sulfamethoxazole (0.5 to 15.0 mg L^{-1}) at constant pH of 6.0 under 2 h of UVA light showed a decreasing trend in the degradation of sulfamethoxazole from 57% to 20% with the sulfamethoxazole concentration increasing from 0.5 mg L^{-1} to 15.0 mg L⁻¹. Borowska et al.²³⁶ investigated the solar photocatalytic degradation of sulfamethoxazole as a contaminant in water by Pt- and Pd-modified TiO2. Their findings established significantly enhanced absorption properties from surface modification achieved by 1%Pd/TiO2 and 1%Pt/TiO₂. As a result, higher removal sulfamethoxazole is observed compared to unmodified TiO₂ in aqueous solution corresponding to a concentration of catalyst of $\sim 50 \text{ mg L}^{-1}$ and a concentration of sulfamethoxazole of 1 mg L^{-1} . This could be explained on the basis of their band gaps (1%Pd/TiO₂: 2.92 eV, 1%Pt/TiO₂: 3.18 eV).

TiO₂ nanotube arrays (TNAs), TiO₂ nanowires on nanotube arrays (TNWs/TNAs), Au-nanoparticle-decorated TNAs, and TNWs/TNAs efficiently degraded sulfamethazine amoxicillin, ampicillin, doxycycline, oxytetracycline, lincomycin, vancomycin and sulfamethoxazole irradiated in water under UV-vis and visible light.¹⁷⁴ Among these, the Au-TNWs/TNAs photocatalyst showed the highest activity towards the degradation of all the antibiotics due to synergistic and surface plasmonic effects. In another study, Cu-TiO₂ (at low mass ratios of 0.016-0.063 wt%) produced nearly complete degradation of sulfamethoxazole by visible light at pH 5.2 for a 4 mg L^{-1} initial concentration of sulfamethoxazole.²³⁷ Further studies revealed the highly stable photoactivity of Cu-TiO₂, as evident from experiments comprising at least 4 cycles. Au, Ag, Cu, Au-Ag and Au-Cu nanoparticles deposited on TiO₂ showed increased photocatalytic activity for the photocatalytic degradation of sulfamethoxazole using UVC light.238

3.3.3 Doped metal oxides. Tsiampalis et al.²³⁹ used irondoped TiO₂ (iron/titania ratios: 0-2%) as a photocatalyst to study the photocatalytic degradation of sulfamethoxazole under simulated solar radiation. These findings showed the highest photocatalytic efficiency (95%) for sulfamethoxazole in ultra-pure water with SMX concentration of 234 μ g L⁻¹, catalyst loading of 1 g L^{-1} and natural pH. The initial activity of the photocatalyst also retained half of its initial value after 5 consecutive experiments. F,Pd-co-doped TiO₂

nanocomposites prepared by а microwave-assisted hydrothermal synthesis method under direct sunlight irradiation degraded ~94.4% and 98.8% of sulfamethoxazole at 20 and 70 min, respectively.²⁴⁰ It was suggested that doping of TiO₂ by F and Pd involved multiple processes.

F,Pt-co-doped photocatalysts have also been employed in photocatalytic degradation using direct solar light.²⁴¹ Fluoride ions and Pt in the TiO2 lattice were chosen in order to control the growth of the photocatalytically active anatase phase and to introduce new energy levels between the valence and conductive bands of TiO₂ to narrow its band gap. These findings demonstrated degradation of sulfamethoxazole under direct solar light and a solar simulator corresponding to about >93% (90 min) and 58% (360 min), respectively. An iodine (I)-potassium (K)-C₃N₄ photocatalyst removed nearly 100% of sulfamethoxazole within 45 min under visible-light irradiation.²⁴² N,Cu-codoped TiO₂ decorated on SWCNTs demonstrated total removal of sulfamethoxazole under a pH of 6.0, catalyst dosage of 0.8 g L⁻¹, light intensity of 200 W, US power of 200 W, and initial sulfamethoxazole concentration of 60 mg L^{-1} in 60 min.²⁴³

Ag metal has been used as a co-dopant in P-doped g-C₃N₄ in order to overcome its poor photocatalytic performance.²⁴⁴ The investigations of Ag (nano)-P-co-doped@g-C₃N₄ (Ag-P@UCN) as a photocatalyst in visible light followed the trend in the removal of sulfamethoxazole in water: Ag(nano)-P@g- C_3N_4 (>99%) > P-doped g- C_3N_4 (68%) > g- C_3N_4 (47%). The presence of silver nanoparticles Ag(nano)-P@g-C₃N₄ enhanced light absorption and also acted as photogenerated electron traps, thereby enabling the effective separation of electron and hole pairs. A mechanism has also been proposed for the degradation of sulfamethoxazole in presence of an Ag-P@UCN photocatalyst. In another study, multi-homojunction gradient-nitrogen-doped TiO₂ exhibited enhanced performance in the removal of sulfamethoxazole from water compared to pristine TiO₂ and non-gradientdoped TiO2 under simulated solar-light irradiation.245 Zammit et al.²⁴⁶ examined the removal of sulfamethoxazole using a cerium-doped zinc oxide (Ce-ZnO) photocatalyst and its comparison with ZnO and benchmark TiO2-P25 in immobilized form on a metallic support and found Ce-ZnO to be most effective under UVA irradiation. In another study,²⁴⁷ Zn (10 wt%)-TiO₂/pBC (pretreated biochar) was investigated for the photodegradation of sulfamethoxazole under visible-light irradiation and a comparison with TiO₂/ pBC and TiO₂ after 3 h took the following order: Zn-TiO₂/ $pBC (80.81\%) > TiO_2/pBC (59.05\%) > TiO_2 (50.07\%).$

3.3.4 Metal oxide-metal oxide based composites. Fernández et al.²⁴⁸ focused on Fe₃O₄/ZnO nanocomposites on the photodegradation performance for sulfamethoxazole, trimethoprim, erythromycin and roxithromycin from surface water under UVA irradiation. Their studies showed complete removal of the antibiotics (100 mg L^{-1}) after 70 min under optimal conditions of pH 7, $[H_2O_2]$ 100 mg L⁻¹ and catalyst dose of 100 μ g L⁻¹. In addition, a reusability evaluation of Fe₃O₄/ZnO after removing it by applying an external magnetic field showed no significant decrease in its performance even after 8 cycles. Investigations were also made on the solar photocatalytic removal of sulfamethoxazole and other micropollutants (carbamazepine, flumequine, ibuprofen) using TiO₂ and its comparison with TiO₂/Fe₃O₄ applied in a photo-Fenton process.²⁴⁹ Magnetically heterogeneous separable Fe₂O₃/WO₃ nanocomposites were also successfully used as a peroxymonosulfate activator to efficiently degrade sulfamethoxazole under visible-light irradiation.²⁵⁰ Wang and others²⁵¹ reported that photogenerated holes played an important role in achieving more than 99% photocatalytic degradation efficiency for sulfamethoxazole (initial solution pH: 3) in 30 min by irradiating a Bi₂O₃-TiO₂/PAC (powdered activated carbon) ternary composite with solar light.

A composite comprising titania nanoparticles/activated carbon prepared by calcination at 400 °C exhibited much better performance in the removal of sulfamethoxazole from deionized water and seawater.²⁵² Clay-TiO₂ nanocomposites prepared via biomass-assisted synthesis showed fast degradation of sulfamethoxazole (>90%) in 30 min under sunlight.²⁵³ An LDH-TiO₂ (10%) nanocomposite has been developed, keeping in view its possible reusability and regeneration after subjection to UVA radiation, to carry out the degradation of sulfamethoxazole.254 These findings established almost complete degradation after 360 min of UVA irradiation, corresponding to initial sulfamethoxazole concentration of 20 mg L⁻¹, pH 10 and LDH-TiO₂ catalyst loading of 50 mg. Recycling and reusability studies were also conducted by dissolving a mass of 50 mg of LDH-TiO₂ in sulfamethoxazole (concentration: 20 mg L^{-1}) and pH 10, irradiated for 8 h under UVA. Further investigations revealed no significant variation in sulfamethoxazole degradation efficiency from the first cycle (100%) to the fifth cycle (90.5%).

According to Długosz *et al.*,²⁵⁵ a floating TiO₂-expanded perlite (referred to as EP-TiO₂-773: where 773 is the calcination temperature in °C) photocatalyst enhanced the photodegradation of sulfamethoxazole in the aqueous medium over a wide range of pH values on irradiation from the near-UV spectral region. However, the fastest decrease in the concentration of sulfamethoxazole was observed for the system irradiated at pH 10. The degradation of sulfamethoxazole followed pseudo-first-order kinetics in accordance with the Langmuir–Hinshelwood model. Their findings also suggested the key role of hydroxyl radical formation in the degradation of sulfamethoxazole. Noroozi *et al.*²⁵⁶ synthesized copper doped TiO₂ decorated with carbon quantum dots (CQDs) and observed its excellent performance in the degradation of SMX during 60 minute time under optimum conditions corresponding to initial SMX concentration, catalyst dosage, pH, visible light intensity and CQDs ratio in the composites of 20 mg L⁻¹, 0.8 g L⁻¹, 6, 75 Wm⁻² and 4 wt% respectively. The photocatalytic degradation of sulfamethoxazole was found to be guided by a pseudo-first-order kinetic model with HO· and O₂·⁻ as active species. Poly(ethylene terephthalate)–TiO₂,²⁵⁷ BiVO₄/SrTiO₃,²⁵⁸ CuO_x–BiVO₄²⁵⁹ and TiO₂@CuCo₂O₄²⁶⁰ were also used for the photocatalytic degradation of sulfamethoxazole.

3.3.5 Graphitic-materials-based composites

3.3.5.1 MWCNT-based composites. WO₃-MWCNT composites with different amounts of functionalized MWCNTs were prepared by a hydrothermal method (named WT-2, WT-4 and WT-8), and SMX degradation was studied under visiblelight irradiation.²⁶¹ Fig. 11(a) shows the highest efficiency of 73.3% within 3 h for WT-8; however, WT-4 with efficiency of 65.2% was preferred due to its better dispersion in water. Further studies on SMX (10 mg L^{-1}) degradation at different catalyst dosages of WT-4 in Fig. 11(b) showed its maximum efficiency (88.5%) corresponding to a loading of 2.00 g L^{-1} . A possible degradation mechanism highlighting the role of O₂⁻ and OH· radicals during the photocatalytic process has also been proposed and is displayed in Fig. 11(c). Awfa al.²⁶² reported $\sim 60\%$ photodegradation et sulfamethoxazole by magnetic carbon nanotube-TiO₂ composites. Martini et al.263 observed almost complete reduction of toxicity using photocatalytic ozonation with H₂O₂ and Fe/CNT.

3.3.5.2 g-C₃N₄-based composites. An Ag (5%)/P-g-C₃N₄ composite synthesized by thermal polymerization combined with a photodeposition method completely degraded sulfamethoxazole within 20 min under visible-light irradiation.²⁶⁴ This is attributed to the formation of holes and superoxide radicals acting as dominant active species. In addition, the surface plasmon resonance effect (Ag) and the formation of a Schottky barrier on the Ag/P-g-C₃N₄ interface could facilitate the enhanced generation of electrons/holes as well as accounting for the recombination of photogenerated electron-hole pairs. A magnetic ZnO@g-C3N4 composite under optimum conditions removed 90.4% of sulfamethoxazole after 60 min.265 In addition, core-shell g-C₃N₄@ZnO,²⁶⁶ peroxymonosulfate (PMS)/g-C₃N₄²⁶⁷ and Ag/g-C₃N₄²⁶⁸ have also been reported in the photocatalytic degradation of sulfamethoxazole.

3.3.5.3 Graphene-based composites. Visible-light-derived rGO–WO₃ composites showed 98% removal of sulfamethoxazole within 3 hours.²⁶⁹ In another study, Ag@Ag₂O–graphene nanocomposites comprising variable graphene concentrations (1.7, 2.5, and 3.4 wt%) were prepared to study the degradation of sulfamethoxazole under simulated solar light ($\lambda > 280$ nm) and visible-light irradiation ($\lambda > 400$ nm), including the stability of the photocatalyst and the mechanism of photocatalytic



Fig. 11 (a) SMX degradation under visible-light irradiation by WO₃, WT-2, WT-4 and WT-8. Conditions: catalyst: 0.50 g L⁻¹, SM: 10 mg L⁻¹. (b) SMX degradation by WT-4 at different catalyst dosage (0.25, 0.50, 1.00 and 2.00 g L⁻¹). Conditions: SMX: 10 mg L⁻¹. (c) Schematic illustration of the proposed mechanism for the enhanced degradation of SMX by WO₃-CNT composites under visible-light irradiation. Reproduced from ref. 261 with permission from Elsevier (2018).

degradation.²⁷⁰ These findings indicated higher activity and comparable stability for the first and second cycles in an Ag@Ag₂O–graphene photocatalyst loaded with 2.5 wt% graphene. Possible charge transfer processes were suggested to take place under visible-light irradiation, and holes were major active species for Ag@Ag₂O–graphene photocatalytic degradation while Ag⁰ acted as an electron capture center. Lin *et al.*²⁷¹ observed 92% degradation of sulfamethoxazole after subjecting an immobilized TiO₂–reduced graphene oxide (rGO) nanocomposite on optical fibers to 180 min of UV irradiation. A visible-light-driven Cu₂O/rGO photocatalyst successfully degraded sulfamethoxazole.²⁷²

Nawaz *et al.*²⁷³ used graphene oxide and titanium dioxide in combination with sodium alginate to synthesize a reduced graphene oxide–TiO₂/sodium alginate (rGOT/SA) aerogel. They observed more than 99% removal of these contaminants taking place within 45–90 min under UVA light, corresponding to an optimal mass ratio of TiO₂ nanoparticles with respect to graphene oxide of 2:1 in an rGOT/sodium alginate aerogel in the presence of 1 wt% sodium alginate solution. Zhou *et al.*²⁷⁴ investigated the photocatalytic decomposition of SMX by Ag_3PO_4 , Ag_3PO_4 -graphene and Ag/Ag_3PO_4 -graphene under simulated solarlight irradiation. They observed that the photocatalytic activities of Ag_3PO_4 -graphene and Ag/Ag_3PO_4 -graphene were no better than pure Ag_3PO_4 . However, these studies indicated the enhanced structural stability of Ag/Ag_3PO_4 -graphene, which would be more practical in real treatment processes.

3.3.6 Heterojunction and Z-scheme-based photocatalysts. WO₃-g-C₃N₄ (WCN) photocatalysts with different g-C₃N₄ amounts (referred to as WCN-4, WCN-6 and WCN-8) were prepared by a hydrothermal method and evaluated for SMX degradation under visible light.²⁷⁵ In view of this, Fig. 12(a) and (b) show the degradation of SMX by (a) WCN-8 at various pH and (b) WCN-8 at different catalyst dosages under visible light. The optimized WO₃-g-C₃N₄ composite (dosage: 1.0 g L⁻¹) showed 91.7% removal efficiency for SMX as a result of Z-scheme heterojunctions between g-C₃N₄ and



Fig. 12 (a) Degradation of SMX by WCN-8 at various pH values under visible light: Conditions: catalyst = 0.5 g L^{-1} , SMX = 10 mg L^{-1} . (b) Degradation of SMX by WCN-8 at different catalyst dosages under visible light: Conditions: SMX: 10 mg L^{-1} , no pH adjustment. (c) Schematic illustration of SMX photodegradation process over WCN composites under visible-light irradiation. Reproduced from ref. 275 with permission from RSC (2017).

WO₃ to account for the separation between photogenerated electron-hole pairs. Alternatively, the role of the larger surface area and better visible-light absorption capability of the photocatalyst in enhancing the removal efficiency of SMX cannot be ruled out. Fig. 12(c) is a schematic illustration of the SMX photodegradation process over WCN composites under visible-light irradiation. Rodrigues *et al.*²⁷⁶ observed 97% (120 min) photocatalytic efficiency for sulfamethoxazole using Ce_{0.8}Gd_{0.2}O_{2- δ}/TiO₂ under UV light.

In another study, $Ag_2S/Bi_2S_3/g-C_3N_4$ heterojunctions exhibited 97.4% degradation of sulfamethoxazole in 90 min in aqueous solution under visible light.²⁷⁷ The stable hierarchical Fe₂O₃/Co₃O₄ heterojunction on nickel foam exhibited enhanced photocatalytic degradation of sulfamethoxazole.²⁷⁸ The photocatalyst was also studied to evaluate its effectiveness in surface water, hospital wastewater, and wastewater treatment. A magnetic quaternary BiOCl/g-C₃N₄/Cu₂O/Fe₃O₄ nano-heterojunction exhibited 99.5% photodegradation of sulfamethoxazole (100 μ M) in 60 and 120 min under visible and natural sunlight, respectively.²⁷⁹ Photocatalysts comprising graphenesupported p–n heterojunction $rGO((U_2O)/BiVO_4)$ composites with different Cu₂O loadings (l, 5, 10, 15 and 20 wt%) were prepared to study their photocatalytic degradation activity for sulfamethoxazole oxidation under LED light at neutral pH.²⁸⁰ All the composites were found to be effective in sulfamethoxazole oxidation owing to the electrical conductivity of rGO and the p–n heterojunction between Cu₂O and BiVO₄.

Zhang *et al.*²⁸¹ evaluated the performance of a Bi₂WO₆/ TiO₂ heterojunction for photocatalytic ozonation degradation of sulfamethoxazole under simulated sunlight. They attained 97.1% removal rate of sulfamethoxazole corresponding to a catalyst dosage of 0.2 g L⁻¹, ozone concentration of 1.5 mg L⁻¹, sulfamethoxazole concentration of 10 mg L⁻¹ and pH 5.25. These studies also established excellent recyclability and stability, as evidenced through 5 cycle experiments. They also proposed a new Z-scheme transfer pathway for electrons and a degradation mechanism. A direct Z-scheme MIL-53(Co/ Fe)/10 wt% MoS₂ heterojunction composite photocatalyst

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displayed 99% removal of sulfamethoxazole (10 mg L⁻¹) in aqueous solution (pH: 6) following visible-light-driven activation of peroxymonosulfate (initial concentration: solution 0.2 g L⁻¹).²⁸² Bi₂O₃/C₃N₄/TiO₂@C quaternary hybrids (fabricated by a hydrothermal and calcination two-step method) exhibited high photocatalytic activity, degrading 100% sulfamethoxazole (SMZ, 5 mg L⁻¹) within 100 min under visible-light irradiation.²⁸³ These investigations further revealed the photocatalytic degradation rates of SMZ by a Bi₂O₃/C₃N₄/TiO₂@C junction to be 5.12, 2.87, and 1.35 times higher than those with Bi₂O₃/C₃N₄, C₃N₄/TiO₂@C, and Bi₂O₃/ TiO₂@C junctions, respectively.

Ren et al.²⁸⁴ examined Ag (0.5, 1 and 2 wt%)nanoparticles/g-C₃N₄/Bi₃TaO₇ as Z-scheme photocatalysts prepared by combining hydrothermal and photodeposition for visible-light-driven performance in the degradation of sulfamethoxazole. It should be noted that the removal efficiency for sulfamethoxazole by Ag (1 wt%)/g-C₃N₄/Bi₃TaO₇ was found to be about 98% after 25 min and adopted the following order compared to g-C₃N₄, Bi₃TaO₇, g-C₃N₄-Bi₃TaO₇ and other Ag/g-C₃N₄/Bi₃TaO₇ composites: Ag (1 wt%)/g-C₃N₄/ $Bi_{3}TaO_{7} > Ag (2 \text{ wt\%})/g-C_{3}N_{4}/Bi_{3}TaO_{7} > Ag (0.5 \text{ wt\%})/g-C_{3}N_{4}/$ $Bi_3TaO_7 > g-C_3N_4/Bi_3TaO_7 > g-C_3N_4 > Bi_3TaO_7$. Such improved performance of Ag (1 wt%)/g-C₃N₄/Bi₃TaO₇ is attributed to the effective separation/transfer of photo-excited electrons and holes. In another study, an in situ prepared Ag₃PO₄/Bi₄Ti₃O₁₂-20% heterojunction composite photocatalyst under visible-light irradiation exhibited much better photocatalytic activity in degrading sulfamethoxazole and stability compared to Ag₃PO₄ or pure Bi₄Ti₃O₁₂.²⁸⁵ This is attributed to the formation of a direct Z-scheme improving the stability and activity of the Ag₃PO₄/Bi₄Ti₃O₁₂ composite.

An Ag₂O-KNbO₃ (0.15Ag-Nb) composite fabricated by an *in situ* deposition method exhibited improved degradation of sulfamethoxazole under visible-light irradiation compared to the corresponding pure KNbO3 and Ag₂O.²⁸⁶ The apparent rate constant of the composite was found to be 0.40 and 8 times those of KNbO3 and Ag₂O, respectively. According to these studies, a type-I and Ag₂O heterojunction formed between KNbO₃ significantly enhanced the separation of photo-induced holes and electrons and accounted for sulfamethoxazole degradation. The rate constant value of the visible-lightdriven optimal 0D/1D AgI/MoO₃ (0.13 min⁻¹) Z-scheme heterojunction photocatalyst in sulfamethoxazole degradation was found to be \sim 22.4 times and 32.5 times those of MoO_3 (0.0058 min⁻¹) and AgI (0.0040 min⁻¹), respectively.²⁸⁷ In addition, Z-scheme Ag₃PO₄/g-C₃N₄,²⁸⁸ Fe₃O₄-ZnO@g-C₃N₄,²⁸⁹ $CeO_2/g-C_3N_4$ (CeO₂: 5% mass ratio)²⁹⁰ N-SrTiO₃/NH₄V₄O₁₀²⁹¹ and S-scheme-based photocatalysts have also been evaluated for the removal of sulfamethoxazole from water.

Table 4 records the performance data of different photocatalysts on the removal of sulfamethoxazole in wastewater.

3.4 Ibuprofen

Ibuprofen (IPF) is a drug belonging to the class of propanoic acid derivatives and is extensively used in the treatment of fever, pain in human beings, inflammatory disorders, muscle problems, including migraines, rheumatoid arthritis, analgesic and painful menstrual periods.^{22,292} It is slightly soluble in water, stable, is eliminated from the body through urine and does not undergo biodegradation. As a result, it can be found in water samples of different origins originating from municipal wastewater treatment plant effluents, groundwater through leaching and natural water and cannot be treated through conventional wastewater treatments. The presence of ibuprofen even in low concentration through water affects the reproduction of aquatic animals, including the photosynthesis of aquatic plants. Ibuprofen can leach into ground water and soil in daily life. In view of this, several studies have been made using metal oxide and graphitic material related photocatalysts to make wastewater free from ibuprofen.^{293–357}

3.4.1 Metal oxides. The photocatalytic degradation of ibuprofen has been reported in the literature using TiO₂, ZnO and other metal oxides.²⁹⁴⁻³⁰⁶ Jallouli et al.²⁹⁴ used a TiO₂/UV-LED system to study the photocatalytic degradation of ibuprofen present in ultrapure water (UP), the secondary treated effluent of a municipal wastewater treatment plant (WWTP) and pharmaceutical industry wastewater (PIWW). They observed the removal of ibuprofen below the detection limit in the case of UP and PIWW compared to municipal water. Their investigations inferred the higher degradation of IBU at near natural pH (5.3) of UP and PIWW compared to acidic (3.0) and alkaline (9.0) pH. In another study, the photocatalytic degradation of ibuprofen in water was carried out using TiO₂ nanoparticles/UV light.²⁹⁵ The emerging findings established the faster depletion of ibuprofen with TiO₂/UV (pH: 5.05) and followed pseudo-first-order kinetics $(k: 1.0 \text{ min}^{-1})$. TiO₂ (0.03 g) resulted in almost 100% (5 min) photodegradation of ibuprofen in aqueous solution (pH: 5.0) on irradiation by a mercury lamp (125 W).²⁹⁶

The photodegradation of ibuprofen has been tested as a function of catalyst type (TiO₂ and ZnO), loading (50-500 mg L^{-1}), initial drug concentration (10, 40, 80 mg L^{-1}) and wavelength (200-600 nm) of irradiation.²⁹⁷ The photocatalytic efficiency was found to be greater than 90% in 15 min under UVA and visible-light irradiation corresponding to an initial concentration of ibuprofen of 10 mg L⁻¹ and amount of photocatalysts (TiO₂ and ZnO) of 100 mg L⁻¹. These findings also indicated over 90% conversion of the drug within 8 min with k-values of 0.382 and 0.326 min⁻¹ under UVA for TiO_2 and ZnO, respectively, and it correspondingly decreased to 0.199 and 0.144 min⁻¹ under visible light. Tanveer and others²⁹⁸ used UV and solar irradiation to compare the photocatalytic degradation of ibuprofen in water using TiO₂ and ZnO. A much higher rate of degradation was observed in UV for TiO₂ (99%) compared to ZnO (86%) after 15 min compared to solar degradation.

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 Table 4
 Performance data on removal of sulfamethoxazole in water using variety of photocatalysts

| Photocatalyst | Preparative method | SMX | Catalyst dose | Hq | Light source and other details | Degradation/removal (time) | Rate constant |
|---|--|--|---------------------------|------------|---|----------------------------------|--|
| TiO ₂ : mainly of anatase | Commercial | 20 mg L^{-1} | $1~{ m g~L}^{-1}$ | 5 | Xenon lamp: 400 W | 96% (180 min) | 0.026 min ⁻¹ |
| (80%), (P25 Degussa) ²¹⁹ TiO ₂ , P-25 Degussa ²²² | Commercial | 20 mg L^{-1} | $0.5 	ext{ g L}^{-1}$ | Natural | $(200 \text{ nm} < \lambda < 700 \text{ nm})$ UV lamp equipped with | 100% (180 min) | I |
| ç Î | | , 0 | , 0 | | UV C (260 nm) | | |
| TiO ₂ Degussa P25 ²²³ | Commercial | 100 mgL^{-1} | $1.0 { m ~g~L^{-1}}$ | 5 | Xenon lamp (1000 W) with $\lambda_{curt-off} < 290 \text{ nm}$ | 88% (360 min) | 0.054 min ⁻¹ |
| TiO ₂ Merck ²²⁴ | Commercial | 20 mg L^{-1} | $0.08 { m ~g~L^{-1}}$ | 3 | Low-pressure mercury | 96.5% (60 min) | |
| Biochar supported TiO, ²²⁸ | Sol-gel method | $10 \text{ mg L}^{-1} (0.1 \text{ L})$ | 0.5 g | 4 | UV lamp-UVC (15 W), 254 nm | 91% (6 h) | I |
| TiO ₂ immobilized on plass snheres ²²⁹ | By dip coating on glass | $100 \ \mu g \ L^{-1}$ | 0.335 g L^{-1} | 7.82 | Solar UV radiation (2 < 400 nm) | 100% (120 min) | 0.030 min ⁻¹ (first cycle) |
| F-ZnO ²³² | Commercial | 1 mM (NH .F: 2.505 mM) | $1.48 { m ~g~L^{-1}}$ | 4.7 | UVC lamp: 10 W | 97% (30 min) | 0.099 min^{-1} |
| ZnO ²³³ | Hydrothermal | 10 mg L^{-1} | 200 mg L^{-1} | 7.5 | UVA lamp | 84% (60 min) | 0.030 min^{-1} |
| TiO ₂ nanoparticles (sioma-Aldrich) ²³⁴ | Commercial | 50 mg L^{-1} | 500 mg L^{-1} | 4 | UV lamp | 100% (90 min) | 0.0356 min ⁻¹ |
| WO ₃ commercial | Commercial | $25~{ m mg~L}^{-1}$ | $750 { m ~mg~L^{-1}}$ | Э | UV lamp | 100% (90 min) | 0.0093 min ⁻¹ |
| $Pd/TO_2 (1\%)^{236}$ | UV-reduction | 1 mg L^{-1} | $\sim 50 { m ~mg~L}^{-1}$ | I | Natural sunlight | 100% (10 min) | $52.1 \pm 5.1 \times 10^{-2} \text{ min}^{-1}$ |
| ${ m Pt/TiO_2}~(1\%)^{236}$ | UV-reduction | 1 mg L^{-1} | $\sim 50 { m ~mg~L}^{-1}$ | I | Natural sunlight | \sim 90% (10 min) | $7.6 \pm 501 \times 10^{-2} \text{ min}^{-1}$ |
| Cu (0.045 wt%)–TiO ₂ ²³⁷ | Microwave assisted impreorpation method | $4 \text{ mg L}^{-1} (20 \text{ mL})$ | $1~{ m g~L}^{-1}$ | 5.2 | Lamps: 8 W, 77 mW cm^{-2} | 100% (120 min) | 0.0506 min ⁻¹ |
| TiO ₂ Evonik P25 ²³⁸ | Sol-gel procedure | 30 mg L^{-1} | 0.5 g L^{-1} | I | UVC | 100% (90 min) | 0.046 min^{-1} |
| TiO ₂ Evonik P25 ²³⁸ | Sol-gel procedure | 30 mg L^{-1} | 0.5 g L^{-1} | | Simulated solar light | 100% (240 min) | 0.022 min^{-1} |
| 1.5% au/TiO ₂ ²³⁸ | Deposition precipitation method | 30 mg L^{-1} | $0.5~{ m g~L}^{-1}$ | I | UVC light (254 nm) | 100% (90 min) | 0.071 min ⁻¹ |
| 1.5% au/TiO ₂ ²³⁸ | Deposition precipitation method | 30 mg L^{-1} | $0.5 \mathrm{~g~L}^{-1}$ | I | Simulated solar light | 100% (180 min) | 0.039 min ⁻¹ |
| 1.5% Ag/TiO ₂ ²³⁸ | Deposition precipitation method | 30 mg L^{-1} | $0.5~{ m g~L}^{-1}$ | I | UVC light (254 nm) Simulated solar light | 100% (45 min) 100% (240 min) | 0.201 min^{-1} 0.027 min^{-1} |
| 1.0% Cu/TiO ₂ ²³⁸ | Deposition precipitation method | 30 mg L^{-1} | $0.5~{ m g~L}^{-1}$ | I | UVC light (254 nm) Simulated solar light | 100% (240 min) 100% (240 min) | 0.186 min^{-1} 0.028 min^{-1} |
| Au–Ag/TiO ₂ ²³⁸ | Deposition precipitation method | 30 mg L^{-1} | $0.5~{ m g~L}^{-1}$ | | UVC light (254 nm) Simulated solar light | 100% (45 min) 100% (240 min) | 0.143 min^{-1} 0.025 min^{-1} |
| Au-Cu/TiO ₂ ²³⁸ | Deposition precipitation method | 30 mg L^{-1} | $0.5~{ m g~L}^{-1}$ | | UVC light (254 nm) Simulated solar light | 100% (45 min) 100% (240 min) | 0.145 min^{-1} 0.026 min^{-1} |
| Fe-doped Titania (Fe/Ti molar ratio: 0.04%) ²³⁹ | Co-precipitation method | 234 mg L^{-1} | $1~{ m g~L}^{-1}$ | Natural pH | Xenon ozone free lamp (100 W) | 95% (120 min) | 29×10^{-3} min ⁻¹ |
| F-Pd co-doped TiO ₂ ²⁴⁰ | Microwave assisted | 30 mg L^{-1} | $1~{ m g~L}^{-1}$ | I | Sunlight | 98.4% (40 min) | |
| F–Pd co-doped Ti O_2^{240} | hydrothermal metnoo Microwave assisted hvdrothermal method | 30 mg L^{-1} | $1~{ m g~L}^{-1}$ | l | Solar simulator | 98.5% (220 min) | |

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| Photocatalyst | Preparative method | SMX | Catalyst dose | Нd | Light source and other details | Degradation/removal (time) | Rate constant |
|--|--|--|---|---------------------|--|-------------------------------|---|
| F-Pt co doped TiO_2^{241} | Microwave assisted | $20 \text{ mg L}^{-1} (50 \text{ mL})$ | 50 mg | ~ 5.1 | Solar light | >93% (90 min) | |
| F-Pt co-doped TiO2 ²⁴¹ | nyurourerman methou Microwave assisted hvdrothermal method | $20 \text{ mg L}^{-1} (50 \text{ mL})$ | 50 mg | ~ 5.1 | Simulated solar light | ~58% (360 min) | I |
| N–Cu co doped TiO,@f-SWCNT ²⁴³ | Sol-gel method | 60 mg L^{-1} | $0.8~{ m g~L}^{-1}$ | 9 | Xenon lamp (200 W) | 100% (60 min) | 0.0512 min^{-1} |
| Ag,P-co-doped $g-C_3N_4^{244}$ | Pyrolysis method | 5 mg L^{-1} | 1000 mg L^{-1} | 0.6 | Visible lamps (8 W each), λ : 465 ± 40 nm | >99% (30 min) | 2.06×10^{-1} min ⁻¹ |
| Ce-doped ZnO ²⁴⁶ | Spray coating | 6.332 µg L ⁻¹ | Catalyst immobilized on 11.5 cm dia discs of area 104 cm ² | 6.28 | UVA lamp (36 W) | Ι | 1.09×10^{-2} min ⁻¹ |
| Zn-TiO ₂ /pBC ²⁴⁷ | Modified sol-gel method | 10 mg L^{-1} (160 mL) | 0.2 g | 5.03 | Xenon lamp (50 W) with 420 nm cut-off filter | 80.8% (180 min) | 0.0085 min ⁻¹ |
| Fe ₃ O ₄ /ZnO, (H ₂ O ₂ :100 mg L^{-1}) ²⁴⁸ | Polyol-mediated preparation | 100 μg L ⁻¹ (20 mL) | 200 mg L^{-1} | | UVA lamp (15 W), λ : 365 nm, 4 mW cm ⁻² | ~100% (240 min) | I |
| $\mathrm{Bi}_2\mathrm{O}_3\mathrm{-TiO}_2\mathrm{/PAC}^{251}$ | Two-stage calcination method | 20 mg L ⁻¹ (250 mL) | 0.05 g | 11 | Solar light-xenon arc lamp (300 W) | $\sim 100\% (30 \text{ min})$ | 0.159 min ⁻¹ |
| LDH-TiO ₂ ²⁵⁴ | Impregnation process | $20 \text{ mg L}^{-1} (100 \text{ mL})$ | 50 mg | 10 | UVA lamp (2: 300–400 nm. 300 W) | 100% (360 min) | |
| Poly(ethylene terephthalate)- 10% TiO ₂ ²⁵⁷ | Solvent casting method | $1 \text{ mg L}^{-1} (100 \text{ mL})$ | 50 mg L^{-1} | I | Xenon lamp (simulated solar light): 1.5 kW, 500 W m ⁻² | 98% (360 min) | 0.015 min ⁻¹ |
| BiVO ₄ /SrTiO ₃ (1 %) ²⁵⁸ | Self-template method under hvdrothermal condition | 10 mg L^{-1} (50 mL) | 0.05 g | | Xenon lamp (500 W) | 91% (60 min) | |
| 0.75 CuO _x -BiVO ₄ | Polyol-reduction method | 0.5 mg L^{-1} | 500 mg L^{-1} (persulfate: 100 mg L^{-1}) | I | Simulated solar light | 100% (30 min) | 0.0991 min ⁻¹ |
| WO ₃ -MWCNT ²⁶¹ | Hydrothermal method | 10 mg L^{-1} | $2.0 { m ~g~L}^{-1}$ | I | Solar simulator-xenon arc lamp (300 W), 420-630 nm | 88.5% (180 min) | I |
| Magnetic میں@میدر N ²⁶⁵ | In situ growth | $30 \text{ mg L}^{-1} (1000 \text{ mL})$ | $0.65~{ m g~L}^{-1}$ | 5.6 | UVC lamp (10 W) | 90.4% (60 min) | 0.0384 min ⁻¹ |
| 5 wt% Ag/g-C ₃ N ₄ | Photo-reduction method | 10 µM (100 mL) | 5 mg | Natural pH | Xenon lamp (300 W) with a 400 nm cut-off filter | 97.5% (60 min) | Ι |
| rGO-WO ₃ ²⁶⁹ | Hydrothermal method | $10~{ m mg~L}^{-1}$ | $1.0 \mathrm{~g~L}^{-1}$ | No pH adiustment | Xenon arc lamp: 200 W (420–630 nm) | >98% (180 min) | $1.607 \ h^{-1}$ |
| Ag@Ag_O-2.5 wt% graphene ²⁷⁰ | Precipitation method | 1 mg L^{-1} | $0.05~{ m g~L^{-1}}$ | | Xeron lamp (300 W) with a cut-off filter $(\lambda > 280 \text{ nm})$, 37.7 mW cm ⁻² | ~100% (90 min) | 0.038 min ⁻¹ |
| Immobilized TiO ₂ -2.7% rGO ²⁷¹ | Polymer assisted hydrothermal deposition method | 5 mg L^{-1} | Bundle of thirty 10 cm photocatalyst-coated SOF (25 mL) placed on a petri disc | Q | High-pressure UV mercury vapor lamp (160 W) | 92% (180 min) | $0.757 \ h^{-1}$ |

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Table 4 (continued)

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Table 4 (continued)

| Photocatalyst | Preparative method | SMX | Catalyst dose | Hq | Light source and other details | Degradation/removal (time) | Rate constant |
|---|--|---|--|---------------------|--|-------------------------------|--|
| Cu ₂ O/rGO-80 (80 refers amount of GO (mg) used in preparation of rG0) ²⁷² | Wet chemical method | 5 mg L^{-1} (80 mL) | 20 mg | 1 | Xe lamp: 300 W (420 nm cut-off filter) | 50% (120 min) | 0.00525 min ⁻¹ |
| rGO-TiO ₂ /sodium alginate (1:3) ²⁷³ | Hydrothermal method | 10 ppm (200 mL) | $0.5~{ m g~L}^{-1}$ | Neutral | High-pressure mercury lamp (100 W) | >99% (45–90 min) | 0.108 min ⁻¹ |
| WO_3 -g- C_3N_4 (referred as WCN-8) ²⁷⁵ | Hydrothermal method | 10 mg L^{-1} | $1.0~{ m g~L}^{-1}$ | No pH adjustment | Xenon arc lamp (300 W), 420–630 nm | 91.7% (240 min) | |
| $Ce_{0.8}Gd_{0.2}O_{2-\delta}/TiO_2^{276}$ | Modified Pechini method | $25 \text{ mg L}^{-1} (300 \text{ mL})$ | 30 mg | , | Mercury lamp (15 W) | 97% (120 min) | 0.2959 mg^{-1} min ⁻¹ |
| ${ m Ag_2S/Bi_2S_3/g}{ m -C_3N_4}^{277}$ | Hydrothermal | 20 mg L^{-1} | 0.25 mg mL^{-1} | 7 | Xenon lamp (visible light): 300 W | 97.3% (90 min) | 0.0642 min ⁻¹ |
| $BiOCl/g-C_3N_4/Cu_2O/Fe_3O_4^{279}$ | Co-precipitation method | 100 µM | $0.2~{ m g~L}^{-1}$ | 6.5 | Xenon lamp | 99.5% (60 min) | 0.0543 min^{-1} |
| rGO@Cu ₂ O/BiVO ₄ ²⁸⁰ Bi ₂ WO ₆ /TiO ₂ ²⁸¹ | Solution method Hydrothermal method | 0.5 mg L^{-1} 10 mg L ⁻¹ , [ozone]: 1.5 mg L ⁻¹ | $100 \text{ mg} (250 \text{ ml}) 0.2 \text{ g} \text{ L}^{-1}$ | 7 5.25 | LED light (30 W) Simulated sunlight | ~97.1% (180 min) ~97.1% | $\frac{-}{1.83\times 10^{-2}}$ min ⁻¹ |
| MIL-53(Co/Fe)/10 wt% MoS ₂ ²⁸² | Hydrothermal through <i>in situ</i> growth | 10 mg L^{-1} , (peroxymonosulfate: $0.2 \text{ or } L^{-1}$) | $0.01 { m ~g~L^{-1}}$ | 9 | Visible light | 99% (60 min) | I |
| ${ m Bi_2O_3/C_3N_4/TiO_2@C^{283}}$ | Hydrothermal and calcination | 5 mg L^{-1} | $1~{ m g~L}^{-1}$ | 5 | Visible light | 100% (100 min) | |
| Ag (1 wt%)/g-C ₃ N ₄ /Bi ₃ TaO ₇ ²⁸⁴ Ag ₃ PO ₄ /Bi ₄ Ti ₃ O ₁₂ -20% ²⁸⁵ | Photo deposition method In situ growth method | 5 mg L^{-1} 5 ppm (50 mL) | 25 mg (50 mL) — | | Xenon lamp (300 W) Xenon lamp: 300 W $(\lambda > 400 \text{ nm})$ | 98% (25 min) ~77% (40 min) | 0.1499 min ⁻¹ 0.0372 min ⁻¹ |
| Ag ₂ O-KNbO ₃ (Ag-Nb molar ratio: 0.15/1) ²⁸⁶ | In situ growth | 5 ppm | 0.3 mg mL^{-1} | | Visible-light irradiation | 91% (40 min) | 0.0603 min ⁻¹ |
| 97.9% Ag ₃ PO ₄ /2.1% g-C ₃ N ₄ | In situ precipitation method | $1 \text{ mg L}^{-1} (100 \text{ mL})$ | 5 mg | Neutral pH | Xenon lamp (300 W), $\lambda > 400 \ { m nm},$ 138 7 mW cm ⁻² | ~99% (90 min) | 0.063 min ⁻¹ |
| $\mathrm{Fe_3O_4^-ZnO@g-C_3N_4^{289}}$ | In situ growth | $30~{ m mg~L}^{-1}$ | $0.5~{ m g~L}^{-1}$ | 7 | UVC lamp (10 W) | 95% (90 min) | 0.0351 min ⁻¹ |

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The degradation of ibuprofen using a heterogeneous ZnO photocatalyst irradiated with UVC achieved 82.97% removal efficiency within a reaction time of 95 min under optimized conditions (pH: 6.7, ZnO loading: 583 mg L⁻¹, initial IBP concentration: 1.5 mg L^{-1} , humic acid concentration: 54 mg L^{-1}).²⁹⁹ The reactive species responsible for oxidizing ibuprofen were found to be h^+ , $O_2 \cdot \bar{}$, $H_2 O_2$, and $\cdot OH$. In another experiment, ZnO-Ce (0.50 g L^{-1}) showed 60% removal of ibuprofen (20 ppm) under acidic conditions after 120 min under UVC irradiation.³⁰⁰ Holes played a vital role in the degradation process of ibuprofen and it displayed good degradation activity even after 3 cycles under UV light. Hexagonal α -Fe₂O₃ flakes have removed up to 80% of ibuprofen in a combination of adsorption treatment followed by UV (265 nm) irradiation.³⁰¹ TiO₂ immobilized on glass coupled with simulated solar irradiation also eliminated ibuprofen and its derivatives.³⁰² Investigations on the photocatalytic activity of TiO2,303,304 ZnO,304,305 and ZnO membrane³⁰⁶ have also been reported in the remediation of water from ibuprofen.

3.4.2 Doped metal oxides. N,S-co-doped TiO₂ exhibited high photocatalytic activity in the degradation of ibuprofen under simulated solar irradiation due to the synergistic effects of N and S co-doping in TiO₂ owing to the separation of photogenerated electrons and holes and higher visible-light adsorption.³⁰⁷ Reusability tests of the N,S-TiO₂ photocatalyst showed that its catalytic activity was not significantly altered even after 6 cycles. C,N,S-co-doped TiO₂ prepared by thermally treating hydrothermally prepared mesoporous TiO₂ (anatase/brookite) and thiourea in a 1:1 wt. ratio demonstrated complete degradation of ibuprofen under visible light within 5 h in contaminated water.³⁰⁸

Bi (0.25 wt%) and Ni (0.5 wt%) doped TiO₂ photocatalysts synthesized by a sol–gel method under irradiation of solar light for 6 h achieved degradation of ibuprofen by 89% and 78% repectively.³⁰⁹ The degradation of ibuprofen followed kinetics in accordance with the Langmuir–Hinshelwood model. In addition, La³⁺-doped TiO₂ monolith,³¹⁰ Cu-doped LaFeO₃,³¹¹ Cu₂O-doped TiO₂ nanotube arrays,³¹² C,N-co-doped mesoporous TiO₂³¹³ and TiO₂ co-doping with urea and functionalized CNT³¹⁴ photocatalysts also displayed enhanced photocatalytic degradation of ibuprofen in aqueous solution.

3.4.3 Metal oxide-metal oxide composites. Lin *et al.*³¹⁵ prepared TiO_2 nanofibers wrapped in BN nanosheets by an electrospinning method, which were examined as a photocatalyst for the removal of ibuprofen from contaminated water under UV irradiation. The ibuprofen was almost completely removed after 2 h owing to wrapping of the BN nanosheets to facilitate improved light absorption and efficient separation of the electron-hole pairs. Investigations were also made on the reusability and regeneration capability of the prepared photocatalyst on the degradation of ibuprofen. Activated carbon (90 wt)% impregnated with TiO_2 showed 92% removal efficiency for ibuprofen solution under UV light within 4 h due to the

synergy of adsorption and photodegradation.³¹⁶ FeO,³¹⁷ Fe₃-O₄(a)MIL-53(Fe),³¹⁸ Fe₃O₄/Bi₂WO₆,³¹⁹ BiOBr_{0.9}I_{0.1}/Fe₃-O₄(a)SiO₂,³²⁰ and Ag/Ag₂O³²¹ nanocomposites also displayed enhanced removal of ibuprofen under visible-light irradiation.

Ag and Fe_3O_4 co-modified WO_{3-x} (Ag/Fe₃O₄/WO_{3-x}) fabricated hydrothermal and composites were by photodeposition processes and showed almost complete photocatalytic-Fenton degradation of ibuprofen (and diclofenac), as evident from (Fig. 13(a) and (b)).³²² This is attributed to the surface plasmon resonance effect of Ag, separation of photogenerated carriers and heterostructures of Ag/Fe₃O₄/WO_{3-x}. In addition, the possibility of absorption of light greatly improving the photocatalytic-Fenton degradation efficiency cannot be ruled out. The fabricated Ag/Fe₃O₄/ WO_{3-x} also exhibited good photocatalytic-Fenton stability in the photodegradation of ibuprofen (and diclofenac), as indicated by the almost unchanged degradation rate of the antibiotic in (Fig. 13(c) and (d)). The degradation and charge transfer mechanism involved in the removal of the ibuprofen and diclofenac have also been proposed and are displayed in Fig. 13(e).



Fig. 13 Photocatalytic-Fenton degradation of (a) ibuprofen and (b) diclofenac by Fe_3O_4 , WO_{3-x} , Fe_3O_4/WO_{3-x} , and $Ag/Fe_3O_4/WO_{3-x}$ samples. (c and d) Corresponding recycling study and stability of Ag/ Fe_3O_4/WO_{3-x} . (e) Schematic illustration of the possible catalytic degradation mechanism and charge transfer of Ag/ Fe_3O_4/WO_{3-x} under light irradiation (modified image). Reproduced from ref. 322 with permission from ACS (2021).

Lenzi et al.³²³ showed that the photocatalytic degradation of ibuprofen (10 ppm) solution (pH: 7) by 0.3 g L^{-1} of Ag/ ZnO/CoFe₂O₄ (5 wt%) exhibited removal efficiencies of 80% and 47% under artificial and solar radiation, respectively. These studies also confirmed the recovery and reuse of the catalyst after 3 cycles without significant loss of catalytic activity. Visible-light-driven mesoporous hierarchical BiOBr/ Fe_3O_4 (a)SiO₂ (dose: 1 g L⁻¹) photocatalyst degraded ibuprofen (initial concentration: 2 mg L⁻¹) almost completely in 60 min.³²⁴ Further studies have shown BiOBr/Fe₃O₄(a)SiO₂ maintaining its initial photocatalytic activity (~80%) even after five cycles. In another study, a magnetically separable Fe₃O₄-SiO₂-coated TiO₂ composite demonstrated excellent photocatalytic activity.325 An immobilized TiO₂/ZnOphthalocyanine sensitized copper(II) heterostructure displayed about 80% degradation of ibuprofen (initial conc.: 5 mg L^{-1}) after 4 h of irradiation under 365 nm UV.³²⁶ The studies revealed a small decline in the IBF degradation (77%) WO3@TiO2,327 cycle. PANI-coated after the 5th (PAN)-MWCNT/TiO₂-NH₂,³²⁸ polyacrylonitrile TiO₂ nanoparticles and C-nanofiber-modified magnetic Fe₃O₄ nanospheres (TiO₂@Fe₃O₄@C-NF),³²⁹ carbon dots/Fe₃-O4@carbon sphere pomegranate-like composites,330 PVDF-ZnO/Ag₂CO₃/Ag₂O,³³¹ and PAN-MWCNT nanofiber crosslinked TiO2-NH2 nanoparticles332 have also been examined for their photodegradation performance for ibuprofen.

3.4.4 Graphitic materials. Hernández-Uresti et al. 333 observed the following order for the degradation of different pharmaceutical compounds in aqueous solution (pH \sim 5.5) using g-C₃N₄ under UV-vis irradiation: tetracycline (86%) > ciprofloxacin (60%) > ibuprofen (20%). Wang and coworkers³³⁴ undertook investigations on the degradation of pharmaceutical contaminants by bubbling a gas-phase surface discharge plasma combined with $g-C_3N_4$ photocatalysis. These findings disclosed 82% and 100% removal of ibuprofen and tetracycline hydrochloride after 25 min, corresponding to initial concentrations of 60 and 200 mg L^{-1} , respectively. A photocatalytic study of hydrothermally prepared reduced-graphene-oxide-loaded HoVO₄-TiO₂ revealed enhanced photodecomposition efficiency of rGO-HoVO₄-TiO₂ (~96%) compared to rGO-HoVO₄ (75%), HoVO₄ (67%), rGO-TiO₂ (30%) or TiO₂ (10%) in the removal of ibuprofen over 60 min.335 The findings also showed ibuprofen decomposition to depend mainly on superoxide radicals photogenerated from rGO-HoVO₄-TiO₂ under visible-light illumination.

Acidified g-C₃N₄/polyaniline/rGO@biochar (0.5 mg L⁻¹) nano-assemblies degraded ibuprofen (20 mg L⁻¹) to the extent of 98.4% in 50 min under exposure to visible light.³³⁶ Such significant performance is attributed to multiple reasons, such as highly separated charges, enhanced visible absorption and diffusion. The major reactive species in the degradation process for ibuprofen involved hydroxyl and superoxide radical anions. Akbarzadeh *et al.*³³⁷ explored the photodegradation of

ibuprofen solution in the presence of a hydrothermally fabricated g-C₃N₄/Ag/AgCl/BiVO₄ microflower composite as photocatalyst under visible light and compared its performance with BiVO₄, g-C₃N₄/BiVO₄ and Ag/AgCl/BiVO₄. These findings revealed remarkably enhanced degradation efficiency of g-C₃N₄/Ag/AgCl/BiVO₄ (94.7%) compared to g-C₃N₄ (6.5%), BiVO₄ (11.4%), g-C₃N₄/BiVO₄ (68.6%), or Ag/ AgCl/BiVO₄ (88.3%) in 1 h corresponding to a photocatalyst dosage of $0.25 \text{ g} \text{ L}^{-1}$ and initial concentration of 2 mg L^{-1} . The reduced band gap energy and recombination rate of the g-C₃N₄/Ag/AgCl/BiVO₄ photocatalyst are ascribed to charge transfer along the heterojunction. The photocatalytic degradation performance of IPF increases with the (121)/(040) XRD plane intensity ratio of BiVO₄, Ag/AgCl/BiVO₄, g-C₃N₄/BiVO₄ and g-C₃N₄/Ag/ AgCl/BiVO₄ and is found to be in good agreement with the photoluminescence findings.

A hierarchical assembly of Ag (7%)/g-C₃N₄/kaolinite composite fabricated following an in situ calcination and photodeposition process exhibited 99.9% degradation of ibuprofen (k: 0.01128 min^{-1}) after 5 h under visible-light irradiation compared to g-C₃N₄, g-C₃N₄/kaolinite and Ag/g-C₃N₄.³³⁸ This outcome is due to the stronger adsorption property, efficient separation and transfer of electron-hole pairs. In addition, the presence of monodispersed Ag nanoparticles in the g-C₃N₄/kaolinite sheets led to more active sites, accounting for this. The efficient photocatalytic degradation of ibuprofen has also been reported in aqueous graphene quantum dots/AgVO₃ solution using nanoribbons,339 composites,³⁴⁰ $g-C_3N_4/MIL-68(In)-NH_2$ graphene oxide and TiO₂ heterostructures doped with F,³⁴¹ reduced-graphene-oxide-TiO2/sodium alginate 3-dimensional structure aerogel²⁷³ and Fe₃O₄/graphene/S-doped g-C₃N₄³⁴² also exhibited enhanced visible-light photocatalytic activity for the degradation of ibuprofen.

3.4.5 Heterojunction and Z-scheme-based photocatalysts. A $TiO_2/g-C_3N_4$ (5%) photocatalyst exhibiting a sea urchin morphology with interface effects was synthesized by a solvothermal method.³⁴³ Its application in the photocatalytic degradation of ibuprofen showed significantly enhanced performance under irradiation by visible light for 60 min. The formed superoxide radicals and holes were assigned as the main active species involved in the photodegradation of ibuprofen. The photocatalytic performance of this catalyst after 5 cyclic experiments indicated its good stability. Wang et al.344 fabricated atomic-scale g-C3N4/Bi2WO6 comprising ultrathin g-C₃N₄ nanosheets and monolayer Bi₂WO₆ nanosheets (1:4 mol ratio) by a hydrothermal reaction. Such an assembly of 2D/2D heterojunctions removed 96.1% ibuprofen under visible-light irradiation within 60 min due to a synergistic effect.

Kumar and others³⁴⁵ synthesized a magnetically recyclable direct-contact Z-scheme $g-C_3N_4/TiO_2/Fe_3O_4$ (a)SiO₂ heterojunction nanophotocatalyst and recorded 97% removal of ibuprofen solution (pH: 3) after 15 min under irradiation by visible light (~330 W m⁻²). Such excellent performance of

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magnetically recyclable direct-contact Z-scheme nanophotocatalyst was attributed to the low recombination rate of photogenerated e⁻ and h⁺. Visible-light-assisted persulfate activation by an SnS₂ (0.5%)/MIL-88B(Fe) Z-scheme heterojunction achieved 100% removal of ibuprofen in 120 min.³⁴⁶ This was found to be 54 and 4 times higher than SnS₂ and SnS₂ (0.5%)/MIL-88B(Fe), respectively. Such findings could be ascribed to the structure and crystallinity of the photocatalysts. In another reported study, an optimized Z-scheme based 1D/2D FeV₃O₈/g-C₃N₄ composite comprising 10% FeV₃O₈ achieved a maximum degradation rate for ibuprofen of 95% at 85 min under visible-light irradiation.347 Kinetic studies established that the rate constant is 4 times that of $g-C_3N_4$ nanosheets. However, the presence of 30% FeV₃O₈ in g-C₃N₄ decreased the degradation efficiency to 52.8%.

Heterostructure g-C₃N₄/Bi₂WO₆/rGO nanocomposites prepared by microwave- assisted treatment for 120 min in a hydrothermal method undertook the maximum photocatalytic degradation of ibuprofen (93.9%) under visible-light illumination.³⁴⁸ In addition, g-C₃N₄@NiO/ Ni@MII-101,³⁴⁹ Bi₅O₇I-MoO₃,³⁵⁰ AgSCN/Ag₃PO₄/C₃N₄,³⁵¹ N-α-SnWO₄/UiO-66(NH₂)/g-C₃N₄,³⁵⁵ CdS/Fe₃O₄/TiO₂³⁵⁶ and Ag₂-CO₃/Ag₂O/ZnO³⁵⁷ heterojunctions also exhibited excellent photocatalytic degradation of ibuprofen.

Table 5 records the performance data of different photocatalysts on the removal of ibuprofen from wastewater.

3.5 Norfloxacin

Norfloxacin (NOR) is an effective antibacterial agent of the fluoroquinolone family and is widely used as a drug in clinical treatments for bacterial infections of urinary, biliary, and respiratory tracts, and gastrointestinal and skin infections.^{358–360} Norfloxacin has frequently been detected in municipal/wastewater treatment plants, is difficult to biodegrade and is predicted to be a potential risk to human beings and the environment. Therefore, it is considered a potential threat to the water environment and human health.^{361–422}

3.5.1 Metal oxides. Reduced TiO_2 (TiO_{2-x}) samples comprising Cat.I-A (anatase), Cat.II-R (rutile) Cat.III-B (brookite) and a series of Cat.IV-A&R (anatase/rutile phases) mixed in different ratios showed about ~100% photocatalytic degradation of norfloxacin in visible light (>400 nm).³⁶¹ Such degradation of norfloxacin is guided by the specific surface area, concentration of Ti³⁺ and the density of oxygen vacancies of the photocatalysts. Haque and Muneer³⁶² reported Degussa P25 (anatase: 75%, rutile: 25%) acting as an efficient photocatalyst for the photodegradation of norfloxacin in aqueous suspensions compared to other TiO₂ powders. Cu₂O particles prepared by a hydrothermal method showed a high degradation rate for norfloxacin (79.8%) with

·OH and ·O₂⁻ species playing major roles.³⁶³ The removal of norfloxacin has also been explored in a broad operating pH range *via* simulated solar-light-mediated bismuth tungstate Bi_2WO_6 .³⁶⁴

3.5.2 Metal-metal oxides composites. Sayed et al.³⁶⁵ prepared immobilized {001}-faceted TiO₂/Ti film by placing Ti plate water/2-propanol solvent and 0.02 M HF (pH: 2.62) under hydrothermal conditions at 180 °C for 3 h and exhibited the following order for the degradation of norfloxacin (10 mg L⁻¹) under UV irradiation: Milli-Q-water $(70.5\%, k: 0.0504 \text{ min}^{-1}) > \text{tapwater} (\sim 55.1\%, k: 0.03 \text{ min}^{-1})$ > river water (44.9%, k: 0.009 min⁻¹) > synthetic wastewater (39.89%, k: 0.005 min⁻¹). Triangular silver nanoplates (T-Ag)/ ZnO nanoflowers significantly enhanced the photocatalytic degradation of norfloxacin under visible light due to synergistic effects in the different water matrices.³⁶⁶ It was concluded that the degradation efficiency for norfloxacin by T-Ag/ZnO nanoflowers is guided by the choice of water source. In another report, Zhang et al.³⁶⁷ prepared triangular Ag nanoplate coated ZnO nanoflowers by a hydrothermal/ dual-reduction method and studied its performance in the photocatalytic degradation of NF in aqueous solutions under visible-light irradiation. It should be noted that the improved photocatalytic degradation of NF activity could be ascribed to the synergetic effect and the unique surface plasmon resonance of triangular silver nanoplates in T-Ag/ZnO. In addition, photogenerated holes are considered to be the main oxidative species that account for the photocatalytic degradation of NF by T-Ag/ZnO composites under visible light. A chemically doped Prussian blue in CeO₂ (doping 10%) photo-Fenton catalyst showed 88.93% ratio: degradation of norfloxacin in 30 min with •OH acting as the major reactive species.368

3.5.3 Doped metal oxides. The effect of ion doping on the properties of photocatalysts has been receiving considerable attention in exploring their better performance for wastewater treatment applications.³⁶⁹ In this regard, the photocatalytic degradation of norfloxacin has been studied using an N-doped TiO₂ catalyst under visible-light irradiation. Jin et al.³⁷⁰ also fabricated TiO₂ doped with nitrogen to enhance its optical response through reduction in the band gap and carried out the photocatalytic degradation of norfloxacin under visible-light irradiation. These investigations indicated almost complete removal of norfloxacin within 30 min under optimum conditions (pH: 6.37, catalyst dose: 0.54 g L⁻¹, norfloxacin: 6.03 mg L⁻¹). Aldoped TiO₂ achieved 93% norfloxacin removal in 2 h which was found to be ~ 5 times higher than undoped TiO₂ nanoflakes under visible light.371 The norfloxacin was completely degraded by visible-light-mediated C-doped TiO₂ in 20 min corresponding to a concentration of 0.0313 mM and catalyst dosage of 2.0 g L^{-1} .³⁷² It was established that the hydroxyl radical plays an important role in the degradation process.

The photocatalytic degradation of norfloxacin (and ciprofloxacin) was found to be 90–93% under optimized

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| Photocatalyst | Preparation method | IPF | Catalyst dose | pН | Light source | % degradation | Rate constant |
|---|-----------------------|------------------------|---------------------------------|---------|---|-----------------------|--------------------------------------|
| TiO ₂ Degussa P25 | Commercial | 213 mg | 2.5 ° L ⁻¹ | 5 0-5 3 | UV-LEDs (10 W) | 100% | 24×10^{-3} |
| 80% anatase and $20%$ rutile) ²⁹⁴ | Commercial | L^{-1} | 2.0 8 1 | 0.0 0.0 | $365 \text{ nm}, 375 \text{ W m}^{-2}$ | (5 min) | \min^{-1} |
| riO ₂ nanoparticles | Commercial | $5 \ \mu g \ mL^{-1}$ | 134.5 mg | 5.5 | UV light: 15 W, | 100% | 1.0 min^{-1} |
| Degussa P25) ²⁹⁵ | | (50 mL) | | | 365 nm | (10 mi) | |
| G_2 (Vetec, 98% of purity) ²⁹⁶ | Commercial | 10^{-4} M | 0.03 g | 5 | Mercury lamp | 100% | _ |
| | | (100 mL) | -1 | | (125 W) | (5 min) | 1 |
| iO ₂ P-25 Degussa | Commercial | 10 mg L^{-1} | 100 mg L^{-1} | 4 | UVA | ~100% | 0.382 min^{-1} |
| 75:25 w/w mixture of | | | | | | (18 min) | |
| natase: rutile) | Commercial | 10 mg I^{-1} | 100 mg J^{-1} | 4 | 1 15/4 | - 1000/ | 0.226 min^{-1} |
| no sigina Aldrich | Commercial | 10 mg L | 100 mg L | 4 | UVA | $\sim 100\%$ (18 min) | 0.320 11111 |
| iO ₂ P-25 Degussa | Commercial | 10 mg L^{-1} | $100 \text{ mg } \text{L}^{-1}$ | 4 | Visible | ~94% | 0.199 min^{-1} |
| 75:25 w/w mixture of | | | | | | (18 min) | |
| natase : rutile) ²⁹⁷ | | | | | | () | |
| nO Sigma Aldrich ²⁹⁷ | Commercial | 10 mg L^{-1} | 100 mg L^{-1} | 4 | Visible | ~90% | 0.144 min^{-1} |
| - | | | | | | (18 min) | |
| iO ₂ (Sigma-Aldrich) ²⁹⁸ | Commercial | 20 mg L^{-1} | 1.5 g L^{-1} | 3 | UV lamp (40 W) | 99% | 0.54 min^{-1} |
| (| | -1 | -1 | | | (15 min) | 1 |
| nO (Sigma-Aldrich) ²⁵⁶ | Commercial | 20 mg L 1 | 1.0 g L ⁻ | 7 | UV lamp (40 W) | 86% | 0.31 min ¹ |
| no (Nana nara Enadana) ²⁹⁹ | Commoraial | 5 mg I ⁻¹ | $500 \text{ mg} \text{ J}^{-1}$ | 7 | 105 W modium processo | (15 min) | |
| no (Nano pars Spadana) | Commercial | 5 IIIg L | 500 mg L | / | Hg lamp (LWC) | 98% (100 min) | |
| | | acid: 50 | | | Tig lattip (0vC) | (100 1111) | |
| | | $mg L^{-1}$ | | | | | |
| nO-Ce ³⁰⁰ | Precipitation | 20 ppm | 0.5 g L^{-1} | 3 | UV light: 125 W Hg | 60% | 6.86×10^{-3} |
| | method | 11 | 0 | | without bulb | (120 min) | \min^{-1} |
| nO–Ce; H_2O_2 : | Precipitation | 20 ppm | 0.5 g L^{-1} | 3 | UV light: 125 W Hg | 70% | _ |
| .5 m mole per L ³⁰⁰ | method | | | | without bulb | (120 min) | |
| iO_2 (Degussa P25) | Commercial | 25 mg L^{-1} | 0.2 g L^{-1} | 4.5 | Solar simulator exposed | ~95% | 0.2378 mg L^{-1} |
| dispersed powder ³⁰² | | | | | to xenon lamp irradiation | (150 min) | min ⁻¹ (zero |
| | | | | | | | order), 0.0251 |
| | | | | | | | order) 0.0034 |
| | | | | | | | $L mg^{-1} min^{-1}$ |
| | | | | | | | (second order |
| O ₂ immobilized on | Chemical vapour | 25 mg L^{-1} | 0.2 g L^{-1} | 4.5 | Solar simulator and | 100% | 0.0124 mg L^{-1} |
| e active coated glass ³⁰² | deposition | U | U | | exposed to xenon lamp | (1480 min) | min ⁻¹ (zero |
| | | | | | irradiation | | order), 0.0012 |
| | | | | | | | min ⁻¹ (first |
| | | | | | | | order), 0.0001 |
| | | | | | | | L mg ⁻¹ min ⁻¹ |
| O Demand (D 25) ³⁰³ | Commencial | 4 | 20 mm t ⁻¹ | 7.0 | | > 0.00/ | (second order |
| IO_2 Degussa (P-25) | Commercial | 4 mg L | 20 mg L | 7.8 | 125 W Hg vapor lamp, | >98% | _ |
| iO ₂ Degussa P25 | Commercial | 5 mg | $50 \text{ mg} \text{ dm}^{-3}$ | _ | Mercury lamp (150 W) | ~89% | 0.0425 min^{-1} |
| ref. 304) | Commercial | dm^{-3} | oo mg um | | $\lambda < 300 \text{ nm}$ | (60 min) | 0.0120 11111 |
| nO Degussa P25 | Commercial | 1 mg | $50 \text{ mg } \text{dm}^{-3}$ | _ | Mercury lamp (150 W), | 60% | 0.0328 min^{-1} |
| ref. 304) | | dm ⁻³ | 8 | | $\lambda < 300 \text{ nm}$ | (30 min) | |
| nO nanoparticles ³⁰⁵ | Chemical | 60 ppm | 10 mg L^{-1} | _ | Four UV-vis solarium lamps | 24% | $0.055 \mathrm{~min}^{-1}$ |
| - | method | | - | | (60 W) | (180 min) | |
| VDF- ZnO/Ag ₂ CO ₃ /Ag ₂ O | Casting solution | 10 ppm | 1.96 wt% | _ | White light-emitting | 49.96% | _ |
| nembrane ³⁰⁶ | using wet phase | (300 mL) | (membrane | | diode lamp | (180 min) | |
| | inversion | | area: 12.56 | | $(\lambda > 400 \text{ nm}, 100 \text{ W})$ | | |
| C as deped TiO | method | 5 mg I ⁻¹ | $cm^{-})$ | c | Cimulated color | 050/ | 0.060 min^{-1} |
| anoparticles ³⁰⁷ | bydrothermal | 5 IIIg L | 2.0 g L | 0 | radiation: 350 W | 85% | 0.062 11111 |
| unoparticies | methods | (30 IIII) | | | xenon lamp | (30 mm) | |
| -N-S co-doped TiO ₂ ³⁰⁸ | Thermal | 20 ppm | 0.5 g L^{-1} | _ | LED lamp | ~100% | 0.021 min^{-1} |
| | treatment | (200 mL) | 010 8 2 | | $(\lambda_{max}: 420 \text{ nm},$ | (300 min) | 01021 11111 |
| | method | . , | | | 1 mW cm^{-2} | | |
| i (0.25 wt%) doped TiO_2^{309} | Sol-gel method | 25 ppm | 2 g L^{-1} | 6 | UV (36 W, 254 nm) | 89% | $0.0064~\mathrm{min}^{-1}$ |
| | - | | - | | | (360 min) | |
| i (0.5 wt%) doped TiO ₂ ³⁰⁹ | Sol-gel method | 25 ppm | 2 g L^{-1} | 6 | UV (36 W, 254 nm) | 78% | 0.0046 min^{-1} |
| | | | | | | (360 min) | |

Table 5 (continued)

| -1 | Preparation | | Catalyst | | | % | |
|---|--|---|------------------------------|---------------|--|----------------------------------|---|
| Photocatalyst | method | IPF | dose | рН | Light source | degradation | Rate constant |
| La ³⁺ (2%)-doped TiO ₂ monolith ³¹⁰ | Sol–gel method | 50 mg L^{-1} (70 mL) | 0.1 g | 5 | Sunlight | 96.9% (150 min) | 2.2×10^{-2} min ⁻¹ |
| C,N-co-doped mesoporous | Hydrothermal method | 20 ppm (220 mL) | $0.5 \mathrm{g L}^{-1}$ | — | High-pressure Hg lamp | 98.9% (120 min) | 0.0377 min ⁻¹ |
| C,N-doped mesoporous | Hydrothermal | 20 ppm (220 mL) | $0.5~g~L^{-1}$ | — | LED lamp (visible light, $\frac{1}{2}$: 420 nm 1 mW cm ⁻²) | (120 min) | 0.0207 min ⁻¹ |
| N doped CNT COOH/TiO ₂ (anatase/rutile: 20/80) ³¹⁴ | Hydrothermal | 5 mg L^{-1} ppm | $400~mg~L^{-1}$ | Natural pH | LED light: 240 W, 40 mW cm ^{-2} and 410 nm | (120 min) 85–86% (120 min) | 4.45×10^{-3} - 1.22×10^{-2} min ⁻¹ |
| Activated carbon impregnated with TiO ₂ ³¹⁶ | Sol–gel method | 25 mg L^{-1} (20 mL) | $1.6 \mathrm{g L}^{-1}$ | 4.3 | UV lamp: 15 W, 254 nm | 92% (240 min) | |
| Fe ₃ O ₄ @MIL-53(Fe) ³¹⁸ | Calcination (400 °C) | 10 mg L^{-1} (50 mL), H ₂ O ₂ (20 mM) | $0.4~{\rm g~L}^{-1}$ | _ | Xenon lamp (500 W with 420 nm cut-off filter) | 99% (60 min) | 4.71×10^{-2} min ⁻¹ |
| ${\rm Fe_3O_4/Bi_2WO_6}^{319}$ | Two-step approach | 10 mg L^{-1} (70 mL) | 70 mg | 4.7 | Solar light | >80% (120 min) | 0.0144 min^{-1} |
| $Ag/Fe_{3}O_{4}/WO_{3-x}/H_{2}O_{2}$ (10 mM) ³²² | Simultaneous | 10 mg L^{-1} (30 mL) | 30 mg | — | Xenon lamp (500 W) with optical filter ($\lambda > 420$ nm) | $\sim 100\%$ (90 min) | _ |
| Ag/ZnO/CoFe ₂ O ₄ ³²³ | Coating CoFe ₂ O ₄ with ag/ZnO using Pechini method | 10 ppm | $0.3~g~L^{-1}$ | 7 | UV light (125 W medium- pressure Hg lamp) | (50 min) 80% (60 min) | 0.03905 min ⁻¹ |
| BiOBr/Fe ₃ O ₄ @SiO ₂ ³²⁴ | Solvothermal | 2 mg L^{-1} | 1 g L^{-1} (50 ml) | 7 | Fluorescent lamp (visible light) | ~99% (60 min) | 0.08 min^{-1} |
| TiO ₂ /ZnO/copper phthalocyanine (CuPc) ³²⁶ | Multiple steps | 5 mg L ⁻¹ (50 mL) | Film | 6.5 | Hg lamp with 365 nm cut-off filter, 1.2 W cm^{-2} | 80% (240 min) | $0.42 h^{-1}$ |
| PAN-MWCNT/TiO ₂ -NH ₂ ³²⁸ | Electrospinning | 5 mg L^{-1} (100 mL) | 15 mg L^{-1} | 2 | UVA lamp (315–400 nm) of 40 W | $\sim 100\%$ (120 min) | — |
| Carbon dots/Fe ₃ O ₄ @carbon sphere (in presence of persulfate) ³³⁰ | Solvothermal method | $50 \ \mu mol$ L^{-1} | 0.3 g L^{-1} | — | Xenon lamp (350 W) with a glass filter $(\lambda > 420 \text{ nm})$ | (120 min) 96% (120 min) | _ |
| PAN-MWCNT/TiO ₂ -NH ₂ composite nanofibers ³³² | Multiple steps | 5 mg L^{-1} (100 mL) | 15 mg | 2 | Xenon lamp (125 W) with cut-off filter $(\lambda > 400 \text{ nm}), 0.1 \text{ W cm}^{-2}$ | 100% (210 min) | — |
| g-C ₃ N ₄ ³³³ | Polycondensation | 20 mg L^{-1} (200 mL) | 200 mg | 5.5 | Xenon lamp (35 W) | 20% (4 h) | _ |
| Reduced graphene oxide-HoVΩ₄-TiO₂ ³³⁵ | Hydrothermal | 10 mg L^{-1} | 40 mg L^{-1} | 7 | Tungsten lamp (150 W), $(\lambda > 4900 \text{ nm})$ | ~96% (60 min) | _ |
| g-C ₃ N/ag/AgCl/BiVO ₄ ³³⁷ | Hydrothermal | 2 mg (50 mL) | $0.25~g~L^{-1}$ | 4 | Visible light | 94.7% (60 min) | _ |
| Ag (7%)/g-C ₃ N ₄ /kaolinite ³³⁸ | Two steps | 5 ppm (50 mL) | 50 mg | — | Xenon lamp (500 W with 400 nm cut-off filter) | (300 min) | 0.01128 min ⁻¹ |
| Graphene quantum dots (3 wt%)/AgVO3 ³³⁹ | Hydrothermal | 10 mg L^{-1} (50 mL) | 0.01 g | — | Xenon lamp (350 W with $\lambda > 420$ nm) | ~100% (180 min) | 0.1678 min ⁻¹ |
| g-C ₃ N ₄ (10 wt%)/MIL-68(In)–NH ₂ composites ³⁴⁰ | <i>In situ</i> solvothermal assisted by ultrasonication | $20 \text{ mg } \text{L}^{-1}$ | 0.15 g | 4 | Xenon lamp (300 W with $\lambda > 420$ nm) | 93% (120 min) | 0.01739 min ⁻¹ |
| Graphene oxide/TiO ₂ doped with F (BrO ₂ ^{-100 µg L⁻¹)³⁴¹} | Hydrothermal | $_L^{100}~\mu g$ | $0.05~{\rm g~L}^{-1}$ | 5.2 | Low-pressure Hg lamp (10 W), (26 μ W cm ⁻²) | ~100% (60 min) | 0.4504 min ⁻¹ |
| rGO-TiO ₂ /sodium alginate ²⁷³ | Hydrothermal | 10 ppm (200 mL) | $0.5~g~L^{-1}$ | 7 | High-pressure Hg lamp (100 W) , $(13.5 \text{ W} \text{ m}^{-2})$ | ~100% (90 min) | 0.047 min^{-1} |
| $TiO_2/5\%$ g-C ₃ N ₄ ³⁴³ | Solvothermal | 5 mg L^{-1} | 50 mg | 7 | Xenon lamp | $\sim 90\%$ (60 min) | 0.03833 min ⁻¹ |
| $g-C_3N_4/Bi_2WO_6$ (1:4 molar ratio) ³⁴⁴ | Hydrothermal | 25 μΜ | $0.2~g~L^{-1}$ | — | Xenon lamp (300 W) with 420 nm cut-off filter | ~96.1% (60 min) | 0.062 min^{-1} |
| g-C ₃ N ₄ /TiO ₂ /Fe ₃ O ₄ @SiO ₂ ³⁴⁵ | Sol-gel method | 2 mg L^{-1} (50 mL) | 50 mg | 7 | Visible light, 330 W m^{-2} | 97% (15 min) | _ |
| $FeV_{3}O_{8}$ (10%)/g- $C_{3}N_{4}^{347}$ | Dispersion, grinding and calcination | 10 ppm (30 mL) | 10 mg | _ | Xenon lamp (300 W) with UV cut-off filter (λ: 420 nm) | 95% (85 min) | 0.03 min ⁻¹ |

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Table 5 (continued)

| Photocatalyst | Preparation method | IPF | Catalyst dose | рН | Light source | % degradation | Rate constant |
|--|--|-----------------------------------|-------------------------|------|--|--------------------|--------------------------|
| $g\text{-}C_3N_4/Bi_2WO_6/rGO^{348}$ | Microwave assisted hydrothermal preparation | 5 mg L^{-1} | 1.0 g L^{-1} | 4.3 | Xenon lamp (300 W), $\lambda > 420$ nm | 93% (240 min) | 0.011 min ⁻¹ |
| $g\text{-}C_3N_4/Bi_2WO_6/rGO^{348}$ | Microwave assisted hydrothermal preparation | 5 mg L^{-1} | $1.0~\mathrm{g~L}^{-1}$ | 4.3 | Sunlight | 98.6% (240 min) | _ |
| AgSCN/Ag ₃ PO ₄ /C ₃ N ₄ (molar % of AgSCN: 11.3) ³⁵¹ | Precipitation reaction | 5 mg L^{-1} (100 mL) | 50 mg | — | Sunlight (500 W halide lamp) | 91% (6 min) | 0.46 min ⁻¹ |
| N-TiO ₂ @SiO ₂ @Fe ₃ O ₄ ³⁵² | Sol-gel method | 2 mg L^{-1} (50 mL) | 50 mg | — | Fluorescent lamps (9 W), 320 μ W cm ⁻² | 94% (300 min) | _ |
| $g-C_3N_4/CQDs/CdIn_2S_4^{353}$ | Hydrothermal | 80 mg L^{-1} (100 mL) | 0.1 g | _ | 300 W xenon lamp with 420 nm cut-off filter, 200 mW cm ⁻² | 91% (60 min) | — |
| $Co_3O_4/BiOI(1:2)^{354}$ | Solvothermal | 10 ppm (50 mL) | 40 mg | 11.3 | 60 W LED lamp with 420 nm cut-off filter | 93.87% (60 min) | 0.0945 min ⁻¹ |
| $\alpha \text{-SnWO}_4/\text{UiO-66}(\text{NH}_2)/\text{g-C}_3\text{N}_4^{-355}$ | Solvothermal | 10 mg L^{-1} (100 mL) | 50 mg | _ | Simulated sunlight using high-pressure 300 W xenon lamp | 95.5% (120 min) | 0.017 min ⁻¹ |

conditions in B and Ce doped TiO₂, irradiated by sunlight.³⁷³ Bi³⁺ and Fe²⁺ ion doped ZnO showed significant photocatalytic degradation of norfloxacin with the addition of HSO₅⁻ under solar irradiation and followed pseudo-first-order kinetics.³⁷⁴ The co-doped ZnO exhibited a lower band gap, which accounted for the increased absorption of solar irradiation and reduced electron and hole recombination, which facilitated high norfloxacin degradation compared to undoped ZnO. Fe-doped CeO₂ exhibited about 95% photocatalytic degradation of norfloxacin in aqueous solution (pH: 8.0) within 180 min corresponding to an initial norfloxacin concentration of 2.5 mg L⁻¹ and catalyst dose of 0.1 g L⁻¹.³⁷⁵ An Ag-doped TiO₂/CFA (coal fly ash) photocatalyst has also been used to monitor the photocatalytic degradation of norfloxacin.³⁷⁶

3.5.4 Metal oxide-metal oxide composites. A mesoporous Fe2O3-TiO2 photocatalyst showed complete norfloxacin removal from aqueous solution (pH: 7) within 120 min under UV illumination with a stoichiometric amount of H₂O₂.³⁷⁷ Trang et al.378 used an ordered SBA-15 mesoporous silica support synthesized by a sol-gel method using the triblock copolymer Pluronic P123 and immobilized with different amounts of photocatalyst TiO₂ (TiO₂:SiO₂ ratios of 0, 0.25, 1.0 and 5.0). Subsequent investigations on the removal of norfloxacin revealed the better photocatalytic activity of 1.0TiO₂/SBA-15 hybrid material in achieving 96.6% degradation of norfloxacin in 150 min under UV-light irradiation. Fe-complex/TiO₂ composites comprising $[Fe^{II}(dpbpy)_2 (H_2O)_2]/TiO_2$, $[Fe^{II}(dpbpy)(phen)_2]/TiO_2$ and [Fe^{II}(dpbpy)(bpy)₂]/TiO₂ (dpbpy: 2,2'-bipyridine-4,4'diphosphoric acid, phen: 1,10-phenanthroline, bpy: 2,2-bipyridyl) photocatalysts exhibited 98.5% degradation of norfloxacin in water under visible-light irradiation after 3 h.³⁷⁹ Further, the photocatalytic performance and cyclic stability of these composites were found to be much better than those of pure TiO_2 or P25. An Ag_2O/TiO_2 -zeolite composite fabricated through a modified sol–gel method exhibited high performance in the decomposition of norfloxacin under simulated solar-light illumination.³⁸⁰ This is a consequence of the narrow band gap of the photocatalyst, its enhanced light absorbance ability in the visible region and high charge separation efficiency.

 $FeVO_4/Fe_2TiO_5$ (2:1) synthesized via a one-pot hydrothermal method exhibited high photocatalytic activity and excellent stability for the removal of norfloxacin in aqueous solution under visible-light irradiation.³⁸¹ This is ascribed to the synergistic effect of photogenerated electronholes with radical OH· and h⁺. MIL-101(Fe)-NH₂ immobilized on an α -Al₂O₃ sheet has also been investigated for effective norfloxacin elimination via a photo-Fenton process.³⁸² Ag/ AgCl-CeO₂ composite photocatalysts fabricated by in situ interspersal of AgCl on CeO2 and subsequent photoreduction of AgCl to Ag exhibited enhanced photocatalytic activity in the photodegradation of norfloxacin under visible-light irradiation.³⁸³ Fig. 14(a) shows the highest degradation efficiency (91%) for norfloxacin achieved by sample Ag/AgCl-CeO₂ composites with an Ag mass ratio of 13.94 wt% (denoted AC-3) within 90 min under visible-light irradiation. It is also apparent from Fig. 14(b) and (c) that the photodegradation process followed a pseudo-first-order kinetic model with the highest rate constant $(0.02279 \text{ min}^{-1})$ for AC-3 compared to CeO₂, Ag/AgCl, Ag/CeO₂ and other AC composites. Fig. 14(d) shows the time-dependent UV-vis spectra of NOF solution for the AC-3 sample. ZnO/ ZnS@biochar,³⁸⁴ ZnFe₂O₄/hydroxyapatite–Sn^{2+,385} (BiO)₂CO₃– Bi-TiO₂,³⁸⁶ and Ag/AgCl/Ag₂MoO₄³⁸⁷ composites have also been reported as promising photocatalysts in the degradation of norfloxacin in water under UV irradiation.


Fig. 14 (a) Photocatalytic degradation NOF curves; (b) kinetic curves of NOF degradation; (c) apparent rate constants for the degradation of NOF; (d) time-dependent UV-vis spectra of NOF solution for AC-3 sample (Ag/AgCl-CeO₂). Reproduced from ref. 383 with permission from Elsevier (2017).

3.5.5 Graphitic composites

3.5.5.1 g- C_3N_4 -based composites. Fei et al.³⁸⁸ investigated the photocatalytic degradation of norfloxacin in the presence of a sunlight-driven mesoporous g-C₃N₄. The results showed 90% decomposition of norfloxacin in 1.5 h under simulated sunlight irradiation. Co/g-C₃N₄, Co/g-C3N4/H2O2 and Co/g-C3N4/PMS composite photocatalysts exhibited better performance compared to pure g-C3N4 in the photocatalytic degradation of norfloxacin under visiblelight irradiation.³⁸⁹ The optimization and variations of different parameters have been used to study the photocatalytic degradation of norfloxacin in the presence of ZnO/g-C₃N₄/Fe₃O₄ under visible light.³⁹⁰ These findings indicated a removal rate of norfloxacin greater than 90% in 120 min for a catalyst concentration of 1.43 g L^{-1} , solution pH 7.12 and norfloxacin concentration of <8.61 L^{-1} . Shuttle-like CeO₂/g-C₃N₄ combined with mg persulfate³⁹¹ and NiWO₄ nanorods anchored on g-C₃N₄ nanosheets³⁹² also exhibited enhanced degradation of norfloxacin under visible light.

3.5.5.2 Graphene-based composites. A TiO₂/Bi₂WO₆/rGO (0.5%) photocatalyst attained about 87.79% removal of norfloxacin in water under visible-light irradiation after 60 min and was found to be superior to its individual components under optimal conditions.393 Such enhanced catalytic activity of TiO2/Bi2WO6/rGO arises due to the ligand-metal electron transfer mechanism. According to Zhao et al.,³⁹⁴ an rGO/Bi₂WO₆ composite exhibited outstanding photocatalytic activity for norfloxacin degradation in an aquatic environment under visible-light irradiation, as evident from the time-dependent-UV spectrum and time-dependent-HPLC spectrum displayed in Fig. 15(a) and (b), respectively. Fig. 15(c) and (d) indicate about 87.49% degradation of norfloxacin within 180 min compared to Bi₂WO₆, under visible-light irradiation. Additional investigations revealed ·OH and e playing dominant roles in the photocatalytic degradation of norfloxacin. N-doped TiO2/graphene exhibited enhanced photocatalytic degradation under UV-light irradiation.³⁹⁵ It is suggested that graphene acts as an efficient "electron pump",

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Fig. 15 (a) The time-dependent UV spectrum, (b) the time-dependent-HPLC spectrum, (c) the photodegradation curve, and (d) photocatalytic degradation rate of norfloxacin. Reproduced from ref. 394 with permission from Elsevier (2021).

thereby promoting the separation of carriers to account for the observed photodegradation.

Wu *et al.*³⁹⁶ reported a UV-assisted nitrogen-doped reduced graphene oxide/Fe₃O₄ composite by a simple hydrothermal–co-precipitation method and investigated the degradation of norfloxacin with activated peroxodisulfate. These findings demonstrated 100% degradation efficiency of norfloxacin (pH: 3.0) within 13 min due to an excellent synergistic effect at $m(NGO-Fe_3O_4):m(PDS)$ of 4:1, and concentrations of NOR and $S_2O_8^{2-}$ of 100 mg L⁻¹ and 1 mM, respectively. According to this, *in situ* generated ·OH was considered to be the main active free radical. rGO-coupled manganese oxynitride,³⁹⁷ immobilized Ag₃PO₄/GO on 3D nickel foam³⁹⁸ and γ -Fe₂O₃-MIL-53(Fe)–GO³⁹⁹ photocatalysts also displayed efficient degradation of norfloxacin.

3.5.6 Heterojunction, Z- and S-scheme-based composites. Ni-doped ZnO/MWCNTs were tested for complete degradation of norfloxacin corresponding to initial concentrations in mg L^{-1} (time in min) of 10 (30), 20 (60), 50 (120), 100 (160) and 10 (40), 20 (70), 50 (150), 100 (200) under visible and UV radiation, respectively.400 The findings also suggested that MWCNTs can act as a charge transfer channel for accelerating electron transfer between Ni and ZnO nanoparticles. This could subsequently effectively decrease the recombination of electron-hole pairs in the Ni-doped ZnO/MWCNTs composite, accounting for the degradation of norfloxacin by the Ni-doped ZnO/MWCNTs photocatalyst. A Bi-containing glass-ceramic defect-rich heterojunction photocatalyst originating from the removal of chloride ions achieved 98%, 73%, and 36% degradation of norfloxacin

NIR under UV-vis-NIR, vis-NIR, and irradiation, respectively.401 Guo et al.402 prepared Co3O4/Bi2MoO6 p-n heterostructure photocatalysts via an in situ calcination process and applied them to activate peroxymonosulfate (PMS) in the degradation of norfloxacin under irradiated visible light. These findings indicated 87.68% removal of norfloxacin within 30 min by selecting a 5 wt% Co₃O₄/Bi₂-MoO₆/PMS photocatalyst owing to the synergistic effect. A CoTiO₃/UiO-66-NH₂ p-n junction mediated heterogeneous photocatalyst showed 90.13% degradation of norfloxacin in 1 h under optimized conditions and followed a type-II p-n heterojunction charge transfer mechanism.403 An LaOCl/LDH Z-scheme heterojunction catalyst containing oxygen vacancies showed a 82.5% (150 min) removal rate for norfloxacin owing to the synergistic effect of the Z-scheme heterojunction and oxygen vacancies.404 Further, the degradation of norfloxacin followed pseudo-first-order kinetics with the rate constant of LaOCl/LDH twice that of the individual components.

Z-Scheme ternary heterojunctions comprising phosphatedoped BiVO₄/graphene quantum dots/P-doped g-C₃N₄ (BVP/ GQDs/PCN) produced an 86.3% degradation rate for norfloxacin under visible light.⁴⁰⁵ Such an excellent performance of the photocatalyst is guided by interfacial charge transfer efficiency and a broadened visible-light response range compared to binary type-II heterojunction phosphate-doped BiVO₄/PCN. CoWO₄ nanoparticles assembled with g-C₃N₄ nanosheets fabricated by a hydrothermal method showed 3.18 and 2.69 times higher photocatalytic degradation of norfloxacin under visible light compared to g-C₃N₄ and CoWO₄, respectively.⁴⁰⁶ Such enhanced performance of $CoWO_4/g-C_3N_4$ is attributed to the synergism between $CoWO_4$ and $g-C_3N_4$ inhibiting the fast recombination of photogenerated electron-hole pairs. Investigations involving radical scavengers suggested that $\cdot OH$ rather than O_2^{--} plays a dominant role in the degradation of norfloxacin. Fig. 16 shows the possible mechanism responsible for the photodegradation of norfloxacin by this synthesized $CoWO_4/g-C_3N_4$, a phenomenon driven through a Z-scheme mechanistic pathway.

A Bi₂Sn₂O₇/heated perylene diimide (PDIH) Z-scheme heterojunction photocatalyst reached 98.71% degradation of norfloxacin in 90 min under visible light.407 The apparent rate constant of norfloxacin was found to be 3.65 and 20 times those of PDIH and Bi₂Sn₂O₇, respectively. The fabricated Bi2Sn2O7/PDIH heterojunction catalyst also facilitated the separation of charge carriers and preserved the redox capability. In another study, piezo-photocatalytic degradation of norfloxacin by the S-scheme heterojunction BaTiO₃/TiO₂ was found to be 91.7% (60 min) with a rate constant of 43 \times 10⁻³ min⁻¹.⁴⁰⁸ Free radical trapping investigations indicated h⁺ and ·OH to be the main active species in the degradation process. The heterojunction also showed excellent stability and cyclability, as evident after 5 cycles. An LaFeO₃/g-C₃N₄ heterojunction showed 95% photocatalytic degradation of norfloxacin under visible light in 180 min, which was found to 9.32 times higher than pristine g-C₃N₄.⁴⁰⁹ Zhang et al.⁴¹⁰ prepared an optimized AgBr (3%)/LaNiO₃ (30%)/g-C₃N₄ (100%) dual Z-scheme composite system via ultrasound-assisted hydrothermal method considering energy band matching and observed 92% photodegradation of norfloxacin within two hours under visible light owing to a synergistic effect. These studies also



Fig. 16 Schematic illustration of possible Z-scheme photocatalytic mechanism. Reproduced from ref. 406 with permission from Elsevier (2019).

indicated an almost unaltered photodegradation rate (>90%) even after six cycles.

Ag₃PO₄/CNTs exhibited an efficiency of about 93% for the photoelectrocatalytic degradation of NOR within 30 min.411 This is explained based on the Z-scheme mechanism that significantly promoted the separation of electron-hole pairs. Further, h^+ and $\cdot O_2^-$ made a major contribution to the degradation process to oxidize NOR. An oxygen-vacancy-rich CuWO₄/BiOCl composite exhibited excellent photocatalytic degradation of norfloxacin (96.69%) in 120 min under a 300 W xenon lamp due to a Z-scheme structure compared with pure CuWO₄ and oxygen-vacancy-rich BiOCl.⁴¹² A dual Z-scheme mechanism has been proposed for Ag (0.3 wt%) (a)BiPO₄/BiOBr/BiFeO₃ that enabled 98.1% and 99.1% degradation of norfloxacin (20 mg L^{-1}) in 90 min and in less than 45 min under visible and UV light exposure, respectively.⁴¹³ It is suggested that the synergistic effects of ternary nanoheterostructures heterojunctions, electron capture and the surface plasmon resonance effect of Ag lead to such high photocatalytic activity. Immobilized Z-scheme CdS/Au/TiO₂ nanobelts displayed 64.67% (60 min) degradation of norfloxacin under xenon-light-simulated sunlight irradiation which was ascribed to the synergistic effect.414

The formation of an S-scheme in the heterojunction of a photocatalyst facilitates the separation of photogenerated electron-hole pairs and reduces the recombination of charge carriers. In view of this, an S-scheme heterojunction comprising N-ZnO/g-C₃N₄ prepared by calcining ZIF-L/g-C₃N₄ in a mass ratio of 15% showed more than 90% degradation of norfloxacin in 90 min under a visible system.415 The corresponding rate constant was 4.15 times and 4.65 times higher than g-C3N4 and N-ZnO, respectively. The effective light capture capacity and migration and separation of carriers accounted for such behavior. Further, holes and superoxide radicals are reported to be the active species in the photodegradation of norfloxacin. The degradation rate of norfloxacin on a 10% g-C₃N₄/Bi₈(CrO₄)O₁₁ heterojunction photocatalyst is about 1.38 and 2.33 times higher than that of pure Bi₈(CrO₄)O₁₁ and g-C₃N₄, respectively.⁴¹⁶

Efficient photocatalytic performance for norfloxacin degradation has also been reported in chitosan/TiO₂(a)g-C₃N₄,⁴¹⁷ AgI/MFeO₃/g-C₃N₄ (M: Y, Gd, La),⁴¹⁸ Bi₂Sn₂O₇/g-C₃N₄,⁴¹⁹ Ag/graphitic carbon nitride quantum dots (CNQDs)/g-C₃N₄,⁴²⁰ BiOBr/iron oxides,⁴²¹ and CdS QDs/CaFe₂-O₄(a)ZnFe₂O₄⁴²² photocatalysts.

Table 6 records the performance data of different photocatalysts on the removal of norfloxacin from wastewater.

3.6 Ciprofloxacin

Ciprofloxacin (CIP) is a synthetic antimicrobial agent of the fluoroquinolone class and considered to be a very promising and efficacious drug for use in the treatment of various community-acquired and nosocomial infections.^{360,423,424} It

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 Table 6
 Performance data on removal of norfloxacin in water using various photocatalysts

| Photocatalyst | Preparation | NOR | Catalyst dose | pН | Light type | Degradation (time) | Rate constant |
|--|---|--|-----------------------------|---------|--|--------------------------------|---|
| TiO _{2-x} ³⁶¹ | Combustion method | $100 \ \mu M \ L^{-1}$ | 0.1 g L^{-1} | 7 | Xenon lamp: | ~100% | 0.0361 |
| Cu_2O^{363} | Hydrothermal | 20 mg L^{-1} , | 50 mg | _ | Xenon lamp | (240 mm) 79.87% | 0.0081 |
| Bi_2WO_6 with [Fe ³⁺]: 0.3 mmol L ⁻¹³⁶⁴ | Ultrasonic spray pyrolysis | (50 mL) 0.0313 mM L^{-1} (100 | $0.5 \mathrm{~g~L}^{-1}$ | 9 | (500 W) Xenon lamp: 300 W | (210 min) 89.7% (20 min) | min^{-1} 0.1006 min^{-1} |
| TiO_2/Ti film with exposed {001} facets (HF: 0.02 M) ³⁶⁵ | Hydrothermal | mL) 10 mg L^{-1} | _ | 2.62 | Low-pressure mercury lamp (10 W), $\frac{1}{2}$: 254 pm | 70.5% (90 min) | 0.0504 min ⁻¹ |
| ZnO nanoflowers ³⁶⁶ | Sol–gel method | 10 mg L^{-1} | $0.1 \mathrm{~g~L}^{-1}$ | 11 | Fluorescent lamp: 8 W | ~72% (100 min) | 3.93×10^{-2} |
| Triangular Ag nanoplates coated ZnO nanoflowers ³⁶⁶ | Sol-gel method | 10 mg L^{-1} | $1.0 \mathrm{g L}^{-1}$ | 11 | $\begin{array}{l} (0.55 \text{ mW cm}^2) \\ \text{Fluorescent lamp} \\ (8 \text{ W}), 0.55 \text{ mW cm}^{-2} \end{array}$ | ~97% (100 min) | min^{-1} 3.93 × 10^{-2} min^{-1} |
| Triangular Ag nanoplates coated ZnO nanoflowers ³⁶⁷ | Hydrothermal method and dual-reduction method | 10 ppm (3 mL) | — | — | Fluorescent lamp (8 W), 0.55 mW cm ⁻² | 92.2% (270 min) | 9.2×10^{-3} |
| Prussian blue doped CeO_2 (ratio: 10%) with H_2O_2 : 9 mM ³⁶⁸ | Physical and chemical loading approaches | 16 mg L^{-1} (50 mL) | $0.6~g~L^{-1}$ | 6 | W fluorescent lamp $(0.55 \text{ mW cm}^{-2})$ | 88.93% (30 min) | |
| N doped TiO ₂ ³⁷⁰ | Hydrothermal method | 6.03 mg L^{-1} | 0.54 g L^{-1} | 6.37 | Xenon lamp (300 W), 350–780 nm, 150 mW cm ⁻² | 99.53% (30 min) | _ |
| Al (1 Mol%)-doped TiO ₂ nanoflakes ³⁷¹ | Solvothermal | $2 \times 10^{-4} \text{ M}$ | 15 mg (50 ml) | 10.1 | Visible light | 93% (120 min) | $0.0143 \ { m min}^{-1}$ |
| C-TiO ₂ ³⁷² | Solution phase carbonization method | 0.0094 mM | 0.2 g L ⁻¹ | Neutral | Low-pressure mercury lamps (420 nm) | ~100% (70 min) | 5.44×10^{-4} [NFX] ₀ -1 + 0.10 [C- TiO ₂] - 1.99 × 10^{-2} min ⁻¹ |
| $\mathrm{Bi}^{3^{+}}$ and $\mathrm{Fe}^{2^{+}}$ doped ZnO^{374} | Sol-gel method | 10.0 mg L^{-1} | $1.0 \mathrm{g L}^{-1}$ | 8 | Xenon lamp (300 W), 45.2 mW cm^{-2} | 80% (120 min) | — |
| Bi ³⁺ and Fe ²⁺ doped ZnO (0.2 mM HSO_5^{-1}) ³⁷⁴ | Sol–gel method | 10.0 mg L^{-1} | 1.0 g L^{-1} | 8 | Xenon lamp (300 W), 45.2 mW cm ⁻² | (120 min) 99% (120 min) | 9.8 × 10^9 M^{-1} s^{-1} (·OH), 9.0 × 10^9 M^{-1} s^{-1} (SO ₄ · ⁻) |
| [FeII(dpbpy)(phen) ₂]/TiO ₂ ³⁷⁹ | Hydrothermal | 0.313 mM | 1 g L^{-1} | 5 | Xenon lamp (300 W), $\lambda > 420 \text{ nm},$ 140 mW cm ⁻² | 98.5% (180 min) | 0.0412 min^{-1} |
| Ag ₂ O/TiO ₂ -zeolite ³⁸⁰ | Sol-gel method | 5 mg L^{-1} | 50 mg | — | Xenon lamp (35 W), 6.7 mW cm^{-2} | 98.7% | — |
| $FeVO_4/Fe_2TiO_5 (2:1)^{381}$ | One-pot hydrothermal method | 10 mg L^{-1} | 0.05 g | _ | 500 W Xe lamp | (00 min) 95% (30 min) | — |
| Ag/AgCl–CeO ₂ (Ag mass ratio: 13.94 wt%) ³⁸³ | <i>Via</i> urea hydrolysis and calcination | $(30 \text{ mL})^{-1}$ $(50 \text{ mL})^{-1}$ | 30 mg | — | Xe lamp: 300 W (equipped with a UV cut-off filter) | (30 min) 91% (90 min) | 0.02279 min ⁻¹ |
| ZnO/ZnS $@$ biochar (ZnSO ₄ /poplar sawdust ratio: 1 : 1) ³⁸⁴ | Impregnation-roasting method | 0.025 g L^{-1} (50 mL) | $0.5 \mathrm{g L}^{-1}$ | 7 | UV-light | 95% (180 min) | $\begin{array}{c} 0.021\\ \text{min}^{-1} \end{array}$ |
| Ag/AgCl/Ag ₂ MoO ₄ ³⁸⁷ | In situ photoreduction | 10 mg L^{-1} | 30 mg | — | Xenon lamp: 300 W, $(\lambda > 420 \text{ nm})$ | $\sim 65\%$ | — |
| $ZnO/g-C_3N_4-Fe_3O_4^{390}$ | Hydrothermal | 8.61 mg L^{-1} | $^{1.43}_{ m L^{-1}}{ m g}$ | 7.12 | Xenon lamp with 280 nm UV filter | >90% (120) min | $0.0117 \ { m min}^{-1}$ |
| CeO ₂ /g-C ₃ N ₄ (mass ratio of CeO ₂ to g-C ₃ N ₄ :5 and PS: 5 mM) ³⁹¹ | Mixing method | 10 mg L^{-1} (50 mL) | 0.05 g | 2 | 150 W high-pressure xenon lamp with cut-off $\frac{1}{20}$ nm | 88.6% (60 min) | 0.03573 min ⁻¹ |
| NiWO ₄ nanorods/g-C ₃ N ₄ ³⁹² | Hydrothermal followed | 10 mg L^{-1} | 50 mg | — | W lamp (visible light), | 97% | 0.0547 |

Table 6 (continued)

| Photocatalyst | Preparation | NOR | Catalyst dose | рН | Light type | Degradation (time) | Rate constant |
|---|--|---|---------------------------|-----|--|---------------------------------|--|
| rGO/Bi ₂ WO ₆ ³⁹⁴ | by sonication Hydrothermal | 10 mg mL^{-1} (100 mL) | (100 mL) 50 mg | | 150 mW cm ⁻² Xenon lamp (300 W) | (60 min) 87.79% (180 min) | min ⁻¹ |
| N–TiO ₂ /graphene ³⁹⁵ | Three-step method | 30 mg L^{-1} (20 mL) | | | Mercury lamp (250 W), 365 nm | 50% (160 min) | 0.0051 min^{-1} |
| N-doped rGO/Fe ₃ O ₄ $[m(N-GO-Fe_3O_4):$ m(peroxodisulfate) $= 4:11^{396}$ | Hydrothermal-co-precipitation | 100 mg L ⁻¹ , S ₂ O ₈ ²⁻ : 1 mM | $1 \mathrm{g L}^{-1}$ | 3 | UV lamp: 15 W, 254 nm, 44 µW cm ⁻² | 100% (13 min) | 0.238 min ⁻¹ |
| Ni foam supported $Ag_3PO_4/GO (16.78 \text{ wt}\%)^{398}$ | Dip-coating | 15 mg L^{-1} (120 mL) | _ | _ | Xenon lamp (250 W) with 400 nm cut-off filter, 100 mW cm^{-2} | 83.68% (100 min) | 0.426 min ⁻¹ |
| $\gamma\text{-}\mathrm{Fe_2O_3\text{-}MIL\text{-}53(Fe)\text{-}GO^{399}}$ | Multiple steps | 10 mg L^{-1} | 20 mg | | 500 W Xe lamp (100 mW cm ^{-2}), (420 nm cut-off filter) | 92.8% (90 min) | — |
| Ni-doped ZnO/MWCNTs ⁴⁰⁰ | Dispersion method | 100 mgL ⁻¹ (100 mL) | _ | 6.8 | UV Visible | 100% (200 min) 100% | — |
| Bi contained glass-ceramic ⁴⁰¹ | Multiple steps | 20 mg L^{-1} (20 mL) | 20 mg | _ | UV-vis–NIR | (160 min) ~53% (180 min) | 6.76×10^{-3} |
| Bi contained glass-ceramic ⁴⁰¹ | Multiple steps | 20 mg L^{-1} (20 mL) | 20 mg | _ | Visible | ~35% (180 min) | 2.52×10^{-3} min ⁻¹ |
| Bi contained glass–ceramic ⁴⁰¹ | Multiple steps | 20 mg L ⁻¹ (20 mL) | 20 mg | | UV | ~52% (180 min) | 4.05×10^{-3} min ⁻¹ |
| LaOCl/LDH ⁴⁰⁴ | Precipitation method | 10 mg L^{-1} (50 mL) | 20 mg | 7 | Xenon lamp: 300 W | 85% (80 min) | 0.014min^{-1} |
| Phosphate-doped BiVO ₄ /graphene quantum dots/P-doped g- $C_3N_4^{405}$ | Hydrothermal | $20 \text{ mg } \text{L}^{-1}$ (50 mL) | 50 mg | 9.6 | Xenon lamp (300 W) with a 420 nm cut-off filter | 86.3% (120 min) | 0.0148 min ⁻¹ |
| $CoWO_4/g$ - $C_3N_4^{406}$ | Hydrothermal method, followed by ultrasonication | 10 mg L^{-1} (100 mL) | 50 mg | _ | 250 W halogen lamps (visible light) | 91% (80 min) | $0.0283 \ {\rm s}^{-1}$ |
| $LaFeO_x/g-C_3N_4^{409}$ | Ultrasound assisted hydrothermal method | 20 mg (100 mL) | 20 mg L^{-1} | _ | Xenon lamp with 420 nm cut-off filter | 95% (180 min) | 0.01371 min ⁻¹ |
| 3 wt% AgBr/30 wt% LaNiO_3/100% g-C_3N_4 $^{\rm 410}$ | Ultrasound-assisted hydrothermal method | 20 mg L^{-1} (100 mL) | 20 mg | 7 | Xenon lamp (500 W) with a 420 nm cut-off filter | 92% (120 min) | 0.01790 min ⁻¹ |
| 0.3 wt% ag@BiPO ₄ /BiOBr/BiFeO ₃ ⁴¹³ | Precipitation-wet impregnation-photo deposition method | 20 mg L^{-1} | 0.3 g | 7.3 | Visible | 98.1% (90 min) | 0.04123 min ⁻¹ |
| 0.3 wt% ag@BiPO4/BiOBr/BiFeO3 ⁴¹³ | Precipitation-wet impregnation-photo deposition method | 20 mg L^{-1} | 0.3 g | 7.3 | UV | 99.1% (45 min) | 0.07023 min ⁻¹ |
| Immobilized CdS/au/TiO ₂ ⁴¹⁴ | Multiple steps | 5 mg L^{-1} (35 mL) | 4 cm^3 | — | Xenon lamp (35 W) | 64.67% (60 min) | 0.018 min^{-1} |
| $\mathrm{AgI}/\mathrm{LaFeO_3/g}\text{-}\mathrm{C_3N_4}^{418}$ | Ultrasound-assisted hydrothermal approach | 20 mg L^{-1} (100 ml) | 0.2 g | _ | Xenon lamp (500 W), (40 mW cm ⁻²) | 95% (180 min) | 0.0188 min ⁻¹ |
| $20\% \ Bi_2Sn_2O_7/g\text{-}C_3N_4^{\ 419}$ | Ultrasound-assisted hydrothermal method | 20 mg L^{-1} (100 mL) | 0.02 g | — | 500 W xenon lamp with a UV cut-off filter | 94% (180 min) | 0.01261 min ⁻¹ |
| BiOBr/iron oxides ⁴²¹ | <i>In situ</i> co-precipitation method | 10 mg L^{-1} (50 mL) | 0.5 g | ~7 | 800 W xenon lamp with 420-nm cut-off filter | 99.8% (90 min) | ~ 0.076 min ⁻¹ |

is not easily biodegradable and is considered a potential risk to human health. The presence of ciprofloxacin in water acts as pollutant and can be removed by means of a photocatalytic approach.^{425–524}

3.6.1 Metal oxides

3.6.1.1 TiO₂. The photocatalytic degradation of ciprofloxacin as a micropollutant in water has been receiving

considerable attention in the presence of metal oxides. Zeng et al.424 used carbon-dot-doped TiO2 to investigate the kinetics, mechanism and pathway following heterogeneous photocatalytic ozonation degradation of ciprofloxacin. It was noted that 1.0 wt% introduction of carbon dots enhanced the degradation of CIP by 91.1% compared to pristine TiO₂ (64%) in 30 min. Several studies have been made on

ciprofloxacin degradation using commercial TiO₂ as a photocatalyst irradiated with simulated solar light, ^{425,426} artificial sunlight, ⁴²⁶ simulated sunlight⁴²⁷ and UVA/LED⁴²⁸ and UVC radiation.⁴²⁹ TiO₂ nanoparticles irradiated with UVA light demonstrated removal of ciprofloxacin (300 μ g L⁻¹) from water in less than 6 minutes.⁴³⁰ The hydrothermally synthesized mesoporous TiO₂ exhibited 96% photocatalytic degradation of ciprofloxacin hydrochloride (CIP·HCl) under artificial sunlight compared to that prepared by calcination of a titanium glycolate precursor and subsequent hydrothermal-calcination.⁴³¹ This is ascribed to the higher electron–hole separation and charge transfer capability.

Li *et al.*⁴³² fabricated 3D tripyramid TiO₂ (TP-TiO₂) architectures and rod-like morphology of TiO₂ (RL-TiO₂) and studied their application in the photocatalytic degradation of ciprofloxacin hydrochloride under UV-vis-light irradiation. They observed relatively superior removal efficiency (90% within 60 min) for ciprofloxacin and its significantly higher rate constants in the presence of TP-TiO₂ compared to RL-TiO₂. This is ascribed to the key role played by superoxide radicals and photogenic holes in the degradation of ciprofloxacin. Usman *et al.*⁴³³ used TiO₂ nanoparticles (50 mg) in the ~91% degradation of ciprofloxacin aqueous solution (pH: 5.5) on irradiation by a white mercury UV lamp for 5 hours.

3.6.1.2 ZnO and other oxides. ZnO (125 nm) is found to be a very effective photocatalyst in removing 300 μ g L⁻¹ ciprofloxacin from aqueous solution treated by UVA in less than 6 minutes.⁴³⁰ ZnO nanoparticles prepared by a chemical precipitation method on irradiation with UV light (365 nm) for 60 min degraded ciprofloxacin (~48%) in aqueous solution (pH: 10) and also followed pseudo-first-order kinetics (~0.00437 min⁻¹).⁴³⁴ ZnO nanoparticles synthesized by a solgel method were used to examine the degradation of ciprofloxacin in contaminated water under UVC light.435 These findings showed complete photodegradation in 140 minutes corresponding to an initial concentration of ciprofloxacin of 10 mg L^{-1} , pH 5, ZnO loading of 0.15 g L^{-1} and irradiation time of 140 min. According to Ulyankina et al.,436 UVA-irradiated ZnO nanoparticles synthesized by a pulse alternating current electrochemical method reached 93.6% removal efficiency in 30 min under optimal conditions (initial CIP concentration: 5 mg L^{-1} , pH: 6.5, catalyst dosage: 0.5 g L^{-1} , UV light intensity: 2.0 mW cm⁻²). Such performance of ZnO nanoparticles is attributed to their higher surface area and increased charge carrier separation compared to commercial ZnO. In another study, ZnO nanoparticles prepared by chemical precipitation immobilized on a glass plate showed 69.5% degradation efficiency for an aqueous solution (pH: 6.8) of ciprofloxacin (10 mg L⁻¹) under UVC irradiation (180 min).⁴³⁷ A ZnO nanostructure prepared by a pyrolysis method achieved 95.5% ciprofloxacin degradation in 60 min under visible light.438

A ZnO nanotube photocatalyst on irradiation with the terrestrial solar spectrum showed about 2.9 times faster degradation of ciprofloxacin compared to TiO_2 Degussa P25.⁴³⁹ The flower-like ZnO architectures assembled with nanorods displayed 96% efficiency (240 min) for the

degradation of ciprofloxacin (initial conc.: 0.015 μ M) in aqueous solution under a UV lamp as a light source.⁴⁴⁰ Finčur *et al.*⁴⁴¹ undertook comparative studies by examining the photocatalytic properties of TiO₂, ZnO and MgO nanopowders prepared by a sol–gel method in the removal of ciprofloxacin from water under UV/simulated sunlight. The corresponding efficiencies of 93.4%, 86.9% and 59.6% suggested TiO₂ to be most efficient nanopowder for this. The photocatalytic activity of CdO nanoparticles synthesized *via* a green route imparted 95% degradation of ciprofloxacin in aqueous media under sunlight (60 minutes).⁴⁴² In another work, ZnO nanorod irradiated with UV lamp recorded 92% degradation of ciprofloxacin in 60 minutes.⁴⁴³

3.6.2 Metal-metal oxides. A photocatalyst of mesoporous TiO₂ modified with Fe (1.5%) and N (2.5%) degraded nearly 70% of ciprofloxacin under visible light in 6 h.444 Ag (0.5 to 4%) nanoparticles grown on the surface of TiO2 exhibited highly enhanced degradation of ciprofloxacin under solar light at low pH.445 A mechanism has also been proposed based on the formation of intermediates identified during the oxidation of ciprofloxacin. A simple reduction method has been used to prepare Cu@TiO2 hybrids of varying Cu/ TiO_2 wt. ratios (0.1–50) and their photocatalytic performance was examined for ciprofloxacin hydrochloride under sunlight simulated by a 500 W xenon lamp.446 These findings revealed its complete removal in 3 h, corresponding to a Cu/TiO₂ wt. ratio of 0.1 in Cu@TiO2 due to the best charge separation and transfer efficiency of photogenerated electrons and holes compared to pure TiO₂.

 TiO_2 modified with monometallic and bimetallic nanoparticles comprising 1.5%-Au/TiO₂, 1.5%-Ag/TiO₂, 1.0%-Cu/TiO₂, 1%Au-0.5%Ag/TiO₂ and 1.0%Au-0.5% Cu/TiO₂ were fabricated by a deposition-precipitation method and used as photocatalysts in the degradation of ciprofloxacin in pure water under UVC-light irradiation.⁴⁴⁷ These investigations revealed 100% degradation of ciprofloxacin for all these modified TiO₂ catalysts corresponding to 60, 30, 60, 90 and 45 min, respectively. This is ascribed to the lower recombination of the hole–electron pairs arising from the electron trap effect by metal nanoparticles.

3.6.3 Doped metal oxides. The removal of ciprofloxacin from water has been studied in the presence of metals, nonmetals and conducting polymers as dopants in metaloxide-based photocatalysts. Suwannaruang et al.448 used a hydrothermal method to synthesize nitrogen (12.5%) doped TiO₂ particles by selecting urea as a source of nitrogen. Subsequent investigation of its photocatalytic activity showed maximum degradation of ciprofloxacin (94.29%) after 4 h of UV-light irradiation. This is attributed to the integration of nitrogen into the TiO₂ lattice and the increased formation of OH radicals. Nitrogen-doped TiO₂ (N/Ti wt. ratio: 0.34%) prepared by a sol-gel method and immobilization on glass spheres resulted in 93.5% removal of ciprofloxacin in 90 min under visible-light irradiation.449 The photodegradation of ciprofloxacin followed first-order-kinetics and the

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photocatalyst exhibited excellent stability even after 5 cycles. Visible-light-irradiated P-doped TiO₂ with surface oxygen vacancies (SOVs) exhibited 100% degradation efficiency for ciprofloxacin.⁴⁵⁰ This is explained on the basis of the synergistic effect as a result of P doping and SOVs on TiO₂ significantly enhancing the transfer and separation efficiency of photogenerated charge carriers. Polyaniline (PANI)-doped ZrO₂ on UV-light irradiation showed 96.6% photodegradation of ciprofloxacin under optimum conditions (PANI/ZrO₂: 30 mg, ciprofloxacin conc: 4×10^{-5} M) in 120 min.⁴⁵¹

A ZnO-modified g-C₃N₄ photocatalyst removed 93.8% ciprofloxacin from water, corresponding to an amount of 0.05 g L^{-1} and pH value of $8.^{452}$ Further studies have shown the degradation rate of ciprofloxacin by ZnO-doped g-C₃N₄ to be 4.9 times faster than that of undoped g-C₃N₄. The photocatalyst also exhibited high reusability, as evident from 89.8% efficiency after 3 cycles. Boron-doped TiO₂ and cerium-doped TiO_2 demonstrated about 90-93% photocatalytic degradation of ciprofloxacin and norfloxacin under solar light.373 Such enhanced photocatalytic activity was explained on the basis of the narrowed band gap and electron-hole separation. In addition, metal-doped metal oxides, such as Fe⁰/TiO₂,⁴⁵³ Fe-doped ZnO⁴⁵⁴ Zn-doped Cu₂O,⁴⁵⁵ and Cu-doped ZnO,⁴⁵⁶ have also been successfully reported in the photodegradation of ciprofloxacin.

Several investigations have also been reported on codoped metal oxides for their applications as photocatalysts in the removal of ciprofloxacin from water. According to Nguyen and others,⁴⁵⁷ the UV-visible-light-driven photocatalytic degradation of ciprofloxacin hydrochloride (30 mg L⁻¹) by N, S-co-doped TiO₂ exhibited a removal efficiency of 78.7% at pH 5.5 for a catalyst dose of 0.05 g. The synthesized N,C-codoped TiO₂ under optimum conditions demonstrated the highest photocatalytic activity in the removal of ciprofloxacin in water under visible light.⁴⁵⁸ It was concluded that photogenerated holes and superoxide radicals play an active role in the degradation of ciprofloxacin. ZnO nanowires doped with copper and cerium oxides displayed 88.9% removal of ciprofloxacin under UV irradiation.⁴⁵⁹

3.6.4 Metal oxide composites. In recent years, several studies have been reported on the photodegradation of ciprofloxacin using a variety of composite materials.⁴⁶⁰⁻⁴⁷¹ A graphitized mesoporous carbon-TiO₂ nanocomposite facilitated an almost complete photocatalytic performance in the degradation of ciprofloxacin under UV irradiation.460 A Co/Mn oxide photocatalyst (1.00 g L⁻¹) prepared by a sol-gel method displayed maximum discoloration (56.3%) of ciprofloxacin (10.00 mg L⁻¹) in water (pH: 4) at about 120 min under sunlight.⁴⁶¹ TiOF₂/TiO₂ prepared at 160 °C under hydrothermal conditions exhibited 95.3% degradation of ciprofloxacin hydrochloride under simulated solar light after 90 min.⁴⁶² In all likelihood, such a combination of TiO₂ and TiOF₂ composites generates more charge carriers, including an improvement in the transmission and separation efficiency of photogenerated electron-hole pairs. TiO₂/ Montmorillonite,⁴⁶³ 3D γ-Fe₂O₃(a)ZnO core-shell⁴⁶⁴ and rGO-

BiVO₄-ZnO⁴⁶⁵ photocatalysts have also shown enhanced degradation of ciprofloxacin.

Teixeira et al.⁴⁶⁶ made an assessment of the optimization and reusability of Fe₃O₄/SiO₂/TiO₂ magnetic photocatalytic particles in the degradation of ciprofloxacin. These studies have shown 95% degradation of ciprofloxacin (pH: 5.5) after 90 min under UV with no significant loss even after five uses. Ternary core-shell Fe₃O₄/SiO₂/TiO₂ nanocomposite photocatalysts showed good synergistic properties on the removal efficiency for ciprofloxacin under UVA-light irradiation.⁴⁶⁷ The photocatalytic degradation of ciprofloxacin hydrochloride by Ag-SrTiO₃/TiO₂ composite nanostructures under simulated sunlight resulted in 97.6% degradation of ciprofloxacin due to an increase in the carriers and separation between electron-hole pairs.468

Metal oxide/hydroxyapatite,⁴⁶⁹ CuFe₂O₄@methyl cellulose,⁴⁷⁰ TiO₂-modified $Bi_2MOO_6^{471}$ and $Ag_2O/Ag_2CO_3/$ MWNTs⁴⁷² have also been examined successfully as composite photocatalysts for the enhancement of ciprofloxacin degradation in water under UV, UVC and visible light, respectively.

3.6.5 Carbonaceous-material-based composites

3.6.5.1 g-C₃N₄ and carbon-dot-based composites. Hernández-Uresti et al.³³³ used polymeric g-C₃N₄ powder and observed 60% degradation of ciprofloxacin in aqueous solution (pH: 5.5) after 240 min under UV-vis irradiation. Recent studies on exfoliated g-C₃N₄ (2 g L⁻¹) showed 78% degradation of ciprofloxacin (20 ppm) irradiated under solar light for 1 h.473 In another finding, a 3D g-C₃N₄/TiO₂/kaolinite heterogeneous composite displayed ~92% degradation efficiency for ciprofloxacin in 240 min under visible-light irradiation.474 This is ascribed to the larger surface area and the availability of more reactive sites, and the efficient separation and longer lifetimes of photogenerated electron-hole pairs. Chuaicham et al.475 observed 98% decomposition of ciprofloxacin (10 mg L^{-1}) within 120 min after irradiation with visible light of a Zn-Cr layered double oxide/fly ash composite photocatalyst in aqueous conditions. The formation of new electronic levels accounted for such enhanced photocatalytic performance. In situ synthesized 3D g-C₃N₄/La-N-TiO₂ also showed complete degradation of ciprofloxacin (5 mg L^{-1} starting concentration) at a pH of about 6.5 in about 60 min under exposure to light.476 dots/Bi₄O₅Br₂⁴⁷⁷ solar Carbon simulated nanocomposites also displayed improved visible-light photocatalytic degradation of ciprofloxacin.

3.6.5.2 Composites of graphene oxide and graphene. Graphene oxide and reduced graphene have been used to fabricate binary and ternary composites and they have been used as photocatalysts in the removal of ciprofloxacin from al.⁴⁷⁸ water. Sponza et prepared nano-GO-Fe₃O₄ adding water-dispersed nanocomposites by Fe₃O₄ nanoparticles to an aqueous solution of GO. This irradiated with sunlight produced 80% removal efficiency for ciprofloxacin in water under optimum conditions (initial conc. of ciprofloxacin: 1 mg L⁻¹, original pH: 6.5, nano-GO/M concentration: 2 g L⁻¹, irradiation time: 250 min). ZnO-

particle-coated carboxyl-enriched GO (ZnO@cGO) degraded almost 100% ciprofloxacin in water (pH: 7) within about 5 min under visible irradiation (initial concentration of CIP: 25 μ g mL⁻¹, catalyst: 0.5 mg mL⁻¹).⁴⁷⁹ It was concluded that degradation of ciprofloxacin depends mainly on O₂⁻ and h⁺. An rGO-supported BiVO₄/TiO₂ heterostructure nanocomposite achieved 80.5% degradation rate for ciprofloxacin in acidic ambient (pH: 5) within 150 min, 2.06 times higher than BiVO₄/TiO₂.⁴⁸⁰ A nanostructured ZnO–CdO incorporated rGO photocatalyst showed degradation of ciprofloxacin of around 99.28% in 75 min under UV light.⁴⁸¹ This is attributed to the effective separation of charge carriers consequential on the production of more reactive oxygen species after incorporation of rGO nanosheets with ZnO–CdO.

The performance of ZnAl mixed metal-oxide (MMO)/rGO_x (x: wt% of rGO) composites was tested and compared with ZnAl MMO and pure ZnAl MMO in the photodegradation of ciprofloxacin hydrochloride in aqueous solution under visible light.⁴⁸² It was found to show the following order of photodegradation efficiency at the end of 2 h of irradiation time: ZnAl MMO/rGO20 (~90.58%) > ZnAl LDH/rGO20 $(\sim 67.74)\%$ > ZnAl MMO (50.96%) > ZnAl LDH (36.47%). Such enhanced performance of the ZnAl MMO/rGO20 photocatalyst has been ascribed to the synergistic effect of the heterogeneous structure. The degradation mechanism of ciprofloxacin has been clearly explained based on the heterostructure that accounts for efficient charge separation and inhibition of the recombination of photogenerated carriers. It is believed that O_2 radicals and h⁺ predominantly contribute to the degradation of ciprofloxacin. TiO₂ (64.3 wt%)-pillared multilayer graphene nanocomposites showed better photodegradation efficiency of 78% than TiO₂ (42%) under light-emitting diode irradiation for 150 min.483 The photodegradation followed pseudo-first-order kinetics with the rate constant of graphene/TiO₂ composite about 3.89 times that of pristine TiO₂. The graphene/TiO₂ composite also exhibited high stability and reusability even after five consecutive photocatalytic cycles. Urus et al.484 used a GO@Fe₃O₄@TiO₂-type core@shell@shell nanohybrid (10 mg) as a catalyst to remove 91.5% of ciprofloxacin (10 ppm) from water solution (pH: 7) after 240 min. In addition, the photocatalytic removal of ciprofloxacin has also been evaluated using 3D-structured flower-like bismuth tungstate/ graphene nanoplates485 and magnetic Ag2CrO4/Ag/ BiFeO₃@rGO photocatalysts.486

Huo *et al.*⁴⁸⁷ synthesized an N-doped ZnO/CdS/graphene oxide ternary composite *via* a two-step method and tested its photocatalytic activity in the degradation of ciprofloxacin hydrochloride under visible light and compared it with pure CdS, N–ZnO, and N–ZnO:CdS (2:1, 1:1, 1:2, 1:3). The highest degradation rate of about 86% was shown for the 2:1 molar ratio of N–ZnO and CdS. This is explained in terms of heterostructure and the contribution from GO in N–ZnO/CdS promoting photogenerated electron transfer and suppressing the recombination of electron–hole pairs. The proposed schematic suggested that charge transfer

and holes played a major role in the photocatalytic system.

3.6.6 Heterostructures, heterojunctions and Z-schemebased photocatalysts. An Ag₃PO₄/TiO₂ heterojunction has been fabricated following the corn-silk-templated synthesis of TiO₂ nanotube arrays with Ag₃PO₄ nanoparticles.⁴⁸⁸ Its application as a photocatalyst in the removal of ciprofloxacin showed degradation efficiency of 85.3% within 60 minutes under simulated solar-light irradiation. Deng et al.489 observed 92.6% removal efficiency for ciprofloxacin by Agmodified P-doped g-C₃N₄/BiVO₄ nanocomposites under visible-light irradiation (>420 nm). It was suggested that a synergistic effect could account for such improvements as a result of reduced electron-hole recombination. ZnO-Ag₂O/ porous g-C₃N₄ ternary composites achieved 97.4% degradation efficiency for ciprofloxacin compared to ZnO (8.2%), g-C₃N₄ (25.4%), Ag₂O (42.3%), and ZnO-Ag₂O (69.4%) within 48 min under visible-light irradiation.490

Magnetic g-C₃N₄/MnFe₂O₄/graphene composites have been examined for the photocatalytic degradation of ciprofloxacin in the presence of persulfate as an oxidant under visible-light irradiation.⁴⁹¹ Graphene-layer-anchored TiO₂/g-C₃N₄ showed enhanced photocatalytic performance (degradation rate: 61.7%, *k*: 0.01675 min⁻¹) under visible light compared to graphene-layer-anchored TiO₂, g-C₃N₄ and g-C₃N₄/TiO₂.⁴⁹² This is explained on the basis of accumulation of g-C₃N₄ electrons with high reduction capability and TiO₂ holes with high oxidation capability. Enhanced photocatalytic activity has also been displayed by a visible-light-driven mesoporous TiO₂@g-C₃N₄ hollow core@shell heterojunction in the degradation of ciprofloxacin.⁴⁹³

A heterostructure comprising Ag nanoparticles deposited on the surface of ZnO nanoplates and Fe₂O₃ nanorods exhibited superior solar-light-driven photocatalytic activity in ciprofloxacin degradation (76.4%) under optimized conditions (initial ciprofloxacin concentration: 10 mg L⁻¹; pH 4; catalyst loading: 0.3 g L^{-1}).⁴⁹⁴ The e⁻, h⁺, ·OH and ·O₂⁻ played important roles as reactive species in the photocatalytic degradation process. The efficient separation of charge carriers and migration of e⁻/h⁺ across the heterostructure interface accounted for this. Zhao et al. 495 achieved 95.6% removal of ciprofloxacin under visible-light irradiation for 40 min by a ternary Mn₂O₃/Mn₃O₄/MnO₂ (molar ratio of 3:1:2) valence state heterojunction with dual heterostructures under visible light. Such a performance is derived from its enhanced surface area, light absorption and charge separation of the Mn₂O₃/Mn₃O₄/MnO₂ heterostructure. Further studies established that holes and superoxide radicals play an important role in the degradation of ciprofloxacin. Other studies comprising a unique 2D/3D/ 2D rGO (3%)/Fe₂O₃ (4%)/g-C₃N₄ heterojunction showed almost 100% degradation of ciprofloxacin (pH: 7) compared to pristine g-C₃N₄ nanosheets under visible-light irradiation for 40 minutes.496 Such photocatalytic properties of a heterojunction nanocomposite system are accounted for in terms of enhanced charge migration and separation.

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Chen et al.497 noted the enhanced degradation of ciprofloxacin over Bi₂O₃/(BiO)₂CO₃ heterojunctions compared to pristine (BiO)₂CO₃ and Bi₂O₃ in the presence of simulated solar light. The decay process for ciprofloxacin followed pseudo-first-order kinetics with the rate constant increasing with decreasing concentration of CIP. In addition, CdS/ BiOBr,⁴⁹⁸ Cu₂O/Cu₂(PO₄)(OH),⁴⁹⁹ Sm-doped g-C₃N₄/Ti₃C₂-MXene,⁵⁰⁰ CeO₂/La₂O₃/TiO₂,⁵⁰¹ g-C₃N₄/NH₂-MIL-88B(Fe)⁵⁰² polypyrrole-sensitized and а ZnFe₂O₄/g-C₃N₄ n–n heterojunction⁵⁰³ have also displayed enhanced photocatalytic degradation of ciprofloxacin.

Costa *et al.*⁵⁰⁴ observed ~98% photodegradation of ciprofloxacin (initial concentration: 5 ppm) at neutral pH in the presence of a Z-scheme TiO₂/SnO₂ nanostructure photocatalyst. These findings also revealed the active role of oxygen singlets, holes, and superoxide radicals as the main species in the photodegradation of ciprofloxacin. Li et al.⁵⁰⁵ prepared an oxygen-vacancy-rich TiO₂/Ta₃N₅ composite by a solvothermal method and used it as a direct Z-scheme heterojunction photocatalyst. They observed 95.7% (90 min) degradation rate of ciprofloxacin hydrochloride under visiblelight irradiation. It was suggested that oxygen vacancies form an intermediate energy level in TiO₂ that accounts for the separation of photogenerated electrons and holes. In addition, the formation of a Z-scheme energy band structure by oxygen-vacancy-rich TiO2 and Ta3N5 is likely to enable more photogenerated carriers to participate in the photocatalytic reaction. This was also inevitable from the excellent photocatalytic degradation of ciprofloxacin delivered by an oxygen-vacancy-rich TiO2/Ta3N5 composite under visible light. CeO₂/ZnO nanocomposites prepared by a co-precipitation method displayed twice the activity in the photocatalytic degradation of ciprofloxacin compared to undoped ZnO and was ten times more active than pristine CeO₂.⁵⁰⁶ Such enhanced formation of a Z-scheme heterojunction is attributed to the migration of photo-excited electrons from the conduction band of ZnO to the valence band of CeO₂.

N-doped carbon quantum dot (NCQD)-decorated Bi2O2-CO₃ heterojunction nanosheets exhibited remarkably enhanced photocatalytic activities for ciprofloxacin photodegradation mediated by radiation in the ultraviolet to near-infrared region.⁵⁰⁷ It is suggested that NCQDs act as photosensitizers (hole reservoirs) to harvest solar light and a type-II heterojunction facilitates efficient charge carrier separation to account for this. The mechanisms and pathways of ciprofloxacin degradation mediated by different lights were also discussed. N-doped carbon dots (NCDs) decorated onto a $Bi_2MoO_6/g-C_3N_4$ (BMCN) nanocomposite photodegraded ciprofloxacin by 98% (30 min) under visible-light irradiation.508 It is proposed that NCDs play a role as a mediator to transfer electrons from the conduction band to the valence band of Bi₂MoO₆ and g-C₃N₄, respectively. The findings also revealed ·OH and $\cdot O_2^{-}$ radicals acting as the dominant reactive species. The photocatalyst also displayed good stability and reusability after five consecutive cycles of ciprofloxacin photodegradation.

A Z-scheme involving a TiO_2 nanorod/g- C_3N_4 (30 wt%) nanosheet nanocomposite showed 93.4% degradation of ciprofloxacin (initial concentration: 15 mmol L⁻¹) aqueous solution (pH: 6.3) under simulated sunlight irradiation in 60 min.⁵⁰⁹ It was also concluded that h⁺ and •OH played a major role in the degradation of ciprofloxacin. In another study, a biochar@ZnFe2O4/BiOBr Z-scheme heterojunction photocatalyst prepared by a solvothermal method under visible-light irradiation ($\lambda > 420$ nm) showed no significant degradation efficiency for ciprofloxacin (65.26%).⁵¹⁰ Wen et al.⁵¹¹ fabricated CeO₂-Ag/AgBr composite photocatalysts with a Z-scheme configuration by following the in situ interspersal of AgBr on CeO2 and subsequently studied the photodegradation of ciprofloxacin under visible-light irradiation (Fig. 17(a)). According to this, CeO₂ itself has almost no ability to degrade ciprofloxacin, though it can be partly eliminated in the presence of pristine Ag/AgBr. However, CIP concentration decreased further to some extent for CeO₂ decorated with Ag/AgBr in CeO₂-Ag/AgBr composites with 21.26 wt% of Ag (denoted CAB-21.26) exhibiting the most pronounced photocatalytic activity. This is ascribed to the accelerated interfacial charge transfer process and the improved separation of the photogenerated electron-hole pairs. Furthermore, the kinetic behavior followed pseudofirst-order kinetics and exhibited higher k-values for the CeO₂-Ag/AgBr hybrids (Fig. 17(b)). Another Z-scheme-based $AgBr/Ag/Bi_2WO_6$ heterostructure achieved 57% (5 h) photocatalytic degradation of ciprofloxacin under visible-light irradiation in pure water.⁵¹² Such a performance was ascribed the synergistic effect of the AgBr/Ag/Bi₂WO₆ heterostructure compared to its single components.

Z-Scheme-guided g-C₃N₄/Bi₂WO₆,⁵¹³ Fe₃O₄/Bi₂WO₆,⁵¹⁴ g-C₃N₄/Ti₃C₂/MXene/black phosphorus,⁵¹⁵ g-C₃N₄/Ag₃PO₄/chitosan,⁵¹⁶ Ag/AgVO₃/g-C₃N₄,⁵¹⁷ CeO₂/Co₃O₄ p-n hetrojunctions,⁵¹⁸ Bi nanodots/2D Bi₃NbO₇ nanosheets,⁵¹⁹ Bi₂WO₆/Ta₃N₅,⁵²⁰ g-C₃N₄@Cs_{0.33}WO₃,⁵²¹ ZnO/SnS₂,⁵²² g-C₃N₄/rGO/WO₃,⁵²³ and CuS/BiVO₄⁵²⁴ have also displayed enhanced photocatalytic degradation of ciprofloxacin.

Table 7 records the performance data of different photocatalysts on the removal of norfloxacin from wastewater.

3.7 Tetracycline

Tetracycline (TC) is invariably used as an antibiotic against different bacterial infections, such as urinary tract infections, acne, gonorrhea, chlamydia, mycoplasma, rickettsia, cholera, brucellosis, plague and syphilis.⁵² It finds extensive application in the medical field, for veterinary purposes, and as a feed additive in the agricultural sector. However, extensive applications of tetracycline mean its presence in surface water, groundwater, wastewater, domestic wastewater and other source-related environments, causing a serious threat to the environment. Therefore, several approaches



Fig. 17 (a) Photocatalytic degradation CIP curves and (b) apparent rate constants for the degradation of CIP solution for a CAB-21.26 sample. Reproduced from ref. 511 with permission from Elsevier (2018).

have been made to develop a highly efficient approach to remove antibiotics by a photocatalysis approach. $^{525-662}$

3.7.1 Metal oxides

3.7.1.1 TiO2. Several investigations have been reported using TiO₂ as a photocatalyst in water treatment for the removal of tetracycline. According to Palominos et al.,⁵²⁷ an aqueous suspension of TiO₂ has been used to facilitate the photocatalytic oxidation of tetracycline on irradiation with simulated solar light. Studies indicated the rapid degradation of tetracycline, undergoing 100% completion after 15 min under optimum conditions (tetracycline: 20 mg L^{-1} , TiO₂: 1.5 g L^{-1} , pH: 8.7). The mechanism of photocatalytic tetracycline oxidation involved active roles for holes and OH radicals. The nanosized TiO2 achieved more than 95% removal of tetracycline within 40 min under UV irradiation for a tetracycline concentration of 40 mg L⁻¹ and catalyst dose of 1000 mg L⁻¹.⁵²⁸ Safari *et al.*⁵²⁹ also used nanosized TiO₂ (1.0 g L^{-1}) to study the degradation kinetics of a tetracycline hydrochloride (TC·HCl) aqueous solution (55 mg L^{-1} , pH: 5) under ultraviolet irradiation. They observed 100% degradation after 30 min on adding H_2O_2 (100 mg L⁻¹) compared to 91.4% degradation after 90 min for TiO₂/UV. The photocatalytic degradation of tetracycline over commercial TiO₂-P25 showed 94.8% (120 min) removal efficiency under visible light (λ = 700 nm).⁵³⁰ Recently, a crosslinking method has been followed for immobilizing TiO₂ (P25) nanoparticles in chitosan film, which showed promising photocatalytic activity in the purification of water containing tetracycline hydrochloride under UV irradiation.531 The stability and reusability of this composite film in four consecutive cycles revealed a significant decrease in removal efficiency after the second run, from 87% to 57%. Tetracycline hydrochloride degradation has also been studied using a green and low-cost approach, involving the preparation of immobilized titania samples by depositing two successive TiO₂ layers on two different commercial supports.532

3.7.1.2 ZnO and other oxides. Palominos et al. 527 carried out the photocatalytic oxidation of tetracycline in an aqueous suspension containing ZnO and found its performance comparable to TiO_2 (~100% degradation) under simulated solar light. According to the suggested mechanism, the contribution towards photocatalytic tetracycline oxidation on ZnO is mainly guided by hydroxyl radicals. UV-irradiated ZnO/peroxymonosulfate has shown about 95.6% degradation of tetracycline (10 mg L⁻¹, pH: 7) in 90 min compared to UV/ ZnO (50.14%), attributed to the formation of SO_4 . In addition, HSO₅⁻ acts as an electron acceptor and inhibits electron-hole pair recombination, thereby allowing the formation of more ·OH radicals. Iron oxide nanoparticles,⁵³⁴ nanospherical α-Fe₂O₃ supported on 12-tungstosilicic acid,⁵³⁵ SnO₂ hollow microspheres,⁵³⁶ polyaniline coated on magnetic MoO₃⁵³⁷ and BiFeO₃⁵³⁸ have also been studied in the photocatalytic degradation of tetracycline aqueous solutions.

3.7.2 Metal-loaded metal oxides. A solution casting method has been used to fabricate membranes by mixing previously prepared core-shell Au (0.1, 0.3, 0.5 g)-TiO₂ nanocomposites and PVDF and they were examined for their performance in the degradation of tetracycline under the influence of visible light.⁵³⁹ It is inferred that an Au (0.3)-TiO₂/PVDF nanocomposite enhanced the photocatalytic degradation rate by 75% within 120 min under visible light. These findings clearly ensured first-order kinetics for Au-TiO₂/PVDF composites, following the order: Au (0.3)-TiO₂/ $PVDF (0.00599 \text{ min}^{-1}) > Au (0.1) - TiO_2/PVDF (0.00449 \text{ min}^{-1})$ > Au (0.5)-PVDF $(0.01212 \text{ min}^{-1})$. Excellent regeneration stability and its easy separation have also been achieved by this method. Gold-containing zinc-titanium oxide films⁵⁴⁰ and Ag/Bi₂O₃⁵⁴¹ have also been reported in the photocatalytic degradation of tetracycline in aqueous media.

Liu *et al.*⁵⁴² studied the photoactivity of an Au-ZnO nanomotor system based on vertically aligned ZnO in the photocatalytic degradation of tetracycline as a function of

Table 7 Data on performance data on removal of ciprofloxacin using different photocatalysts

| Photocatalyst | Preparative method | CIP ^a /CIP·HCl ^b | Catalyst dose | pH | Light source | Degradation (time) | Rate constant |
|---|--|---|--|-----|---|-----------------------|---|
| P25 TiO ₂ (anatase : rutile = 80 : 20), [H ₂ O ₂]: 82.5 mg L ^{-1 425} | Commercial | 0.030 mmol $L^{-1 a}$ (500 mL) | $0.5 \mathrm{g L}^{-1}$ | 6 | Simulated solar irradiation, 800 | ~100% (90 min) | $0.022 \ min^{-1}$ |
| Degussa P-25 TiO ₂ (80:20% w/w anatase-to-rutile) ⁴²⁶ | Commercial | 100 mg $L^{-1 b}$ | $1 \mathrm{g L}^{-1}$ | 9 | Simulated solar irradiation (850 $W \text{ cm}^{-2}$) | ~100% (160 min) | 0.108 min ⁻¹ |
| Degussa P-25 TiO ₂ (80:20% w/w anatase-to-rutile) ⁴²⁸ | Commercial | 20 mg L ^{-1 <i>a</i>} (100 mL) | $\begin{array}{c} 100 \ mg \\ L^{-1} \end{array}$ | 6.0 | UVA/LED lamp (3 W), 10 mW cm ⁻² , $\lambda > 365$ nm | _ | 0.2217 ± 0.0179 min ⁻¹ |
| TiO ₂ (80% anatase and 20% rutile) immobilized on glass | Multiple steps | 60 μmol L ^{-1 a} (500 mL) | TiO_2 (7.5 g L ⁻¹) | 9 | UVC lamp: 15 W 254 nm | ~98% (120 min) | $\sim 25 \times 10^{-3}$ min ⁻¹ |
| TiO_2 P25 and ZnO^{430} | Commercial | 300 μg L ^{-1 a} (50 mL) | $1~g~L^{-1}$ | — | UVA (1.6 to 1.7 mW cm ⁻²) | 100% (6 min) | _ |
| Mesoporous TiO ₂ nanoparticles ⁴³¹ | Hydrothermal | 160 mg $L^{-1 b}$ (40 ml) | 0.01 g | _ | Xenon lamp (500 W), 200–1000 nm | 96.05% (360 min) | 0.45 min ⁻¹ |
| 3D tripyramid TiO ₂ architectures ⁴³² | Hydrothermal method | 32.6 μM ^a (50 mL) | 5 mg | _ | UV-vis light | 90% (60 min) | 4.03×10^{-2} min ⁻¹ |
| ZnO nanoparticles ⁴³⁴ | Chemical precipitation method | $4 \text{ mg } \text{L}^{-1 a}$ (3 mL) | $20 \text{ mg} \ \mathrm{L^{-1}}$ | 10 | Xenon lamp (365 nm) | ~48% (60 min) | 0.0043 ± 0.003 min ⁻¹ |
| ZnO nanoparticles ⁴³⁵ | Sol-gel method | $10 \text{ mg L}^{-1 a}$ | $0.15 \mathrm{~g~L}^{-1}$ | 5 | Low-pressure mercury-vapour lamps (9 W) | 100% (140 min) | $\frac{0.032}{\min^{-1}}$ |
| Nano-ZnO ⁴³⁶ | Pulse electrochemical synthesis | $5 \text{ mg L}^{-1 a}$ | $0.5~g~L^{-1}$ | 6.5 | UV light (2.0 mW cm^{-2}) | 93.6% (30 min) | — |
| Immobilized ZnO nanoparticles ⁴³⁷ | Heat attachment method | $10 \text{ mg L}^{-1 a}$ | $14 \times 14 \times 15 \text{ cm}^3$ | 6.8 | UV lamp (15 W, 42 W m^{-2}) | 69.5% (180 min) | ~ 0.008 min ⁻¹ |
| ZnO nanotubes ⁴³⁹ | Modified published protocol | $2 \times 10^{-5} \text{ mol}$ L ^{-1 a} (0.4 L) | 14 mg | 8.0 | 300 W xenon lamp with AM1.5 filter (1000 W m ⁻²) | 12% (120 min) | 9.61×10^{-4} min ⁻¹ |
| Flower-like ZnO ⁴⁴⁰ | Thermionic vacuum arc | 0.015 μM ^a | ZnO deposited on 2×2 cm ² (Si wafer) | _ | UV lamp, 1 Ŵ m ⁻² , 253.7 nm | 96% (240 min) | 14.8 × 10 ⁻³ min ⁻¹ |
| $TiO_2^{441} (NH_4)_2 S_2 O_8: 0.125 \text{ mM}$ | Sol–gel method | 0.05 mM^a | $0.5 \text{ mg} \text{mL}^{-1}$ | _ | High-pressure Hg lamp (125 W), 1.4×10^{-2} W cm ⁻² in UV region | 93.4% (60 min) | _ |
| ZnO ⁴⁴¹ | Sol–gel method | 0.05 mM ^a | $0.5 \mathrm{~g~L}^{-1}$ | _ | High-pressure Hg lamp (125 W) in UV region, 1.4×10^{-2} W cm ⁻² | 86.9% (60 min) | _ |
| CdO ⁴⁴² | Green approach | 10 ppm ^a (50 mL) | 50 mg | — | Sunlight | 95% (60 min) | 0.04722 min ⁻¹ |
| ZnO–Ag-Graphite ⁴⁴³ | Hydrothermal method | $5 \text{ mg L}^{-1 a}$ (50 mL) | 0.3 g L^{-1} | _ | 24 W UV lamp, λ: 254 nm | 98% (60 min) | 0.05983 min ⁻¹ |
| 2.5% N-1.5% Fe-TiO ₂ ⁴⁴⁴ | Hydrothermal method | 20 mg L ^{-1 <i>a</i>} (300 mL) | 0.3 g | — | LED illumination source | 70% (360 min) | 5.52×10^{-3} min ⁻¹ |
| Ag nanoparticles (a) TiO ₂ ⁴⁴⁵ | Sonicating TiO ₂ and aq. AgNO ₃ + aq. Na ₂ CO ₃ | 1.0 mM^a (100 mL) | 1.0 mg L^{-1} | 7 | UV light (120 W Hg lamp) | 85.21% (14 500 s) | 1.53 mM s ⁻¹ |
| Ag nanoparticles (a) Ti ${\rm O_2}^{445}$ | Sonicating TiO_2 and aq . AgNO ₃ + aq. Na ₂ CO ₃ | $1.0 \text{ mM}^{a'}$ (100 mL) | 1.0 mg L^{-1} | 7 | Sunlight | 75.58% (14 500 s) | 1.210 mM s ⁻¹ |
| Mesoporous Cu (0.1 wt\%) $($ 3TiO_2^{446} | Reduction method | $40 \text{ mg L}^{-1 b}$ (40 mL) | 0.01 g | — | 500 W xenon lamp (sunlight) | ~100% (3 h) | 1.16 h ⁻¹ |
| 1.5%-Au/TiO ₂ ⁴⁴⁷ | Deposition–precipitation method | $30 \text{ mg L}^{-1 a}$ (250 mL) | 0.5 g L^{-1} | — | UVC light irradiation (15 W low-pressure | 100% (60 min) | 0.06 min ⁻¹ |

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Table 7 (continued)

| Photocatalyst | Preparative method | CIP ^a /CIP·HCl ^b | Catalyst dose | рН | Light source | Degradation (time) | Rate constant |
|---|---|---|--------------------------------|-----|---|--|---|
| 1.5%-Ag/TiO ₂ ⁴⁴⁷ | Deposition-precipitation method | 30 mg L ^{-1 a} (250 mL) | $0.5~{ m g~L}^{-1}$ | _ | Hg lamp, 254 nm 44 W m ⁻²) UVC light irradiation (15 W low-pressure Hg lamp, 254 | 100% (30 min) | 0.117 min ⁻¹ |
| 1.0%-Cu/TiO ₂ ⁴⁴⁷ | Deposition-precipitation method | 30 mg L ^{-1 a} (250 mL) | $0.5 { m g L}^{-1}$ | _ | nm 44 w m) UVC light irradiation (15 W low-pressure Hg lamp, 254 nm 44 W m ⁻²) | 100% (60 min) | 0.072 min ⁻¹ |
| 1% Au–0.5% Ag/TiO ₂ ⁴⁴⁷ | Deposition-precipitation method | 30 mg L ^{-1 <i>a</i>} (250 mL) | 0.5 g L^{-1} | _ | UVC light irradiation (15 W low-pressure Hg lamp, 254 nm 44 W m ⁻²) | 100% (90 min) | 0.053 min ⁻¹ |
| 1.0% Au–0.5% Cu/TiO ₂ ⁴⁴⁷ | Deposition-precipitation method | 30 mg L ^{-1 a} (250 mL) | $0.5 {\rm ~g~L^{-1}}$ | _ | UVC light irradiation (15 W low-pressure Hg lamp, 254 nm 44 W m ⁻²) | 100% (45 min) | 0.099 min ⁻¹ |
| N (12.9%) doped-TiO ₂ nanorice particles ⁴⁴⁸ | Hydrothermal method | 20 ppm ^a | $0.3~g~L^{-1}$ | 5.5 | UVA lamps: 20 W, 365 nm, 0.493 mW cm^{-2} | 94.29% (240 min) | _ |
| N doped–TiO ₂ (N/Ti wt ratio:0.34%) immobilized on glass spheres ⁴⁴⁹ | Sol–gel method followed by immobilization | 20 mg L ^{-1 <i>a</i>} (20 mL) | 3 g L^{-1} | _ | Xenon lamp: 500 W and $\lambda >$ 420 nm | 93.5% (90 min) | 0.02859 min ⁻¹ |
| P-doped TiO ₂ (using 50 mg NaH ₂ PO ₂) ⁴⁵⁰ Polyaniline doped ZrO ₂ ⁴⁵¹ | Heat treatment under flowing NH ₃ <i>In situ</i> oxi. Polym. | 5 ppm ^a (50 mL) $4 \times 10^{-5} M^{a}$ (100 mL) | 25 mg 30 mg | _ | Visible-light irradiation UV-light irradiation ($\lambda >$ | 100% (60 min) 96.6% (120 min) | 0.065 min ⁻¹ — |
| TiO ₂ /Fe ⁰⁴⁵³ | Liquid-phase reduction process | $30 \text{ mg L}^{-1 a}$ | $1.0~g~L^{-1}$ | 3.0 | 400 nm) UV-lamp: 10 W, 254 nm, 2.0 W | 94.6% (60 min) | — |
| Fe doped ZnO nanoparticles ⁴⁵⁴ | Precipitation route | $5 \text{ mg L}^{-1 b}$ | 150 mg L^{-1} | 9 | Sunlight, 650 W m^{-2} , 80 000 ± 3000 lux | ~80% (210 min) | — |
| Zn-doped Cu ₂ O (by adding 0.05 g of $ZnCl_2$) ⁴⁵⁵ | Solvothermal method | 20 mg L ^{-1 <i>a</i>} (50 mL) | 30 mg | _ | 5000 W metal halide lamp, λ < 400 nm filter | 94.6% (240 min) | 0.0038 min ⁻¹ |
| N-S-doped TiO_2^{457} | Sol-gel method | 30 ppm ^a | 0.05 mg | 5.5 | Halogen lamp: 500 W (360–780 nm) | 78.7% (220 min) | 0.0065 min ⁻¹ |
| Graphitized mesoporous carbon–TiO ₂ ⁴⁶⁰ | Extended resorcinol-formaldehyde method | 15 mg L ^{-1 a} (200 mL) | 70 mg | _ | 14 W UV lamp, 254 nm | 100% (120 min) | 0.102 min ⁻¹ |
| Mo/co oxides ⁴⁶¹ | Sol–gel method | $10 \text{ mg L}^{-1 a}$ | 1 g L^{-1} | 4 | Sunlight | 56.3% (180 min) | 7.9×10^{-2} min ⁻¹ |
| TiOF ₂ /TiO ₂ ⁴⁶² | Hydrothermal (160 °C) | 20 mg L ^{$-1 b$} (50 mL) | 50 mg | _ | Xenon lamp: 300 W with a UV-cut-off filter (420 nm) | ~95% (90 min) | 0.034 min^{-1} |
| Core-shell 3D γ-Fe ₂ O ₃ @ZnO ⁴⁶⁴ rGO-BiVO ₄ -ZnO ⁴⁶⁵ | Hydrothermal-sintering and atomic layer deposition Hydrothermal method | 10 mg L ^{-1 a} (100 mL) $4 \times 10^{-5} M^{a}$ (100 mL) | 0.5 g L ⁻¹ 30 mg | 5.8 | (420 mm) Xenon lamp (300 W) W lamp (150 mW cm ⁻²), ($\lambda <$ | 92.5% (60 min) 98.4% (60 min) | 0.0419 min ⁻¹ |
| Fe ₃ O ₄ /SiO ₂ /TiO ⁴⁶⁶ | Sol–gel synthesis (calcined at 600 °C) | $5 \text{ mg L}^{-1 a}$ | $1 \mathrm{g L}^{-1}$ | 5.5 | 400 nm) UV irradiation, (365 nm, 1.6 mW cm $^{-2}$) | 95% (90 min) | 0.032 min ⁻¹ |
| Core–shell Fe ₃ O ₄ /SiO ₂ /TiO ₂ (100 °C) ⁴⁶⁷ | Microwave-assisted synthesis | 10 mg dm ^{-3 <i>a</i>} (100 cm ³) | 50 mg | 6.5 | UVA lamp (365 nm) | 94.0% (120 min) | $\begin{array}{c} 0.0158\\ \text{min}^{-1} \end{array}$ |

Table 7 (continued)

| | | | Catalyst | | | Degradation | Rate |
|--|--|--|---------------------------------|------|---|--|--|
| Photocatalyst | Preparative method | CIP ^a /CIP·HCl ^b | dose | рН | Light source | (time) | constant |
| Ag-SrTiO ₃ /TiO ₂ ⁴⁶⁸ | Hydrothermal/photoreduction | 20 mg L ^{$-1 b$} (50 mL) | 20 mg | _ | 300 W xenon lamp | 97.6% (60 min) | 0.070 min ⁻¹ |
| TiO ₂ /hap (with 40% by wt% of oxide:Hap) ⁴⁶⁹ | Soft chemical method | 20 ppm ^{<i>a</i>} (100 mL) | $2~g~L^{-1}$ | — | HPK 125 W lamp- UV light | 100% (15 min) | — |
| ZnO/HAp (with 40% by wt% of oxide:Hap) ⁴⁶⁹ | Soft chemical method | $20 \text{ mg L}^{-1 a}$ | $2~g~L^{-1}$ | — | HPK 125 W lamp-UV light | 100% (20 min) | _ |
| $CuFe_2O_4$ @methyl cellulose ⁴⁷⁰ | Microwave-assisted method | $3 \text{ mg L}^{-1 a}$ | 0.2 g | 7 | UVC lamps (low pressure, 6 W, Philips) | (20 min) 72.87% (90 min): real sample | $0.902 \ min^{-1}$ |
| $\rm TiO_2/Bi_2MoO_6~(TiO_2~content: 0.41~wt\%)^{471}$ | Solvothermal–calcination process | 10 mg L ^{-1 <i>a</i>} (50 mL) | 30 mg | — | Xenon lamp 350 W with a UV cut-off filter | 88% (150 min) | $\sim 8 \times 10^{-3}$ min ⁻¹ |
| Ag ₂ O/Ag ₂ CO ₃ /MWNTs ⁴⁷² | Calcination (10 min) | 10 mg L ^{-1 <i>a</i>} (100 mL) | 0.05 g | _ | Xenon lamp: 300 W (visible light) | 76% (60 min) | _ |
| g-C ₃ N ₄ ³³³ | Polycondensation of melamine | $10 \text{ mg L}^{-1 a}$ | 200 mg (200 mL) | _ | Xenon lamp (35 W): UV-vis radiation source | 60% (240 min) | $\begin{array}{c} 4\times 10^{-5} \\ s^{-1} \end{array}$ |
| Exfoliated g-C ₃ N ₄ ⁴⁷³ | Green route | 20 ppm ^a | 1 gL^{-1} | _ | Solar-light irradiation | 78% (60 min) | 23×10^{-3} \min^{-1} |
| g-C ₃ N ₄ /TiO ₂ /kaolinite ⁴⁷⁴ | Sol–gel method/chemical stripping/self-assembly | 10 ppm ^{<i>a</i>} (100 mL) | 0.2 g | _ | Xenon lamp (90 mW cm ⁻² with 400 nm cut-off filter) | ~92% (240 min) | 0.00813 min ⁻¹ |
| Zn–Cr LDH/fly ash (molar ratio = $2:1$) ⁴⁷⁵ | Coprecipitation method followed by dispersion method | 10 ppm ^a (50 mL) | $1.0 {\rm ~g~L}^{-1}$ | | Xenon lamp (500 W) with UV cut-off filter | ~98% (150 min) | _ |
| g-C ₃ N ₄ /La–N–TiO ₂ ⁴⁷⁶ | In situ synthetic method | $10 \text{ mg L}^{-1 a}$ | 0.75 g L^{-1} | ~6.5 | Xenon lamp; (300 W), $\lambda >$ 420 nm | 96.8% (60 min) | — |
| Nano graphene oxide–magnetite ⁴⁷⁸ | Mixing and dispersion | $1 \text{ mg L}^{-1 a}$ | 2 g L^{-1} | 6.5 | Sunlight irradiation at 80 W power | 80% (250 min) | _ |
| ZnO-CdO/rGO ⁴⁸¹ | Refluxing method | 10 mg L ^{-1 <i>a</i>} (50 mL) | 10 mg | 7 | UV light, 800 W xenon lamp with 420-nm cut-off filter | 99.28% (75 min) | |
| ZnAl mixed metal oxides/rGO ⁴⁸² | Hydrothermal combined with calcination | 10 mg L ^{-1 <i>a</i>} (50 ml) | 10 mg | — | 800 W xenon lamp with 420 nm cut-off | 90.58% (120 min) | 0.01893 min ⁻¹ |
| TiO ₂ (64.3 wt%)-pillared multilayer graphene (35.7 wt%) ⁴⁸³ | Hydrothermal | 15 mg L ^{$-1 a$} (40 mL) | 20 mg | 5.8 | LED lamp (5 W), $\lambda > 420~\mathrm{nm}$ | 78% (150 min) | 0.99111 min ⁻¹ |
| GO@Fe ₃ O ₄ @TiO ₂ ⁴⁸⁴ | In situ method | 10 ppm ^a (100 mL) | 10 mg | 7–8 | Solar simulator: 300 W | 91.5% (240 min) | 0.0079 min ⁻¹ |
| $Ag_2CrO_4/Ag/BiFeO_3$ Wt ratio of rGO ⁴⁸⁶ | Dispersion method | 10 mg L^{-1a} | $0.2 \text{ mg} \text{mL}^{-1}$ | 7 | Xenon lamp (300 W) with 400 nm cut-off filter, 450 mW cm^{-2} | 96% (60 min) | 0.0638 min ⁻¹ |
| N-ZnO/CdS/GO ⁴⁸⁷ | Hydrothermal | 15 mg L ^{-1 <i>a</i>} (100 mL) | 50 mg | — | Xenon lamp (300 W) with λ > 420 nm | 86% (60 min) | _ |
| $0.6Ag_3PO_4/TiO_2$ nanotube arrays (600 °C) ⁴⁸⁸ | In situ growth method | 10 mg L ^{-1 <i>a</i>} (40 mL) | 40 mg | _ | Xenon lamp (300 W), 200 mW cm ⁻² | 85.3% (60 min) | 0.02499 min ⁻¹ |
| P-doped ultrathin g-C ₃ N ₄ /BiVO ₄ ⁴⁸⁹ | Impregnated process | $10 \text{ mg L}^{-1 a}$ | $1 \mathrm{g L}^{-1}$ | 6.72 | Visible-light irradiation ($\lambda > 420 \text{ nm}$) | 92.6% (120 min) | 0.0203 min ⁻¹ |
| ZnO–Ag ₂ O/porous g-C ₃ N ₄ ⁴⁹⁰ | Hydrothermal | 20 mg L ^{-1 a} (100 mL) | 50 mg | — | W lamp (500 W), $\lambda \ge 420$ nm | 97.4% (48 min) | 0.057 min ⁻¹ |

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Table 7 (continued)

| Photocatalyst | Preparative method | CIP ^a /CIP·HCl ^b | Catalyst dose | рН | Light source | Degradation (time) | Rate constant |
|---|---|---|---------------------------------|---------|---|--|--|
| Graphene layers anchored TiO_2/g - $C_3N_4^{492}$ | In situ calcination method using 40 g of Ti_3C_2 | $3 \text{ mg L}^{-1 a}$ (100 mL) | 60 mg | _ | Xenon lamp (300 W), $\lambda >$ 400 nm, 300 mW cm ⁻² | 61.7% (60 min) | 0.01675 min ⁻¹ |
| Ag/Fe ₂ O ₃ /ZnO ⁴⁹⁴ | Ultrasonic-assisted hydrothermal method | 10 mg L ^{$-1 a$} (100 mL) | $0.3~g~L^{-1}$ | 4 | Solar illumination | 76.4% (210 min) | 0.3036 h ⁻¹ |
| $Mn_{2}O_{3}/Mn_{3}O_{4}/MnO_{2}^{\ 495}$ | Hydrothermal and <i>in situ</i> method | $10 \text{ mg L}^{-1 a}$ (120 mL) | $0.2~g~L^{-1}$ | 7 | Xenon lamp (300 W), 900 mW cm ⁻² | 95.6% (40 min) | _ |
| rGO/Fe ₂ O ₃ /g-C ₃ N ₄ ⁴⁹⁶ | Embedding approach | $50 \text{ mg L}^{-1 a}$ | 100 mg | 7 | Halogen lamp: 500 W | ~100% (40 min) | 1.0878 min ⁻¹ |
| Bi ₂ O ₃ /(BiO) ₂ CO ₃ ⁴⁹⁷ | Hydrothermal/calcination | $10 \text{ mg L}^{-1 a}$ | 0.5 g L^{-1} (100 mL) | 7 | Xenon lamp: 300 W, 0.641 W cm ⁻² | (40 min) 93.4% (30 min) | $\frac{0.476}{\text{min}^{-1}}$ |
| CdS/BiOBr-1: 3 ⁴⁹⁸ | Solvothermal route | $10 \text{ mg L}^{-1 a}$ | 50 mg | 7 | Sunlight | 99.1% | 0.00692 |
| Cu ₂ O/Cu ₂ (PO ₄)(OH) ⁴⁹⁹ | Reflex method | (200 mL) 20 mg L ^{-1 a} | 100 mg | — | Direct sunlight | $\sim 98\%$ (120 min) | |
| $CeO_{2}/La_{2}O_{3}/TiO_{2}^{\ 501}$ | Sol–gel followed by calcination | 10 ppm^{a} (50 mL) | 50 mg | 6-7 | Visible light using tungsten lamp (300 W cm^{-2}) | (120 min) 100% (120 min) | _ |
| $\mathrm{TiO_2/SnO_2}^{504}$ | Hydrothermal and ion exchange | $2.5 \times 10^{-3} \text{ g L}^{-1 a}$ | 2.5×10^{-3} g | Neutral | UVC lamps with 35 W each (253 nm) | 92.8% (120 min) | 22.4×10^{-3} min ⁻¹ |
| CeO ₂ /ZnO ⁵⁰⁶ | Co-precipitation method | 15 mg L ^{-1 a} (100 mL) | 0.25 g L^{-1} | 3.2 | 200 W mercury-xenon lamp with 365 nm filter | ~60% (60 min) | 0.0130 min ⁻¹ |
| 5 wt% N-doped carbon quantum dots decorated Bi ₂ O ₂ CO ₃ ⁵⁰⁷ | Hydrothermal method | 10 mg L ^{-1 a} (80 mL) | 40 mg | _ | UV-vis light Visible | 91.1% (60 min) 92.8% (60 min) | ~ 0.0325 min ⁻¹ ~ 0.02 min ⁻¹ |
| $Bi_2 MoO_6/g\text{-}C_3 N_4^{508}$ | Hydrothermal method | $5 \text{ mg L}^{-1 a}$ | $1.0~g~L^{-1}$ | 8 | Visible lamps (77 mW cm^{-2}) | 98% (30 min) | 0.12 min ⁻¹ |
| TiO_2 nanorod/30 wt% g-C ₃ N ₄ | Mixing followed by | 15 μ mol L ^{-1 <i>a</i>} | 10 mg | 6.3 | Xenon lamp: | 93.4% | 0.0381 |
| 5 wt% biochar@ZnFe ₂ O ₄ /BiOBr ⁵¹⁰ CeO ₂ -21.26 wt% Ag/AgBr ⁵¹¹ | Solvothermal/photodeposition/ precipitation In situ | $15 \text{ mg L}^{-1 a}$ | 50 mg (100 mL) 50 mg | _ | Xenon lamp: 300 W Xenon lamp | (60 min) 65.26% (60 min) 93.05% | 0.02011 |
| 5552 21120 (16/6 11 <u>5</u> /11 <u>5</u> /1 | | (50 mL) | 00 mg | | (300 W) with a | (120 min) | min ⁻¹ |
| ${\rm Bi_2WO_6/ag/AgBr^{512}}$ | Precipitation followed by dispersion | 30 mg L ^{-1 <i>a</i>} (250 mL) | 125 mg | — | Phillips lamp (50 W), $\lambda =$ 380–800 nm | 57% (5 h) | — |
| $g\text{-}C_{3}N_{4}/Bi_{2}WO_{6}^{513}$ | Solvothermal and grind calcination method | 15 mg L ^{$-1 a$} (100 mL) | 0.1 g | — | Xenon lamp:300 W. $\lambda < 400 \text{ nm}$ | 98% (120 min) | — |
| $\operatorname{Fe_3O_4/Bi_2WO_6}(4\% \text{ iron content})^{514}$ | Hydrothermal method | $10 \text{ mg L}^{-1 a}$ (100 mL) | 30 mg | — | Visible-light irradiation ($\lambda > 420$ nm) | ~99.7% (15 min) | _ |
| g- C_3N_4/Ti_3C_2 MXene/black P^{515} | Calcination process | 20 mg L ^{$-1 a$} (100 mL) | 20 mg | _ | Xenon lamp: 300 W, $\lambda > 420$ | >99% (60 min) | $0.048 \\ \text{min}^{-1}$ |
| $g\text{-}C_3N_4/Ag_3PO_4/chitosan^{516}$ | Multiple steps | $20~{\rm mg~L}^{-1a}$ | 2.0 mg | 7 | Visible light | 90.34% | 0.01771 |
| 0.5 wt% Ag/AgVO ₃ /g-C ₃ N ₄ ⁵¹⁷ | Wet-impregnation method | 10 ppm ^{<i>a</i>} (100 mL) | 0.1 g | _ | Halogen lamp (500 W): visible light | (80 min) 82.6% (120 min) | |
| Bi (7%) nanodots/Bi ₃ NbO ₇ nanosheets ⁵¹⁹ | Two-step wet chemical reaction | 10 mg L ^{-1 <i>a</i>} (100 mL) | 50 mg | — | Xenon lamp: 300 W with 400 | 86% (120 min) | 0.01427 min ⁻¹ |
| Bi ₂ WO ₆ /Ta ₃ N ₅ (1.0/1 mole ratio) ⁵²⁰ | Electrospinning–calcination– solvothermal route | 20 mg L ^{-1 a} (100 mL) | 40 mg | 3 | Xenon lamp: 300 W with a cut-off filter (λ > 400 nm), 97 mW cm ⁻² | 81.1% (120 min) | 0.0105 min^{-1} |

Table 7 (continued)

| Photocatalyst | Preparative method | CIP ^a /CIP·HCl ^b | Catalyst dose | рН | Light source | Degradation (time) | Rate constant |
|--|------------------------|--|-------------------|----|--|-----------------------|---|
| g-C ₃ N ₄ @Cs _{0.33} WO ₃ ⁵²¹ | Solvothermal | 20 ppm | 20 mg (100 mL) | 3 | Xenon lamp (500 W), λ: 230–2500 nm, 0.25 W cm ⁻² | 97% (145 min) | 14.9 × 10 ⁻³ min ⁻¹ |
| g-C ₃ N ₄ /rGO/WO ₃ ⁵²³ | Photo reduction method | 20 mg L ^{-1 a} (50 mL) | 10 mg | _ | High-pressure xenon arc lamp with 400 nm cut-off filter and 100 mW cm ⁻² | 85% (180 min) | _ |
| CuS/BiVO ₄ (mass ratio: 7%) ⁵²⁴ | In situ | 10 mg L ^{-1 a} (100 mL) | 100 mg | _ | Xenon lamp (300 W) with a 420 nm cut-off filter | 86.7% (90 min) | 0.02151 min ⁻¹ |



Fig. 18 Photocatalytic degradation of TC. (a) Dynamic curves of different photocatalysts (initial conditions: 40 mg L⁻¹, TC, 0.2 g L⁻¹ photocatalyst, and 350 mW cm⁻² UV light). (b) The impact of UV light intensity (initial conditions: 40 mg L⁻¹ TC and 0.2 g L⁻¹ Au–ZnO nanomotors). (c) Cycling tests (initial conditions: 30 mg L⁻¹ TC: 0.2 g L⁻¹, Au–ZnO nanomotors, and 350 mW cm⁻² UV light). (d) Proposed photocatalytic mechanism for TC degradation. Reproduced from ref. 542 with permission from RSC (2022).

different photocatalysts, UV light intensity and cycling tests, as presented in Fig. 18(a)-(c), respectively. The findings revealed that the respective degradation rates of tetracycline within 30 min and rate constants corresponding to pseudofirst-order kinetics follow the order: Au-ZnO nanorod motors (Au–ZnO-M): 99.3% > Au–ZnO nanorod array (Au–ZnO-A): 95.5% > ZnO (86.5%), and k 'Au–ZnO nanorod motors (k (Au–ZnO-M): 0.1451 min⁻¹ > k (Au–ZnO-A): 0.1120 min⁻¹ > k (ZnO): 0.0542 min⁻¹). It was suggested that the Au layer in the Au-ZnO heterojunction nanoarrays acted as an electron reservoir to facilitate charge separation, thereby lowering the possibility of photogenerated carrier recombination. A possible photocatalytic mechanism for the photocatalytic degradation of tetracycline by Au-ZnO nanomotors under UV-light irradiation is displayed in Fig. 18(d). According to this, electrons in Au could react with O_2 to form O_2^- , accounting for the degradation of tetracycline. In contrast, h⁺ in the VB of ZnO could directly degrade tetracycline to a stable product.

3.7.3 Doped photocatalysts

3.7.3.1 Doped TiO2 and ZnO. Several studies have been carried out on the performance of doped TiO₂ and ZnO photocatalysts and subsequently used in the removal of tetracycline from water.^{543–546} Red mud and modified red mud originating from industrial solid waste discharged from the aluminum industry have been investigated as lowcost, effective photocatalysts under irradiated visible light.⁵⁴³ Xu et al.⁵⁴⁴ developed a C-doped TiO2polymethylsilsesquioxane (PMSQ) aerogel followed by thermal treatment at 400 °C in air. They used it to achieve 98% removal of tetracycline hydrochloride from aqueous solution in 180 min and ascribed it to enhanced charge separation. In another study, hydrothermally prepared carbon (3 wt%)-doped TiO2 with metal (Ni/Co/Cu) nitrate hydroxide was used as a nanocomposite photocatalyst.545 The photocatalytic activity of this catalyst displayed 97% removal of tetracycline hydrochloride within 60 min. TiO₂ doped with acetylene black, 546 N-doped $\rm TiO_2/diatomite, ^{547}$ nitride tubes P-doped carbon combined with peroxydisulfate (PDS),⁵⁴⁸ N,S-doped TiO₂ and N,S-doped ZnO modified chitosan, 549 and C,N,S-tri-doped TiO₂ 550 photocatalysts have also been investigated for the degradation of tetracycline.

Metal-doped photocatalysts have also received a lot of attention for their application in the photocatalytic degradation of tetracycline in aqueous solution. Nb-doped ZnO (Nb:Zn molar ratio: 1:1) showed 93.2% degradation efficiency for tetracycline in 180 min under visible light and also possessed superior recyclability and stability.⁵²⁵ Zhang *et al.*⁵⁵¹ fabricated Ag-doped TiO₂ (Ag⁺:Ti⁴⁺ mole ratio: 0, 0.5, 1.0, 2.0, 3.0, and 5.0%) hollow microspheres following an applied hydrothermal process by a template-free method. It was noted that Ag-doped TiO₂ (Ag⁺:Ti⁴⁺ mole ratio: 3.0%) exhibited maximum removal of tetracycline hydrochloride following first-order kinetics with OH· and h⁺ playing an active role. Ce (2%)-doped TiO₂/halloysite nanotubes and Ce

(2%)-TiO₂/halloysite nanotubes enabled about 78% tetracycline removal within 60 min under visible-light irradiation.⁵⁵² TiO₂ composite nanofibers doped with CuO were also studied for the photocatalytic degradation of pharmaceutical wastewater.⁵⁵³ Bembibre *et al.*⁵⁵⁴ used Cadoped ZnO nanoparticles in the removal of tetracycline under a visible-light-driven sonocatalytic process.

3.7.3.2 Doped graphitic materials. Doped graphitic materials have attracted a lot of attention as photocatalysts in the removal of tetracycline from water.555 Nitrogen-selfdoped g-C₃N₄ nanosheets prepared by a combination of Nself-doping and thermal exfoliation showed higher photocatalytic activity for tetracycline degradation than bulk g-C₃N₄, N-self-doped g-C₃N₄ or g-C₃N₄ nanosheets.⁵⁵⁶ This is attributed to the enlarged visible-light absorption ability, reduced recombination and prolonged lifetime of photogenerated charge carriers. Chen et al.557 reported the removal of tetracycline hydrochloride from wastewater (pH: 5) using an S-g-C₃N₄/PTFE membrane under irradiated visible light. These findings indicated 98.1% photocatalytic degradation corresponding to an initial concentration of tetracycline hydrochloride of 10 mg L^{-1} , catalyst dosage of 1 g L^{-1} , and S-g-C₃N₄ loading of 50 mg. Further, the S-g-C₃N₄/ PTFE membrane displayed good recovery performance and photocatalytic stability. Ba (2%)-doped g-C₃N₄ demonstrated significant influence on the photocatalytic activity owing to its low band gap and the effective separation of photoinduced e⁻-h⁺.558

Er-doped g- C_3N_4 ,⁵⁵⁹ Cd-doped g- C_3N_4 ,⁵⁶⁰ S-doped carbon quantum dot loaded hollow tubular g- C_3N_4 ,⁵⁶¹ single-atom Ni,S-co-coped g- C_3N_4 ,⁵⁶² nitrogen defect/boron dopant engineered tubular g- C_3N_4 ,⁵⁶³ Ag-g- C_3N_4 ,⁵⁶⁴ Bi-nanoparticledecorated g- C_3N_4 nanosheets (10 wt%),⁵⁶⁵ Co-doped TiO₂rGO,⁵⁶⁶ rGO-doped ZnAlTi-LDH,⁵⁶⁷ and graphene oxide/ magnetite/cerium-doped titania⁵⁶⁸ photocatalysts also acted as efficient photocatalysts in the degradation of tetracycline.

3.7.4 Metal oxide composites. Several studies have been reported on the evacuation removal of tetracycline from water using a combination of metal oxides. Wang et al.526 observed 81% (10 min) photocatalytic degradation of tetracycline by irradiating a 5% carbon quantum dots/TiO2 composite prepared by a hydrothermal method with visible light. Such performance of the composite is attributed to the improved separation efficiency of photogenerated electrons and holes. According to Liu et al.,569 excellent catalytic performances is observed for 3%-CuO_x/ γ -Al₂O₃ in the simultaneous degradation of tetracycline hydrochloride in a wide pH range of 3.10-9.47 under irradiation by a 300 W xenon lamp (190-1100 nm). In another study, a sol-gel-synthesized calcite/TiO₂ photocatalyst accounts for 90% tetracycline removal under UV light in aqueous solution (pH: 7) corresponding to 1.5 g L⁻¹ of catalyst and 50 mg L⁻¹ of tetracycline.⁵⁷⁰ Hunge et al.⁵⁷¹ studied the effect of catalyst loading for the MoS_2 (20 wt%)/TiO2 composite and solution pH, in the degradation of tetracycline under UV-vis irradiation of composites and

observed its superior performance (95%) compared to TiO₂ and MoS₂. ZnO/ γ -Fe₂O₃ demonstrated an important role in achieving ~89% degradation efficiency for tetracycline in water under UV-visible light after 150 min.⁵⁷²

The degradation of tetracycline in water has been investigated on TiO₂ decorated on magnetically activated carbon as a function of different parameters under ultraviolet and ultrasound irradiation.⁵⁷³ These findings revealed 93% tetracycline removal at the end of 180 min under optimum conditions corresponding to an optimum intensity of 70 W US power, pH 6.0, catalyst loading of 0.4 g L⁻¹, and initial concentration of tetracycline of 30 mg L⁻¹. ZnO rod-activated carbon fiber,⁵⁷⁴ Fe₃O₄/FeP,⁵⁷⁵ spatially confined Fe₂O₃ in hierarchical SiO₂@TiO₂ hollow spheres,⁵⁷⁶ La-enriched titania-zirconia oxide,⁵⁷⁷ Ni(OH)₂-decorated TiO₂,⁵⁷⁸ IO-TiO₂-CdS,⁵⁷⁹ and WO_{2.72}/ZnIn₂S₄⁵⁸⁰ have also been demonstrated as efficient photocatalysts for the removal of tetracycline from water.

Wang et al.⁵⁸¹ converted harmful algae into bionanohybrid materials by immobilizing Microcystis aeruginosa cells onto PAN-TiO2/Ag hybrid nanofibers. They observed about 96% degradation efficiency for tetracycline hydrochloride under visible light compared to PAN/TiO₂/Ag nanofiber (77%) and M. aeruginosa (49%) due to a synergistic effect. It is suggested that enhanced degradation in M. aeruginosa/PAN-TiO₂/Ag could be caused by algae facilitating the effective separation of photogenerated electron-holes on TiO₂. The presence of ZnO, carbonaceous layers and Ag nanoparticles improved the optical absorption property in the Ag/ZnO/C structure, resulting in 95.8% (35 min) and 90.6% (280 min) degradation of tetracycline hydrochloride under UV- and visible-light irradiation, respectively.582 This is ascribed to efficient photogenerated electron separation and transportation and an increase in the active reaction sites. According to Wei *et al.*,⁵⁸³ an SiO₂-TiO₂-C ($n_{\rm C}$: $n_{\rm Ti}$ mol ratio: 3.5) aerogel composite displayed 80.01% degradation efficiency for tetracycline hydrochloride within 180 min under visible light and also retained its high stability and reusability. $\cdot O_2^-$ and $\cdot OH$ were considered as the active species responsible for the photocatalytic degradation of tetracycline. In addition, ternary chitosan comprising chitosan-TiO₂-ZnO over graphene,⁵⁸⁴ palygorskite-supported Cu₂O/TiO₂,⁵⁸⁵ CuO/Fe₂O₃,⁵⁸⁶ ZnO@zeolitic imidazolate,⁵⁸⁷ and bimetallic oxide/carbon588 have also been tested for the photocatalytic degradation of tetracycline in water.

3.7.5 Graphitic materials

3.7.5.1 g- C_3N_4 . Insufficient sunlight usage, low surface area and rapid charge recombination of electron and hole pairs are a major hinderance contributing towards the low photocatalytic performance of g- C_3N_4 .⁶⁵ As a result, several investigations have been made into the photodegradation of tetracycline using g- C_3N_4 and its composites. Hernández-Uresti *et al.*³³³ prepared a graphite-like C_3N_4 photocatalyst by the polycondensation of a melamine precursor and observed the following trend for the photodegradation of four different pharmaceuticals in aqueous solution under UV-vis irradiation: tetracycline > ciprofloxacin > salicylic acid > ibuprofen. The active species responsible for the degradation of tetracycline were considered to be photogenerated holes, OH radicals and H_2O_2 . Self-assembly-based g- C_3N_4 nanoflakes showed up to 70% removal efficiency for tetracycline (20 ppm) within 180 min under light irradiation (420 nm).⁵⁸⁹

Shi et al.590 studied the degradation performance of tetracycline in real water systems by metal-free g-C₃N₄ microspheres under various conditions through visible-light catalysis and PMS activation synergy. According to this, the rate constant values for the degradation of tetracycline by photocatalysis, Fenton-like catalysis, and photo-Fenton-like catalysis are 0.013, 0.025, and 0.028 min⁻¹, respectively. The observed superior degradation performance of photo-Fentonlike catalysis is attributed to the synergetic effect between PMS activation and photocatalysis. In another study, Wang and others⁵⁹¹ used graphitic carbon nitride microspheres and recorded 80.54% degradation efficiency for the removal of tetracycline hydrochloride under visible-light irradiation for 2 h, corresponding to a photocatalyst dose of 1.0 g L^{-1} , initial concentration of tetracycline hydrochloride solution of 10 mg L⁻¹ and initial pH 7. Porous g-C₃N₄,⁵⁹² GQDs/g- C_3N_4 ,⁵⁹³ S-doped graphitic carbon nitride,⁵⁹⁴ hexagonal BN/g- C_3N_4 ,⁵⁹⁵ poly-*o*-phenylenediamine (POPD)/g- C_3N_4 ,⁵⁹⁶ and N– CNT/mesoporous g-C₃N₄⁵⁹⁷ photocatalysts have also been evaluated for the removal of tetracycline.

Jiang et al.⁵⁹⁸ studied the degradation of tetracycline in aqueous solution using P and S doped g-C₃N₄ under visible light ($\lambda \ge 420$ nm) and showed higher photocatalytic than bare g-C₃N₄ or single-doped g-C₃N₄. According to this, P and S doping in g-C₃N₄ inhibited the recombination of electronhole pairs and facilitated the efficient separation of photogenerated charges. The h^+ and $\cdot O_2^-$ were the dominant active species responsible for the degradation of tetracycline. Porous $g-C_3N_4/TiO_2$ ($g-C_3N_4:TiO_2$ mass ratio: 12:1) photocatalysts removed 88.43% of tetracycline from aqueous solution under a xenon lamp for 90 min, which was ascribed to the synergistic effect.⁵⁹⁹ In another study, a ZrO₂embedded MoS₂/g-C₃N₄ nanocomposite exhibited 94.8% tetracycline degradation in aqueous solution in 90 min under visible light owing to the dual charge-transfer channel between the layers of MoS₂/g-C₃N₄ and ZrO₂ nanoparticles.⁶⁰⁰ Poly-N-isopropylacrylamide (PNIPAM)/Fe₃O₄/g-C₃N₄ prepared by a hydrothermal method and thermal photoinitiation under visible-light irradiation decomposed tetracycline into harmless small molecules.⁶⁰¹ The catalytic activity remain more or less unaltered even after 5 repeated uses and could be easily separated. In addition, CDs/g-C₃N₄/BiPO₄,⁶⁰² ZnO/Ndoped g-C₃N₄,⁶⁰³ and g-C₃N₄/H₃PW₁₂O₄₀/TiO₂⁶⁰⁴ exhibited enhanced photocatalytic degradation performance for tetracycline under visible light.

3.7.5.2 Graphene. Binary and ternary graphitic composite materials have been reported as photocatalysts in the removal of tetracycline from aqueous solution.⁶⁰⁵⁻⁶²¹ According to Ren *et al.*,⁶⁰⁵ a red mud/graphene oxide (mass

ratio: 93:7) composite attained the best degradation rate for tetracycline (79.8%) compared to raw red mud under visible light within 80 min owing to its enhanced specific surface area, light absorption and charge separation. Porous hydroxyapatite (Hap) hollow microspheres as a source of cheap and green photocatalysts have been harnessed in fabricating rGO/Hap composites.606 Investigations revealed significantly enhanced photocatalytic activity of rGO (1.5 wt%)/Hap in tetracycline degradation (92.1%, 30 min) under a xenon lamp (300 W) for full-spectrum irradiation. This is explained on the basis of the photogenerated electrons accumulating at rGO (acting as an electron acceptor) that could interact with O_2 to form O_2^- . In addition, separated positive holes in the VB of porous hollow Hap (acting as an electron donor) microspheres directly participate in the oxidation of tetracycline.

Heteropoly acid (H₃PMo₈W₄O₄₀)/graphene oxide nanocomposites based on UiO-66 have been synthesized following an *in situ* growth hydrothermal method and tested as photocatalysts in tetracycline photodegradation under visible-light irradiation.⁶⁰⁷ The photocatalytic degradation efficiency for tetracycline was found to be significantly higher (95%: 120 min) compared to GO or heteropoly acid. An Fe₃O₄/GO/ZnO magnetic nanocomposite showed 74% (100 min) degradation of tetracycline hydrochloride under visiblelight irradiation.⁶⁰⁸ This is explained on the basis of ZnO and Fe₃O₄/GO in Fe₃O₄/GO/ZnO contributing to the generation of the electron-hole pairs under visible light and promoting the transfer of photogenerated electrons, respectively. In another study, graphene quantum dot decorated ZnO-ZnF₂O₄ nanocage ternary composites, prepared by a one-step deposition method exhibited superior performance in the degradation of tetracycline hydrochloride under visible light compared to ZnO or ZnO-ZnFe₂O₄.⁶⁰⁹ According to Chakraborty et al.,610 an rGO-ZnTe (1:1) photocatalyst facilitated the degradation of tetracycline due to a synergistic effect. It is suggested that the 2D wrinkled surface of rGO contributes in minimizing the recombination probabilities of photoinduced electron-hole pairs. N-doped TiO₂ nanoparticles deposited on rGO exhibited more pronounced photodegradation activity for tetracycline hydrochloride than pure TiO₂ or N-doped TiO₂.⁶¹¹ Subsequent studies on the reusability of N-doped TiO₂/rGO also established the stability of the composite photocatalyst.

Kumar *et al.*⁶¹² fabricated ZnO quantum dots (1.5 wt%)/ rGO by a hydrothermal method and observed 68% removal of tetracycline from wastewater (pH: 5) after 120 min under visible light. Fe₃O₄/g-C₃N₄/rGO exhibited 86.7% degradation rate of tetracycline hydrochloride, following pseudo-secondorder kinetics.⁶¹³ The proposed mechanism suggested $O_2^$ and OH radicals as the most reactive species in the photocatalytic degradation of tetracycline. Ghoreishian *et al.*⁶¹⁴ reported sonophotocatalytic degradation of tetracycline using a flower-like rGO/CdWO₄ composite under simulated visible-light irradiation. These findings under optical conditions (pH: 5.7, initial concentration of tetracycline: 13.54 mg L^{-1} , catalyst dosage: 0.216 g L^{-1} , time: 60 min) revealed its photocatalytic catalytic activity to be 1.5 and 3 times higher than that of commercial nano-ZnO and TiO₂, respectively.

Interfacial growth of a TiO₂-rGO composite by the Pickering emulsion approach showed 94% removal efficiency for tetracycline hydrochloride (10 ppm) after 40 min under the visible light.⁶¹⁵ Such significant enhancement in the photocatalytic efficiency of TiO₂-rGO is ascribed to its 2D sandwich-like structure. Porous hollow hydroxyapatite microspheres decorated with rGO,⁶¹⁶ rGO-CdS,⁶¹⁷ rGO-CdS/ZnS,⁷² Ag/TiO₂ nanosheets/rGO,⁶¹⁸ Ag/TiO₂ nanosheets,⁶¹⁹ Ag/TiO₂ nanosheets-rGO,⁶²⁰ and TiO₂/rGO/activated carbon⁶²¹ have also been harnessed as photocatalysts in the degradation of tetracycline in aqueous solution.

3.7.6 Heterojunction-based photocatalysts. Heterojunction photocatalysis have attracted attention for the degradation/ removal of tetracycline in aqueous solution by various heterojunctions.51 In this regard, a core-shell g-C3N4@Co-TiO₂ heterostructured nanofibrous membrane exhibited excellent visible-light-driven degradation of tetracycline hydrochloride.⁶²² Huang et al.⁶²³ observed 74.7% degradation efficiency for tetracycline hydrochloride within 30 min by a hierarchical Au (2%)-g-C₃N₄-ZnO heterostructure under xenon lamp irradiation. Mesoporous TiO2-modified ZnO quantum dots (8%) immobilized on linear low-density polyethylene (LLDPE) under fluorescent light irradiation showed 89.5% removal of tetracycline (initial concentration: 40 mg L⁻¹) from water (pH: 9) within 90 min.⁶²⁴ g-C₃N₄/CuO (7%)⁶²⁵ and ZnO globular (15 wt%)/g-C₃N₄⁶²⁶ showed 55% and 78.4% degradation of tetracyclines in 60 and 50 min under simulated solar light ($\lambda > 365$ nm) and artificial visible sunlight illumination ($\lambda \ge 400$ nm), respectively.

 $Ti_{0.7}Sn_{0.3}O_2/g-C_3N_4$ (mass ratio: 10 wt%) achieved 83% degradation of tetracycline hydrochloride in 40 min under irradiated visible light.⁶²⁷ This is explained on the basis of an S-scheme between $Ti_{0.7}Sn_{0.3}O_2$ and $g-C_3N_4$ to increase and transport photogenerated charges. The ultrasonic-assisted precipitation method has been used to fabricate a ZnO (20 wt%)/GO (2 wt%)/Ag_3PO_4 heterojunction and it has been used as a photocatalyst in the elimination of tetracycline hydrochloride from wastewater.⁶²⁸ These findings showed 96.32% (75 min) degradation under visible light corresponding to initial concentration of tetracycline of 30 mg L⁻¹ and catalyst dose of 1.0 g L⁻¹.

The degradation rate of tetracycline was found to be about 10 times higher in a g-C₃N₄/C/Fe₃O₄ ternary nanocomposite compared to its individual or binary components under simulated solar light.⁶²⁹ The degradation process followed a first-order kinetics model with a much higher apparent rate constant for g-C₃N₄/C/Fe₃O₄ (0.0063 min⁻¹) compared to g-C₃N₄ (0.0029 min⁻¹) or carbon (0.0003 min⁻¹). The photoinduced h⁺ and \cdot O₂⁻ free radicals are suggested to act as the main active components in the degradation. The enhanced activity of g-C₃N₄/C/Fe₃O₄ in tetracycline degradation is attributed to heterojunction formation and is due to the effective separation of the photocarriers. In addition, the introduction of C into $g-C_3N_4/C/Fe_3O_4$ facilitates an enhancement of the optical response range and effective electron transfer.

Liao et al.⁶³⁰ examined the utility of a core-shell BiFeO₃/ TiO_2 heterostructure with a p-n heterojunction as a photocatalyst prepared by forming nanospheres of TiO₂ on BiFeO₃ (nanocubes) in tetracycline degradation under visiblelight irradiation. The findings indicated much higher degradation efficiency of BiFeO₃/TiO₂ (72.2%) compared to BiFeO₃ (64.9%) and TiO₂ (38.3%) after 180 min of visible illumination. A BiFeO₃/TiO₂ p-n heterojunction photocatalyst showed superior degradation efficiency for tetracycline due to its enlarged specific surface area and higher sensitivity to visible light, improved separation and transfer efficiency of photoelectron-hole pairs and a synergistic effect. Fibershaped Ag₂O/Ta₃N₅ p-n heterojunctions designed as efficient photocatalysts showed enhanced photocatalytic activity with good stability in photocatalytic activity for tetracycline under visible light ($\lambda > 400$ nm) due to the synergistic effect.⁶³¹ It is anticipated that photogenerated holes and superoxide radicals played prominent roles in the photocatalytic process.

others⁶³² and fabricated an α -Bi₂O₃/g-C₃N₄ Chen heterostructure modified by plasmonic metallic Bi and oxygen vacancies and observed a remarkably high degradation rate for tetracycline (90.2%) under visible light after 180 min. Such enhancement is attributed to the formation of a p-n junction arising from a combination of n-type $(g-C_3N_4)$ and p-type $(\alpha-Bi_2O_3)$ semiconductors, which is beneficial in a ternary photocatalyst. It is suggested that Bi nanoparticles and the presence of oxygen vacancies favor the consumption and separation of the photogenerated electrons and holes in the ternary heterojunction photocatalyst. Several other heterojunction photocatalysts, such as C₃N₄(a)MnFe₂-CuO@ZnO,637 ZnO/SnO₂,⁶³⁸ Cu₂O-TiO₂,⁶³⁹ MoS₂/Ag/g- C_3N_4 , 640 g- C_3N_4 /Zr O_{2-x} , 641 and needle Sn O_2 nanoparticles anchored on exfoliated g-C₃N₄⁶⁴² have also shown enhancement and stability in the degradation of tetracycline.

N-doped ZnO- MoS_2 binary heterojunctions have been fabricated by a hydrothermal method and used to study its photocatalytic activity for the degradation of tetracycline under visible-light irradiation.⁶⁴³ Fig. 19(a)-(d) show



Fig. 19 (a) Kinetic curves for the degradation of TC, (b) $\ln(C/C_0)$ vs. time curve for the degradation of TC, (c) a histogram showing a comparative degradation rate (%) of TC under visible light illumination and (d) a bar graph showing the values of rate constants for all the photocatalysts (N-doped ZnO nanorods loaded 0.2, 0.5, 1, 2 and 3 wt% of with MoS₂ nanoflowers (MNF) are referred to as NZM0.2, NZM0.5, NZM1, NZM2, and NZM3, respectively). Reproduced from ref. 643 with permission from RSC (2017).

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corresponding findings based on variations in the degradation of TC with time, corresponding $\ln(C/C_0)$ vs. time plots, a histogram showing a comparative degradation rate (%) of TC under visible light illumination and a bar graph showing the values of rate constants for all the photocatalysts. It should be noted that photocatalytic degradation of tetracycline followed pseudo-first-order fabricated kinetics. In addition, semiconductor heterojunctions demonstrated enhanced performance for the degradation of tetracycline due to the synergistic effect. Furthermore, the enhanced photostability of the photocatalyst over three cycles for a period of 360 min is ascribed to the transfer of holes from the valence band of N-doped ZnO to the valence band of MoS₂.

A novel type-II $Bi_2W_2O_9/g$ - C_3N_4 heterojunction has been fabricated and studied for its photocatalytic performance in the removal of tetracycline under simulated solar irradiation and it was compared with $Bi_2W_2O_9$ and g- C_3N_4 , as displayed in Fig. 20(a).⁷² It is inferred that $Bi_2W_2O_9/g$ - C_3N_4 yields high photodegradation (~95%) compared to the degradation observed for pristine g- C_3N_4 (75%) or $Bi_2W_2O_9$ (~60%). This is attributed to the $Bi_2W_2O_9$ semiconductor acting as a trap for photogenerated holes and electrons. A photocatalytic mechanism has also been proposed for the $Bi_2W_2O_9/g$ - C_3N_4 system in Fig. 20(b).

Z-scheme WO₃/g-C₃N₄ composite hollow microspheres fabricated by an *in situ* hydrolysis and polymerization process showed an enhanced degradation rate towards tetracycline hydrochloride (82% in 120 min) under visible-light irradiation.⁶⁴⁴ The enhanced separation of photoinduced electrons and holes and the synergistic effect of g-C₃N₄ and WO₃ are considered to be a few reasons for this. In addition, the presence of hollow cavities could enable trapping of the incident photons and facilitate availability of more electrons and holes in the photocatalytic process. In another study, a Z-scheme mesoporous $Sn_3O_4/g-C_3N_4$ heterostructure exhibited superior photocatalytic performance in degrading tetracycline hydrochloride present in water.645 A possible photocatalytic reaction mechanism has also been examined in detail for this. In another study, BiOI/g-C₃N₄/CeO₂ (3 wt%) photocatalyst possessed the best photocatalytic activity for degradation of tetracycline (91.6%) under visible-light irradiation.⁶⁴⁶ It is anticipated that CeO₂/g-C₃N₄ and BiOI/g-C₃N₄ catalysts block the recombination of photoinduced pairs electron-hole through the formation of a heterojunction.

Dai *et al.*⁷³ *in situ* prepared 3D-20% polyaniline/perylene diimide (PANI/PDI) and found the degradation rate for tetracycline under visible-light irradiation in a static system, by 15.3 times and 17.0 times those of pure PDI and PANI, respectively. The main reactive species in the degradation of tetracycline comprised superoxide radicals, hydrogen peroxide and holes. Fig. 21(a) and (b) schematically show the electron-hole pair separation process and TC degradation mechanism of a 3D 20%-PANI/PDI heterojunction under visible-light irradiation. Scanning electron microscopy images of 3D PANI/PDI in Fig. 21(c and d) indicate a significant decrease in size after the dissolution/assembly process and the PDI are uniformly/orderly dispersed in the 3D network structure of PANI.

In addition, $TiO_{2-x}/ultra$ thin g- C_3N_4/TiO_{2-x} ,⁶⁴⁷ K-doped g- $C_3N_4/TiO_2/CdS$,⁶⁴⁸ γ -Fe₂O₃ nanospheres anchored on g- C_3N_4 ,⁶⁴⁹ CQDs/g- C_3N_4 ,⁶⁵⁰ Ag₃PO₄/MIL-88A(Fe),⁶⁵¹ BiOBr/MoS₂/GO,⁶⁵² g- $C_3N_4/MnO_2/GO$,⁶⁵³ BiVO₄@polypyrrole/g- C_3N_4 ,⁶⁵⁴ AgI/BiOBr/rGO,⁶⁵⁵ graphene-bridged Ag₃PO₄/Ag/BiVO₄,⁶⁵⁶ g- C_3N_4 , nanoparticles/WO₃ hollow microspheres,⁶⁵⁷ CuIn₂S₂/g- C_3N_4 ,⁶⁵⁸ Ag₃PO₄/g- C_3N_4/ZnO ,⁶⁵⁹ g- C_3N_4 nanosheet/Ag₃PO₄/ α -Bi₂O₃,⁶⁶⁰ LaNiO₃-modified C₃N₄,⁶⁶¹ and ultrafine TiO₂ nanoparticle



Fig. 20 (a) Photocatalytic degradation of tetracycline antibiotic ($C_0 = 10 \text{ mg L}^{-1}$, pH = 4.89) as a function of irradiation time over Bi₂W₂O₉, g-C₃N₄ and Bi₂W₂O₉/g-C₃N₄ samples. (b) Proposed photocatalytic mechanism for the Bi₂W₂O₉/g-C₃N₄ system under solar-like irradiation. Reproduced from ref. 72 with permission of Elsevier (2020).



Fig. 21 (a) Morphological structure of PANI/PDI. (b) Photocatalytic mechanism of PANI/PDI heterojunction photocatalysts under visiblelight irradiation: direct Z-scheme heterojunction mechanism. (c and d) Scanning electron microscopy images of 3D PANI/PDI. (Modified) Reproduced from ref. 73 with permission of Elsevier (2020).

modified g-C₃N₄⁶⁶² heterojunction photocatalysts have also been harnessed in the removal of tetracycline in water.

Table 8 records the performance data of different photocatalysts used in the removal of tetracycline from water.

3.8 Diclofenac

Diclofenac (DCF), an important non-steroidal antiinflammatory drug, finds multifaceted applications as a painkiller primarily for dysmenorrhea, rheumatoid arthritis and inflammation.663,664 The intake of diclofenac even at low levels by humans and other living organisms is reported to have an adverse biochemical effect. The solubility and high polarity of diclofenac in water and lower degradability account for its water pollution. Further, it can accumulate in food chains owing to its migration through the aquatic medium (surface water, drinking water, underground water) in food chains. In view of this, the following photocatalytic methods have been used in the removal of diclofenac from water.665-748

3.8.1 Metal oxides. Rizza et al.⁶⁶⁷ studied the degradation of diclofenac sodium by UV/TiO2 for a wide range of initial DCF concentrations (5–80 mg L^{-1}) and photocatalyst loadings $(0.2-1.6 \text{ g L}^{-1})$ in a batch reactor system. These results showed 100% removal of DCF compared to $\sim 3\%$ and 14% for TiO₂ (dark conditions) and photolysis (UV) corresponding to the initial concentration of 5 mg L⁻¹ and catalyst dosage of 0.2 g L^{-1} . The photocatalytic degradation of real pharmaceutical wastewater (pH: 9) including diclofenac and other drugs by TiO₂/H₂O₂ was found to be 45.11% under UVmediated irradiation within 120 minutes.⁶⁶⁸ TiO₂ nanofilm membranes fixed on glass panels have also been explored in

Performance data of tetracycline on its removal in water using different photocatalysts

constan 56 ± 2 10^{-3} 0.018min⁻¹ $7.25 \times 10^{-3} \text{ min}^{-1} \text{ min}^{-1} \sim 3.8 \times 10^{-2} \text{ min}^{-1} \text{ min}^{-1} \text{ min}^{-1} \text{ min}^{-1} \text{ min}^{-1}$ ~ 0.03 min⁻¹ Rate Degradation 94.8% (120 min) 100% (15 ~25% (12 100% (30 min) 95.6% (90 100% (15 87% (360 and time 95% (60 min) 90% (35 min) min) min) min) min) UV lamp (30 W), λ_{max} : 360 nm Low-pressure UV lamp (6 W), Xenon lamp, 250 ${
m Wm}^{-2}$, 300-Xenon lamp, 250 Wm⁻², 300-Medium-pressure mercury lamp (UV), $\lambda < 290 \text{ nm } 525$ Xenon lamp 300 W, 20 mW felosil HG500 UV lamp, 30 JV lamp: 18 W, λ: 254 nm, Visible light LED 50 W cm^{-2} , λ : 350 nm $2500 \ \mu W \ cm^{-2}$ λ: 254-258 nm Light source $mW cm^{-2}$ $uW cm^{-2}$ 800 nm 800 nm Ηd 6.0 7.0 8.7 17 6 10 Catalyst dose 1000 mg 0.2 g L^{-1} 1.5 g L^{-1} 1.0 g L300 mg 0.12 g Ľ 30 mg ъс аð CIP^a/CIP·HCl^b $30 \text{ mg L}^{-1 b}$ $L^{-1 b}$ 20 mg L^{-1} 10 mg L^{-1} (100 mL) 50 mg L^{-1} 55 mg L^{-1} 20 mg L^{-} 40 mg L 35 ppm^b (100 mL)250 mL) 100 mL (40 ml) 100 Lmg 10 Modified sol-gel method (product calcined at 400 °C) Biosynthesis Preparative method Dispersion method Comme rcial Solvothermal Commercial Commercial Commercial Commercial Nanosized TiO $_2$ (P25) with 70% anatase and 30% rutile⁵²⁸ $m FiO_2-P25$ (80% anatase and 20% rutile) 20% rutile in presence of $m H_2O_2~(100~m_{2})$ Nanosized TiO₂ with 80% anatase and $m TiO_2$ (P25) immobilized in chitosan⁵³¹ Nanometric and immobilized $\operatorname{TiO}_2^{532}$ in presence of $\rm H_2O_2~(100~mg~L^{-1})^{530}$ ZnO nanoparticles (peroxy monosulfate:2 mM)⁵³³ ZnO (Sigma Aldrich)⁵²⁷ TiO₂ (P25 Degussa)⁵²⁷ Photocatalyst Table 8 $\operatorname{TiO}_2^{526}$ -1)529

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| Table 8 (continued) | | | | | | | |
|---|---|---|----------------------|---------|---|----------------------------|---------------------------------------|
| Photocatalyst | Preparative method | CIP ^a /CIP·HCl ^b | Catalyst dose | Hq | Light source | Degradation and time | Rate constant |
| Iron oxide nanoparticles ⁵³⁴ | Co-precipitation | 83 μM^b (10 mL) | 10 mg | 7 | Hg quartz lamp (280 W), λ: 180 nm to 623 nm | 40% (60 min) | 0.0092 min ⁻¹ |
| Nanospherical α -Fe ₂ O ₃ supported on 12-tungstosilicic acid (H ₂ O ₂ : 0.1 | Solid state dispersion | 30 ppm ^a | 150 ppm | 8 | Hg lamp (15 W), <i>λ</i> : 254 nm | 97.39% (50 min) | 0.0098 0.0098 min ⁻¹ |
| ppm.200 mJ SnO2 hollow microspheres (SnCl ₂ ·2H ₂ O:Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O mole ratio = 1 · 4) ⁵³⁶ | Hydrothermal method | 50 mg $L^{-1 b}$ (40 ml) | 50 mg | | Hg lamp, <i>ì</i> : 365 nm | 76% (140 min) | 0.00861 min ⁻¹ |
| BiFeO ₃ (in presence of H ₂ O ₂ : 9.8 mM) ⁵³⁸ | Calcination of gel formed from bi and Fe nitrates at 600 من | $40 \text{ mg L}^{-1 a}$ | $2~{ m g~L}^{-1}$ | 4 | Hg lamp (300 W), λ = 365 nm | 100% (210 min) | 0.02650 min ⁻¹ |
| $_{11}^{(11)}$ Nb doped TiO ₂ (Nb: Zn molar ratio of $1:1)^{525}$ | Green synthesis | $150 \text{ mg L}^{-1 a}$ (100 mL) | $0.25~{ m g~L}^{-1}$ | Ч | 250 W xenon arc lamp with a 420 nm cut-off filter | 91. 5% (180 min) | 7.3×10^{-3} |
| Au-TiO ₂ $(0.3 \text{ g})/\text{PVDF}^{539}$ | Three-step synthesis strategy | 20 ml ^a | 0.1 g | | Xenon lamp (300 W), $\lambda < 420$ | 75% (120 min) | 0.01212 |
| C-doped TiO ₂ (in PMSQ) ⁵⁴⁴ | Multiple steps | $10 \mathrm{mg}\mathrm{L}^{-1}^{b}$ | 0.5 g | ~ | W halogen lamp (100 W) with | 98% (180 | |
| Ti O_2 /acetylene black with PS: 3 mM L^{-1546} | Mixing method | (30 mL) 30 mg L ^{-1 b} (100 mL) | $0.5~{ m g~L}^{-1}$ | 4.1 | LED lamp ($x > 420$ mm) LED lamp (30 W), λ : 400–780 nm, 50 W m ⁻² | mm) 93.3% (120 min) | 2.2×10^{-2} |
| N doped TiO ₂ diatomite ⁵⁴⁷ | Mixing followed by calcination | $20 \mathrm{~mg~L}^{-1~b}$ | $5~{ m g~L}^{-1}$ | 9 | Xenon lamp (150 W), $\lambda < 400$ | 91% (300 | - uim |
| P doped carbon nitride tube (peroxydisulfate: 1.0 g $\rm L^{-1})^{548}$ | Hydrothermal calcination | $20 \text{ mg L}^{-1 a}$ (100 mL) | $0.3~{ m g~L}^{-1}$ | 4.59 | Xenon lamp (300 W) with a cut-off filter of λ : 400 nm, 180 | 96.4% (60 min) | 0.0492 min ⁻¹ |
| Chitosan modified N,S-doped Ti O_2^{549} | Sol-gel-hydrothermal method | $10 \text{ mg L}^{-1 a}$ | $0.6~{\rm g~L}^{-1}$ | 8.2 | LED lamp: 18 W | 91% (20 in) | 0.048 |
| C,N,S-tri-doped TiO ₂ ⁵⁵⁰ | Sol-gel method (thiourea-to-Ti molar ratio of 0.05:1 and calcined at 450) | $5.0 \text{ mg L}^{-1 a}$ | $0.5~{ m g~L}^{-1}$ | 6 | Solar stimulator equipped with xenon arc lamp (150 W), | 98% (180 min) | 24.6×10^{-3} |
| Ag-doped TiO_2 (Ag^+ to Ti^4+molar ratio: $3.0\%)^{551}$ | Template-free route (hydrothermal) | $30 \text{ mg L}^{-1 b}$ | 100 mg | I | $\chi < \frac{4.0}{3}$ x = 4.0 mm ($\lambda > 420$ nm) | ~88% (30 min) | 6.77×10^{-2} |
| Ce (2%)-TiO ₂ /halloysite nanotubes ⁵⁵² | Modified sol-gel method | $20 \text{ mg L}^{-1 a}$ | 50 mg | I | Xenon lamp (300 W), $\lambda > 420$ | 78% (60 | |
| TiO ₂ composite nanofibers doped with CitO ⁵⁵³ | Electrospinning technique | 100 ppm^a | $1.0~{\rm g~L}^{-1}$ | Neutral | Xenon lamp (400 W) | 71% (60 min) | Ι |
| N self-doped g-C ₃ N ₄ ⁵⁵⁶ | Combination of N self-doping and thermal | $10 \text{ mg L}^{-1 a}$ | $0.5~{\rm g~L}^{-1}$ | I | Xenon lamp (300 W), $\lambda > 350$ | 89.14% (60 | Ι |
| S-g-C ₃ N ₄ /PTFE membrane ⁵⁵⁷ | Ultrasonic device method | $10 \text{ mg L}^{-1 b}$ | 50 mg | 5 | 300 W xenon light irradiation | 98.1% (120) 98.1% (120) | 0.03348 |
| Ba (2%)-doped g- $C_3N_4^{558}$ | Facial thermal condensation method | $20 \operatorname{mg} \mathrm{L}^{-1 a}$ | 50 mg | 10 | Xenon lamp (150 W) with 400 | 91.94% (120 min) | 0.0175 |
| Er (0.0035 g)-doped g- $C_3N_4^{559}$ | Calcination | $25 \text{ mg L}^{-1 a}$ | 25 mg | 4 | Xenon lamp (35 W) | $\sim 90\% (90$ | 0.0204 |
| Cd (4.6 wt%) doped g-C ₃ N ₄ ⁵⁶⁰ | Thermal polymerization method | $10 \text{ mg L}^{-1 a}$ | $0.8~{\rm g~L^{-1}}$ | 5 | Xenon lamp (300 W) with $\lambda > 120$ um | 98.1% (60 min) | |
| S-doped CQDs loaded hollow tubular $g-C_3N_4^{561}$ | Ultrasonic assisted synthesis strategy | 20 mg L ^{-1 a} | $1~{ m g~L}^{-1}$ | Ι | Xenon lamp (300 W), 0.33100 W cm ⁻² | 82.67% (60 min) | 0.0293 min ⁻¹ |

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| Dhotoratalvst | Drenarative method | Стр ^а /Стр.нСl ^р | Catalvst dose | Hu | Licht source | Degradation and time | Rate |
|---|--|--|-----------------------------|-----|---|--|---|
| Ni s so sound a C NI ⁵⁶² | Thornel notionization followed by | 10 mm ^b (20 | | | Vonce [ame (200 III) 100 III | 01 7707 (CD | 0.021 |
| INI-S co-coped g-C3N4 | t nermat polymerization followed by calcination | nu ppm (30 mL) | gm c | n | хепоп іапір (зоо w), 100 w cm ⁻² | 91.77% (60 min) | 0.031 min ⁻¹ |
| Ag doped g-C ₃ N ₄ ⁵⁶⁴ | Heating melamine and urea mixture | $20 \text{ mg L}^{-1 a}$ | $0.1\mathrm{g}$ | 7 | Solar light | 96.8% (120 | |
| | | $(50 \text{ mL})^{1}$ | | | | min) | |
| Bi nanoparticle-decorated g-C ₃ N ₄ nanocheet (10 ur4%) ⁵⁶⁵ | Ultrasound-assisted electrostatic self-assembly method | 10 mg L^{-1} | 40 mg | | Lamp (300 W), <i>λ</i> : 420–780 nm | 90.7% (70 min) | |
| Co $(0.20 \text{ wt}\%)$ doped TiO ₂ /rGO ⁵⁶⁶ | One-pot hydrothermal method | $30 \text{ mg L}^{-1 b}$ | 100 mg | | Halogen lamp: 500 W (400 nm | 60% (180 | |
| | | (100 mL) | | | cut-off filter) | min) 62.6267 (1960 | |
| magneuc graphene oxue-Ce (10%) mass ratio) doped titania ⁵⁶⁸ | Dispersion memor | 25 mg L (100 mL) | gill Uc | | zenon iamp: 300 W, 400 nm cut-off filter | 82.92% (180 min) | cuusu.u min ⁻¹ |
| $MoS_2 (20 vt\%)^T TiO_2^{571}$ | Hydrothermal route | $10 \text{ mg L}^{-1 a}$ | 100 mg | 5.5 | Metal halide lamp: 400 W | 95% (100 | 0.0276 |
| ZnO/γ -Fe ₂ O ₃ ⁵⁷² | Microwave-assisted solution method | $30 \text{ mg L}^{-1 a}$ | 0.5 mg L^{-1} | 6.7 | UV-VIS light source) Halogen lamp, 100 mW cm ⁻² | min) 88.52% (150 | 0.01321 |
| Magnetic activated C@TiO _{2⁵⁷³} | Impregnation method | (20 mL) 10 mg L ^{-1 a} | $0.4~{\rm g~L^{-1}}$ | 9 | UVC lamp (40 W), (2: 254 nm) | $m_{ m in}) \sim 100\% \ 180$. | 0.19^{-1} |
| ZnO rod-activated carbon fiber $(ACF)^{574}$ | Microwave | 40 mg $L^{-1 a}$ (150 mL) | One piece (5.5 cm of ZnO | ø | UV lamp (20 W), <i>λ</i> : 8365 nm | mın >99% (60 min) | uim – |
| | | 4 | rod-ACF) | | | `````````````````````````````````````` | |
| Fe ₃ O ₄ /FeP (molar ratios of Fe:P at 1: 6) ⁵⁷⁵ | Hydrothermal synthesis and partial phosphating annealing method | 50 mg L ^{-1 b} (40 mL) | 20 mg | | Xenon lamp (1000 W) | 88% (180 min) | 0.00984 min ⁻¹ |
| Hierarchical hollow | Dispersion/ <i>in situ</i> polymerization/sol-gel | $10 \text{ mg L}^{-1 a}$ | 0.2 mg mL^{-1} | 3-7 | Simulated solar-light | 100% (140 | |
| Fe ₂ O ₃ in hierarchical SiO ₂ @TiO ₂ hollow | approacn Dispersion/ <i>in situ</i> polymerization/sol-gel | $10 \text{ mg L}^{-1 a}$ | $0.2~{ m mg~mL}^{-1}$ | I | Irrautation Natural sunlight irradiation | 100% (80) | I |
| sphere ⁵⁷⁶ 1.aTiOZrO. ⁵⁷⁷ | Sol-oel nrovess | (50 mL) 10 mo L ^{-1 a} | 0 35 mo 1 ⁻¹ | Ľ | IIV lamn | min) 100% (120 | 0.0359 |
| | | (100 mL) | 1 2 III C | 2 | | min) | min ⁻¹ |
| Ni(OH) ₂ decorated rutile TiO _{2⁵⁷⁸} | Deposition of Ni(OH) ₂ on hydrothermally | 100 mg $L^{-1 a}$ | 200 mg | | 200 W Hg xenon lamp, $\lambda < 100$ mm (and other filters) | 76% (150 | 0.0090 |
| 3D IO-TiO ₂ -CdS ⁵⁷⁹ | prepared 1102 nanorods using 0.2 M 11014 Hydrothermal synthesis | (20 mL) 30 mg L ^{-1 b} | 30 mg | I | Xenon lamp $(\lambda < 420 \text{ nm})$ | ////////////////////////////////////// | |
| 1D/2D WO _{2.72} /ZnIn ₂ S ₄ ⁵⁸⁰ | Hydrothermal reaction | $50 \text{ mg L}^{-1 b}$ | 30 mg | | Xenon lamp: 300 W ($\lambda > 420$ | min) 97.3% (60 | I |
| POL | | $(300 \text{ mL})^{1}$ | · | | (uu | min) | |
| PAN/TiO₂/Ag nanofiber² ³⁸¹ | Immobilizing <i>M. aeruginosa</i> cells onto PAN/TiO ₂ /Ag | 20 mg L^{-1} (500 mL) | $1\mathrm{gL}^{-1}$ | 9 | Halogen lamp: 500 W ($\lambda < 420$ nm) | 96% (240 min) | 5.62×10^{-3} min ⁻¹ |
| Ag/ZnO/C ⁵⁸² | Calcination and photodeposition route | $20 \text{ mg L}^{-1 b}$ | 100 mg | | Xenon lamp: 500 W, $\lambda > 400$ | 81% (280 | |
| Ag/ZnO/C ⁵⁸² | Calcination and photodeposition route | (100 mL) 20 mg L ^{-1 b} | 100 mg | | nm UV lamp: 250 W, λ _{max} : 365 nm | min) 95.8% (35 | I |
| SiO ₂ -TiO ₂ -C $(n_{\rm c}:n_{\rm Ti}: 3.5)^{583}$ | Sol-gel method | (100 mL) 10 mg L ^{-1 b} | I | | Visible light $(\lambda > 420 \text{ nm})$ | m_{10} $80.31\% (180$ | 0.00831 |
| Chitosan-TiO ₂ -ZnO ⁵⁸⁴ | Sol-gel and ultrasound-assisted method | (50 mL) 20 mg L ^{-1 a} | $0.5 \mathrm{~g~L}^{-1}$ | 4 | UV | min) 97.2% (180 min) | , uim – |
| Palygorskite-supported Cu ₂ O/TiO ₂ ⁵⁸⁵ | Liquid phase reduction method | $30 \text{ mg L}^{-1 b}$ | 1.0 mg | 8.7 | Xenon lamp: 500 W | 88.81% (240 | 0.0129 |
| CuO/Fe ₂ O ₃ ⁵⁸⁶ | Green synthesis | (50 mg L ^{-1 a} | 40 mg | ~ | UV irradiation | 88% (80 | 0.048 |
| Zr _{0.3} Ti/C ⁵⁸⁸ | Calcination | $10 {\rm ~mg~L}^{^{-1}a}$ | I | I | Xenon lamp (300 W) | min) 98% (30 | min 0.84 L |

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Table 8 (continued)

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Table 8 (continued)

| Photocatalyst | Preparative method | CIP ^a /CIP·HCl ^b | Catalyst dose | Hq | Light source | Degradation and time | Rate constant |
|--|---|---|-------------------------|-----|---|---------------------------|--|
| | | | | | | min) | Mol ⁻¹ min ⁻¹ |
| Polymeric g-C ₃ N ₄ ³³³ | Polycondensation | $20 \text{ mg L}^{-1 a}$ | 200 mg | 5.5 | Xenon lamp (35 W) | 86% (240 | |
| g-C ₃ N ₄ nanoflakes ⁵⁸⁹ | Thermal condensation followed by heat | (200 mL) | I | | LED (6 W), <i>λ</i> : 365 nm | mm) 70% (180 …in) | I |
| Self-assembled g- C_3N_4 microsphere ⁵⁹¹ | ureaument Supramolecular self-assembly with | 10 mg $\mathrm{L}^{^{-1}b}$ | 1.0 g L^{-1} | | Xenon lamp: 500 W ($\lambda > 420$ | 80.54% (120 | Ι |
| Porous g-C ₃ N ₄ ⁵⁹² | post-neating treatment Calcination of bulk g-C ₃ N ₄ | $20 \text{ mg L}^{-1 b}$ | 30 mg | 6 | Nenon lamp (300 W) with UV | min) 91.8% (60 | I |
| 0.5 wt% GQDs/g- $C_3N_4^{593}$ | Electrostatic interaction method | (50 mL) 20 mg L ^{-1 b} | 25 mg | | cut-off filter 420 nm 300 W xenon arc lamp, $\lambda >$ | $\sim 67\% (120$ | I |
| S-doped graphitic carbon nitride ⁵⁹⁴ | Thermal induction copolymerization | $30 \text{ mg L}^{-1 a}$ | $0.01~{ m g~L}^{-1}$ | 4 | 400 nm Solar light | min) 93.8% (60 | I |
| h-BN (2.0 mg)/g-C ₃ N ₄ ⁵⁹⁵ | In situ method | $10 \text{ mg L}^{-1 a}$ | $1.0~{ m g~L}^{-1}$ | | Xenon lamp (300 W, $\lambda > 400$ | 79.7% (60 | 0.02775 |
| $POPD/g-C_3N_4^{596}$ | Suspension polymerization | (100 mL) 10 mg L ^{-1 b} (50 mI) | $0.5~{ m g~L}^{-1}$ | | Xenon lamp (300 W) | 86.0% (120 min) | |
| N doped CNT/mpg-C ₃ N ₄ ⁵⁹⁷ | Thermal polycondensation | $20 \text{ mg L}^{-1 b}$ | $1.0~{\rm g~L}^{-1}$ | I | Xenon lamp (300 W) | 67.1% (240 min) | I |
| P,S-doped g-C ₃ N ₄ (hexachloro triphosphazene: 50 mg) ⁵⁹⁸ | In situ thermal copolymerization | $10 { m mg \ L}^{-1 \ a}$ | $1.0~{ m g~L}^{-1}$ | | 300 W xenon lamp, $\lambda > 420$ nm | 85.85% (60 min) | 0.03823 min ⁻¹ |
| Porous g-C ₃ N ₄ /TiO ₂ nanoparticles ⁵⁹⁹ | Reaction carried out under autoclave | $10 \text{ mg L}^{-1 a}$ (70 mL) | 70 mg | 5 | Xenon lamp irradiation | 88.43% (90 min) | I |
| $ m ZrO_2$ nanoparticles@MoS_/g-C_3N_4^{600} | Multiple steps | $20 \text{ mg L}^{-1 a}$ | 50 mg | 3 | Xenon lamp (300 W), $\lambda > 420$ | 94.8% (90 | 0.0230 |
| $PNIPAM/Fe_{3}O_{4}/g-C_{3}N_{4}^{601}$ | Thermal photoinitiation technology | (100 mL) 20 mg L ^{-1 a} | 0.1 g | | Xenon lamp (300 W): visible | $\sim 78\% (120$ | - |
| CDs doped g- $C_3N_4//BiPO_4^{602}$ | Hydrothermal method | (100 mL) 10 mg L ^{-1 b} | $1~{ m g~L}^{-1}$ | 4 | Renon lamp (500 W), under | 75.50% (220 | 0.0005 |
| 20% ZnO/N doped g- $C_3N_4^{603}$ | Self-assembled method through electrostatic | $20 \text{ mgL}^{-1 b}$ | 0.1 mg L^{-1} | | visible light Xenon lamp (300 W) under | min) 81.3% (15 | 0.1016 |
| Red mud modified with graphene oxide | attraction Ultrasonic mixing | (200 mL) 10 mg L ^{-1 a} | 50 mg | 6.9 | VISIDIE LIGHT Xenon lamp (300 W), $\lambda > 420$ | min) 79.8% (80 | 0.02011 |
| (mass ratio: 93 : /) rGO (1.5 wt%) hydroxyapatite microsphere ⁶⁰⁶ | Hydrothermal method | $60 \text{ mg L}^{-1 a}$ | $1.0~{ m g~L}^{-1}$ | 2 | nın Xenon lamp (300 W) with full snectrum irradiation | min) 92.1% (30 min) | 0.1816 min^{-1} |
| Heteropoly acid/GO/UiO-66 ⁶⁰⁷ | In situ growth hydrothermal method | $20 \text{ ppm}^a (50 \text{ m}^3)$ | 0.02 g | 7 | Hg lamp 500 W ($\lambda > 400 \text{ nm}$) | 95% (120 | |
| ${\rm Fe_3O_4/GO/ZnO^{608}}$ | Dispersion, followed by hydrothermal treatment | 111L 50 mg L ^{-1 b} | 1 mg L^{-1} | I | Under simulated light irradiation (intensity: 1 kW | 74% (100 min) | 14×10^{-3} min ⁻¹ |
| CODe (1 m1)/7n0_7mEa O 609 | Ona-stan danssition mosass | 30 mor I $^{-1}$ b | 30 mg (50 mI) | | m^{-2}) Vence lown (500 m) counted | 2010,000 | |
| 64D8 (1 1111)/2110-211.6204 | one-step deposition process | 70 III DZ | (TIII AC) SIII AZ | | with 420 nm cut-off filter | ~90% (2/ min) | min ⁻ |
| $rGO/ZnTe(1:1)^{610}$ | Single-pot one-step solvothermal process | $10 \text{ mg L}^{-1 a}$ | 100 mg (50 mL) | | Solar simulator (AM 1.5, 100 mW cm ⁻²) | \sim 70% (40 min) | 0.033 min ⁻¹ |
| N doped-TiO ₂ /rGO ⁶¹¹ | Photoreduction method | $10 { m ~mg~L}^{-1 b}$ | 50 mg | | Xenon arc lamp (300 W) with | 98% (60 min) | 0.05655 min ⁻¹ |
| 1.5 w% ZnO quantum dots/rGO ⁶¹² | Precipitation and hydrothermal methods | $20 \text{ ppm}^a (50 \text{ ml})$ | 50 mg L^{-1} | c) | Non halogen lamps (24 V, 250 W) | 68% (120 min) | 0.00961 min ⁻¹ |

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| Photocatalyst | Preparative method | $\mathrm{CIP}^a/\mathrm{CIP}\mathbf{\cdot}\mathrm{HCl}^b$ | Catalyst dose | Hq | Light source | Degradation and time | Rate constant |
|---|--|---|---------------------------|--------|--|----------------------------|---|
| ${\rm Fe_3O_4/g-C_3N_4/rGO^{613}}$ | Ultrasonic dispersion | 20 mg $L^{-1 b}$ (100 ml L^{-1}) | 0.1 g | ~ | Xenon lamp (500 W) | 86.7% (60 min) | 0.0306 min ⁻¹ |
| rGO/CdWO ₄ ⁶¹⁴ | Heating method | $13.54 \text{ mg}_{1^{-1a}}$ | $0.216~{\rm g~L}^{-1}$ | 5.7 | Simulated solar light | 100% (60 min) | 0.0693 min ⁻¹ |
| rGO/CdS ⁶¹⁷ | Solvothermal | 0.08 mmole^{a} | 40 mg | | Solar light | 83.25% (16 | 0.13 |
| Ag/TiO ₂ /rGO ⁶¹⁸ | Ultrasonic impregnation assisted | (40 mm) 20 mg L ^{-1 a} (50 mJ) | $1~{ m g~L}^{-1}$ | Ч | Hg lamp (300 W), $\lambda < 400~\mathrm{nm}$ | $\sim 100\% (60$ | 0.1578 |
| TiO ₂ /rGO/activated carbon ⁶²¹ | photoreuteron strategy Hydrothermal method | $5 \times 10^{-4} \mathrm{M}^{b}$ | $2.0~{ m g~L}^{-1}$ | I | Xenon lamp (solar simulator) | $\sim 95\% (100$ | 0.0286 |
| Core–shell g-C ₃ N ₄ @Co–TiO ₂ ⁶²² | Electrospinning approach/thermal | 20 mg $L^{-1 b}$ | $2 \times 2 \text{ cm}^2$ | 4 | Xenon lamp (300 W), $\lambda > 420$ | 90.8% (60 min) | 0.038 min^{-1} |
| Hierarchical 2% Au-g-C ₃ N ₄ -ZnO ⁶²³ | <i>In situ</i> preparation of g-C ₃ N ₄ ZnO nanorods on <i>g</i> -C ₃ N ₄ nonosheets and the deposition of Au | (10 mL) 50 mg L ^{-1 a} (50 mL) | 10 mg | 9.3 | Xenon lamp | 74.7% (30 min) | 3.998×10^{-2} |
| Mesoporous TiO ₂ -modified ZnO QDs immobilized on 11 DDF ⁶²⁴ | nanopartuctes Casting method | 40 mg $L^{-1 a}$ | I | 6 | Fluorescent lamp: 48 W | 89.5% (90 min) | 0.01312 min ⁻¹ |
| 7% CuO/g-C ₃ N ₄ ⁶²⁵ | Dispersion method | $50 \text{ mg}^{b} (1000)$ | 0.2 g | | Xenon lamp (500 W), $\lambda > 365$ | 55% (60 | 0.014 |
| ZnO globular (15 wt%)/g- $C_3N_4^{626}$ | In situ growth | mL) 20 mg $L^{-1 a}$ | 20 mg | | nm PLS-SXE300 (300 W), L.I: 9.6 | min) 78.4% (50 | , uim – |
| ZnO (20 wt%)/GO (2 wt%)/Ag_3PO_4^{628} | Ultrasonic-assisted precipitation method | (100 mL) 30 mg L ^{-1 b} | $1.0~{\rm g~L}^{-1}$ | 9 | w m ⁻ , 400–780 nm Visible lamp: 65 W | min) 96.32% | I |
| $g-C_3N_4/C/Fe_3O_4^{629}$ | Sonication and <i>in situ</i> precipitation technique | (50 mL) 10 mg L ^{-1 a} (40 mT) | 10 mg | Ι | Xenon lamp (500 W) | 96.4% (120 | 0.0292 |
| Core–shell BiFeO ₃ /TiO ₂ ⁶³⁰ | Hydrolysis and precipitation method | (40 mL) 20 mg L ^{-1 a} | $1~{ m g~L}^{-1}$ | D. | UV light | 67.9% (180 | - |
| Core–shell BiFeO ₃ /TiO ₂ ⁶³⁰ | Hydrolysis and precipitation method | (300 mL) 20 mg L ^{-1 a} | $1~{ m g~L}^{-1}$ | 2 J | Visible light | min) 72.2% (180 min) | I |
| Fiber-shaped $\rm Ag_2O/Ta_3N_5$ (molar ratios: $0.3/1)^{631}$ | Electrospinning-calcination-nitridation method, followed by <i>in situ</i> anchoring of Ag ₂ O | $(10 \text{ mg L}^{-1 a})$ | I | | Xenon lamp (300 W), $\lambda > 400$ nm | mm) 78.3% (60 min) | 0.0079 min ⁻¹ |
| BiVO4/TiO2/rGO ⁶³³ | ue position Reaction under Teflon reactor | 10 $\mu \mathrm{g} \ \mathrm{L}^{^{-1} a}$ | Ι | | Xenon lamp (1000 W), $\lambda > 420$ | 96.2% (120 min) | 0.02613 min ⁻¹ |
| g-C ₃ N ₄ /AgBr/rGO ⁶³⁴ | Mixing followed by heating | $20 \text{ mg L}^{-1 a}$ | 0.05 g (100 mL) | Ι | Xenon lamp (250 W) | 78.4% (90 min) | |
| $\mathrm{C}_{3}\mathrm{N}_{4}$ (2) MnFe $_{2}\mathrm{O}_{4}$ -rGO (491 | Impregnation approach | $20 \text{ mg L}^{-1 a}$ (50 mL) + PS | 50 mg | I | Xenon lamp (300 W) with 400 nm cut-off filter | 94.5% (60 min) | 0.0337 min ⁻¹ |
| BiOl/exfoliated C_3N_4 (mass ratio: 0.4) ⁶³⁶ | Combination of thermal exfoliation and | $20 \text{ mg L}^{-1 a}$ | $1.0~{ m g~L}^{-1}$ | 9 | Xenon lamp (500 W) with 420 | 86% (30 | 0.0705 min ⁻¹ |
| 3.0 wt% CuO@ZnO ⁶³⁷ | One-pot method | 20 ppm^a | $1.5~{ m g~L}^{-1}$ | | Xenon lamp (300 W), λ_{cutoff} : 420 nm, 45.2 mW cm ⁻² | 100% (45 min) | 113.50×10^{-3} min ⁻¹ |
| ZnO/5 wt% SnO ₂ ⁶³⁸ | Solvothermal process | $1 \mathrm{g} \mathrm{L}^{-1 b} (100 \mathrm{mm})$ | 60 mg | I | Xenon lamp (300 W), <i>λ</i> : | $\sim 90\%$ (60 | 0.0385 |
| Cu ₂ O-TiO ₂ ⁶³⁹ | Surfactant-free preparation method (TiO ₂ : C_{15} , $O = 0.4 \cdot 0.2 \cdot 0.3$) | $50 \text{ mg}^a (100 \text{ mL})$ | 30 mg | I | Xenon lamp (300 W) | 91% (60 min) | 0.0432 min ⁻¹ |
| 10 wt% $MoS_2/Ag/g$ - $C_3N_4^{640}$ | Ag deposition and MoS ₂ coupling is applied co-modify g-C ₃ N ₄ nanosheets | 20 mg L ^{-1 a} (50 mL) | 10 mg | 5.5 | Xenon lamp (300 W), $\lambda > 420$ nm | 90.1% (30 min) | 0.0507 min ⁻¹ |

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Table 8 (continued)

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Table 8 (continued)

| Photocatalyst | Preparative method | CIP ^a /CIP·HCl ^b | Catalyst dose | Hd | Light source | Degradation and time | Rate constant |
|---|---|--|----------------------|------|--|----------------------------|--|
| g-C ₃ N ₄ (7.1 wt%)/ZrO _{2-x} ⁶⁴¹ | Anodic oxidation and thermal deposition method (0.06 g melamine taken) | 10 ppm ^b (5 mL) | 2 mg | | Xenon lamp (300 W), $\lambda > 420$ nm | 90.6% (60 min) | 0.0474 ${ m min}^{-1}$ |
| 3 wt% needle SnO ₂ needle nanoparticles anchored on exfoliated e-C,N, ⁶⁴² | Hydrothermal method | $30 mg L^{-1 a}$ (100 ml) | 50 mg | | Xenon lamp (250 W) with a cut-of filter of 420 nm | 95.90% (120 min) | 0.0205 min ⁻¹ |
| s 35.14 N-doped ZnO nanorods-MoS2 nanoflowers (1 wt% MoS2 loaded in N-ZnO) ⁶⁴³ | Hydrothermal strategy | $0.01 { m ~g~L}^{-1 a}$ | 25 mg (50 mL) | | CFL lamp (45 W), $\lambda \ge 420 \text{ nm}$ | 84% (120 min) | 14.43×10^{-3} min ⁻¹ |
| $WO_3/g-C_3N_4^{644}$ | In situ hydrolysis and polymerization process | 25 mg $L^{-1 b}$ (100 mL) | 50 mg | | Xenon lamp (300 W) with a 420 nm cut-off filter | 82% (120 min) | 0.0164 min ⁻¹ |
| Sn_3O_4/g - C_3N_4 (with load ratio of 3%) ⁶⁴⁵ | Two-step hydrothermal process | $10 \text{ mg L}^{-1 b}$ | 50 mg | | Xenon lamp (500 W) | 72.2% (120 min) | 0.0108 min ⁻¹ |
| BiOI/g-C ₃ N ₄ /CeO ₂ (3 wt%) ⁶⁴⁶ | Calcination and hydrothermal treatment | $20 \text{ mg L}^{-1 a}$ | 50 mg | | Xenon lamp (300 W), $\lambda > 420$ | 91.6% (120 | 0.0205 |
| ${ m TiO}_{2-x}/{ m g-C_3N_4}^{647}$ | Grinding and <i>in situ</i> reduction | $10 \text{ mg L}^{-1 b}$ (50 mL) | 50 mg | 6 | Xeon-lamp (300 W), $\lambda > 420$ nm | 87.7% (90 min) | 31.7×10^{-3} |
| K doped g-C ₃ N ₄ /TiO ₂ /CdS ⁶⁴⁸ | Hydrothermal method | $20 \text{ mg L}^{-1 a}$ | 50 mg | | Xenon lamp (300 W), $\lambda > 420$ | 94.2% (30 min) | 0.08554 min ⁻¹ |
| γ -Fe $_2$ O $_3$ nanospheres (5%) anchored on m -C M $_{649}^{649}$ | Anchoring mesoporous γ -Fe ₂ O ₃ nanospheres on α -C.N. nanoshaet surface | $10 \text{ mg L}^{-1 b}$ | 50 mg | | Xenon light source (500 W) with 420 nm out-off filter | 73.8% (120 min) | 0.0134 |
| g-03114 0.50 wt% CQDs/g-C ₃ N ₄ ⁶⁵⁰ | Un g varva nanosneet surrace Low-temperature process | $10 \text{ mg L}^{-1 b}$ | 50 mg | | Xenon lamp (250 W) with 420 | 78.6% (210 | ~ 0.0065 |
| BiOBr/MoS ₂ /graphene oxide ⁶⁵² | Hydrolysis method | (100 mL) 10 mg L ^{-1 b} | 25 mg | I | The UV-cut-off filter Xenon lamp (300 W) with | min) >98% (40 | 0.04277 |
| $\mathrm{g}\mathrm{-C}_3\mathrm{N}_4/\mathrm{MnO}_2/\mathrm{GO}^{653}$ | Wet-chemical method | 10 mg L^{-1} ^b | $0.5~{\rm g~L}^{-1}$ | 9 | 380-nm cut-off filter Xenon lamp (300 W) with a | m_{11}) 91.4% (90 | , uim – |
| $BiVO_4 @Polypyrrole/g-C_3 N_4^{654}$ | Dispersion method | (100 mL) 30 mg L ^{-1 a} | 30 mg | | 420 nm filter Xenon lamp (300 W), $\lambda > 420$ | min) 90% (120 | |
| AgI/BiOBr/rGO ⁶⁵⁵ | Solvothermal method followed by <i>in situ</i> | (50 mL) 20 mg L ^{-1 a} | 50 mg | I | nm Xenon lamp (5.00 W), | min) 94.2% (80 | 0.018 |
| Ag/Ag ₃ PO ₄ /BiVO ₄ /rGO ⁶⁵⁶ | precipitation <i>In situ</i> deposition method followed by nhoto-reduction | (100 mL) 10 mg $\mathrm{L}^{-1 a}$ | $0.5~{ m g~L}^{-1}$ | 6.75 | simulated sunlight Xenon lamp (300 W) | min) 94.96% (60 min) | min ⁻ |
| g-C ₃ N ₄ /WO ₃ ⁶⁵⁷ | Dispersion method | $10 \text{ mg L}^{-1 b}$ | 40 mg | | Xenon lamp (500 W), 320–780 nm $100 \text{ mW} cm^{-2}$ | 79.8% (180 min) | |
| (50%)CuIn ₂ S ₄ /g-C ₃ N ₄ ⁶⁵⁸ | Synthesis under autoclave | $20 \text{ mg L}^{-1 a}$ | $0.5~{ m g~L}^{-1}$ | Ι | Xenon lamp (300 W), $\lambda > 420$ nm cut-off filter | 83.7% (60 min) | 0.02583 min ⁻¹ |
| ${\rm TiO}_2/{\rm g}{\rm -C}_3{\rm N}_4^{662}$ | Co-annealing process | $\begin{array}{c} \begin{array}{c} 1 \\ 20 \\ 10 \\ \end{array} \\ \begin{array}{c} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 $ | 250 mg | М | Xenon lamp (150 W) | 99.40% (120 min) | 3.70×10^{-4} min ⁻¹ |

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the removal of diclofenac sodium from wastewater under UV irradiation.⁶⁶⁹ Schulze-Hennings et al.⁶⁷⁰ studied the durability of the coating containing TiO₂ on glass for the photocatalytic degradation of diclofenac sodium in water using UVA irradiation. The effectiveness of ZnO and V2O5 has also been tested in the photocatalytic degradation of diclofenac sodium in water under solar and UV irradiation.671 The emerging findings indicated 100% photodegradation efficiency for V2O5 compared to ZnO under UV and solar irradiation corresponding to the initial DCF concentration of 300 mg L^{-1} , catalyst dosage of 1.0 g L^{-1} and pH 4. The relatively higher rate constant values of V₂O₅ under UV (k: 0.0196 min⁻¹) and solar (k: 0.0141 min⁻¹) irradiation compared to the corresponding values for ZnO in the photodegradation of DCF also supported this. In another report, investigations were made to study the factors affecting diclofenac decomposition in water by UVA/TiO2 photocatalysis.⁶⁷² According to Bagal et al.,⁶⁷³ UV/TiO₂/H₂O₂ fabricated by a hydrodynamic cavitation approach showed 95% degradation of diclofenac sodium under the optimized operating conditions.

ZnO showed highly photodegradation of active diclofenac sodium in aqueous solution under UV lamp irradiation compared to solar radiation.⁶⁷⁴ Mimouni et al.675 investigated the effect of heat treatment on the photocatalytic activity of α -Fe₂O₃ nanoparticles towards diclofenac elimination. The findings in Fig. 22(a) and (b) show the highest degradation for α -Fe₂O₃ (calcinated at 300 °C) and the value of the degradation rate constant corresponds to 0.060 min⁻¹. The generation of extremely active OH· radicals is responsible for the total photodegradation of DCF, as schematically described in Fig. 22(c). Meroni et al.676 achieved 70% degradation of diclofenac (25 ppm) by a piezo-enhanced sonophotocatalytic approach based on ZnO (0.1 g L⁻¹) subjected to UV-light irradiation for 360 min. In addition, ZnO modified with



Fig. 22 (a) Conversion plots for photodegradation of DCF in the presence of α -Fe₂O₃ calcinated at different temperatures. (b) The degradation rate of different samples at 120 min. (c) Schematic presentation on the generation of OH· radicals in α -Fe₂O₃. Reproduced from ref. 675 with permission from Springer (2022).

rare earth elements (Ce, Yb) and Fe,⁶⁷⁷ Ni_xZn_{1-x} Fe₂O₄ (x = 0, 0.3, 0.7),⁶⁷⁸ cobalt ferrite,⁶⁷⁹ MgO,⁶⁸⁰ and WO₃⁶⁸¹ photocatalysts have also been investigated for the removal of diclofenac from aqueous solution.

3.8.2 Metal-metal oxides. Chakhtouna and coworkers682 reviewed the role of Ag nanoparticles in enhancing the photocatalytic activity of Ag/TiO2 in the removal of pharmaceutical pollutants from aqueous solutions under UV and visible light. Espino-Estévez et al.⁶⁸³ synthesized Ag and Pd nanocomposites of TiO₂ (TiO₂-Ag and TiO₂-Pd) by a solgel method and observed almost 100% (120 min) photocatalytic degradation of diclofenac sodium salt in water under a UV light source. It was also noted that photocatalytic degradation of DCF follows first-order kinetics. In another study, Ag@Ag₂O/WO₃ and Ag@Ag₂S/WO₃ were prepared by following a deposition hydrothermal route and used as photocatalysts.684 Subsequent studies have shown high degradation of DCF (60 mg L⁻¹, pH: 12) in the presence of H_2O_2 (1 × 10⁻⁴ M) under visible light ($\lambda > 420$ nm, 160 W) in the presence of Ag@Ag₂O/WO₃ ($k = 32.0 \times 10^{-3} \text{ min}^{-1}$) and Ag@Ag₂S/WO₃ ($k = 7.3 \times 10^{-3} \text{ min}^{-1}$) catalysts. Further investigations have also revealed that $\cdot O_2^-$ plays an important role in the degradation of DCF.

3.8.3 Doped metal oxides. Nguyen et al. 685 removed diclofenac from wastewater using a submerged photocatalytic membrane reactor comprising immobilized N-TiO2 under visible irradiation. It was also noted that DCF removal efficiency is enhanced under visible irradiation by coupling H_2O_2 with the photocatalytic process. C-doped TiO₂ synthesized by a microwave digestion method showed almost complete removal of diclofenac after about 160 min under visible light corresponding to diclofenac concentration of 50 mg L⁻¹, catalyst concentration of 250 mg L⁻¹ and light intensity of 8000 lx.686 The doping of titania with 25 wt% Mg resulted in 55% and 48% degradation of diclofenac sodium under UV and visible irradiation, respectively.95 An Mn (0.6 mol%) and Ag (0.5 mol%) co-doped TiO₂ aerogel exhibited 86% removal of diclofenac under UVA-light irradiation after 4 h.687 The photodegradation rates followed first-order kinetics with a highest apparent rate constant of 0.0064 min^{-1} .

The photocatalytic performance of a sodium diclofenac solution (pH: 6.5) in F-doped (20 wt%) ZnO under simulated solar radiation indicated the complete degradation of diclofenac sodium of concentration: 10 mg L^{-1} under the optimized experimental conditions (ZnO-F concentration: 1 g L^{-1}).⁶⁸⁸ The enhanced photocatalytic activity of F-doped TiO₂ is ascribed to the reduction in the recombination rate of electron-hole pairs. In another similar study, fluorine (0.25, 0.5 and 1 at%)-doped ZnO nano- and meso-crystalline ZnO showed high rates of diclofenac degradation in water compared to bare ZnO.689 Chaudhari and others690 used a sol-gel method to prepare Mn/CeO2, Cu/CeO2 Ag/CeO2 (metal semiconductors) and Agl/CeO₂ (an n-p semiconductorsemiconductor) by doping with Mn, Cu, Ag and AgI, respectively. Further investigations have been made to compare their photocatalytic degradation for diclofenac

sodium in water under the same optimal conditions (pH: 7, diclofenac concentration: 10 ppm) within 90 min exposure to UV light. It is noted that AgI-doped CeO₂ (1 g L⁻¹) exhibited higher degradation of diclofenac sodium solution (95%) compared to Mn/CeO₂, Cu/CeO₂ or Ag/CeO₂, such enhancement in the photocatalytic activity of AgI/CeO₂ is attributed to its larger surface area and charge separation efficiency.

In addition, Ce@TiO₂,⁶⁹¹ granular activated carbon modified with N-doped TiO₂,⁶⁹² C,N-co-doped TiO₂,⁶⁹³ Ce, Mn-co-doped TiO₂,⁶⁹⁴ N,S-co-doped carbon quantum dots/TiO₂,⁶⁹⁵ TiO₂ doped with B, F, N, P,⁶⁹⁶ and S,N,C-tri-doped TiO₂⁶⁹⁷ photocatalysts have been investigated for the removal of diclofenac from aqueous solution.

3.8.4 Metal oxide composites. Alalm et al.¹⁸² investigated the solar photocatalytic degradation of pharmaceuticals, namely amoxicillin, diclofenac, and paracetamol, using TiO₂ immobilized on powdered activated carbon (TiO₂/AC). According to this, degradation corresponding to the initial concentration of pharmaceuticals of 50 mg L⁻¹ and TiO₂/AC dosage of 1.2 g L^{-1} followed the order: amoxicillin (100%: in 120 min) > diclofenac (83% beyond 180 min) > paracetamol (70% in 180 min). TiO₂-WO₃ (molar ratio: 10:1) synthesized by a hydrothermal method was the most effective catalyst in the photocatalytic removal of diclofenac under visible-light irradiation compared to pure TiO2.698 The composite catalyst successfully degraded diclofenac almost completely in 270 min corresponding to pH 5, initial diclofenac concentration of 25 mg L^{-1} and catalyst concentration of 0.6 g L^{-1} . Subsequent studies showed the catalyst retained 80% catalyst efficiency after four consecutive reaction cycles. N-doped WO₃/TiO₂ synthesized by a sol-gel method enhanced the degradation of diclofenac sodium using simulated solar light owing to the synergistic effect and narrowing of the bandgap.⁶⁹⁹ The visible-light-irradiated photocatalytic degradation of diclofenac sodium using ZnO-WO₃ has shown better catalytic activity than bare ZnO.700 These studies revealed ZnO-WO₃ (Zn:W mole ratio: $\approx 10:1$) exhibiting ~76% degradation efficiency at a given pH (6), DCF diclofenac concentration (20 mg L⁻¹) and catalyst loading (0.8 $g L^{-1}$).

Cordero-García *et al.*⁷⁰¹ studied the effect of carbon doping on WO₃/TiO₂ on the photocatalytic degradation of diclofenac sodium and observed its higher photocatalytic activity compared to WO₃/TiO₂ and TiO₂. Hydroxyapatite/TiO₂ (dose: 4 g L⁻¹) in water degraded DCF (initial concentration: 5 ppm) by 95% in 24 h on irradiating it with simulated solar light.⁷⁰² According to Sun *et al.*,⁷⁰³ the intensity of UV irradiation plays a more significant role in the significant removal of diclofenac by a nano-TiO₂/diatomite composite in a photocatalytic reactor. According to this, diclofenac degraded completely at 30 min under higher UV irradiation intensity at a flux of 3.0 L h⁻¹. A visible-light-responsive TiO₂/ Ag₃PO₄ (10:1) nanocomposite immobilized in a spherical polymeric matrix showed almost complete removal of diclofenac (*k*: 0.018 min⁻¹) in 120 min corresponding to initial drug concentration of 20 mg L^{-1} bead loading of 10 g L^{-1} , and reaction volume of 0.8 $L^{.704}$ The ·OH radical and h⁺ are reported to be the primary reactive oxygen species in the photodegradation of diclofenac.

Ag-Ag₂O/reduced An TiO_2 nanophotocatalyst demonstrated 99.8% degradation of diclofenac after 50 min of visible irradiation.⁷⁰⁵ This is attributed to the effective charge separation, enhanced visible light absorbance and localized SPR of nanocrystalline Ag⁰. Silvestri et al.⁷⁰⁶ synthesized PPy-ZnO (25:1) via a polymerization method and studied the degradation of DCF under simulated solar light. In this regard, the composite catalyst $(1 \text{ g } \text{L}^{-1})$ facilitated 81% (60 min) degradation of diclofenac (10 mg L^{-1}) with h^+ the main reactive species involved in the reaction. This performance is ascribed to the mesoporous structure, superior surface area and reduced band gap of PPy-ZnO. According to Das et al.,⁷⁰⁷ a titania-zirconia (Zr/Ti mass ratio of 11.8 wt%) composite catalyst exhibited a reasonably higher removal of DCF (\sim 92.41%) compared to the anatase form of titania without zirconia.

Attempts have been made to eliminate diclofenac sodium from wastewater through the photocatalytic degradation of hydrothermally prepared TiO₂–SnO₂ (Ti–Sn molar ratio: 1:1, 5:1, 10:1, 20:1 and 30:1) under various operating conditions.⁷⁰⁸ The results indicated the TiO₂–SnO₂ catalyst with a molar ratio of 20:1 to be the most effective photocatalyst compared to the other binary composites. The catalyst achieved complete degradation of diclofenac under optimum conditions comprising initial drug concentration of 20 mg L⁻¹, catalyst loading of 0.8 g L⁻¹ and pH 5. The photocatalyst also displayed excellent repeatability and better stability over repeated reaction cycles. Fe₃O₄/Ti_xO_y/activated carbon,⁷⁰⁹ Fe₃O₄ (nanosphere)/Bi₂S₃ (nanorod)/BiOBr (nanosheet)⁷¹⁰ TiO₂@ZnFe₂O₄/Pd,⁷¹¹ nanotubular titanium







Fig. 23 (a) C_t/C_0 versus time plots of different photocatalysts. (b) Respective kinetic curves (inset) and apparent reaction rate constants of diclofenac (conditions: $[DCF]_0 = 10 \text{ mg } L^{-1}$, $[Catal.] = 1 \text{ g } L^{-1}$, no pH adjustment and pH_{initial} = 5.05) and (c) possible mechanism for the photodegradation of DCF and CBZ under LED lamp irradiation over 30% BCCNT composites. Reproduced from ref. 719 with permission from Elsevier (2019).

dioxide–polyethersulfone (PES) membrane,⁷¹² $A_{l2}O_{3}$ – Nd_2O_3 ,⁷¹³ and TiO_2 –zeolite⁷¹⁴ based photocatalysts have also been evaluated for the photocatalytic degradation of diclofenac.

3.8.5 Graphitic materials

3.8.5.1 g- C_3N_4 and its composites. Carbon quantum dot (CQD)-modified porous $g-C_3N_4$ (dose: 200 mg L⁻¹) synthesized using 20 mL of CQD stock solution showed almost complete degradation of diclofenac solution (pH: 9) of an initial concentration of 10 mg L⁻¹ in 12 min under visible light.⁷¹⁵ This is attributed to the tuning of the band structure and enhanced separation of charge carriers. The studies also suggested DCF degradation to be dominated by a mechanism. photosensitization-like The CQD/g-C₃N₄ photocatalyst also exhibited excellent reusability, as evident from studies in the 5th cycle (>90%). Pd quantum dots (1 wt%) deposited on g-C₃N₄ (dose: 0.5 g L^{-1}) achieved 100% removal of diclofenac solution (initial concentration: 1 mg L^{-1} , pH: 7) within 15 min under solar light.⁷¹⁶ The rate constant (0.72 min⁻¹) was found to be 8 times higher than that of g-C₃N₄. Such enhanced photocatalytic activity has been explained based on its narrowed bandgap, reduction in the recombination of photogenerated charge carriers and availability of a photosensitization-like electron transfer pathway.

Graphite-like C₃N₄-modified Ag_3PO_4 nanoparticles exhibited highly enhanced photocatalytic activity under visible-light irradiation owing to the synergistic effect.⁷¹⁷ This is mainly ascribed to the matching band potentials between Ag₃PO₄ and g-C₃N₄, effectively suppressing recombination of electron-hole pairs and promoting their separation efficiency. Diclofenac sodium and ibuprofen (5 mg L^{-1}) achieved complete degradation (180 min) in the presence of carbon microspheres (dia: 0.9-1.9 µm) supported on an anatase phase of TiO_2 (mass ratio TiO_2 to C microspheres: 2) heterostructure photocatalyst under solar light.⁷¹⁸ Further studies revealed the high performance of the photocatalyst even after five successive cycles (80%) as evident from the findings in the first cycle (94%).

Hu *et al.*⁷¹⁹ fabricated eco-friendly 2D heterojunction photocatalyst composites (BCCNT) comprising C-doped supramolecule based g-C₃N₄ (BCCN) layers and TiO₂ nanoparticles and corresponding findings are displayed in Fig. 23(a). It should be noted that degradation of diclofenac solution (10 mg L⁻¹, initial pH: 5.05) by 1 g L⁻¹ of 30% C-doped supramolecular based g-C₃N₄ (BCCNT) reached 98.92% within 30 min under LED lamp illumination owing to \cdot O₂⁻ and h⁺ as the main active species. Further investigations established that the degradation kinetics of DCF fitted the pseudo-first-order equation (Fig. 23(b)) with an apparent reaction rate constant (k_{app} : 0.1796 min⁻¹) about 29.4 times higher than BCCN (0.0061 min⁻¹). A possible mechanism for the photodegradation of DCF under LED lamp irradiation is also displayed in Fig. 23(c).

An AgI/gC_3N_4 (AgI molar mass ratio: 45%) composite photocatalyst exhibited almost complete degradation of

diclofenac sodium in 6 min under visible-light irradiation compared to AgI and g-C₃N₄.⁷²⁰ The reaction rate constant value of AgI/gC₃N₄ (k: 0.561 min⁻¹) was found to be ~12.5 and 43.2 times higher than those achieved by AgI (0.045 min^{-1}) and $g-C_3N_4$ (0.013 min^{-1}). The photocatalytic degradation of diclofenac was guided by photogenerated holes and superoxide anion radicals as the main reactive species. Such enhanced photocatalytic activity of AgI/g-C₃N₄ is ascribed to the heterojunction between g-C₃N₄ and AgI that facilitated interfacial charge transfer and prevented the recombination of electron-hole pairs. Ag/g-C₃N₄ (mass ratio of Ag: 54%) heterostructure photocatalysts prepared by photodeposition under ambient conditions showed complete degradation of DCF compared to g-C₃N₄ under visible-light irradiation and followed pseudo-first-order kinetics. The rate constant was $k = 0.0429 \text{ min}^{-1.721}$ The rate constant of diclofenac degradation over Ag/g-C3N4 was almost 3.1 times higher than that of pure g-C₃N₄. Further investigations also revealed generated holes as the main reactive species in diclofenac degradation and also established the excellent stability of Ag/g-C₃N₄. CNT-Ni@TiO₂:W nanoparticles⁷²² and C₃N₄/NH₂-MIL-125 (ref. 723) have also shown remarkable performance in the removal of diclofenac present in water.

3.8.5.2 Graphene composites. The removal of diclofenac (and amoxicillin) has been reported by maltodextrin/reduced graphene and maltodextrin/reduced graphene/copper oxide nanocomposites.⁷²⁴ Kovacic *et al.*⁷²⁵ fabricated S-doped TiO₂/ rGO by a one-pot solvothermal method to study the removal of diclofenac sodium in aqueous medium (pH 4) under simulated solar irradiation. These findings revealed strong dependence on rGO loading of the photocatalytic performance of S-TiO₂/rGO in the degradation of DCF. Accordingly, 5 wt% rGO in TiO₂ showed improved diclofenac photocatalytic activity compared to bare TiO₂ owing to the effective photogenerated charge separation, as inferred from a photoluminescence study. John et al.726 investigated sunlight-mediated removal of diclofenac sodium from water (25 mg L^{-1}) using TiO₂-reduced graphene oxide (75 mg L^{-1}) and persulfate (20 mg L⁻¹). They achieved an efficiency of more than 98% within 30 min under sunlight illumination. The diclofenac degradation followed the Langmuir-Hinshelwood mechanism and pseudo-first-order kinetics with a pseudo-first-order rate constant (99.4 \times 10³ min⁻¹) about twice that of TiO_2 -rGO (50.9 × 10⁻³ min⁻¹). A hydrothermally synthesized BiOCl-GO composite showed 100% and 47.88% removal of DCF from solution (25 mg L^{-1}) under UV light and visible spectrum solar light, respectively.727 Li et al.728 also used a hydrothermal method to synthesize an Ag-BiOI-rGO nanocomposite. They observed the complete removal of diclofenac (10.0 mg mL⁻¹) by 5 mol% Ag-BiOI-rGO (5 wt%) in 80 min under visible-light irradiation compared to pure BiOI, Ag-BiOI or BiOI-rGO photocatalysts (50 mg in 50 mL). This is attributed to the enhanced charge separation and reduced recombination of photogenerated charge carriers due to Ag and rGO in BiOCl. Other studies reported ~93% decomposition of diclofenac

sodium (25 mg L⁻¹) solution (pH: 6) within 6 min by cubic Ag/AgBr/GO (0.030 g) on illumination with sunlight.⁷²⁹ It is suggested that the large surface area of the catalyst as well as the superior charge separation and transfer efficiency accounted for this. UV-light-assisted activation of persulfate by rGO-Cu₃BiS₃ (30 mg) reportedly achieved 81% degradation of DCF in 60 min.⁷³⁰ An AgFeO₂-graphene/Cu₂(BTC)₃ MOF heterojunction has also been studied under sunlight for the degradation of diclofenac in aqueous solution.²⁰⁹

3.8.6 Heterojunctions, S- and Z-scheme-based composites. Co₃O₄/WO₃ nanocomposites were fabricated by dispersing WO_3 in a solution of cobalt acetate (pH: 7) followed by heating at 90 °C.731 It showed 90.8% degradation of diclofenac sodium salt (15 ppm) solution (pH: 10.7) under visible-light irradiation. According to this, the formation of a monoclinic phase of WO₃ and a p-n heterojunction maximizing the generation of non-selective OH radicals and reducing electron-hole pair combination and the strong absorption of visible light account for such a performance. A Fe₃O₄(a)SrTiO₃/Bi₄O₅I₂ solar-active heterojunction photocatalyst imparted 98.4% diclofenac removal in 90 min under simulated solar-light irradiation.732 A vis-NIR-driven Sscheme, an WO_{3-x}/S-doped g-C₃N₄ nanocomposite, exhibited ~99.5% degradation rate for diclofenac. 733 g-C_3N_4/BaBiO_3 heterojunctions contributed enhanced photocatalysis of diclofenac sodium under visible light through interfacial charge transfer.734 The photocatalytic activity of g-C3N4/ BaBiO₃ is reported to be 6.5 and 5 times higher than BaBiO₃ and g-C₃N₄, respectively. Visible-light-responsive N,S-co-TiO2@MoS2,735 S,B-co-doped doped g-C₃N₄ nanotube@MnO2,736 oxygen-doped-g-C₃N₄/ZnO/ TiO₂@halloysite nanotubes,⁷³⁷ and Pt-TiO₂-Nb₂O₅⁷³⁸ also displayed enhanced photocatalytic degradation of diclofenac.

The optimal BiOCl/CuBi₂O₄ exhibited a 90% degradation rate for aqueous DCF in 60 min under visible-light irradiation.⁷³⁹ The degradation followed pseudo-first-order kinetics (*k*: 0.03539 min⁻¹), much higher than CuBi₂O₄ (*k*: 0.00139 min⁻¹) or BiOCl (*k*: 0.00319 min⁻¹). Such enhanced photocatalytic performance of BiOCl/CuBi₂O₄ is most likely to be due to the upgraded charge separation and transfer caused by the formation of an S-scheme heterojunction and the presence of oxygen vacancies. Chen *et al.*⁷⁴⁰ investigated the photocatalytic performance and mechanism of a Z-scheme CuBi₂O₄/Ag₃PO₄ photocatalyst in the degradation of diclofenac sodium under visible-light irradiation. Studies have also been reported on Z-scheme CuBi₂O₄/Ag₃PO₄ to study the effects of pH, H₂O₂, and S₂O₈²⁻ on the visible-light driven degradation of diclofenac sodium.⁷⁴¹

Visible-light-driven $\text{TiO}_2/\text{g-C}_3\text{N}_4$ achieved maximum degradation efficiency (93.49%) for the removal of diclofenac sodium from aqueous solution (5 ppm) and the process followed pseudo-first-order kinetics.⁷⁴² Such a Z-scheme photocatalyst successfully prevents the fast recombination of electron-hole pairs. Elangovan and others⁷⁴³ prepared a TiO₂-CdS heterojunction following a two-step hydrothermal

treatment. Subsequent use of this as a photocatalyst achieved 86% diclofenac degradation within 4 h under visible-light irradiation. It was suggested that the direct Z-scheme heterojunction structure accounts for the direct charge transfer between heterojunction catalysts. Investigations of a TiO₂–CdS photocatalyst in five successive reaction cycles established its appreciable photochemical stability and reusability. $ZnSnO_3/Bi_2WO_6$,⁷⁴⁴ $Ag_3PO_4/g-C_3N_4$,⁷⁴⁵ $V_2O_5-B-doped g-C_3N_4$,⁷⁴⁶ $MOS_2/Cd_{0.9}Zn_{0.1}S^{747}$ and $MOO_3@ZrO_2^{748}$ photocatalysts have also shown enhanced degradation of diclofenac and diclofenac sodium.

Table 9 records the data on the performance of metal oxides and carbonaceous materials based photocatalyst in the removal of diclofenac from water under optimum conditions.

3.9 Atenolol

Atenolol (ATL) belongs to the group of β -blockers and is extensively used in the treatment of cardiovascular diseases, such as hypertension, coronary arterial disease and cardiac arrhythmia.⁷⁴⁹ As a result, it has been widely detected in sewage effluent, surface water and wastewater treatment plants on its release into the environment through urban discharges. Atenolol can prevent the growth of human embryonic cells and is toxic to water species. Therefore, it is essential to develop simple and cost-effective technologies for the effective removal of ATL in wastewater before release into natural water.^{750–780}

3.9.1 Metal oxides. Several studies have been done into carrying out the degradation of atenolol using commercial as well as synthetic TiO₂ compared to ZnO.⁷⁵⁰⁻⁷⁵² Hapeshi et al.⁷⁵³ used a variety of commercially available TiO₂ as photocatalysts and found the following relative catalytic activity for the conversion of atenolol: Degussa P25 (67%) >Hombicat UV 100 (39%) > Tronox A-K-1 (30%) > Aldrich (15%) > Tronox TRHP-2 (10%) > Tronox TR (9%) In another study, nano-TiO₂ crystal phase (anatase TiO₂, rutile TiO₂, and mixed phase) coupled with UV-LED was used to study the influence of several parameters on atenolol photodegradation.754 It was noted that the mixed phase completely degraded atenolol in 60 min under UV-LED (365 nm) corresponding to the ATL concentration of 18.77 µM, catalyst dosage of 2.0 g L^{-1} , light intensity of 774 μ W cm⁻² and pH 7.6. This is in all likelihood due to several contributions originating from the large specific surface area of the catalyst, excellent charge separation efficiency, and the influence of light absorption. The photodegradation of atenolol followed pseudo-first-order kinetics (k: 0.064 min⁻¹).

Among the different commercial TiO₂ catalysts, TiO₂ (Degussa P25) aqueous suspensions (250 mg L⁻¹) delivered 80% photocatalytic conversion of atenolol (10 mg L⁻¹) under irradiation by a 1 kW Xe-OP lamp in 120 min.⁷⁵⁵ TiO₂ (Degussa P25) has been tested for the removal by degradation of atenolol, acetaminophen, sulfamethoxazole in hospital wastewater.⁷⁵⁶ Rimoldi *et al.*⁷⁵⁷ evaluated the degradation of tetracycline hydrochloride, paracetamol, caffeine and

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Table 9 Performance data on removal of diclofenac in water presence of various photocatalysts

| Photocatalysts | Preparative method | DCF | Catalyst dose | рН | Light source | Degradation and time | Rate constant |
|--|--|--|-------------------------------------|---------|--|--|--|
| TiO ₂ ⁶⁶⁵ | Sol–gel method | 5 ppm (100 mL) | 50 mg | 6 | Xenon arc lamp, 300 W, 70 mW cm ⁻² , $\lambda_{cut-off}$: 420 | ~80% (120 min) | _ |
| TiO ₂ ⁶⁶⁵ | Sol-gel method | 5 ppm (100 mL) | 50 mg | 6 | Natural sunlight | ~72% (120 min) | _ |
| TiO ₂ P25 ⁶⁶⁶ | Commercial | 2 mg L^{-1} | $200~mg~L^{-1}$ | — | Blacklight Philips TLK05 (40 W), 290–400 nm | (120 min) 100% (60 min) | ~ 0.09 min ⁻¹ |
| TiO_2SG^{666} | Commercial | $2 \text{ mg } \text{L}^{-1}$ | $200~{\rm mg~L^{-1}}$ | — | Blacklight Philips TLK05 (40 W), 290–400 nm | 100% (30 min) | ~ 0.13 min ⁻¹ |
| TiO_2 aerogel P25 $(Degussa)^{667}$ | Commercial | 5 mg L^{-1} (100 mL) | $0.2~g~L^{-1}$ | — | 125 W black light fluorescent lamp: | 100% (80 min) | 4.24×10^{-2} min ⁻¹ |
| TiO ₂ nano thin film on glass slide ⁶⁶⁹ | Chemical bath deposition | 10 ppm | 25 × 75 mm deposited | 2 | UV lamp | 26% (12 min) | |
| TiO ₂ immobilized on glass ⁶⁷⁰ | Solution method | 0.5 mg L^{-1} | Film of area 144 cm ² | 6.2-7.2 | UVA lamp: 15 W (300–400 nm) | ~100% (26 h) | $0.15 \ h^{-1}$ |
| ZnO (Merck) ⁶⁷¹ | Commercial | 300 mg L^{-1} | 1.0 g L^{-1} | 4 | UV | 90.7% (180 min) | $0.0144 \ { m min}^{-1}$ |
| ZnO (Merck) ⁶⁷¹ | Commercial | 300 mg L^{-1} | 1.0 g L^{-1} | 4 | Solar | 56.5% (190 min) | 0.0044 min ⁻¹ |
| $V_2O_5 (Merck)^{6/1}$ | Commercial | 300 mg L^{-1} | 1.0 g L^{-1} | 4 | UV | ~100% (180 min) | 0.0196 min ⁻¹ |
| V_2O_5 (Merck) ⁶⁷¹ | Commercial | 300 mg L^{-1} | 1.0 g L^{-1} | 4 | Solar | ~100% (180 min) | 0.0141 min ⁻¹ |
| activated carbon ¹⁸² Degussa P25 TiO ₂ (75% A:25% R)/H ₂ O ₂ : | impregnation method Commercial | $\begin{array}{c} 30 \text{ Hg L} \\ (4 \text{ L}) \\ 5 \text{ mg L}^{-1} \end{array}$ | 1.2 g L 250 mg L ⁻¹ | | UVA lamp (9 W lamp) | ~83% (180 min) ~99.5% (60 min) | \min^{-1} |
| 1.4 mM ^{$0/2$} TiO ₂ (anatase and mutile) ⁶⁷³ | Commercial | 20 ppm (5 L) | $0.3 \mathrm{g L}^{-1}$ | 4 | UV lamp: 250 W | 80.25% | 0.0152 |
| TiO ₂ (anatase and rutile)/H ₂ O ₂ : 0.3 g L ^{-1 673} | Commercial | 20 ppm (5 L) | 0.3 g L^{-1} | 4 | UV lamp: 250 W | (120 min) 95.7% (120 min) | 0.0273 min ⁻¹ |
| ZnO ⁶⁷⁴ | Commercial | 30 µM | 0.25 g L^{-1} | 3 | UV lamp: 40 W, 254 nm | 95% (5 min) | 0.403 min ⁻¹ |
| α -Fe ₂ O ₃ nanoparticles (calcinated at 300 °C) ⁶⁷⁵ | Drying followed by heat treatment | 15 mg L^{-1} (100 mL) | 1 g L^{-1} | — | UVC lamp: 15 W, 254 nm | 96% (120 min) | 0.04 min ⁻¹ |
| MgO nanoparticles ⁶⁸⁰ | Direct precipitation method | 10 mg L^{-1} | 0.1 g | 6.5 | UV light source (254 nm) | 100% (60 min) | $0.1191 \ {min}^{-1}$ |
| $TiO_2 - Pd^{683}$ | Sol-gel method | 50 g L^{-1} (0.20 L) | 1 g L^{-1} | 5 | UV light source (15 W), 300–400 nm | 100% (120 min) | ~ 0.05 min ⁻¹ |
| 110_2 -Ag ⁰⁰⁰ | Sol-gel method | 50 mg L ¹ (0.20 L) | 1 g L ⁻ | 5 | UV light source (15 W), 300–400 nm | 100% (120 min) | ~ 0.04 min ⁻¹ |
| $(10^{-4} \text{ mM})^{684}$ | Deposition/hydrotherman | (100 mL) | 0.1 g | 12 | \geq 400 nm | (60 min) | 10^{-3} min ⁻¹ |
| C-doped TiO_2 (anatase phase) ⁶⁸⁶ | Microwave digestion method | $50~\mu g~L^{-1}$ | $250~{\rm mg~L^{-1}}$ | 7.5 | High-pressure W visible lamp (150 W), $\lambda > 400$ nm 8000 lx | ~100% (150 min) | 0.0334 min ⁻¹ |
| Mg (25 wt%)-doped SiO ₂ ⁶⁸⁷ | Mixing of Mg/SiO ₂ with MgCl ₂ | 20 mg L^{-1} (25 mL) | $0.7~g~\mathrm{L^{-1}}$ | 4.3 | UV light | 55% (60 min) | — |
| $Mg'(25 wt\%)$ -doped SiO_2^{687} | Mixing of Mg/SiO ₂ with MgCl ₂ | 20 mg L^{-1} (25 mL) | 0.7 g L^{-1} | 4.3 | Visible light | 48% (60 min) | — |
| F (0.25)-doped ZnO nano ⁶⁸⁹ | Hydrothermal approach | 10 mg L^{-1} (100 mL) | 1.0 g L^{-1} | _ | UV-LEDs strip: 10 W, 365 nm | 85% (30 min) and ~99% (180 min) | 0.06 min ⁻¹ |
| Mn doped CeO ₂ ⁶⁹⁰ | Sol-gel | 10 ppm | $1.0 { m g L}^{-1}$ | 7 | Mercury vapour lamp (125 W) with cut-off wavelength of 455 pm | 48% (60 min) | _ |
| Cu doped CeO_2^{690} | Sol–gel | 10 ppm | 1.0 g L^{-1} | 7 | Mercury vapour lamp (125 W) with cut-off wavelength of 470 nm | 50% (60 min) | |

Table 9 (continued)

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| Photocatalysts | Preparative method | DCF | Catalyst dose | рН | Light source | Degradation and time | Rate constant |
|--|--|--|--|---------------|---|---|--|
| Ag doped CeO ₂ ⁶⁹⁰ | Sol-gel | 10 ppm | $1.0 \mathrm{g L}^{-1}$ | 7 | Mercury vapour lamp (125 W) with cut-off | 57% (60 min) | _ |
| AgI/CeO ₂ ⁶⁹⁰ | Sol–gel | 10 ppm | 1.0 g L^{-1} | _ | wavelength of 510 nm Mercury vapour lamp (125 W) with cut-off wavelength of 460 nm | 88% (60 min) | $1.758 \times 10^4 \text{ L} \text{Mol}^{-1}$ |
| Ce@TiO ₂ ⁶⁹¹ | Precipitation method | 5 μM | 75 mg | — | UV light | $\sim 100\%$ | min - |
| 1% Ce-0.6% Mn/TiO ₂ ⁶⁹⁴ | Sol-gel method | 10 mg L^{-1} | 50 mg L^{-1} | 6 | UV lamp: 30 W, λ: 254 nm | 94% (240 min) | $0.012 \ { m min}^{-1}$ |
| N,S co-doped-CQDs/TiO ₂ ⁶⁹⁵ | <i>Via in situ</i> phase inversion method | 10 ppm (200 mL) | 1.5 g (25 cm ² membrane | _ | Visible-light irradiation (λ > 400 nm) UV light (λ < 380 nm) | (150 min) (150 min) $\sim 55\%$ (150 min) | _ |
| B (5 wt%) doped ${\rm TiO_2}^{696}$ | Sol-gel method | 15 mg dm^{-3} | 250 mg dm^{-3} | _ | UV lamp | (150 min) ~30% (120 min) | 0.0035 |
| P (5 wt%) doped ${\rm TiO_2}^{696}$ | Sol-gel method | 15 mg dm ⁻³ | 250 mg dm^{-3} | — | UV lamp | $\sim 24\%$ (120 min) | 0.0019 min ⁻¹ |
| F (5 wt%) doped TiO_2^{696} | Sol-gel method | 15 mg dm ⁻³ | 250 mg dm^{-3} | _ | UV lamp | $\sim 27\%$ (120 min) | 0.0021 min ⁻¹ |
| C–S–N-tri-doped TiO ₂ (thiourea/Ti molar ratio: $0.2:1$) ⁶⁹⁷ | Sonochemical method | 25 mg L^{-1} (50 mL) | $0.05~{\rm g~L}^{-1}$ | Neutral pH | Sunlight | 76.48% (90 min) | 0.0632 min ⁻¹ |
| TiO_2 -WO ₃ (10:1 molar ratio) ⁶⁹⁸ | Hydrothermal method | 25 mg L^{-1} (100 mL) | 0.6 g L^{-1} | 5 | Metal halide lamp, 400 W, visible light | 100% (210 min) | _ |
| Hydroxyapatite-TiO ₂ ⁷⁰² | Annealing of Ti salt and hydroxyapatite | 5 mg L^{-1} (50 mL) | 4 g L^{-1} | _ | UV lamp, λ : 365 nm, 1.80 mW cm ⁻² | 95% (24 h) | — |
| Nano TiO ₂ /diatomite ⁷⁰³ | Hydrolysis, precipitation and roasting of diatomite and TiCl | 400 $\mu g L^{-1}$ | $0.5 \mathrm{g L}^{-1}$ | _ | UV lamps: 16 W, 254 nm, 1.17 mW cm ⁻² | 100% (30 min) | _ |
| Immobilized (12 wt% TiO ₂)/Ag ₃ PO ₄ (10:1) ⁷⁰⁴ | Sol–gel method | 20 mg L^{-1} | 10 g L ⁻¹ (beads), 0.8 | _ | Visible light source | ~90% (120 min) | $0.018 \ {min}^{-1}$ |
| 4.25-Ag–Ag ₂ O/r-TiO ₂ -0.130 ⁷⁰⁵ | One-step solution reduction strategy | $5 \text{ mg} \cdot \text{L}^{-1}$ (100 mL) | 30 mg | _ | Visible light | 100% (50 min) | 0.04767 min ⁻¹ |
| PPy: ZnO $(25:1)^{706}$ | <i>Via</i> polymerization method | 10 mg L^{-1} (100 mL) | 1 g L^{-1} | 6 | Xenon lamp (250–800 nm) | 81% (60 min) | 0.986 min ⁻¹ |
| $TiO_2\text{-}SnO_2$ (molar ratio: 20 to 1)^{708} | Hydrothermal method | 20 mg L^{-1} | $0.8 \mathrm{g L}^{-1}$ | 5 | UV lamp | 100% (300 min) | $\begin{array}{c} 0.0147 \\ \text{min}^{-1} \end{array}$ |
| $Fe_3O_4/Bi_2S_3/BiOBr$ (with Bi_2S_3 mass ratio of 4%) ⁷¹⁰ | One-pot solvothermal | 10 mg L^{-1} (50 mL) | 0.03 g L^{-1} | 5 | LED lamp (50 W), 475 nm | 93.81% (40 min) | $\begin{array}{c} 0.0527 \\ \text{min}^{-1} \end{array}$ |
| TiO_2 (a) $ZnFe_2O_4/Pd^{711}$ | Photodeposition technique | 10 mg L^{-1} | $0.03 {\rm ~g~L}^{-1}$ | 4 | Solar light | 84.87% (120 min) | 0.0172 min ⁻¹ |
| Nanotubular $\text{TiO}_2\text{-PES}^{712}$ | <i>Via</i> anodization of TiO ₂ nanotubes on polyethersulfone | 5 mg L^{-1} | Circular membranes (Dia: 47 | _ | UVA sunlamp (7.6 mW cm ⁻²) | ~94% (240 min) | 9.96 × 10 ⁻³ min ⁻¹ |
| Al_2O_3 -(15%) $Nd_2O_3^{713}$ | Sol–gel method | 80 ppm | 200 mg (200 mL) | _ | UV lamp, 254 nm, 4400 μW cm ⁻² | >92.0% (40 min) | 9.5×10^{-2} min ⁻¹ |
| CQDs (50 mL) modified g- $C_3N_4^{715}$ | Mixing method | 10 mg L^{-1} (50 mL) | $200~{\rm mg~L^{-1}}$ | 9 | Xenon arc lamp (300 W) with UV cut-off filter ($\lambda \ge 400$ nm), 150 ± 5 mW cm ⁻² | 100% (12 min) | $\frac{0.47}{\min^{-1}}$ |
| TiO ₂ -carbon microspheres (CMS) with Ti : CMS molar ratio = 2^{718} | Solvothermal treatment | 5 mg L ⁻¹ (50 mL) | 250 mg L^{-1} | 6.0 | Xenon lamp (500 W m ⁻²). With light correction filter ($\lambda \le 350$ nm) | 100% (180 min) | |
| 30% TiO ₂ -hybridize C-doped based $r=C_{2}N_{1}^{-719}$ | <i>In situ</i> method | 10 mg L^{-1} (100 mL) | $1 \mathrm{g L}^{-1}$ | 5.05 | LED lamp: 50 W, 380–780 nm | 98.92% (30 min) | 0.1796 min ⁻¹ |
| AgI/g-C ₃ N ₄ (molar ratio of AgI: 45%) ⁷²⁰ | Deposition–precipitation method | 1 mg L^{-1} (100 mL) | 10 mg | _ | Xenon lamp (300 W), $\lambda \ge$ 400 nm, 100 mW cm ⁻² | 100% (6 min) | 0.561 min ⁻¹ |

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Table 9 (continued)

| Photocatalysts | Preparative method | DCF | Catalyst dose | рН | Light source | Degradation and time | Rate constant |
|--|---|--|---------------------------------|------|--|-------------------------|---|
| Ag modified g- C_3N_4 (mass ratio of Ag: 54%) ⁷²¹ | Photodeposition | 100 mg L^{-1} (100 mL) | 10 mg | _ | Xenon lamp: 300 W with cut-off filter ($\lambda \ge 400$ nm), 100 mW cm ⁻² | ~100% (120 min) | 0.0429 min ⁻¹ |
| TiO_2 -rGO in presence of persulfate ⁷²⁶ | Solvothermal treatment (using 5 wt% GO) | 25 mg L^{-1} (50 mL), (persulfate:20 mg L^{-1}) | 75 mg L^{-1} | 4 | Sunlight $(1.25 \times 10^6 \text{ lx})$ | >98% (30 min) | 99.4 × 10 ⁻³ min ⁻¹ |
| BiOCl-GO ⁷²⁷ | One-pot hydrothermal method | 25 mg L^{-1} (100 mL) | 1 g L^{-1} | 5 | Visible spectrum solar light (17.38 mW cm ⁻²) | 47.88% (180 min) | _ |
| 5 Mol% Ag-BiOI-rGO 5 wt% ⁷²⁸ | Hydrothermal strategy | 10.0 $\mu g \text{ mL}^{-1}$ (50 mL) | 50 mg | — | Halogen lamp: 300 W | 100% (80 min) | 0.026 min^{-1} |
| Ag/AgBr/GO ⁷²⁹ | Sonochemical route | 25 mg L^{-1} (25 mL) | 0.030 g | 6.2 | Sunlight irradiation | ~93% (6 min) | — |
| rGO-Cu ₃ BiS ₃ (15%)/PS (5 mM) ⁷³⁰ | Solvothermal process | 10 mg L^{-1} (50 mL) | 30 mg | _ | UV LED light (15 W) | 85% (60 min) | 3.8×10^{-2} min ⁻¹ |
| Co_3O_4/WO_3 (annealed) ⁷³¹ | Dispersion method | 15 ppm (50 ml) | 30 mg | 6.8 | Mercury lamp (80 W) with cut-off of 420 nm | 90.8% (180 min) | 0.1412 min^{-1} |
| Fe ₃ O ₄ @SrTiO ₃ /Bi ₄ O ₅ I ₂ ⁷³² | <i>In situ</i> hydrothermal route | 10 mg L^{-1} | 0.3 mg mL ⁻¹ | 6 | Xenon lamp (300 W) | 98.4% (90 min) | 0.06214 min ⁻¹ |
| N,S co-doped TiO ₂ @MoS ₂ ⁷³⁵ | Hydrothermal method | 0.15 mg L^{-1} | 0.98 g L^{-1} | 5.5 | Visible LED light irradiation | 98% (150 min) | 0.002 min^{-1} |
| S–B-co-doped g- C_3N_4 nanotubes– MnO_2 (PMS: 0.06 mM) ⁷³⁶ | Hydrothermal | 20 mg L^{-1} | $0.5 \mathrm{g L}^{-1}$ | 7 | Visible light (8 × 8 W), 460 nm | 99% (10 min) | _ |
| Pt-TiO ₂ -Nb ₂ O ₅ ⁷³⁸ | Multiple steps | 12.5 mg L^{-1} (100 mL) | $0.5 {\rm g L}^{-1}$ | — | UV-LED | 100% (20 min) | 0.446 min^{-1} |
| BiOCl/CuBi ₂ O ₄ (mass ratio: 40%) ⁷³⁹ | Solvothermal process | 50 mg L^{-1} (40 mL) | 1 mg mL^{-1} | — | Xenon lamp (300 W), $\lambda >$ 420 nm | ~90% (60 min) | 0.03539 min ⁻¹ |
| $CuBi_2O_4/Ag_3PO_4 (1:1)^{740}$ | Combination of hydrothermal and <i>in situ</i> deposition | 10 mg L^{-1} (50 mL) | 0.025 g | — | Xenon lamp (300 W) with cut-off filter at $\lambda \ge 400$ nm | ~90% (120 min) | 0.0143 min ⁻¹ |
| $CuBi_2O_4/Ag_3PO_4$ (mass ratio of 3 : 7) ⁷⁴¹ | Hydrothermal synthesis and <i>in situ</i> deposition method | 10 mg L^{-1} | 25 mg (50 mL) | 4.42 | Xenon lamp (300 W), $\lambda >$ 400 nm | 82% (60 min) | 0.0072 min ^c |
| CuBi ₂ O ₄ /Ag ₃ PO ₄ (mass ratio of $3:7$)/S ₂ O ₈ ²⁻ : 1- 06 mM ⁷⁴¹ | Hydrothermal synthesis and <i>in situ</i> deposition method | 10 mg L^{-1} | 25 mg (50 mL) | 4.42 | Xenon lamp (300 W), $\lambda >$ 400 nm | 100% (60 min) | 0.0272 min ⁻¹ |
| CuBi ₂ O ₄ /Ag ₃ PO ₄ (mass ratio of $3:7$)/H ₂ O ₂ : 1 mM ⁷⁴¹ | Hydrothermal synthesis and <i>in situ</i> deposition method | 10 mg L^{-1} | 25 mg (50 mL) | 4.42 | Xenon lamp (300 W), $\lambda > 400 \text{ nm}$ | 98.40% (60 min) | $0.0162 \ {min}^{-1}$ |
| $\mathrm{TiO}_2/\mathrm{g-C}_3\mathrm{N_4}^{742}$ | Wet impregnation method | 5 ppm | 0.3 g | 5 | W halogen lamp (1000 W) | 93.49% (90 min) | 0.0324 min ⁻¹ |
| $Ag_{3}PO_{4}/g$ - $C_{3}N_{4}(30\%)^{745}$ | Deposition–precipitation method | 1 mg L^{-1} (100 mL) | $0.1 {\rm g L}^{-1}$ | _ | Xenon lamp (300 W) with filter ($\lambda \ge 400 \text{ nm}$) | ~100% (12 min) | 0.453 min ⁻¹ |
| 50% V ₂ O ₅ –g-C ₃ N ₄ (molar ratio: 30%) ⁷⁴⁶ | Mixing method | 10 mg L^{-1} | $0.2 \text{ mg} \text{mL}^{-1}$ | >7 | Monochromatic blue lamps (8 W), 465 \pm 40 nm | 100% (<105 min) | ~ 0.53 min ⁻¹ |
| MoS ₂ /Cd _{0.9} Zn _{0.1} S ⁷⁴⁷ | One-step hydrothermal method | 20 μM (50 mL) | 25 mg | _ | Xenon lamp (300 W) with 420 nm cut-off filter | 86% (30 min) | _ |

individual pollutants in atenolol, both as and mixtures, using UV and simulated-solar-mediated TiO₂. According to Ponkshe and Thakur,758 degradation of atenolol $(2 \times 10^{-4} \text{ M})$ using different commercially available TiO₂ (0.03 g L^{-1}) as photocatalysts in a 100 mL reaction solution (natural pH) under UV light for 120 min followed the order: Aeroxide TiO_2 P25 (94%) > TiO_2 Hombikat UV 100 (68%) > Merck TiO_2 (60%) > TiO_2 Kronoclean 7000 (45%). Rogé et al.⁷⁵⁹ prepared ZnO nanowires by metal organic chemical vapor deposition and investigated their photocatalytic activity in a solution containing atenolol and sulfadimidine under low-power 365 nm UV light (2.28 mW cm⁻²). The corresponding pseudo-first-order rate constants in these pollutants were found to be 6.5×10^{-3} and 2.3×10^{-3} min⁻¹. Several other studies also reported the photocatalytic degradation of atenolol in aqueous solution using Degussa TiO₂ P25 suspension,⁷⁶⁰ TiO₂,⁷⁶¹ TiO₂/salicylaldehyde–NH₂-MIL-101(Cr)⁷⁶² and ZnO.⁷⁶³

3.9.2 Metal-doped and metal-metal oxides. Ramasamy *et al.*¹⁰⁴ fabricated an Ag-doped ZnO photocatalyst to study its performance as a photocatalyst in the visible-light region

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for the photocatalytic degradation of atenolol (and acetaminophen) in a water medium. The corresponding removal efficiencies were found to be about 70 and 91% for $[ATL]_{int} = [ACT]_{int}$: 5 mg L⁻¹, pH: 8.5, time: 120 min, and Ag-ZnO: 1 g L⁻¹. These findings also confirmed that the removal process takes place through the OH· pathway in the removal of the pollutants. Fe–TiO₂ and Ag–TiO₂ mediated visible-light photocatalysis removed atenolol from aqueous solution under optimum conditions by 75.5% (98 min) and 68.3% (120 min), respectively.⁷⁶⁴

Atenolol has been removed from domestic wastewater effluent using green-synthesized Fe (0-5%)doped TiO₂ (Fe-TiO₂) under visible-light irradiation.⁷⁶⁵ These findings showed 85% removal of atenolol in the presence of Fe (2 wt%)-TiO₂ after 105 min at solution pH 9, initial atenolol concentration of 10 mg and catalyst dose of $1.25 \text{ g } \text{L}^{-1}$. The degradation L^{-1} atenolol by visible-light-activated Fe-TiO₂ was of attributed to the cleavage of the ether bond, hydroxylation of the aromatic ring and oxidation of amine moieties. Alternatively, the enhanced photocatalytic activity for atenolol by Fe-doped TiO₂ due to the reduced band gap of TiO₂ cannot be ruled out.

Ag-TiO₂ (Ag/Ti molar ratio: 2%) microtubes showed enhanced degradation of atenolol under UV-light irradiation (λ : 365 nm, power: 0.111 mW cm⁻²).⁷⁶⁶ Further investigations revealed Ag acting as a good photogenerated electron acceptor for photocatalysis. Cobalt-doped TiO₂ nanoparticles (dose: 2.0 g L⁻¹) exhibited about 90% photodegradation (ATL: 15 mg L⁻¹, H₂O₂: 2.0 mL, pH: 2) of atenolol in 40 min under UV irradiation.⁷⁶⁷ The photodegradation of atenolol followed first-order kinetics, and the process involved the formation of hydroxyl free radicals and superoxide oxygen anions as active species.

3.9.3 Metal oxide composites. A Bi₂O₃/TiO₂ composite was successfully synthesized by a solvothermal method and its photocatalytic performance was tested for the removal of atenolol removal from aqueous solution under UVC and visible-light irradiation.⁷⁶⁸ The investigations revealed the decomposition of atenolol to be better for Bi₂O₃/TiO₂ (68.92%) than Bi₂O₃ (22.58%) after 60 minutes under optimum conditions (pH: 7, catalyst dosage: 400 mg L^{-1} and initial concentration of atenolol: 10 mg L^{-1}). Stojanović et al.⁷⁶⁹ fabricated a TiO₂/zeolite composite by a solid-state dispersion method and investigated the photocatalytic degradation of atenolol from an aqueous solution (pH ~ 6.5) under simulated solar light. These findings indicated ~94% and 88% degradation of atenolol after 70 min for ZSM-5 combined with P25 TiO₂ and ZSM-5/TiO₂ nanocrystals, respectively. Corchero et al.⁷⁷⁰ prepared Fe₃O₄@AgCl and Fe₃-O4@TiO2 nanocatalysts using an ionic liquid. Subsequent evaluation of their effectiveness as photocatalysts under UV light (30 min) showed the degradation of atenolol by 66.0% and 43.7%, respectively. The photocatalytic degradation of atenolol has also been reported using BiOCl@Fe₃O₄⁷⁷¹ and immobilized titania/silica on glass slides.772

3.9.4 Graphitic material composite. A hydrothermally prepared graphene oxide– TiO_2 (1.5 g L⁻¹) composite showed 72% degradation of atenolol (25 ppm) solution (pH: 6) under visible-light irradiation after 1 h.⁷⁷³ The inclusion of graphene oxide in the composite facilitated enhanced electron–hole pair separation. The photocatalytic activities of immobilized graphene– TiO_2^{774} and graphene oxide/ZnO composite⁷⁷⁵ have also been examined for the photocatalytic degradation of atenolol under UV and solar irradiation, respectively. A metal-free exfoliated g-C₃N₄ photocatalyst



Fig. 24 (a) Photocatalytic activities of photocatalysts for atenolol degradation of Ag₃PO₄, Y-Ag₃PO₄, BiVO₄, Y-Ag₃PO₄/BiVO₄, Y-Ag₃PO₄/CQDs and Y-Ag₃PO₄/CQDs/BiVO₄ for the degradation of atenolol and (b) Z-scheme photocatalysis mechanism for atenolol degradation by Y-Ag₃PO₄/CQDs/BiVO₄, Reproduced from ref. 779 with permission from Elsevier (2020).

showed the efficient removal of atenolol from urban wastewater under visible light.⁷⁷⁶ In another study, carbon nitride modified by graphene quantum dots exhibited 86% photocatalytic degradation efficiency for atenolol, which still remained above 83% after five cycles.⁷⁷⁷

3.9.5 Heterojunctions and Z-scheme-based photocatalysts. Kumar et al.⁷⁷⁸ used recycled LiFePO₄ from batteries in combination with B@C₃N₄ and CuFe₂O₄, which were harnessed as sustainable nanojunctions to study xenonlamp-mediated atenolol degradation and showed 99.5% and 85.3% (60 min) degradation efficiency by B@C₂N₄/LiFePO₄/ CuFe₂O₄ and B@C₃N₄/LiFePO₄/CuFe₂O₄ (30%)photocatalysts. Z-Scheme Y-Ag₃PO₄/CQDs/BiVO₄ exhibited 90.9% degradation efficiency for atenolol under visible light (6 h) compared to Y-Ag₃PO₄ and BiVO₄ (Fig. 24(a)).⁷⁷⁹ This could be attributed to an increase in the visible-light absorption and electron mediators as a result of the synergistic effect. The kinetic constant in the photocatalytic degradation of atenolol was found to be ~2.8 times that of pristine Ag₃PO₄ in the presence of Y-Ag₃PO₄/CQDs/BiVO₄ and a possible mechanism has also been proposed, as shown in Fig. 24(b). Both Y-Ag₃PO₄ and BiVO₄ generated photogenerated carriers under visible-light illumination. CQDs not only increase the visible-light absorption of Y-Ag₃PO₄/CQDs/BiVO₄ but also act as electron mediators. Simultaneously, oxygen defects caused by the doping of Y^{3+} into Ag₃PO₄ are a capture centre for photogenerated electrons to generate O_2^{-} , inhibiting the recombination of photogenerated electron-hole pairs. In another study, a Z-scheme rGO/CuFe₂O₄/CdS/Bi₂S₃ double ODs nanoheterojunction exhibited ~76.5% degradation of atenolol photo-Fenton-assisted photocatalytic degradation of atenolol in 360 min under visible-light irradiation.780 The degradation of atenolol was attributed to enhanced surface oxygen vacancies, the formation of OH· and h⁺ and the photo-Fenton reaction.

Table 10 records data on the performance of different photocatalysts on removal of diclofenac from water under optimum conditions.

4 Future scope and perspectives

Pharmaceutical pollutants found in water supplies through human and animal consumption of antibiotics, antipyretics, analgesics, *etc.* are considered potential hazards to the environment, humans and aquatic life.⁷⁸¹ However, conventional wastewater treatment methods are ineffective in eliminating them completely. In view of this, the photocatalytic degradation of these pharmaceutical pollutants using semiconducting materials is considered an effective method.

An efficient semiconducting material acting as an efficient photocatalyst is guided by enhanced visible-light absorption, facilitating charge carrier migration and a reduced recombination rate. In view of this, TiO₂, WO₃, ZnO, Fe₂O₃,

CdS, MoS₂ etc. are widely used photocatalysts for the photodegradation of pharmaceutical pollutants in water.²³⁻³⁹ However, the large band gaps of photogenerated charge carriers, *i.e.* rapid recombination rate (*i.e.*, short lifetimes) of photogenerated charge carriers, instability in an aqueous medium, reusability of the photocatalyst and poor absorption ability for visible light, are a few drawbacks that limit the practical applications of metal oxide as photocatalysts. Therefore, increasing attention has been focused on achieving the effective separation of photogenerated charge carriers, improvements in the visible-light response and other factors⁷⁸² through designing and constructing advanced light energy harvesting assemblies for environmental remediation.783 This problem has been overcome by modifying semiconducting metal oxides through doping, composite formation, immobilizing semiconducting materials on supports and heterojunction formation for the removal of drugs from contaminated water. In addition, the combination of these semiconducting metal oxides with carbon-based materials, such as activated carbon, biochar, carbon nanotubes, carbon dots, g-C₃N₄ and graphene, has also attracted a lot of attention in the removal of pharmaceutical pollutants present in wastewater. However, there are still several research gaps in the removal of antibiotics by photocatalysts. These future challenges are described below.

The expensive precursors used in the synthesis of metal oxides limit their large-scale application. Therefore, it is desirable to realize the simple, facile, affordable, low-cost synthesis of photocatalysts. The specific surface area,⁷⁸² crystallite size,⁷⁸⁴ size, shape and overall structure⁷⁸⁵ of photocatalysts play important roles in the photocatalytic activity of emerging pollutants. This needs to be correlated with light trapping, charge separation and pollutant adsorption ability parameters under optimized operational conditions.

Carbon-based materials have also attracted significant interest in recent years due to their unique physicochemical, optical and electrical properties following band-gap tuning, composite formation and heterojunction construction, *etc.*^{40–50} The enhanced photo-efficiency of the corresponding nanocomposites is ascribed to improvement in visible-range absorption, fast charge carrier migration and reduced recombination rate. However, their choices are limited to batch experiments at the laboratory scale rather than the pilot scale. As a result, there is a gap between on-going research and its application.

The literature revealed considerable interest in investigating the photocatalytic degradation of individual pharmaceutical pollutants in water. However, wastewater could contain complex pollutant mixtures, including other organic and inorganic species originating from heavy metals, dyes, personal care products, pesticides and other sources.^{757,786–794} This can affect the degradation process for pharmaceutical pollutants through interference and matrix effects. Therefore, attention also needs to be focused on
Table 10 Performance data on removal of atenolol in water in the presence of different photocatalysts

| Photocatalyst | Preparation method | ATL | Catalyst dose | рН | Light source | Degradation (time) | Rate constant |
|--|--------------------------------------|--|--------------------------------------|------|--|--------------------------------|--|
| TiO ₂ : mixed phase (source: Shandong Xiya Chemical Co) ⁷⁵⁴ | Commercial | 18.77 μM | 2 g L^{-1} | 7.6 | UV-lamp (365 nm) and I_0 : 774 mW cm ⁻² | 100% (60 min) | 0.064 min ⁻¹ |
| TiO_2 (75% A + 25% R) Degussa $P25^{755}$ | Commercial | 10 mg L ⁻¹ | $250~{\rm mg~L}^{-1}$ | 8 | Xenon-OP lamp (1 kW), I_0 : 272.3 W m ⁻² | 80% (120 min) | _ |
| Degussa P25 ⁷⁵⁶ | Commercial | 10 mg L^{-1} | $1.0~g~L^{-1}$ | — | Natural solar irradiation | 100% (400 kJ m ⁻²) | _ |
| Degussa TiO ₂ P25 ⁷⁵⁸ | Commercial | 37.6 mM | 2.0 g L^{-1} (25 mL) | 6.8 | High-pressure Hg lamp (125 W), 365 nm, 31.3 mW m ⁻² | ~100% (60 min) | 0.0570 min ⁻¹ |
| Degussa P25 TiO ₂ ⁷⁶⁰ | Commercial | 37.6 μM | 2.0 g L^{-1} | 7 | UV light | 100% (60 min) | _ |
| TiO_2 immobilized on the clinoptilolite nano particles support ⁷⁶² | Dispersion method | $10 \text{ mg} \\ \text{L}^{-1} (25 \text{ mL})$ | 1.5 g L^{-1} | _ | UV lamp (80 W) | 75% (60 min) | _ |
| TiO ₂ immobilized on Salicylaldehyde-NH ₂ -MIL 101 (Cr) support ⁷⁶² | Dispersion method | 10 mg L ⁻¹ (25 mL) | 1.5 g L^{-1} | _ | Xenon lamp (100 W) | 82% (60 min) | _ |
| ZnO nanoparticles ⁷⁶³ | Synthetic method | 20 mg L^{-1} | 10 mg L^{-1} | 7 | 9 W UVC lamp | 100% (120 min) | _ |
| Fe-TiO ₂ ⁷⁶⁴ | Green method | 5 mg L^{-1} (100 mL) | $1005 {\rm ~mg~L^{-1}}$ | 8 | Xenon arc lamp, 300 W, λ: 650 nm | 71.2% (98 min) | _ |
| Ag-TiO ₂ ⁷⁶⁴ | Green method | 5 mg L^{-1} (100 mL) | 1065 mg L^{-1} | 8 | Xenon arc lamp, 300 W, λ : 650 nm | 65.7% (120 min) | _ |
| Ag–ZnO microtubes ¹⁰⁴ | Solution method | 5 mg L^{-1} | $1 \mathrm{g L}^{-1}$ | 8.5 | W halogen lamp (300 W) | 70.2% (120 min) | 0.01 min ⁻¹ |
| Fe-TiO ₂ ⁷⁶⁵ | Green | 10 mg L^{-1} | $1.25~g~L^{-1}$ | 9 | 300 W halogen lamp | 85% (105 min) | 0.013 min^{-1} |
| Ag–TiO ₂ microtubes (Ag/Ti molar ratio: 2%)/O ₃ ⁷⁶⁶ | Calcination | $\substack{20 \text{ mg} \\ L^{-1}}$ | 0.2 g | 9.11 | Medium-pressure Hg lamp: 365 nm and 0.111 mW cm ⁻² | 92.23% (9 min) | 0.3275 min ⁻¹ |
| Co doped-TiO ₂ (H ₂ O ₂ : 2.0 mL L^{-1}) ⁷⁶⁷ | Mixing followed by calcination | 15 mg L^{-1} | 2.0 g L^{-1} | 2 | UV (200 nm) | 90% (40 min) | 0.059 min^{-1} , $1.75 \times 10^{-4} \text{ g}$ $\text{mg}^{-1} \text{ min}^{-1}$ |
| Bi ₂ O ₃ /TiO ₂ ⁷⁶⁸ | Solvothermal method | 10 mg L^{-1} | $400~mg~L^{-1}$ | 7 | UVC (visible-light irradiation) | 68.92% (60 min) | _ |
| TiO ₂ /zeolites ⁷⁶⁹ | Solid-state dispersion method | $_{\mathrm{L}^{-1}}^{50}\mathrm{mg}$ | $1 \text{ g L}^{-1} (40 \text{ mL})$ | 6.5 | Lamp (Osram Vitalux (300 W)) | ~94% (70 min) | 0.132 ± 0.001 min ⁻¹ |
| TiO ₂ @Fe ₃ O ₄ ⁷⁷⁰ | Mixing method | 10 ppm | $0.75 {\rm ~g~L}^{-1}$ | 5.5 | Low-pressure Hg vapour lamp (UVC. l: 280 nm) | 43.7% (30 min) | _ |
| Fe ₃ O ₄ @AgCl ⁷⁷⁰ | Mixing method | 10 ppm | $0.75 {\rm ~g~L}^{-1}$ | 5.5 | Low-pressure Hg vapour lamp (UVC. l: 280 nm) | 66% (30 min) | _ |
| Fe ₃ O ₄ @TiO ₂ ⁷⁷⁰ | Mixing method | 10 ppm | 0.75 g L^{-1} | 5.5 | Low-pressure Hg vapour lamp (UVC. l: 280 nm) | 66% (30 min) | _ |
| BiOCl@Fe ₃ O ₄ with [PS]: 1.0 mM^{771} | Precipitation process | $_{\mathrm{L}^{-1}}^{2.5}\mathrm{mg}$ | $0.1 \mathrm{g L}^{-1}$ | 6.5 | Xenon lamp (simulated sunlight): 500 W | ~99% (60 min) | $(5.34-6.04) \times 10^{-2} \text{ min}^{-1}$ |
| Graphene oxide-TiO ₂ ⁷⁷³ | Hydrothermal | 25 ppm | 1.5 g L^{-1} (150 mL) | 6 | 1000 W xenon arc lamp, 750 mW cm ^{-2} | 72% (60 min) | _ |
| $Y-Ag_3PO_4/CQDs/BiVO_4^{779}$ | Mixing method | 10 mM (50 mL) | 5 mg photocatalyst | — | 250 W xenon lamp with UV cut-off filter, $\lambda > 420$ nm | 90.9% (6 h) | $0.50 \ h^{-1}$ |

developing photocatalysts capable of simultaneously removing pharmaceuticals even in the presence of other pollutants/interfering substances in the wastewater. Recovery, reusability, and stability remain other issues in the development of high-performing photocatalysts in wastewater treatment. Toxicity assessment is considered to be one of important parameters in the treatment of wastewater by photocatalysis.⁷⁹⁵ This could be ascribed to the formation of

carcinogenic secondary metabolites due to the incomplete mineralization of targeted contaminants.

Nanomaterial-based photocatalysts have shown great promise due to their superior adsorptive and photocatalytic properties in the removal of pharmaceutical pollutants.^{51,57} In this regard, leaching of toxic components could adversely affect the quality of the water environment. This aspect remains a matter of great concern and as a consequence,

extensive investigations are needed to fully understand the role of various photocatalyst nanoparticles and their toxicity risks in aquatic environments.796,797 Therefore, it remains challenging to recover and separate the nanoparticle-based photocatalysts invariably used in water treatment. Recently, this difficulty has been overcome by immobilizing the photocatalysts on various support materials. Therefore, in the future innovations will be needed for effective, eco-friendly, and sustainable immobilization techniques for the separation/recovery and reuse of photocatalytic materials. Existing research has also invariably focused on laboratoryscale photocatalysis in the degradation of emerging pharmaceutical pollutants without much implementation in real water systems. More studies need to be focused at the pilot and industrial scale levels for its commercialization. The fabrication of economical, environmentally friendly and effective photocatalysts taking into account many of these aspects remains a major challenge in this field.

5 Conclusions

Antibiotics have been invariably used in different fields, such as the medical field, agriculture, and veterinary medicine for the purpose of killing or preventing bacterial growth. However, the presence of these pharmaceutical pollutants on entering surface water and groundwater are a potential threat to human and marine lives and need to be eliminated. Considering this, various conventional processes have been developed for the removal of these pharmaceutical pollutants. However, their choice is limited due to their high cost as well as incomplete elimination of contaminants from the contaminated water.

In view of this, the current review highlights recent advances in the applications of different photocatalysts to the removal of emerging pharmaceutical pollutants in wastewater. As a result, the performance of several metal oxides, carbonaceous materials, composites including surface modification, doping with metals/nonmetals, heterojunction formation, and immobilization using support materials, homo- or hetero-materials composed of two or more inorganic phases, inorganic semiconductors coupled with carbon-based materials, inorganic semiconductors hybridized with 2D materials as excellent photocatalysts have been reviewed to find out the optimum removal efficiency for the pollutants (acetaminophen, amoxicillin, sulfamethoxazole, acetaminophen, norfloxacin, ciprofloxacin, tetracycline, diclofenac and atenolol) in water. However, secondary pollution produced by the formation of by-products during the photocatalytic process, leaching of dopants/active components of the photocatalysts, and the generation of excess CO₂ during the photocatalysis process are additional challenges that need to be addressed in future. Further, most of these findings are reported on the laboratory scale, and real-world and industrialscale applications have yet to be fully realized. The further development of low-cost, robust photocatalysts utilizing semiconductors and renewable visible/solar light to solve both the world crises of energy supply and environmental pollution remains a pressing demand for industrial application.

Conflicts of interest

There are no conflicts to declare.

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